World Technology Evaluation Center (WTEC)

NIST

WTEC Workshop Report on

R&D Status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices in the United States

Proceedings of the May 8-9, 1997 Workshop

Richard W. Siegel, WTEC Panel Chair
Evelyn Hu, Panel Co-Chair
M.C. Roco, NSF Coordinator

JANUARY 1998

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WTEC PANEL ON NANOPARTICLES, NANOSTRUCTURED MATERIALS, AND NANODEVICES

Sponsored by the National Science Foundation, the Air Force Office of Scientific Research, the Office of Naval Research, the Department of Commerce (including NIST and Technology Administration, Main Commerce), the Department of Energy, the National Institutes of Health, and the National Aeronautics and Space Administration of the United States Government.

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INTERNATIONAL TECHNOLOGY RESEARCH INSTITUTE
WTEC PROGRAM

The World Technology Evaluation Center (WTEC) at Loyola College (previously known as the Japanese Technology Evaluation Center, JTEC) provides assessments of foreign research and development in selected technologies under a cooperative agreement with the National Science Foundation (NSF). Loyola's International Technology Research Institute (ITRI), R.D. Shelton, Director, is the umbrella organization for WTEC. Paul Herer, Senior Advisor for Planning and Technology Evaluation at NSF's Engineering Directorate, is NSF Program Director for WTEC. Several other U.S. government agencies provide support for the program through NSF.

WTEC's mission is to inform U.S. policymakers, strategic planners, and managers of the state of selected technologies in foreign countries in comparison to the United States. WTEC assessments cover basic research, advanced development, and applications. Panels of typically six technical experts conduct WTEC assessments. Panelists are leading authorities in their field, technically active, and knowledgeable about U.S. and foreign research programs. As part of the assessment process, panels visit and carry out extensive discussions with foreign scientists and engineers in their labs.

The ITRI staff at Loyola College help select topics, recruit expert panelists, arrange study visits to foreign laboratories, organize workshop presentations, and finally, edit and disseminate the final reports.

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WTEC Study on

NANOPARTICLES, NANOSTRUCTURED MATERIALS, AND NANODEVICES

PART 1: PROCEEDINGS OF THE MAY 8-9, 1997 U.S. REVIEW WORKSHOP

JANUARY 1998

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ABSTRACT

This volume is a collection of papers and viewgraphs presented at a workshop reviewing U.S. research and development activities in nanoparticles, nanostructured materials, and nanodevices. The workshop was held in Arlington, Virginia, on May 8 and 9, 1997. This workshop was the first stage in a worldwide assessment of R&D status and trends in nanotechnology being conducted for the U.S. government by a WTEC expert panel. This panel's final report, covering the United States, Japan, Western Europe, and Russia, will be published later in 1998. The May 1997 workshop was intended to provide a broad perspective on U.S. R&D activities in the wide variety of fields related to nanoparticle synthesis and assembly; bulk materials behavior; dispersions and coatings; high-surface-area materials; functional nanostructures (devices); and relevant biological, carbon, and theory issues. Representatives of most of the U.S. government agencies conducting or supporting such research began the workshop by reviewing their research interests. The remainder of the workshop was devoted to paper presentations by leading U.S. researchers reviewing U.S. activities. Paper authors were asked to provide a broad description of all related U.S. work in their respective fields (i.e., not necessarily just the activities in their own laboratories). Authors were chosen to be representative of cutting edge U.S. research in each of the topic areas. The list was not exhaustive; some important research was not included. Following the workshop each of the WTEC panelists drafted a summary of each topic area in an effort to fill in any gaps in coverage of the full spectrum of related U.S. activities. Subsequent to the workshop, WTEC offered each of the paper authors and other presenters an opportunity to revise or extend their contributions for the purposes of producing this proceedings report. Only minimal editing work has been done on the papers, some of which still consist largely of viewgraphs presented at the workshop.

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FOREWORD

The National Science Foundation (NSF) has been involved in funding technology assessments comparing the United States and foreign countries since 1983. A sizable proportion of this activity has been in the Japanese Technology Evaluation Center (JTEC) and World Technology Evaluation Center (WTEC) programs. NSF has supported more than 40 JTEC and WTEC studies over a wide range of technical topics. Both programs are now subsumed under the single name, WTEC, although the JTEC name has remained until recently on reports that cover only Japan.

As U.S. scientific and technological leadership is challenged in areas of previous dominance such as aeronautics, space, and nuclear power, many governmental and private organizations seek to set policies that will help maintain U.S. strengths. To do this effectively requires an understanding of the relative position of the United States and other countries. The purpose of the WTEC program is to assess research and development efforts in other countries in specific areas of technology, to compare these efforts and their results to U.S. research in the same areas, and to identify opportunities for international collaboration in precompetitive research.

Many U.S. organizations support substantial data gathering and analysis efforts directed at nations such as Japan. But often the results of these studies are not widely available. At the same time, government and privately sponsored studies that are in the public domain tend to be “input” studies; that is, they provide enumeration of inputs to the research and development process, such as monetary expenditures, personnel data, and facilities, but do not provide an assessment of the quality or quantity of the outputs obtained.

Studies of the outputs of the research and development process are more difficult to perform because they require a subjective analysis performed by individuals who are experts in the relevant technical fields. The NSF staff includes professionals with expertise in a wide range of disciplines. These individuals provide the technical expertise needed to assemble panels of experts who can perform competent, unbiased, technical reviews of research and development activities.

Specific technologies, such as telecommunications, biotechnology, or microelectromechanical systems, are selected for study by government agencies that have an interest in obtaining the results of an assessment and are able to contribute to its funding. A typical assessment is sponsored by two to four agencies. In the first few years, most of the studies focused on Japan, reflecting concern over Japan’s growing economic prowess.

Beginning in 1990, we began to broaden the geographic focus of the studies. As interest in the European Community (now the European Union) grew, we added Europe as an area of study. With the breakup of the former Soviet Union, we began organizing visits to previously restricted research sites opening up there. These WTEC studies have focused on identifying opportunities for cooperation with researchers and institutes in Russia, the Ukraine, and Belarus, rather than on assessing them from a competitive viewpoint.

In the past several years, we also have begun to substantially expand our efforts to disseminate information. Attendance at WTEC workshops (in which panels present preliminary findings) has increased, especially industry participation. Representatives of U.S. industry now routinely number 50% or more of the total attendance, with a broad cross-section of government and academic representatives making up the remainder. Publications by WTEC panel members based on our studies have increased, as have the number of presentations by panelists at professional society meetings.

The WTEC program will continue to evolve in response to changing conditions in the years to come. We are now implementing initiatives aimed at the following objectives:

- Disseminating the results of WTEC studies via the Internet. Eighteen of the most recent WTEC final reports are now available on the World Wide Web (http://itri.loyola.edu) or via anonymous FTP (ftp.wtec.loyola.edu/pub/). Viewgraphs from several recent workshops are also on the Web server.

- Expanding opportunities for the larger science and technology community to help define and organize studies
- Increasing industry sponsorship of WTEC studies

The latter two objectives are now being served under the WTEC Community-Initiated State-of-the-Art Reviews (CISAR) initiative. CISAR provides an opportunity for the U.S. R&D community to suggest and carry out studies that might not otherwise be funded solely at the initiative of the government. For example, WTEC has formed partnerships with university/industry teams, with partial funding from industry, to carry out three CISAR studies, covering the Korean semiconductor industry, electronics final assembly technologies in Pacific Rim countries, and civil infrastructure technologies in Pacific Rim countries, respectively. Several other topics are under consideration. Further information on the CISAR initiative is available on the WTEC Web server (http://itri.loyola.edu/cisar.htm) or by contacting the WTEC office.

In the end, all government-funded programs must answer the question, How has this investment benefited the nation? A few of the benefits of the WTEC program follow:

- JTEC studies have contributed significantly to U.S. benchmarking of the growing prowess of Japan’s technological enterprise. Some have estimated that JTEC has been responsible for over half the major Japanese technology benchmarking studies conducted in the United States in the past decade. JTEC and WTEC reports have also been widely cited in various competitiveness studies.
- These studies have provided important input to policymakers in federal mission agencies. JTEC and WTEC panel chairs have given special briefings to senior officials of the Department of Energy and Commerce, to the National Aeronautics and Space Administration (NASA) administrator, and to the President’s science advisor. Two recent studies on electronic packaging and related electronics manufacturing issues have had a particularly significant impact in this regard. The 1995 JTEC report on electronic manufacturing and packaging in Japan was cited by the Defense Secretary and the Commerce Secretary in a joint announcement of a $30-40 million government initiative to improve U.S. competitiveness in electronic packaging. The President’s Office of Science and Technology Policy and two senior officials at the Department of Commerce have received briefings on a follow-on WTEC study covering electronic manufacturing in other Pacific Rim countries.
- Studies have been of keen interest to U.S. industry, providing managers with a sense of the competitive environment internationally. The director for external technology at a major U.S. high-technology firm recently told us that that he always looks for a relevant WTEC report first when beginning to investigate a technology for his company, because these reports provide a comprehensive understanding that includes R&D, process technology, and some information on commercial developments. The list of corporate users of the WTEC Web server includes virtually all of the nation’s high-technology sector.

Not the least important is the educational benefit of the studies. Since 1983 over 200 scientists and engineers have participated as panelists in the studies. As a result of their experiences, many have changed their viewpoints on the significance and originality of foreign research. Some have also developed lasting relationships and ongoing exchanges of information with their foreign hosts as a result of their participation in these studies.

As we seek to refine the WTEC program in the coming years, improving the methodology and enhancing the impact, program organizers and participants will continue to operate from the same basic premise that has been behind the program from its inception: the United States can benefit from a better understanding of cutting-edge research that is being conducted outside its borders. Improved awareness of international developments can significantly enhance the scope and effectiveness of international collaboration and thus benefit all of the United States’ international partners in collaborative research and development efforts.

Paul J. Herer
National Science Foundation
Arlington, VA

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(USG funding body indicated in brackets)

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[1] Please note that for ease of reference WTEC has inserted figure numbers into authors' papers wherever practicable; however, many of the contributors' figures were part of slide or viewgraph presentations. In chapters 3 and 6, where figures were not referred to specifically by any accompanying text, figure numbering was omitted. Viewgraphs in chapters 3 and 6 that contain only words (i.e., no graphics) are not listed here.

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CHAPTER 1

INTRODUCTION

M.C. Roco, National Science Foundation

This review of U.S. research and development in nanoparticles, nanostructured materials, and nanodevices was held in Rosslyn, Virginia, on May 8-9, 1997, and included experts from industry, universities, and national laboratories. Twelve U.S. funding agencies and national laboratories participated: the Air Force Office of Scientific Research (AFOSR), the Army Research Office (ARO), the Ballistic Missile Defense Organization (BMDO), the Defense Advanced Research Projects Agency (DARPA), the Department of Commerce (DOC), the Department of Energy (DOE), the National Aeronautics and Space Administration (NASA), the National Institute of Standards and Technology (NIST), the National Institutes of Health (NIH), the National Science Foundation (NSF), the Office of Naval Research (ONR), and the Naval Research Laboratory (NRL). The primary objectives were to highlight major achievements and research programs and to work towards developing better interactions and eventually an interdisciplinary community in the field of nanotechnology (NT). The meeting was coordinated by the World Technology Evaluation Center (WTEC) and NSF.

NT arises from the exploitation of physical, chemical, and biological properties of systems that are intermediate in size between isolated atoms/molecules and bulk materials, where phenomena length scales become comparable to the size of the structure. It is recognized as an emerging technology of the 21st century, along with the already established areas of computer/information technology and biotechnology. NT is now at a level of development comparable to that of computer/information technology in the 1950s. New experimental and simulation tools emerging in the last few years and the discovery of novel phenomena and processes at the “nano” scale have opened revolutionary opportunities for developments in nanoparticles, nanostructured materials, and nanodevices. Nanoparticles, including nano-clusters, -layers, -tubes, and two- and three-dimensional structures in the size range between the dimensions of molecules and 50 nm (or in a broader sense, submicron sizes as a function of materials and targeted phenomena), are seen as tailored precursors for building up functional nanostructures. The precursors’ properties may be controlled during such generation processes as aerosol, colloid, plasma, combustion, molecular self-assembly, bioreplication, and chemical/mechanical comminution. These properties may be significantly different from those of corresponding bulk materials, and desirable novel properties may be obtained.

Engineered nanostructures include nanostructured materials such as ceramics, optical materials, polymers, and metals; nanocomponents such as coatings and connectors; and nanodevices such as sensors, switches, and reactors. Application areas include the pharmaceutical and chemical industries, nanoelectronics, space exploration, metallurgy, biotechnology, cosmetics, the food industry, optics, nanomedicine, metrology and measurement, and ultraprecision engineering — there are practically no unaffected fields. Efficient conversion of energy, materials, and other resources into products of high performance will be a strategic necessity in the next century. There is an evident need to create the infrastructure for science, technology, facilities, and human resources. It is estimated that all U.S. agencies together are spending approximately $115 million per year for NT research. NSF is spending about 60% of the total, and it may be a good place to catalyze a national endeavor in NT.

NT implies direct control of materials and devices on molecular and atomic scales, including fabrication of functional nanostructures with engineered properties, synthesis and processing of nanoparticles, supramolecular chemistry, self-assembly and replication techniques, sintering of nanostructured metallic alloys, use of quantum effects, creation of chemical and biological templates and sensors, surface modification, and films. The purpose is to produce materials and devices that take advantage of physical, chemical, and biological principles whose causes are found in the nanometer scale. New properties are due to size reduction to the point where interaction length scales and physical phenomena become larger than the size of the structure. NT includes development of suitable characterization methods (e.g., scanning probe microscopy, electron holography) and new manufacturing and modification processes (e.g., scanning tunneling microscope lithography, photonic processes). The most revolutionary NT approach is building up from the molecules and nanoparticles, the so-called “bottom-up” (building blocks) approach — versus the “top-down” (extreme miniaturization) approach.

A main objective of this WTEC study is to identify new research and technological opportunities, unexpected phenomena and processes, and overall paradigm shifts that would help researchers make the right choices in the future. This survey, which covers relevant work in academia, industry, and national labs, is issue-driven and interdisciplinary and includes relevant theories, methods, instruments, and technological processes. The study should help capitalize on emerging opportunities and optimize allocation of R&D funds. The May 8-9 workshop focused on establishing the state of the art and benchmarking U.S. activities.

A consensus was developed at the WTEC workshop for the need for interagency collaboration, and an interagency nanotechnology group has been established. Each participating organization has several areas of interest. Several collaborative research and educational activities on nanoparticles and nanostructured materials have been already developed between NSF, NIST, and ONR. An annual nanotechnology forum has been proposed in order to periodically survey research and educational opportunities and funding programs and to promote interactions between the NT community and funding agencies and between research providers and users.

Scientific and technological discoveries in nanotechnology are growing at an unprecedented rate, and an attempt should be made to capitalize on emerging research opportunities. U.S. nano activities in general are fragmented. The current situation can be improved by promoting joint funding of projects and use of facilities in centers of excellence, collaborations among program managers in various agencies, and interdisciplinary activities (cross-disciplinary workshops, university-industry research groups, and use of other mechanisms to facilitate knowledge and technology transfer). Academic interaction with industry is an obvious priority for the Nanotechnology Group. Preparing an interagency memorandum of understanding has been discussed by a group of funding agencies for promoting joint funding on selected interdisciplinary NT areas and leveraging funding for complementary projects.

There is a gap in student education and training in the mesoscopic range (phenomena specific from approximately 1 to 100 nm), in the interval between the molecular description and macroscopic description. Current educational activities related to NT are isolated, and a plan of action to improve this situation would be appropriate.

International interest in nanotechnology is highlighted by the existence of comprehensive programs in Europe. Examples include the European Union’s Phantom program, Nanoparticles in E.S.F., the LINK NT Programme in the U.K., and the Nanotechnology focus at the German Ministry for Research and Education. In Japan, relevant programs include the Science and Technology Agency’s Institutes on Ceramics and Metals, two 10-year programs of the Ministry of International Trade and Industry, and several projects of the Exploratory Research for Advanced Technology (ERATO) program. There are also large efforts in

Switzerland, Sweden, France, Russia, China, Taiwan, and Korea. It is hoped that the second part of the WTEC study, the worldwide survey, will encourage international networking and collaborations.

The technical presentations in this proceedings report have been grouped into the following topics: synthesis and assembly; bulk behavior; dispersions and coatings; high-surface-area materials; devices; and biological, carbon, and theory issues. The WTEC panel views this as a working document for future activities. We would like to thank to all participants for their contributions.

Introduction to WTEC Study on
Nanoparticles / Nanostructures / Nanodevices

- *Looking for paradigm shifts; new research and technological opportunities; unexpected phenomena and processes (including methods, instruments, and technical processes with relevance from nanostructured materials to biotechnology)*
- Overview in ind., univ., nat. labs; discipline neutral; issue-driven
- *Preference for "bottom-up" vs. "top-down" approach*
- Goals: helping U.S. researchers and industry identify and capitalize on emerging opportunities, and allocate future R&D funds
- Need to create scientific/technological base for human resources and experimental scientific and technological facilities for this key technology of the 21st century
- Lifetime of 5-10 years, on Web, disseminated to industry, universities, and government

Nanoparticles / Nanostructures / Nanodevices

- <u>Nanotechnology now:</u>
  - – estimated development level similar to computer technology four decades ago; need for infrastructure
  - – fragmented among disciplines and areas of relevance; need for a focal point of interaction
- Suggestion: "<u>annual nanotechnology forum</u>" for reviewing programs in U.S., highlight special achievements in research, technology, education, and also new products; and develop collaborations (consider this meeting as the first "forum")
- <u>International dimension</u>: centers of excellence abroad, networking opportunities (ex.: PHANTOM in E.C., Atom Technology Project in Japan, Nanoparticles in E.S.F., educational, etc.), share expensive facilities

CHAPTER 2

OVERVIEW OF THE WTEC STUDY

Richard W. Siegel

INTRODUCTION

The National Science Foundation and other agencies of the U.S. government have asked the World Technology Evaluation Center (WTEC) to perform an assessment of status and trends in nanoparticle and nanostructure technology and applications R&D around the world in comparison to the United States. The purposes of this study are to provide the scientific and engineering community with a critical view of the field and identify the most promising areas for research and industrial development; to stimulate the development of an interdisciplinary and international community of nanoparticles/nanostructures researchers; and to identify opportunities for international collaboration in the field.

Sponsors of the study include the Engineering, Math and Physical Sciences, and Biological Sciences Directorates of the National Science Foundation, the Air Force Office of Scientific Research, the Office of Naval Research, the National Institute of Standards and Technology, the Department of Commerce (Asia/Pacific Technology Program), the National Institutes of Health, the National Aeronautics and Space Administration, and the Department of Energy of the U.S. government.

The first phase of the WTEC study is a review of the status of U.S. R&D in related nanotechnology fields, which was accomplished by holding the May 8-9 workshop. This proceedings document is the report of that workshop.

BACKGROUND

Nanoparticle synthesis, processing, and device manufacturing are part of an emerging field referred to as nanotechnology. R&D in this field emphasizes scientific discoveries in the generation of nanoparticles with controlled characteristics; research on their processing into microstructured bulk materials with engineered properties and technological functions; and introduction of new device concepts and manufacturing methods. New properties are due to size reduction to the point where critical length scales of physical phenomena become comparable to or larger than the size of the structure. Applications take advantage of high surface area and confinement effects, which lead to nanostructures with different properties than conventional materials, and which create opportunities for innovative principles of operation for devices and instruments. Synthesis and processing of nanoparticles/nanostructures will require new aerosol, colloid, thermal, plasma, or combustion approaches, and device manufacturing is at the intersection of a broad spectrum of disciplines. R&D in this field is also stimulating understanding of the physics of new phenomena and processes at nanoscales (1-100 nm), furthering the development of new modeling and experimental tools, and generating new device principles and manufacturing methods.

Industry recognizes the extraordinary potential the nanotechnology field offers in the form of bulk, composite, or coating materials to optoelectronic engineering, magnetic recording, ceramics and special metals engineering, bioengineering, and micromanufacturing (building from small to large, unlike microelectromechanical systems). Nanostructured materials or nanoprocessed devices have a broad range of applications, from pharmaceuticals, bioengineering, pigments, and electronics to optical and magnetic devices or structures and coatings with special properties. Large-scale nanotechnology programs, institutes, and research networks have been initiated recently on a wide range of topics in Europe, Japan, China, and other countries.

The importance of nanotechnology was underscored a few years ago with the announcement by Japan's Ministry of International Trade and Industry of two 10-year nanotechnology programs (*Science* 1991, 1303): the Atom Technology Project for $185 million, and the Quantum Functional Devices Project for $40 million. Japan's Science and Technology Agency also funds several research institutes on nanoparticles, nanostructures, and related technologies. It is believed that Japanese companies and research institutions are focused in particular on the processing and manufacturing aspects of nanotechnology, including advanced diagnostics instrumentation and applications in microelectronics.

SCOPE

The sponsors determined that the scope of study should include the topics and issues described below.

Technologies to be Covered

The primary objectives will be to document the research and technological levels of other countries in the following areas:

- nanoparticles
- nanotubes
- nanolayers
- nanostructure synthesis
- processing
- related manufacturing technologies

There is a special focus on nanoparticle processing and manufacturing into new devices and applications. Biological applications are being explicitly addressed. Other issues covered include diagnostics techniques, scale-up, and miniaturization.

Since nanostructured materials are generally metastable with respect to their larger-structured counterparts, this study is also surveying the stability of particle assembly and other nanostructures under the effects of thermal, magnetic, optical, and chemical factors, along with methods to stabilize them.

Education, Infrastructure, and Other Issues

The study is evaluating university and industrial research, education, and technological development, and their interactions. The WTEC panel seeks to establish linkages between centers of excellence abroad and U.S. organizations, and is developing a World Wide Web-based international information center on this topic in the United States (http://itri.loyola.edu/nano/). Other areas of focus include the following:

- assessment of the role of directed R&D versus curiosity-driven research
- assessment of the economic potential of nanoparticles/nanostructures technologies in Japan and other countries and their role in the international arena
- evaluation of the potential for industrial low-cost manufacturing
- identification of the main differences between U.S. and foreign approaches
- identification of conditions that have facilitated the main scientific and technological breakthroughs
- assessment of the role of scientific and technological networking
- reporting on funding levels for both industry and government programs, where data are available
- evaluation of the research and education infrastructure and of international collaboration.

PANELISTS

Based on the above objectives, the following panel of U.S. experts in the relevant fields were recruited to carry out the study:

Richard Siegel (panel chair), Rensselaer Polytechnic Institute
Evelyn Hu (panel co-chair), University of California, Santa Barbara
Donald Cox, Exxon Corporation
Herb Goronkin, Motorola Corporation
Lynn Jelinski, Cornell University
Carl Koch, North Carolina State University
John Mendel, Eastman Kodak Corporation
David Shaw, State University of New York, Buffalo

OUTLINE OF THE STUDY

The sponsors and the panelists agreed on an outline of the study, as detailed below.

Nano materials can be classified into the following categories:

1. clusters with aspect ratios between 1 and infinity
2. multilayers
3. ultrafine grained overlayers
4. nanophase materials

The overall focus of this study is on the building blocks, their assembly in controlled ways to make materials with new properties, and the assembly of these materials into useful “things” (devices, etc.). This hierarchy of (a) atomically engineered building blocks, (b) assembly and materials fabrication, and (c) applications is the basis for organizing this study. What this study aims to give is a “broad-brush, stand-back” view of the world of nanostructures and their applications, both now and in the future, with respect to both short-term and “blue-sky” applications.

Based on this approach, an organizational chart was drawn for the study, as shown in Fig. 2.1. The draft report outline based on this structure calls for a separate chapter for each of the applications boxes at the bottom of this structure, each to be written by one panelist. These will be preceded by a broad “synthesis and manufacturing” chapter to be written by Evelyn Hu and David Shaw (representing the top box in the figure). Thus, the report outline is as follows:

Executive Summary (Richard Siegel)
Introduction and Methodology, Benchmark (Richard Siegel)
Nanoparticles/Nanolayers — Synthesis/Manufacturing of Nanostructures (Evelyn Hu, David Shaw)
Dispersions and Coatings (John Mendel)
High-Surface-Area Materials (Don Cox)
Functional Nanostructures and Nanodevices (Herb Goronkin)
Consolidated Materials and Parts (Carl Koch)
Biological Approaches and Applications (Lynn Jelinski)
Appendices: biographies, site reports, glossary, etc.

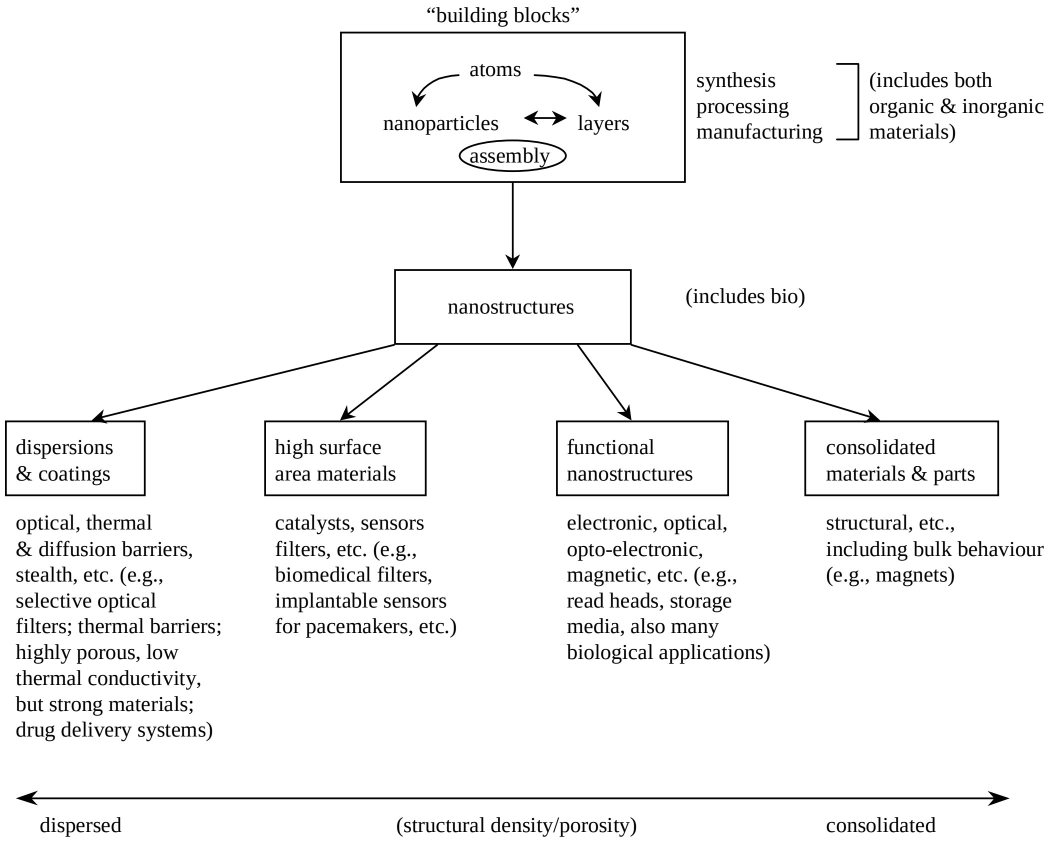


Fig. 2.1. Organizational chart of the WTEC study.

Prof. Jelinski also will work with all of the other chapter authors to assure that biological issues, approaches, and applications are adequately covered throughout the report.

The above outline was also followed in organizing the presentations for the May 8-9, 1997 U.S. review workshop.

CHAPTER 3

REVIEW OF U.S. GOVERNMENT ACTIVITIES AND INTERESTS IN NANOTECHNOLOGY

SUMMARY OF PARTICIPATING U.S. GOVERNMENT AGENCIES' ACTIVITIES

National Science Foundation
Coordinator of the Interagency Nanotechnology Group

Twelve U.S. government agencies involved in nanotechnology (NT) have provided input to this summary, including the Air Force Office of Scientific Research (AFOSR), the Army Research Office (ARO), the Ballistic Missile Defense Organization (BMDO), the Defense Advanced Research Projects Agency (DARPA), the Department of Commerce (DOC), the Department of Energy (DOE), the National Aeronautics and Space Administration (NASA), the National Institutes of Health (NIH), the National Institute of Standards and Technology (NIST), the National Science Foundation (NSF), the Office of Naval Research (ONR), and the Naval Research Laboratory (NRL). Their overall combined level of support for NT research is estimated at about $115 million/year for 1997/98. Most of the reported research is in the precompetitive phase. Approximately 25% of the total funding is spent for applied research as part of development projects. Development funds have not been explicitly reported in this survey. The largest single-agency research expenditure is at NSF, about $65 million/year.

Current interest in NT is broad-based, and there are several common themes among all agencies. A main goal has been to obtain synthesis, processing, properties, and characterization of nanostructured materials, including high rate production of nanoparticles for potential industrial use; thermal spray processing and chemistry-based techniques for depositing multifunctional nanostructured coatings; processing of nanoscale powders into bulk structures and coatings; and researching superlattices and buckminsterfullerene. Nanofabrication with particular focus on the electronics industry is another major theme. This includes development of technologies offering improved speed, power density, and functionality beyond that achieved by simply scaling transistors. Other electronics-related research themes include operation at room temperature, use of quantum well electronic devices, and computational nanotechnology addressing physics- and chemistry-related issues in nanofabrication. Research on nanoscale materials for energy applications has had a focus on synthesis and processing of materials with controlled structures, surface passivation, and interface properties. The initially targeted energy-related applications include catalysts and soft magnets. Neural communication technology and biochip technology have been investigated for biochemical applications and sensor development. Metrology activities for thermal and mechanical properties, magnetism, and thermodynamics of nanostructures have been initiated. Nanoprobes to study nanometer material structures and devices with nanometer length and picosecond time resolution have been developed.

Future research will continue the miniaturization efforts by using established methods and principles to make big things small, and it is expected that most relevant industrial applications in the short term will come from this area. In the longer term, the approach of building up from molecules and nanoparticles, nanotubes, and nanolayers is more promising from the points of view of science, likelihood of innovations, and industrial relevance. Future research opportunities include development of an understanding of the physics and chemistry of the new properties and phenomena found at the nanometer scale; engineering of functional nanostructures from molecules and fine particles; establishment of measuring tools with improved sensitivity, time, and spatial resolution; and advances in the theory and in simulation techniques for systems in the range of 1 to 100 nm. Among targeted functional nanostructures are optoelectronic devices, multifunctional (smart, adaptive) coatings and three-dimensional engineered structures, semiconductor nanostructures for multispectral detector arrays, structures generated by chemistry self-assembly techniques, biomimetics, quantum control, and atom manipulation. Nanocomponents are envisaged for microdevices for sensing, information processing, and telemedicine. There will be a continued interest in low power nanoelectronics, miniaturization of spacecraft systems, carbon nanotube technology for producing nanogears and hydrogen storage, improved molecular beam epitaxy, and silicon-germanium-carbon-based devices in order to enable scaled silicon nanoelectronics. The potential of single-electron devices and molecular electronics will be explored.

The balance of this chapter contains brief reports from the participating U.S. government agencies.

Overview of Nanotechnology Research Sponsored by U.S. Agencies

- 12 participating agencies:
  AFOSR, ARO, BMDO, DARPA, DOC and NIST, DOE, NASA, NIH, NSF, ONR, and NRL
- Current interests:
  - synthesis, processing, properties, and characterization of nanostructured materials
  - nanofabrication with a focus on electronics
  - high rate production of nanoparticles and nanolayers
- Current support: Approx. $115 million/year in 1997/98
- Main research opportunities:
  - fundamental understanding of new properties and phenomena at nanometer scale
  - miniaturization in various areas
  - functional nanostructures (precursors, materials, components, devices)
  - combined chemical, physical, bio-processes

NATIONAL SCIENCE FOUNDATION ACTIVITIES IN NANOTECHNOLOGY

NSF OVERVIEW

Dr. M.C. Roco, National Science Foundation
Coordinator of the Nanotechnology Group

Previous NSF activities in nanotechnology have originated in the disciplinary programs throughout the Foundation, and also result from several relevant interdisciplinary initiatives:

- the Advanced Materials and Processing Program, which deals with generation, properties, and characterization of nanostructured materials
- the Ultrafine Particle Engineering initiative, which covers synthesis and processing of nanoparticles with controlled properties, with a focus on high rate production processes
- the National Nanofabrication Users Network (NNUN), which connects researchers and facilities at five universities to fabricate nanometer-scale structures, initially focused on miniaturization in the electronics industry
- an initiative on Instrument Development for Nano-Science and Engineering (NANO-95), which seeks to develop new instrumentation to advance atomic-scale measurements of molecules, clusters, nanoparticles, and nanostructured materials

A broad spectrum of individual or small-group projects in the areas of materials, chemistry, physics, electrical and chemical engineering, biosciences and bioengineering, computer science, and manufacturing have received support in the area of NT by competing in the disciplinary programs of the NSF Directorates for Mathematical and Physical Sciences (MPS), Engineering (ENG), Biosciences (BIO), and Computer and Information Sciences and Engineering (CISE). The 1997-8 level of NSF investment in nanotechnology research totals approximately $65 million, of which about $41 million is spent in MPS and about $20 million in ENG, with relatively lower expenditures in BIO and CISE.

Several NSF-supported centers in engineering (e.g., the Engineering Research Center on Microelectronics at the University of Illinois) and materials research (e.g., the Material Research Science and Engineering Center at Brown University) have plans targeted at nanosciences and nanotechnology. More detailed information concerning NSF NT activities can be found in the outlines of the NSF areas of support given in the following sections.

High-risk/high-gain research is sought in all aspects of nanosciences and nanotechnology. The “building-up” approach — from molecular and particle levels to nanostructured materials, nanocomponents, and nanodevices — is preferred. In order to succeed, this activity will require an interdisciplinary research and education endeavor. It is expected that the NSF Directorate for Education and Human Resources (EHR) will be also involved. The fundamental research opportunities may be grouped as follows:

- advanced generation and processing techniques to generate nanostructures with controlled properties, including chemistry and bio-self-assembly techniques, and artificially structured materials
- advanced methods to simulate structure growth dynamics and assembly processes at mesoscale
- stability, dynamic properties, and chaotic behavior of nanostructures
- methodologies to characterize nanoscale materials at atomic and molecular scales with increased sensitivity and spatial resolution, including instrumentation and nanosensors based on novel concepts and principles
- tools and concepts of quantum control and atom manipulation, including laser and atomic trapping techniques and optically generated waveguides
- theoretical and computational studies of how biological structures encode and utilize information
- new knowledge of computing systems architecture and nanoscale robotic systems
- novel health-care technologies
- use of cell biology and materials science for functional nanostructures

Previous NSF Activities in Nanoparticles/Nanostructures

- Advanced Materials and Processing Program (including nanostructures, molecular self-assembly, chem., etc.)
- Ultrafine Particle Engineering (synthesis at high rates)
- National Nanofabrication Users Network (a focus on electronics, extending MEMS top-down approach)
- Several other centers (ERC at U. of Ill, Particle Center at Penn State, MRSEC at Brown U., etc.); and individual projects
- Biosciences and Bioengineering projects
- NANO-95 (for instrumentation; increasing the success rate)
- Education opportunities (in centers, collaboration with industry; groups of young researchers to Japan and Europe)

NSF NANOPARTICLE SYNTHESIS AND PROCESSING

Dr. M.C. Roco
Engineering Directorate, NSF

Nanoparticles, including nano-clusters, -layers, -tubes, and self-assembled systems, are seen as precursors of nanostructured materials and devices with tailored properties. An initiative called “Ultrafine Particle Engineering” for new concepts and fundamental research on methods to generate nanoparticles at high rates started in 1991 in NSF’s Engineering Directorate in collaboration with the Directorate for Mathematical and Physical Sciences. The work has included contributions on fundamental physics and chemistry for generation of nanoparticles with engineered properties via aerosols, colloids, plasma, combustion, sol-gel, chemical vapor deposition, molecular and cluster assembling, and other synthesis methods. Emphasis has been placed on awards to small groups for multidisciplinary projects with a focus on fundamental research. The Ultrafine Particle Engineering initiative originated in NSF’s Chemical and Transport Systems Division in the particulate and multiphase processes area; it was developed in collaboration with various disciplinary programs such as “Ceramics, Metals, and Electronic Materials,” “Physical Chemistry,” and “Combustion and Plasmas”; and it has covered a variety of theoretical, process, and instrumentation aspects. NSF’s support was approximately $6 million/year in the last five years. Two review conferences were held in collaboration with NIST: the NSF-NIST conferences on Ultrafine Particle Engineering (1994, proceedings edited by M.C. Roco, R. Shull, and D.T. Shaw) and on Nanoparticles (1997, proceedings edited by D.T. Shaw, M.C. Roco, and R. Shull; both proceedings published by SUNY Buffalo and NSF).

Ultrafine particle engineering involves the synthesis and processing of nanometer-sized particles with controlled properties for applications in advanced materials such as ceramics, metals, optical structures, and semiconductors. Metals and ceramics produced by consolidating nanoparticles with controlled microstructures have been shown to exhibit properties substantially different from materials with coarse microstructures. New properties include greater hardness, higher yield strength, and ductility in ceramic materials. The band gap of nanometer-scale semiconductor structures increases as the size of the microstructure decreases, raising expectations for many possible optical and photonic applications. Novel applications have been proposed: laser ablation of materials to generate nanoparticles used in nanoelectronics; production of polymer semiconductor composites to develop nonlinear optics for waveguides; molecular and nanostructure self-assembly techniques for integrated circuits and chemical sensors; high performance catalysts; control of nanoparticles resulting from combustion and plasma processes; hypersonic plasma expansion for nanostructured coatings; and special sensors applied in chemical plants and the environment.

Future work aims to expand research on nanoparticle processing into nanostructured materials and devices, advanced simulation techniques at mesoscale, and novel instrumentation. NSF will emphasize support of scientific discoveries in generation of nanoparticles with controlled characteristics, research on particle processing into microstructured blocks with engineered properties, introduction of new principles of operation for devices, and development of new modeling and experimental tools.

"UTRAFINE PARTICLE ENGINEERING" INITIATIVE

GOAL:	**SYNTHESIS & PROCESSING OF NANOPARTICLES**
NICHE:	**PRODUCTION AT HIGH RATES; SPECIAL PROPERTIES**
RELEVANCE:	**ENGINEERED MICROSTRUCTURED MATERIALS**

EACH PROJECT HAS 3 CO-P.I.s FROM DIFFERENT DISCIPLINES

Examples

- Nanoparticle Formation Using a Plasma Expansion Process, U. MN
- Nanocrystalline Materials Prepared by Spark Erosion, UCSB
- Controlled Production of Nanoparticles Using Microemulsions, MIT
- Combustion Process for Nanosized Reinforced Composites, U. WA-SL
- High Volume Production Using Laser Ablation of Microparticles, UT
- Particle-particle and Particle-substrate Interactions, Purdue U.

Others

- Submicron Aerosol Agglomeration, UCLA
- Nanophase Composite Materials for Magnetic Refrigeration, SUNY-B
- Effect of Electric Fields in Nanoparticle Flame Reactors, U. Cincinnati

NSF ENGINEERING DIRECTORATE (ENG)

(M.C. Roco, R.P. Khosla, D. Crawford)

NSF/ENG Interest in Nanotechnology

Summarized by M.C. Roco for the ENG Nanotechnology Group

The Current ENG Base Support

NSF participation in NT is broad-based in all engineering disciplines. The participating Engineering Directorate (ENG) divisions — Electrical and Communications Systems (ECS); Chemical and Transport Systems (CTS); Design, Manufacture, and Industrial Innovation (DMII); Bioengineering and Environmental Systems (BES); and Civil and Mechanical Systems (CMS) — have identified NT as an area of future growth with interdisciplinary research opportunities. The annual expenditure in ENG will be approximately $20 million in 1997/1998 (FY '98). ECS and CMS have had a larger interest in the top-down approach (making big things small), including the ECS support for NNUN (see next section). This interest has primarily been driven by the potential advances in microelectronic and photonic components of reduced dimensions, as well generation of materials with higher mechanical and tribological properties. CTS and BES have a larger interest in the "building up" approach (from the molecular level to precursor nanoparticles and then to functional nanostructures). This work includes fundamental contributions on nanoparticles, nanolayers, and nanotubes; characterization and use of precursor nanostructures; and manufacturing processes for miniaturized devices and biosensors. DMII and CMS have a focus on nanofabrication of nanocomponents for MEMS and for coatings.

Research Opportunities

ENG is interested in promoting interdisciplinary research and education in the science and engineering of nanotechnology, and particularly in functional nanostructures. It is most likely that this will involve engineers, biologists, material scientists, chemists, and physicists. Selected examples of research areas suitable for study are as follows:

- Methods to generate and assemble nanoprecursors with controlled composition, size, and surface properties via aerosols, colloids, plasma, combustion, biomolecular macromolecular chemistry, templates, molecular and cluster assembling, sintering, etc.

  Nanostructure design includes innovative techniques for synthesis and processing of active and smart nanolayers and coatings with special properties; generation and assembly of clusters and nanoparticles into functional nanostructures; bio-assisted assembling techniques; nanostructures on surfaces and catalytic particles; monolayer membranes of single-molecule thickness that possess exquisite size and shape distinction characteristics, and ceramic membranes that are derived from biomimetic principles of hierarchical structures; polymers used as templates to confer specific nucleation patterns and generate novel pore structures for ceramic materials; self-assembling nanostructures that are formed by surfactants and polymers leading to novel separation media; block copolymers and hyperbranched and dendritic polymers assembled to higher order structures; and plasma processes that are used to modify particles and other surfaces in a controlled way.

- Physical, mathematical, chemical, and biological modeling and simulation techniques of structure growth dynamics and assembly processes at mesoscale, at length scales where the current theories in physics and chemistry at molecular level (less than 1 nm) and classical thermodynamic theories at macroscopic level (over 100 nm) do not hold: modeling of transport phenomena that account for various transport mechanisms across a diversity of length and time scales including 1 to 100 nm; simulation of hierarchical processing and prediction of nanostructure properties.

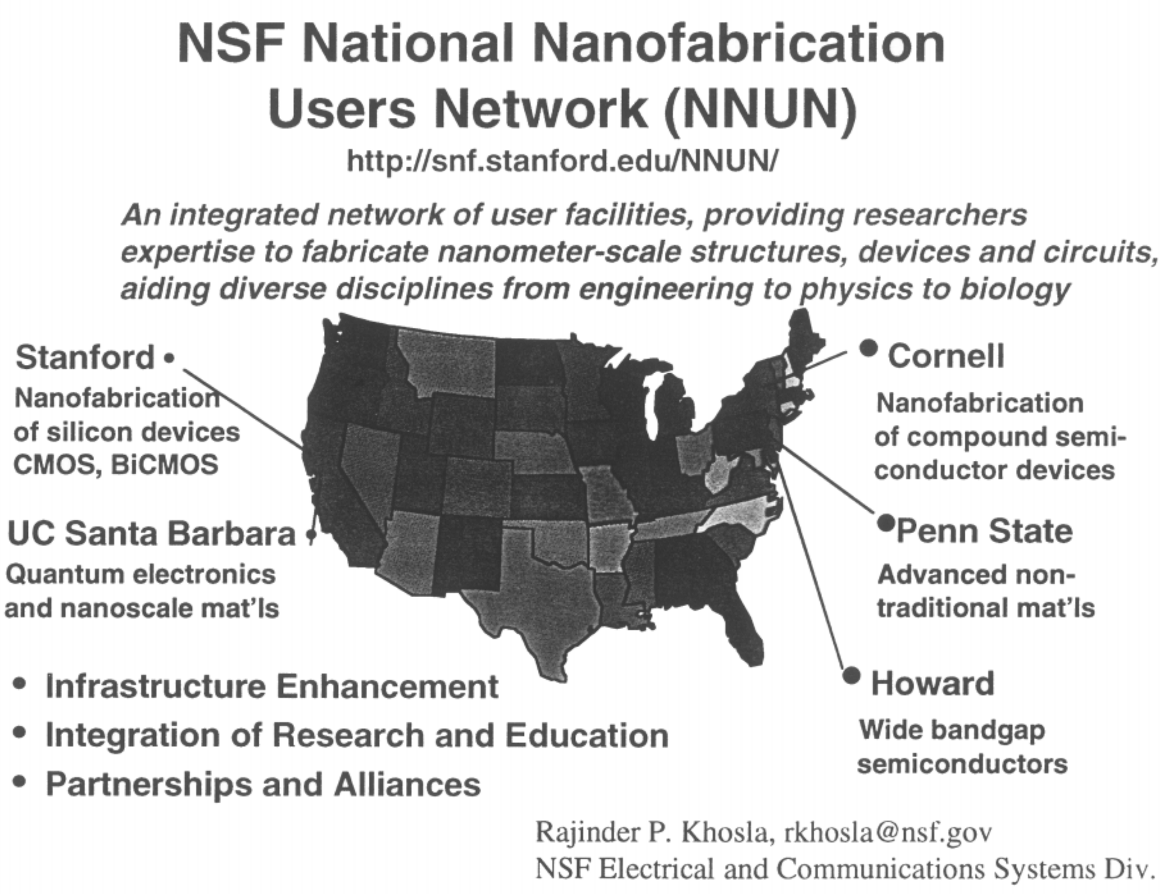
- Instrumentation and sensors based on novel concepts and principles: methods to measure thermophysical properties of submicron scale materials; sensors with nanometer-scale resolution and response time in the microsecond range; infrared detectors that can operate at room temperature; various chemical sensors and biosensors that employ thin film technology; on-line measuring techniques.

- Basic principles of processing techniques: transport (nanofluidics, thermal processing); mixing; separation; nanomechanics; bioseparation; nanosensors to analyze metabolic pathways, morphological, chemical, thermal, and biological stability of nanostructures; the effects of applied electrical and magnetic fields on phenomena at nano scale; and nanofabrication processes.

NSF National Nanofabrication Users Network (NNUN)

Dr. Rajinder P. Khosla
Program Director, NSF

NSF's National Nanofabrication Users Network (NNUN) is an integrated network of user facilities at Cornell University, Howard University, Pennsylvania State University, Stanford University, and the University of California at Santa Barbara that provides researchers with expertise to fabricate nanometer-scale structures, devices, and circuits, aiding diverse disciplines from engineering to materials to biology. NUNN is supported by the NSF Directorates of Biological Sciences, Engineering, and Mathematical and Physical Sciences. The projects span materials science, physics, chemistry, nanoelectronics, biology, biomedicine, and many other interdisciplinary areas. One of the fast-growing applications of micro- and nanostructures is in the area of biology. It is expected that the interaction and collaboration of these disciplines will have a significant impact in the area of nanotechnology. NNUN was started as a network in April 1994. The network's budget at this time is $3.95 million/year.



NSF National Nanofabrication Users Network (NNUN)

http://snf.stanford.edu/NNUN/

An integrated network of user facilities, providing researchers expertise to fabricate nanometer-scale structures, devices and circuits, aiding diverse disciplines from engineering to physics to biology

Stanford
Nanofabrication of silicon devices CMOS, BiCMOS

UC Santa Barbara
Quantum electronics and nanoscale mat'ls

Cornell
Nanofabrication of compound semi-conductor devices

Penn State
Advanced non-traditional mat'ls

Howard
Wide bandgap semiconductors

- Infrastructure Enhancement
- Integration of Research and Education
- Partnerships and Alliances

Rajinder P. Khosla, rkhosla@nsf.gov
NSF Electrical and Communications Systems Div.

NSF National Nanofabrication Users Network (NNUN)

- Supported by the Directorates of Biological Sciences, Engineering, and Mathematical and Physical Sciences.
- Projects span materials science, physics, chemistry, nanoelectronics, biology, biomedical, and other interdisciplinary areas.
- One of the fast growing applications of micro and nanostructures is in the area of biology: A workshop was held in the Fall of ’96 to identify emerging research opportunities in this growing area.
- Provides opportunities for researchers to turn new ideas in nanoscale science and technology into experimental reality.
- Network is committed to education, training, and technical outreach.
- Serves a broad and diverse engineering and scientific community in universities, industry, and government laboratories.

Sample Projects

- “Microchannels for Endothelial Cell Culture and Blood Flow Studies,” Morris, Univ. Of Rochester
- “Fabrication of High Sensitivity Cantilever Magnetometers,” Naughton, Tau Sensors
- “Torsional Oscillator Magnetometer Studies of Nanoscale Magnetic Particles,” Craighead, Cornell
- “SiN Mirror Scanners for a Miniature Microscope,” Kino, Stanford
- “Silicon Nanowires,” Boker, U.C. Berkeley
- “Scanning Electron Micrography of Carbon Nanotubes Deposited in Jet Fuel Combustion Processes,” Schobert, Penn. State; Atria, Wright Patterson AFB

Nanotechnology in ECS

Dr. D.L. Crawford
Program Director, NSF

The Electrical and Communications Systems (ECS) Division of NSF’s Engineering Directorate has invested significant resources in nanotechnology for some time. This interest has primarily been driven by the potential advances in microelectronic and photonics technologies brought about by using components and subsystems of reduced dimensions, which result in concomitant performance advantages in terms of reduced power consumption, increased speed of operation, and so on. In some cases, the development of completely new subcategories of the forementioned technologies with new performance capabilities have resulted, such as resonant tunneling diodes and quantum cascade lasers.

For the most part, however, the drive toward the nanometer dimension has been derived from the “brute force, making big things small” engineering of ultrasmall structures, through the use of advanced epitaxial growth and processing techniques. The ECS Division currently invests approximately $10 million in research and education activities that focus on the engineering of such structures; this includes a $2.2 million annual investment in the National Nanofabrication Users Network described above.

ECS would like to pursue an alternative approach to nanoscale engineering that is most relevant to the electrical and electronic engineering community; this would be a bottom-up approach to engineering these structures, and in some cases, might mirror the “self-assembly” models of biological systems. In order to succeed, this activity would require an interdisciplinary research and education endeavor.

NSF MATHEMATICAL AND PHYSICAL SCIENCES DIRECTORATE (MPS)

(B.A. MacDonald, J. Osteryoung, D. Caldwell, L. Inglehart)

Nanostructured Materials Research in the Division of Materials Research (DMR)

B.A. MacDonald
Division of Materials Research, MPS/NSF

The area of nanostructure science and technology is an extremely active one within the MPS Directorate’s Division of Materials Research (DMR). For the May 8 workshop we asked the program directors of the Individual Investigator Awards (IIA) and of the Materials Research Science and Engineering Centers (MRSECs) to examine their respective programs to list on-going nanoscience/technology activities and provide an estimate of the total funding directed towards these areas. The accompanying viewgraphs indicate that in FY 1996 DMR supported the nanoscience field with over $22.3 million, and that all of the division’s programs give broad support to this field.

Areas of nanoscience within the DMR programs include synthesis, fabrication, processing, structure analysis, characterization, properties, and applications. The Materials Theory Program handles theory, modeling, and simulation science for DMR and accordingly supports a broad range of theoretical work related to clusters, self-assembly, artificially-structured materials, and nanoproperties of materials. The experimental programs explore a variety of material forms, including clusters, nanoparticles, thin films, composites, coatings, and bulk structures. Associated synthesis and fabrication activities make use of a broad range of techniques available for creating and processing nanostructures.

Materials properties of interest include the electronic and photonic areas, superconducting materials, magnetic behavior, mechanical behavior, wear resistance, catalysis, and even potential drug-delivery systems, all of which excite a variety of potential applications. It is apparent that this broad range of nanostructured materials activities offers significant overlap between programs, permitting opportunities for joint support of grants between DMR activities and other parts of the Foundation.

Materials Research in MPS

Division of Materials Research (DMR)

- **IIA Program areas include**
    - Materials Theory
    - Condensed Matter Physics
    - Solid State Chemistry
    - Polymers
    - Metals
    - Electronic Materials
    - Ceramics
- **Materials Research S&E Centers**
- **National Facilities & Instrumentation**

DMR MATERIALS THEORY PROGRAM: NANOSTRUCTURED MATERIALS

- **Clusters and cluster-assembled materials**
- **Self-assembled materials**
- **Mesoscopic properties**
- **Artificially structured materials**
    - **Quantum dots, quantum wires, superlattices**
- **Atomistic simulations of materials properties**
- **Nano-properties of materials**

DMR COND. MAT. PHYSICS PROGRAM: NANOSTRUCTURED MATERIALS

- **Properties of nanoscale conductors, magnets, electron devices**
- **Quantum dots, wires, single electron- and high mobility electron devices, nanomagnets, arrays**
- **Fabrication**
    - **nanolithography, STM, step-edge growth**
- **Properties of interest: electrical, optical, magnetic**
- **Nanoscale physics**
    - **size quantization, e-e Coulomb interaction, localization, disorder, superconductivity; basis for nanoelectronics of the future.**

28 grants ($2.5M)

DMR SOLID STATE CHEMISTRY PROGRAM: NANOSTRUCTURED MATERIALS

- **New synthesis routes to nanostructured materials**
  - **SAMS, hydrothermal methods, molecular precursors**
  - **intercalation/inclusion**
- **Fundamental issues**
  - **synthetic control of particle size and distribution**
  - **chemical reactivity of systems**
  - **physical properties**
- **Applications**
  - **sensing and switching**
  - **high-density memory**
  - **catalysis**

DMR POLYMERS PROGRAM: NANOSTRUCTURED MATERIALS

- **Nanostructured materials - pervasive among polymers**
  - **block copolymers phase separate into structural domains of 20-50 nm size**
  - **crystalline polymers grown in lamellae of ~10 nm thickness**
- **Synthetic chemistry, dendrimers, nanoclusters, 2-D polymerization**
- **Self-assembly, supramolecular structures, LB multilayers, thin films**
- **Blends, copolymers, interfaces, adhesion, coatings**
- **Nanofabrication, processing, associative phenomena, modeling**
- **Electronic and photonic polymers (e.g., lithographic resists, waveguides, electro-optic materials)**
- **Biopolymers, membranes, drug-delivery systems**

DMR METALS RESEARCH PROGRAM: NANOSTRUCTURED MATERIALS

- **Mechanical behavior**
  - **strengthening mechanisms**
  - **superplasticity**
- **Magnetic behavior**
  - **carbon-coated magnetic particles**
  - **magnetic multilayers and networks**
- **Synthesis and phase transformations**
  - **film growth**
  - **stability**

16 grants/$1.7M

ELECTRONIC/PHOTONIC MAT. PROGRAM: NANOSTRUCTURED MATERIALS

- **Synthesis/Processing**
  - **techniques: MBE, MOCVD, CBE, SPE, CVD**
- **Strategies**
  - **facet growth and in-situ fabrication of Si-based nanostructures**
  - **nucleation and ordering processes**
  - **use of morphological transitions during strained layer epitaxial growth to create quantum-nanostructures**
  - **strain stabilized, self limiting growth of coherent Ge islands via Ge/Si heteroepitaxy**
  - **utilization of photochemical interactions to create and operate nanometer scale devices**
  - **composite materials containing gallium nitride and gallium nitride-aluminum nitride quantum dots in glass via non-hydrolytic gel**
  - **use of polynucleotide chains as templates for the fabrication of quantum dot structures of inorganic materials such as cadmium sulfide**

7 grants ($.9M)

- **Science & Tech. Center: Quantized electronic structures**
  - **UCSB STC ($2.9M)**

DMR CERAMIC MATERIALS PROGRAM: NANOSTRUCTURED MATERIALS

- **Processing**
  - **colloidal sol-gel processing**
  - **powder synthesis**
- **Properties**
  - **nanocomposites for electroceramic applications**
  - **controlled porosity materials**

5 grants/$0.6M

DMR MRSECS PROGRAM: NANOSTRUCTURED MATERIALS

High Surface Area Coatings

- **Swollen gels, quenched random systems**
  - **MIT ($400K)**
- **Complex fluids/drug delivery systems**
  - **UCSB ($300K)**
- **Thermal spray coatings**
  - **SUNY Stony Brook ($900K)**

3 centers ($1.6M)

DMR MRSECS PROGRAM : NANOSTRUCTURED MATERIALS

Consolidated Materials

- Granular materials, macroscopic motion
  - Chicago ($300K)
- Electronic films from nanoporous ceramics
  - Northwestern ($200K)

2 centers ($0.5M)

DMR MRSECS PROGRAM: NANOSTRUCTURED MATERIALS

High Surface Area Materials

- Nanoporous materials, fullerines, mesoporous ceramics, heterogeneous polymeric structures - UCSB ($900K)
- Ceramic oxide powders, catalytic membranes
  - Houston ($400K)
- Catalytic oxides (nanocrystalline cerium oxides)
  - MIT ($200K)
- Colloids and emulsions, engineered structures, liquid crystal emulsions - U. Penn ($400K)
- Ultra-low density polymers- U. Mass ($200K)

5 centers ($2.1M)

DMR MRSECS PROGRAM: NANOSTRUCTURED MATERIALS

Functional Electronic/Photonic Nanostructures

- Polymer/metal nanostructures, colloids - Chicago ($400K)
- Single electron devices - Cornell ($500K)
- Superconducting nanostructures - J. Hopkins ($300K)
- Single electron devices, lithography - Harvard ($400K)
- Nanoscale mass transport on surfaces- Maryland ($500K)
- Nanoscale biomembrane templates - U. Mass ($200K)
- Microphotonics, nanostructures polymers, semiconducto nanostructures - MIT ($800K)
- Optoelectronic polymers - Penn ($400K)
- 2-D electronic systems, organic thin films, quantum structures - Princeton (700K)
- Confined semiconductor electronic systems
  - Purdue ($600K)
- Nanoporous polymer films, optical polymer thin films
  - Stanford/IBM/UC Davis ($900K)
- Engineered semiconductor and superconductor nanostructures - Wisconsin ($500K)

12 centers ($6.2M)

DMR MRSECS PROGRAM: NANOSTRUCTURED MATERIALS

Functional Magnetic Nanostructures

- **Nanomagnetics, structure, synthesis,dispersion of particles - Alabama ($500K)**
- **Micromagnetics, read/write heads, GMR, single domain nanoparticles, nanoprobe characterization**
  - **UC-San Diego ($900K)**
- **Nanoparticles, 2-D systems, nanowires, dots**
  - **J. Hopkins ($800K)**
- **Colloidal magneto-resistance effect of reduced dimensionality - Maryland ($500K)**
- **GMR - Michigan State ($200K)**

5 centers ($2.9M)

Chemistry (CHE/MPS) Division Investment in Nanoscience

Janet Osteryoung, Division Director
Division of Chemistry, MPS/NSF

The Chemistry Division of NSF's Mathematical and Physicals Sciences (MPS) Directorate invests about $18 million per year in projects involving the synthesis or characterization of nanostructures and the development of methods for application to nanoscience. These activities span all programmatic areas of the division and range from theoretical investigations to advanced applications.

Work on theory of atomic and molecular clusters includes their dynamic properties, their chaotic and ergotic behavior, the relationship between cluster topography and potential energy surfaces, and electron correlation calculations for clusters composed of three- and four-valence electron atoms. Synthetic efforts include work on chemical vapor deposition, sol-gel chemistry, micromachining, patterned metallization, and patterned, catalyzed polymerization. Development work on techniques and methods for characterizing nanostructures is being carried out in near-field optical spectroscopy, atomic force and scanning tunneling microscopy, and laser microprobe techniques. The following are examples of active nanoscience research projects funded by NSF's Chemistry Division:

- Andrew Hamilton (University of Pittsburgh)
  control of molecular self-assembly through hydrogen bonding
- David Walba (University of Colorado at Boulder)
  synthesis and characterization of ferroelectric liquid crystals
- Eileen Spain (Occidental College)
  deposition of inorganic thin films on chemically modified surfaces by pulsed laser evaporation
- George Whitesides (Harvard University)
  molecular self-assembly based on networks of hydrogen bonds
- Ingrid Fritsch (University of Arkansas)
  fabrication, characterization, and stability of organic thin films suspended across microfabricated structures
- Richard McCullogh (Carnegie Mellon University)
  development of self-assembling conducting oligomers and polymer superstructures
- Joseph Lauher and Frank Fowle (SUNY at Stony Brook)
  strategies for the preparation of designed supramolecular structures

Division of Physics Activities in Nanotechnology

Denise Caldwell
Division of Physics (PHY), MPS/NSF

As nanostructures continue to become increasingly small in size, they approach a limit at which their behavior may become atomic in character, and study of the nanostructure then falls into the arena of basic atomic, molecular, and optical (AMO) physics. Until recently, research in AMO physics centered on the interpretation of the internal structure and dynamics of atoms and molecules through application of the fundamentals of quantum mechanics. However, the past few years have witnessed a major change in this emphasis, brought about by experiments made possible by technological breakthroughs in laser and atomic trapping technology. In this new generation of experiment, the translational motion of the free atom is determined by quantum mechanical, not classical, considerations. Out of this new regime have grown the tools and concepts of quantum control and atom manipulation. Application of these principles has led to advances in both the understanding of basic atomic and molecular physics and the underlying principles of quantum mechanics, and to an increasing number of potential applications.

In the optical fields generated by ultrastable, ultrahigh-resolution laser systems, individual atoms can be cooled, captured, and positioned with incredible precision. Examples of the impact of these control techniques increase in number regularly. Nanowires ten times smaller than the smallest feature on a computer chip are constructed by dropping cold atoms onto a laser field at the surface of a crystal. Atoms are guided through an optically generated waveguide and deposited at predetermined locations on a surface. Interferometers based on atomic matter waves are the new tools for testing fundamental quantum measurement principles appropriate to the quantum behavior of extremely small structures. Laser beams are used as tweezers to stretch and position polymers. Coherent matter waves emerging from atom lasers probe the limits of quantum statistics and offer possibilities for new sources for atom manipulators fashioned from laser beams. And trapped ions are one scheme that points the way to a possible realization of the quantum computer. About $2 million is invested in activities related to these topics in PHY/MPS, roughly 10% of the total AMO physics budget.

NSF NANO-95 for Instrumentation: Instrument Development for Nano Science and Engineering

L.J. Inglehart
Program Director, National Facilities and Instrumentation, Division of Materials Research, NSF

This presentation focuses on a special NSF-wide program initiated in 1995 to address a need, in the area emphasizing atomic-scale capability, for higher-risk proposals with no anticipated product. The NANO-95 program was devised by three directorates at NSF (Engineering, Biology, and Math and Physical Sciences) to seek proposals for the development of new instruments leading to new discoveries and for the advancement of atomic-scale measurements of atoms, clusters, nanoparticles, and nanostructured materials. The intent of the program is to impact the areas of manufacturing, synthesis, and fabrication on the nanometer scale, and to complement computational efforts. The results of the program included funding of seven proposals for a total of $2,625,334. Projects supported included two in the area of biology, two in the area of engineering, and three in the area of materials science; three of the seven projects were cofunded.

NANO 95

- Multidisciplinary cross-Directorate activity (MPS, ENG, BIO)
- Coordinated by DMR with 6 NSF programs
- Support for research leading to development of instruments important for nanoscience and engineering
- Program announcement with March 17, 1995 deadline
- 39 proposals received by NSF (24 DMR)
- NSF-wide panel organized by DMR
- 18% success rate (NSF-wide)

NANO 95

($2,625,334)

BIR	
Schmidt/U. Mich. $359,154	Scanning Laser Force Microscope with Nanometer Resolution for Dynamic Imaging of Single Biomolecules under Physiological Conditions
Roukes/CIT $245,072	Nanofabricated Devices for Picoliter-Scale Analyses of Embryonic Gene Regulation
ECS	
Quate/Stanford $330,000	Scanned Probe Lithography for Nanostructures
CTS/DMR	
Andres/Purdue $450,000	Cluster-Based Probes for Nanostructure Analysis
DMR/CHE	
Chiang/UC-Davis $310,000	Development of a Variable Temperature Ultrahigh Vacuum (UHV) Scanning Tunneling Microscope (STM)/Atomic Force Microscope (AFM)
DMR	
Boland/UNC $186,380	Development of a Dual-Probe STM for Investigating Nanoscale Materials and Devices
DMR/CTS/DMII/OMA	
Smalley/Rice $744,728	Fullerene Nanoprobes

NSF BIOSCIENCES AND ENGINEERING/BIOENGINEERING

(K. Koehler, G. Vermont, G. Devey)

BIO Directorate Support of Nanotechnology

K. Koehler
Directorate for Biosciences (BIO), NSF

Programs in the BIO Directorate at NSF support nanotechnologies both directly and indirectly, with a total of approximately $1.5 million. Direct support involves approaches to the imaging and characterization of biological structures: utilization of nanofabricated electrode arrays, microchannel structures for separations and detection, atomic force microscopies, near-field spectroscopies, and microlithographed nuclear magnetic resonance (NMR) coil structures, to name only a few. In addition to direct support of such studies, the Division of Biological Infrastructure supports NNUN.

Indirect support involves the potential generalization of characterized biological structures and the assembly rules derived from them to directed assembly of nonbiological structures. Such support is at present limited and would be reflected in increased joint review and funding with the MPS Directorate.

Understanding biological self-assembly, and hence more general aspects of self-assembly, involves correlation of structure with functional properties such as association behavior, generally in an aqueous environment. BIO supports the acquisition and development of methodology to characterize interacting macromolecules (and more general binding processes). Some examples include analytical ultracentrifugation, biosensor approaches (BIAcore, etc.), optical scattering, and spectroscopic approaches.

BIO as well as programs in MPS support theoretical and computational studies of the way in which biological structures encode and utilize information.

Current Areas

- Nanoforces
  - optical traps, tweezers, pokers
  - force microscopes
- Nanodetection
  - single molecule spectroscopy
  - single spin detection
  - analysis in nanoliter volumes
  - nmr micro-coils
  - nanoscale electrode arrays/chemical sensors
  - chemical analysis of single cells
  - chemical probes of nanostructures
- Computational Problems
  - large-scale structures
  - various time-scales
- Quantitation of Interactions

Biology at NSF and Nanotechnology

BIOLOGICAL SYSTEMS:

Basic Characteristics

Physical Analysis

Molecular Biological Analysis

Theoretical Analysis

Basic Characteristics of Biological Systems

- Self-Assembly
- Temporal Adaptivity
- Structural Adaptivity
  - cytoskeleton
  - molecular motors
  - muscle contraction (mechanochemical transduction)

Physical Analysis of Biological Systems

- Measurement of forces involving nanostructures and single molecules
  - Near-field optical spectroscopy
  - Raman spectroscopy using small metal clusters
  - force microscopies
- Structure determination of ensembles
  - NMR, X-ray, everything
- Use of oligonucleotide arrays for gene analysis

Molecular Biological Analysis of Biological Systems

- Mutational Effects on Self-Assembly

Theoretical Analysis of Biological Systems

- Computations (molecular dynamics, etc.) of the structure of macromolecules, their intermolecular interactions with solvent, ions, and other small and large molecules
  - (electrostatic funnels)
- Macromolecule: membrane interactions

Nanotechnology in Bioengineering

George Vermont
Bioengineering and Environmental Systems Division, Directorate for Engineering, NSF

All of the bioengineering programs could be considered to be operating on a molecular or cellular "nano" scale. However, for purposes of this discussion I will use the much narrower definition of fabricated nanostructures or nanodevices.

Using that tighter definition, Bioengineering is supporting approximately $500,000 of nanotechnology programs. Two examples are the work of Frances Arnold at Cal Tech and that of Bruce Locke at Florida State. Dr. Arnold ($162,000, 1997) is using simple sugar complexes to template specific-sized holes in heavily cross-linked polymers. The polymer network then serves as a selective detection system for these sugars. Using such technology, an accurate glucose monitor has been developed. Likewise, Dr. Locke ($148,000, 1997) is using rigid oligonucleoside chains to create specific pore dimensions in separation gels. These gel membranes provide very selective separation media. Both processes depend on using molecular species to form specific-sized holes in polymeric networks and then removing the template material by washing in solubilizing solutions.

One area that might profit from additional funds is the development of micro/nano sensors to analyze and elucidate the metabolic pathways within individual microbial and mammalian cells. This need was highlighted at the international conference held in Danvers, MA, 6-11 October 1996, "Recombinant DNA Biotechnology: Focus on Metabolic Engineering."

BIOENGINEERING AND ENVIRONMENTAL SYSTEMS DIVISION (ENG DIRECTORATE)

- Biomedical Engineering
- Biochemical Engineering
- Biotechnology (engineering/life science interdisciplinary)

Biotechnology

- SENSOR AND DETECTOR TECHNOLOGY
  - glucose sensors involving structured environment
- SEPARATIONS TECHNOLOGY
  - nanostructured hydrogels for separations
- SMALL VOLUME ANALYTICAL METHODS
- BIOLOGICAL TRANSFORMATIONS
  - control of metabolism
  - generation of new materials and nanostructures
  - turning peas into beans

Nano-Structured Hydrogels for Macromolecular Separations

Bruce R. Locke
Florida State University

Hydrogels useful for electrophoretic or chromatographic separations are synthesized with approximately 2 - 10 nm channels.

<u>EXAMPLE</u>

Polymerizing acrylamide and a diacrylamide around water soluble rigid, liquid crystal polyanion rods of NDA or xanthan polysaccharide as templates

A Glucose-Sensing Polymer

Guohua Chen, Zhibin Guan,[1] Chao-Tsen Chen,[2] Litian Fu,
Vidyasankar Sundaresan, and Frances H. Arnold*

Division of Chemistry and Chemical Engineering 210-41, California Institute of Technology, Pasadena, CA 91125
[1]Division of Materials Sciences, DuPont Central Research, Experimental Station, Bldg. 328, Wilmington, DE 19880
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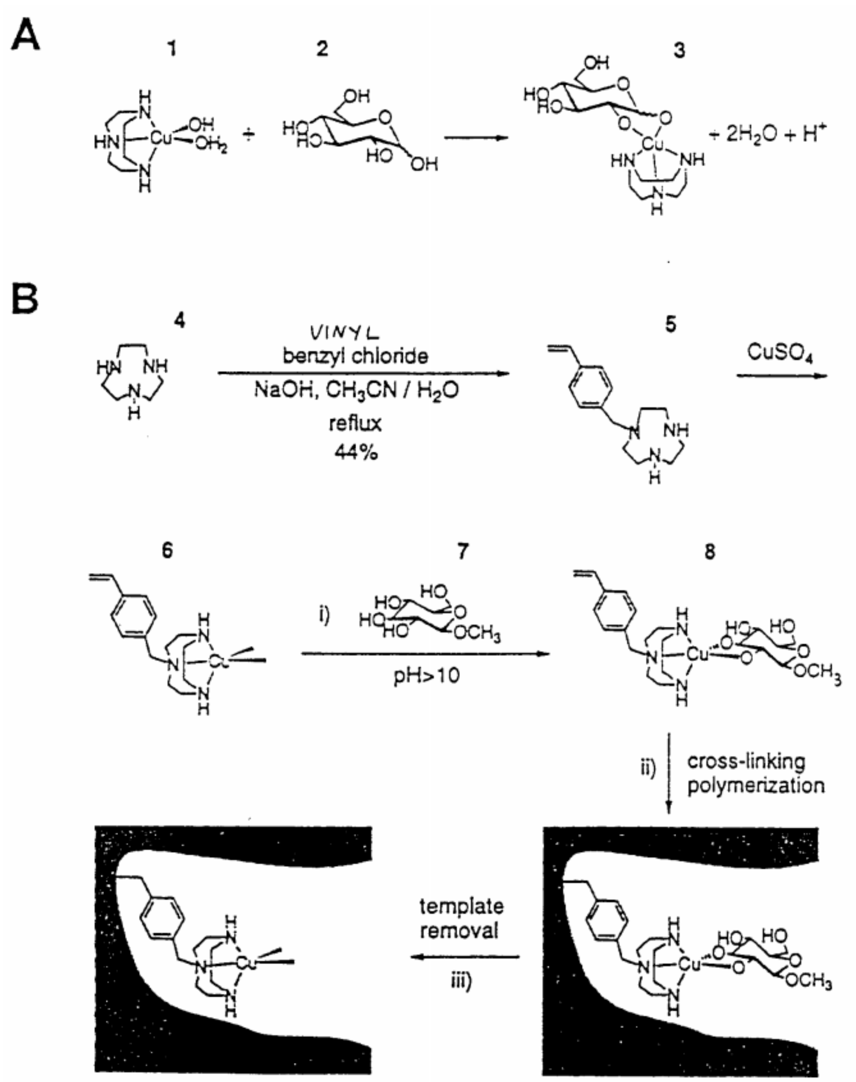


(A) Glucose binding to the TACN-Cu^{2-}complex (1) at alkaline pH results in the release of protons.
(B) Preparation of a glucose-sensing polymer by molecular imprinting with methyl-β-b-glucopyranoside.

Biomedical Engineering and Research to Aid Persons with Disabilities (BERAPD)

Gilbert B. Devey
Bioengineering and Environmental Systems Division (BES), ENG/NSF

No research is currently supported by the BERAPD program that meets the description of nanotechnology as employed in the WTEC study. The program does support biomedical research where smaller and smaller tools (sensors, manipulators, imaging devices, surgical instruments) are required. The following awards illustrate the BES focus:

1. BES 9158507. Presidential Young Investigators Award (Response of cartilage to external mechanical forces). Development of microtools. Martha Gray, Massachusetts Institute of Technology.
2. BES 9501793. CAREER Award (Microsystems for least-invasive medicine). Michael C. Murphy, Louisiana State University.
3. BES 9520501. Cost-Reducing Health Care Technology Award (Image-guided percutaneous robotic assisted therapy). James H. Anderson, Johns Hopkins University.
4. BES 9632962. Efficacy of a neural interface for limb prosthesis (micro sensor and coaxial cable). Michael Zanakis, New York Institute of Technology.
5. BES 9509758. Design and evaluation of artificial retina device to benefit visually impaired. Wental Liu, North Carolina State University.
6. BES 9521719. International workshop: Robotics and computer-assisted medical interventions. Takeo Kanade, Carnegie Mellon University.

Results from the International Workshop (#6 above) were especially useful for our program planning in this area. The BERAPD Program has taken a first step toward encouraging activities in nanotechnology by indicating it as an area of specific interest in the new program brochure, “Exploratory investigations of nanoscale and microscale biological, chemical, and physical phenomena for the development of new health care technologies for minimally invasive applications in medical diagnosis and therapy.”

NSF COMPUTER AND INFORMATION SCIENCE AND ENGINEERING DIRECTORATE (CISE)

M.J. Foster
Division of Microelectronic Information Processing Systems (MIPS), NSF

The CISE Experimental Systems program supports research projects that involve building, evaluating, and experimenting with an information-processing system. These are goal-oriented projects undertaken by teams of designers, builders, and users. The building of the system must itself represent a major intellectual effort, and offer advances in our understanding of information systems architecture. A system supported by the Experimental Systems program will usually include both hardware and software components.

Within this context, CISE currently supports some research in the nanotechnology area. Topics of current interest include biomolecular computing, quantum computation, and the scaling of MEMS systems to smaller dimensions. Our hope is that exploration of these new technologies can provide new knowledge of computing systems architecture and open up new application areas.

The level of funding for nanotechnologies in CISE is about $1.5 million/year. Most of this is in biomolecular computing. Other support for nanotechnology research can be found in the Theory of Computation program, managed by Zeke Zalcstein.

THE OFFICE OF NAVAL RESEARCH MATERIALS DIVISION FUNDING OF R&D ON NANOSTRUCTURED MATERIALS

L. Kabacoff
ONR Materials Division (ONR 332)

The Materials Division of the Office of Naval Research (ONR) has funded research on the synthesis and processing of nanostructured materials for nearly a decade. For most of that time, the primary focus has been on chemical routes to synthesis of nanoscale powder, including the spray conversion process that has now been fully commercialized. With the advent of a large number of viable synthesis techniques and considerable progress in commercialization, funding was shifted to the processing of nanoscale powder into bulk structures and coatings. These structures and coatings may be of interest because of the processing advantages of using nanoscale powder (and may or may not be nanostructured in final form), or may exhibit some outstanding property made possible by an ultrafine microstructure, such as hardness or wear resistance. At the current time, research and development efforts are geared toward materials of interest because of their mechanical properties (including thermal barrier coatings), with little (but not zero) work on optical, electronic, or magnetic materials. In addition, all funding is directed toward three-dimensional nanostructured materials (i.e., no fibers or multilayers), a restriction based on fiscal limitations rather than lack of interest. The current annual level of funding is $3 million.

The largest portion of ONR funding in this area goes to thermal spray processing of nanostructured coatings. This is an integrated program encompassing basic and applied research as well as prototype development and technology insertion. Most of the work is being performed by two large consortia, one concentrating on alloys and cermets, the other on ceramics. The work includes process modeling and process diagnostics (leading to real time process control); fundamental studies of wear, toughness, and corrosion; structure property relationships; and product development. Other ONR-funded efforts include processing of bulk non-oxide ceramics (e.g., AlN), fundamental studies of deformation in hard nanostructured composites, and processing of Al- and Ni-based alloys by cryomilling.

A significant research program is being carried out at the Naval Research Laboratory (NRL), partly funded by NRL internal funding and partly by ONR. This effort emphasizes technological and economical aspects of solution chemistry-based techniques for depositing multilayered, nanostructured metallic, ceramic, and composite coatings with enhanced properties. There is an additional emphasis on multifunctional (smart) coatings and on replacement of environmentally unacceptable coating techniques such as chrome plating.

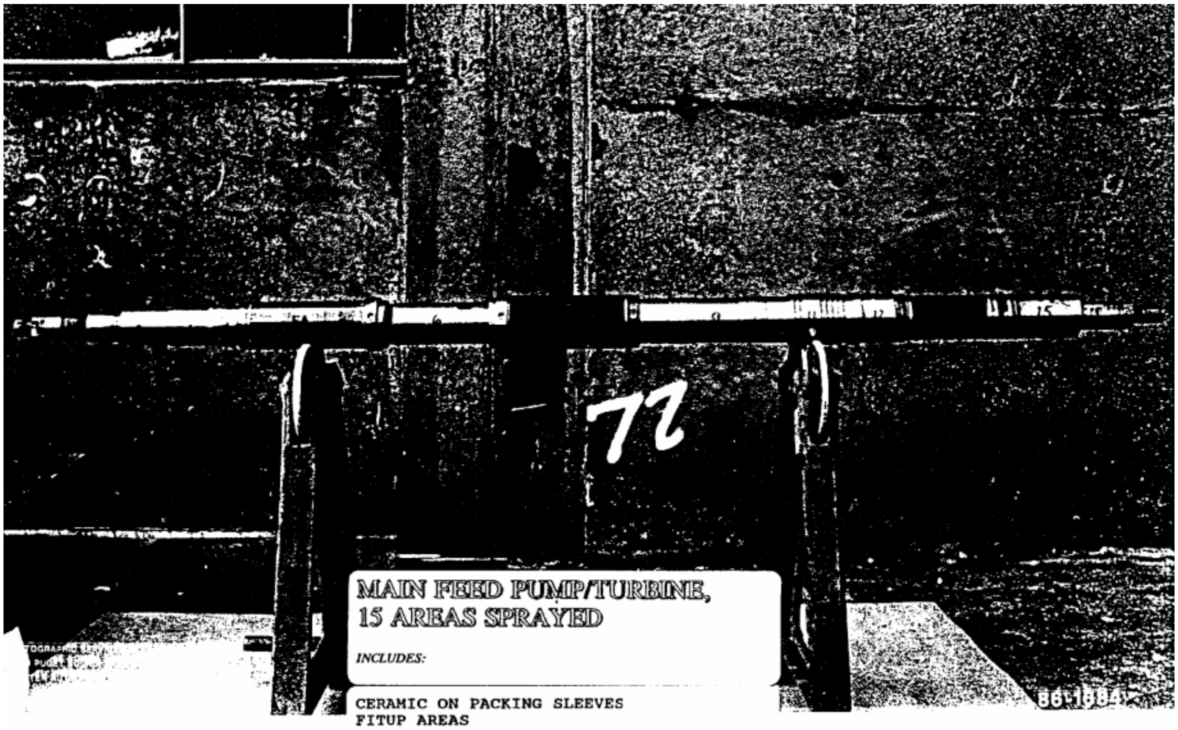
The Materials Division will spend approximately $3 million on nanostructured materials in FY98, a little less in FY99. There is no MURI (multidisciplinary research initiative) component to this ONR program.

Areas of Current Interest

- Processing of Bulk Non-oxide Ceramics from n-Powder Precursors
  - Elimination of sintering aids
  - Enhanced Properties of “coarse material”
- Thermal Spray Processing of n-Materials
- Processing/Structure/Properties Relations

Desired Information

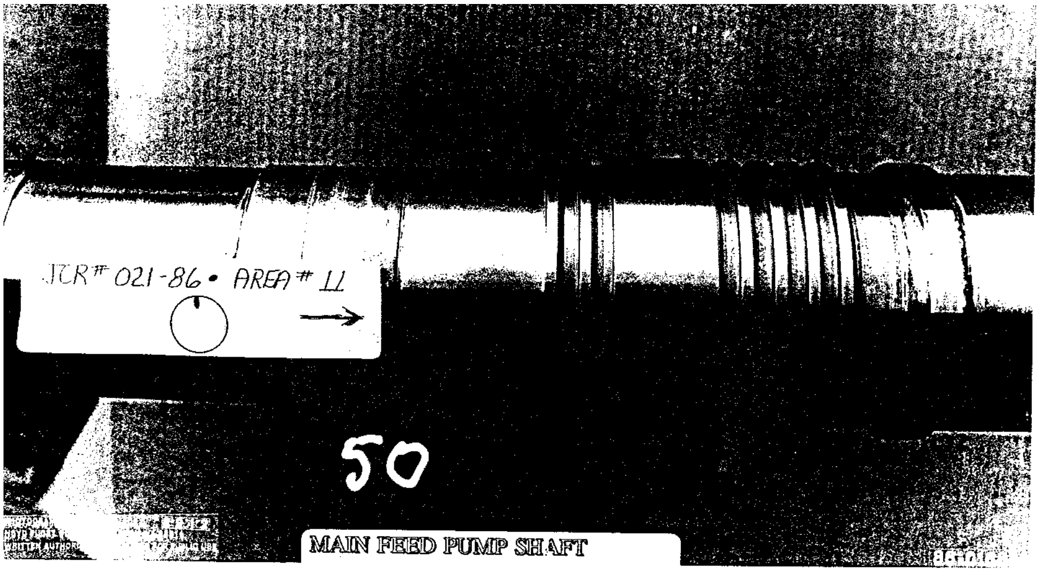
- Level of Activity (Who, What, Where)
- Recent or Potential Breakthroughs
- Commercialization
  - Near term
  - Long Term
- Applications (Is anyone using, or planning to use, this stuff?)



MAIN FEED PUMP/TURBINE,
15 AREAS SPRAYED

INCLUDES:

CERAMIC ON PACKING SLEEVES
FITUP AREAS
BEARING JOURNALS
LABYRINTH SEAL
CARBON SEAL (CERAMIC SPRAYED)



MAIN FEED PUMP SHAFT

LABYRINTH SEAL (CLOSEUP)

MICRO AND NANO ENGINEERING AT THE DEPARTMENT OF ENERGY

R. Goulard
Office of Basic Energy Sciences, DOE

The DOE Office of Basic Energy Sciences (BES) comprises four divisions:

1. Material Sciences ($302 million)
2. Chemical Sciences ($156 million)
3. Energy Biosciences ($25 million)
4. Engineering and Geosciences ($16 million and $20 million, respectively)

The numbers in parentheses are the total operating expenses for each division in Fiscal Year 97, for a grand total of $519 million for BES. It is apparent that energy engineering research is only 3% of BES expenditures. Moreover, the other divisions have traditionally conducted a large part of their research on basic processes involving individual atoms, ions, and molecules in free flight or distributed on a surface; in many cases, these processes are nanometer-scale events. In contrast, engineering research has only recently been involved in sizes small enough that their relevant properties cannot be defined as a statistical average; hence, phenomenological laws are still a dominant feature of engineering research. For these two reasons, the current DOE effort to understand nanostructures is largely conducted in the first three science divisions listed above.

Current Micro and Nano Research in Engineering

The history of technological advances is based on the need to produce devices that can perform a certain function in an optimum way in the context of some unavoidable constraints. Cost is often paramount; so are weight and dimensions. In some instances, large sizes are beneficial (e.g., economy of size in boilers, gas turbines, etc.), but in a number of cases, the trend towards smaller (and thus lighter) devices has accelerated. In particular, electronic chips have been steadily downsized to reduce the electron flight times and thus improve the speed of computer calculations. This has given birth to very efficient lithographic technologies; these, in turn, have led to microscale devices (cantilever beams, motors, burners) in the range between 1 mm and 1 micron. It has also made possible the design of sensors that can measure a range of microsize features inaccessible until recently (atomic force microscopy), and hopefully to control them. The engineering community is very involved with this upsurge of microelectricalmechanical systems (MEMS) technologies (there were 19 sessions on the subject at the Winter 96 ASME annual meeting!).

Another, newer thrust is the growing interest in quantum effects that appear at the next lower scale of events, from 1 micron to 1 nm, the so-called “nanophase.” As mentioned above, these have been studied extensively in pure science-oriented research, that is, often in idealized conditions. In engineering applications, additional concerns are emphasized:

1. the ability to represent phenomena that are likely to play a necessary part in an engineering device
2. the ability to include a range of properties likely to be found in a realistic environment (ambient temperatures, complex geometries)
3. the potential for manufacturing in quantity and at low cost

Projected Research at DOE/BES/Engineering

As mentioned earlier, the BES Engineering Division has a commitment to elucidate phenomena that are likely to become a factor in the operation of future technological devices. As a typical example, the study of multiphase flows has led to a thorough examination of boiling processes, with their variety of interfaces and associated dynamics (bubbles, droplets, slugs, etc.). This decade-long pursuit has led to increasingly lower scales: bubble generation in microcavities (Oregon State University), microsized pipes in heat transmission

(Purdue University), and micron range phenomena near condensing surfaces. Similarly, research in suspensions has led to the study of diagnostics of microsized particulates (University of Minnesota). Very short time signals are also investigated in connection with fluxes through ultrathin materials (University of California, Berkeley). In the nano range itself, laser sources and two-dimensional electron waveguides are being explored (University of Texas, Austin).

Conclusion

Microengineering and nanoengineering research at BES has evolved out of other programs, and is not the result of the sudden creation of a large nanostructures program. This trend towards the phenomenology of smaller scales is likely to amplify in coming years. In addition, it should be kept in mind that a large amount of new nanoscale knowledge keeps being produced in the "pure sciences" divisions of BES, especially in the materials division.

An example of the extensive involvement of the materials division in nanostructure research is the multilaboratory project titled "Nanoscale Materials for Energy Applications," funded at over $7 million in FY 95. The project is one of the focuses of the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials; its activities are discussed throughout the annual report *Materials Sciences Programs FY 95* (DOE/ER-0682, May 1996), and its goals are summarized on p. 95:

> …Consistent with what are believed to be the most pressing needs to advance and utilize this new area of materials science, the project consists of three closely related tasks:
>
> – synthesis and processing for controlled size,
> – surface passivation and interface properties, and
> – interconnections and assemblies.
>
> Metal, semiconductor and outside clusters are of interest, and the synthesis routes being pursued include inverse micelles, arrested precipitation, ball milling, colloidal dispersions, ion implantation, gas condensation, sputtering and sol-gel methods. Initial targeted applications are catalysis, optoelectronics and soft magnets.

U.S. ARMY RESEARCH OFFICE ACTIVITIES IN NANOTECHNOLOGY

Michael A. Stroscio
Senior Research Scientist (ST), Office of the Director, U.S. Army Research Office

U.S. Army Research Office (ARO) programs and highlights may be summarized as follows:

- ARO was established in 1951 on the Duke University campus and has remained in the Research Triangle Park area for forty-six years
- ARO has funded research leading to eight separate Nobel Prizes shared by twelve Nobel Laureates
- Several of these Nobel Prizes were awarded for seminal topics in the field of nanotechnology; these include superlattices and buckminsterfullerene
- Today ARO participates in DOD-wide thrusts on Scientific Research Initiatives (SROs)

SROs of particular relevance to nanotechnology are

- nanoscience
- biomimetics
- smart Structures
- compact power sources

The ARO funding in the areas of nanoscience, biomimetics, and smart structures is about $15 million a year. In addition to that, the OSD funds research centers: the university research initiative centers and the multidisciplinary research initiative centers, the so-called MURI centers.

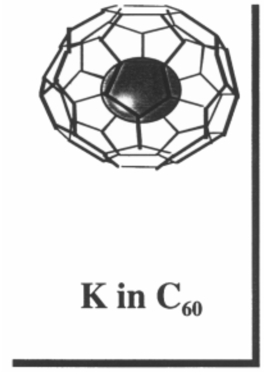
Army needs in the area of nanotechnology include the following:

- lightweight, strong materials
- smart, adaptive structures
- microdevices for sensing, situational awareness, information processing
- microdevices for telemedicine

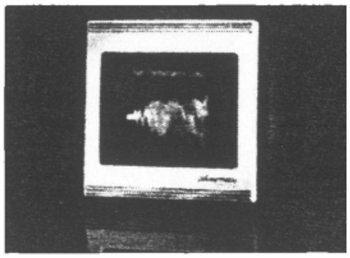
The Army is interested in these things for a lot of reasons, for example, to improve situational awareness — how do you keep the soldiers from being killed? One important factor is for the soldier to know his location, so the Global Positioning System (GPS) is important, microsensors are important, as are chemical and biological detection sensors; many concepts based on unattended ground sensors are key for situational awareness. The idea of miniaturizing power sources is critical. Nanotechnology has a lot to offer there. Higher functionality, smaller mass, and smaller volume are among the advantages ARO seeks from nanotechnology.

Historical Background

- Significant Accomplishments
  - **Nobel Prizes**
    - Semiconductor Engineering (Esaski)
    - Superconductivity (Bardeen, Cooper, Schrieffer)
    - Ion Traps (Dehmelt)
    - Fullerenes (Smalley)
  - **Engineering Feats**
    - Electronic Circuit CAD (Dutton)
    - Photonic Band Engineering (Yablonovitch)
    - Atom Laser (Ketterle)



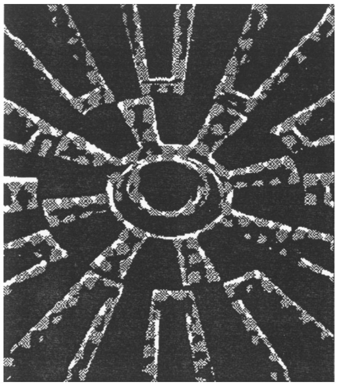
DOD Relevance



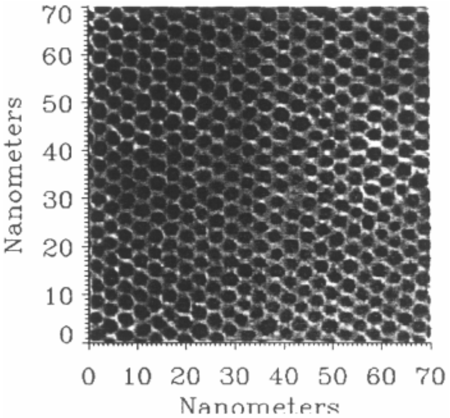
- **Present military applications**
  - Smart weapons
  - Command, control, & communications
  - Agent detection and remediation
- **Dual-use applications**
  - Microprocessors
  - Displays
  - High bandwidth communications
  - Miniature power sources

DOD Relevance

- Future military applications
  - **More functionality per unit weight or volume**
    - low-power, efficient, and cheaper electronics
    - faster processors and denser memories
    - design and analysis of new materials and devices
  - **New functionalities**
    - optical, chemical, and biological sensors
    - dramatically improved wargaming, deployment, and logistics
    - IR low observables and optical limiters



Building Materials from the Ground Up



Self-assembled gold cluster array

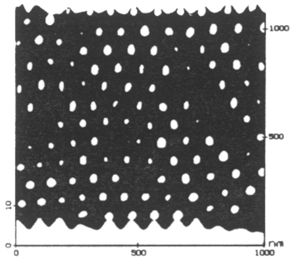
- **Current Fabrication Techniques**
  - Chisel silicon
  - Expensive, ultraclean
- **New Fabrication Techniques**
  - Build atom-by-atom
  - Self-assembly
  - Low-cost and fast

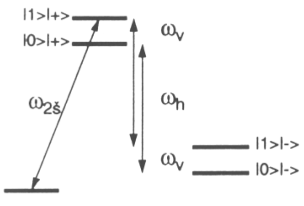
Major Army S&T Areas

- Army Nanoscience Investment Unique
  - **Quantum Mechanics**
    - New functionalities
  - **Nanostructures**
    - Build "from the ground up"
  - **Dynamic nanoanalysis**
    - Understand the science
  - **Engineer the flow of light**
    - Control propagation

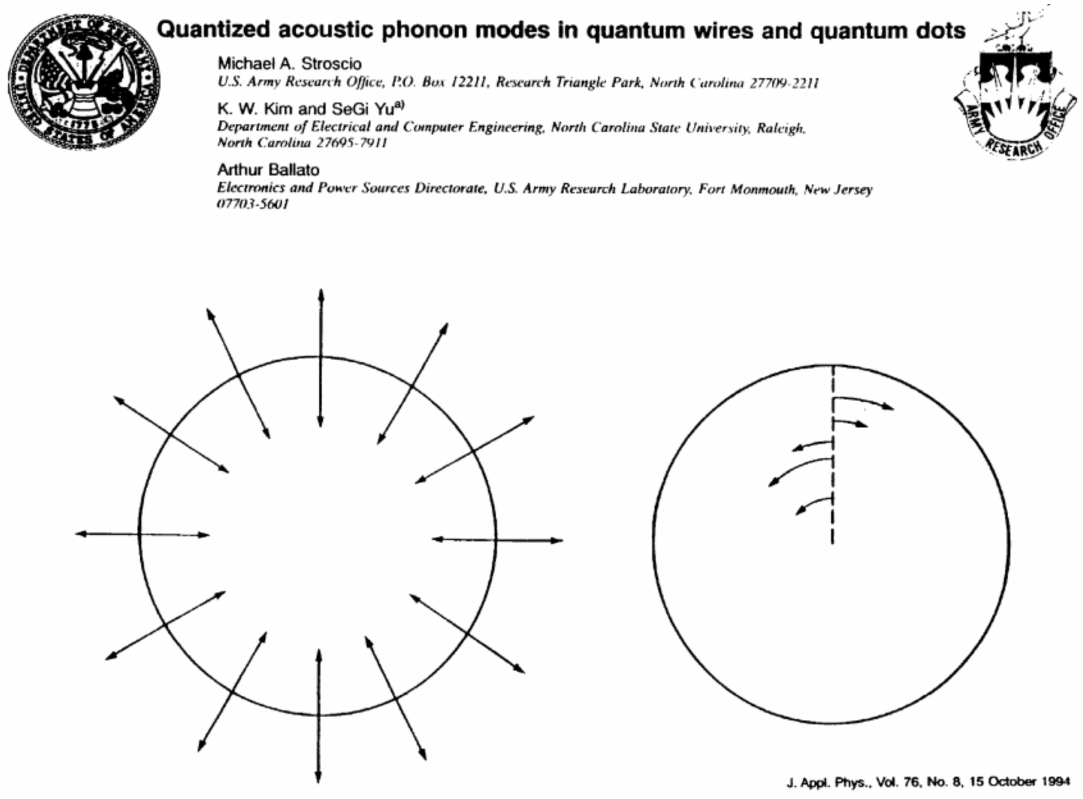
Challenges

- Nanofabrication
  - Small (< 0.1 μm) structures
  - Defect and interface engineering
  - Self-assembly of complex structures
- Quantum Mechanical Control
  - Matter as waves
  - Room temperature operation
  - Quantum computing





(Based on $^9Be^+$ ion)

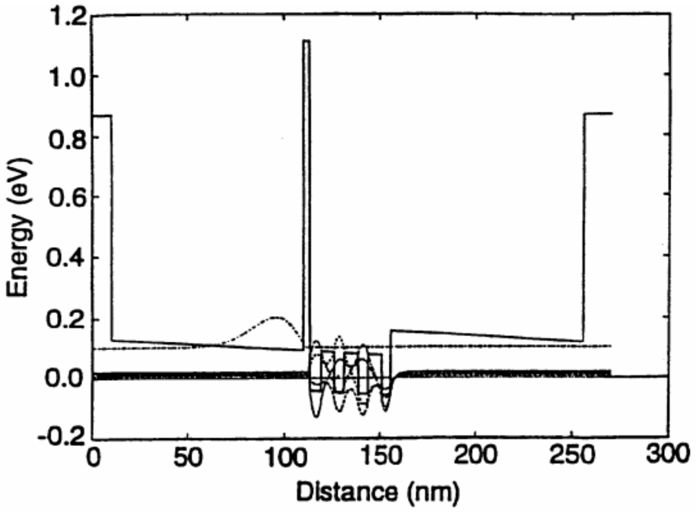


Quantized acoustic phonon modes in quantum wires and quantum dots

Michael A. Stroscio
U.S. Army Research Office, P.O. Box 12211, Research Triangle Park, North Carolina 27709-2211
K. W. Kim and SeGi Yu[a)]
Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina 27695-7911
Arthur Ballato
Electronics and Power Sources Directorate, U.S. Army Research Laboratory, Fort Monmouth, New Jersey 07703-5601

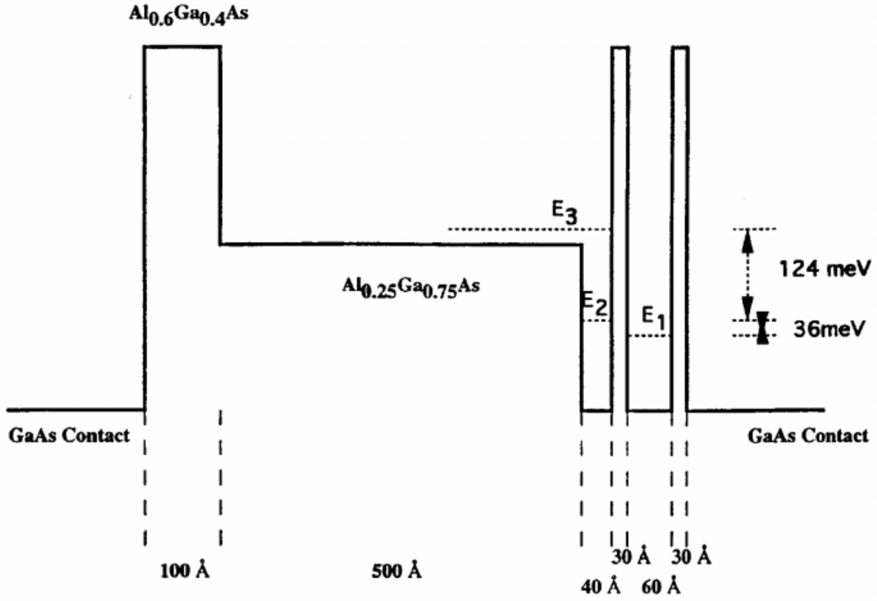
J. Appl. Phys., Vol. 76, No. 8, 15 October 1994

Multiple-Well Quantum-Injection Laser



P. Bhattacharya
Univ. of Michigan
URI on High-Frequency
Microelectronics

Step Quantum Well Laser



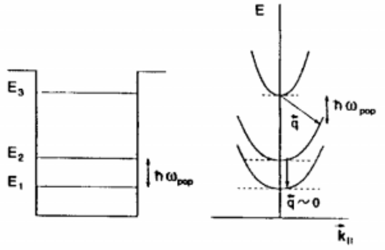
Proceedings of the
International Conference on

Quantum Devices

4–7 June 1996

DISSIPATION AND SCATTERING TIME ENGINEERING IN QUANTUM DEVICES

Scattering Time Engineering in Optoelectronic Devices



JEAN-PIERRE LEBURTON
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Interface-phonon-assisted transitions in quantum-well lasers

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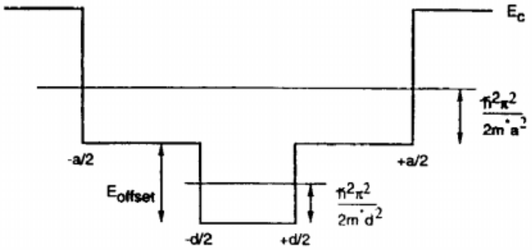


FIG. 1. Schematic of two-level heterostructure.

$$H_{s^+}=\sum_q \left[\frac{\omega_{s^+}e^2}{2\epsilon_0 L^2}\right]^{\frac{1}{2}}[\beta_1^{-1}(\omega_{s^+})\tanh(\tfrac{1}{2}qd)$$

$$+\beta_2^{-1}(\omega_{s^+})]^{-\frac{1}{2}}\frac{1}{\sqrt{2q}}\,e^{i\mathbf{q}\cdot\mathbf{r}}f_s(q,z)[A_{s^+}(q)+A_{s^+}^{+}(-q)]$$

and

$$H_{c_1}=\sum_q \left[\frac{\omega_{L_1}e^2}{2\epsilon_0 L^2}\right]^{\frac{1}{2}}\left[\frac{1}{\kappa_{\infty 1}}-\frac{1}{\kappa_{01}}\right]^{\frac{1}{2}}\left[\frac{2}{d}\right]^{\frac{1}{2}}\frac{1}{[q^2+(\pi/d)^2]^{\frac{1}{2}}}$$

$$\times e^{i\mathbf{q}\cdot\mathbf{r}}\cos\left(\frac{\pi}{d}z\right)[a_1(q)+a_1^{+}(-q)]$$

$$\gamma=\frac{64}{\pi^2}\left(\frac{\omega_{s+}}{\omega_{L1}}\right)\frac{(N_{q_s}+1)}{(N_{q_c}+1)}\frac{\left[\frac{1}{\kappa_{\infty 2}}-\frac{1}{\kappa_{02}}\right]}{\left[\frac{1}{\kappa_{\infty 1}}-\frac{1}{\kappa_{01}}\right]}\frac{\ln\left(\frac{2kT}{\hbar\omega_{s+}'}\right)}{\sqrt{1+\alpha}}$$

$$\alpha=\left(\frac{\pi}{2d}\right)^2\left(\frac{\hbar^2}{2m^*kT}\right)$$

$$f_s(qz)=\begin{cases} e^{q(z+d/2)}, & z\leqslant-\frac{1}{2}d \\ \cosh(qz)/\cosh(\frac{1}{2}qd), & -\frac{1}{2}d\leqslant z\leqslant\frac{1}{2}d \\ e^{-q(z-d/2)}, & z\geqslant\frac{1}{2}d \end{cases}$$

and

$$\beta_n(\omega)=\left[\frac{1}{\kappa_{\infty n}}-\frac{1}{\kappa_{0n}}\right]\frac{\omega_{L_n}^2}{\omega^2}\left[\frac{\omega^2-\omega_{T_n}^2}{\omega_{L_n}^2-\omega_{T_n}^2}\right]^2$$

U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH RESEARCH IN NANOSCIENCE

M. Chipley
Program Manager, Particulate and Fluid Mechanics, AFOSR

In FY 97 and prior years, within the U.S. Air Force Office of Scientific Research (AFOSR), only the Aerospace Materials Sciences Particulate and Fluid Mechanics program was funding efforts in nanosciences technology, with a total effort of approximately $750,000 per year. The emphasis was on material properties, numerical modeling/simulation, and constitutive relationships.

In FY 98, the Director, Defense Research and Engineering (DDR&E) announced a DOD-wide MURI effort in nanosciences. Within AFOSR three directorates will be involved in nanoscience technology: Aerospace Materials and Science, Mathematics, and Physics. Each directorate has submitted proposals to DDR&E for the FY 98 MURI program topic Nanoscience. Under the Nanoscience topic are five subtopics; AFOSR is the lead for two of these. Each sub-area will be funded at approximately $1 million/yr.

FY 98 MURI Nanoscience Topics:

1. Engineering of Nanostructures and Devices
2. Computational Tools for Design, Analysis and Optimization of Nanometer Scale Devices and Operation. AFOSR POCs: Maj. Scott Schreck (202) 767-7902, Capt. Brian Sanders (202) 767-6963.
3. Nanoscience: Size Distribution Control of Self-Assembled Semiconductor Nanostructures for Multispectral Detector Arrays. AFOSR POC: Maj. Michael Prairie (202) 767-4931.
4. Nanoelectronics: Low Power, High Performance Components and Circuits
5. Carbon Clusters and Nanotubes

Complete information on the MURI programs can be found on the websites of AFOSR (http://www.afosr.af.mil), ARO, and ONR.

Based on the increasing effort in the MURI program, the Particulate and Fluids Mechanics program will decrease slightly to an annual effort of approximately $600,000 per year, with an emphasis on constitutive relationships under quasi-static conditions. The majority of the work will be related to clay soils, rock, and concrete experiencing very high strain rate loadings by earth penetrators or blast loads. AFOSR is a Technical Affiliate of the University of Florida Engineering Research Center.

DEPARTMENT OF COMMERCE ROLE IN NANOTECHNOLOGY RESEARCH

A. Duff Mitchell
U.S. Department of Commerce, Technology Administration

Introduction

The Department of Commerce (DOC) Office of Technology Policy is part of the DOC Technology Administration. In broadest terms, the Office of Technology Policy is responsible for 3 functions:

1. developing policies to increase the role of technology in enhancing the economic well-being and competitiveness of the United States
2. developing international science and technology policies that promote U.S. international competitiveness
3. serving as liaison to the private sector to identify barriers to the rapid commercialization of technology, eliciting support for Administration civilian technology policies, and ensuring that industry’s interests are reflected in S&T agreements and civilian technology policy

Nanotechnology Study

U.S. companies and policymakers need to understand how the emerging science of nanotechnology will affect their competitive global positions. The potential impact is considerable — nanostructured materials or nano-processed devices have broad applications from pharmaceuticals, bioengineering, pigments, and electronics to optical and magnetic devices and structures and coatings with special properties. In keeping with our mission to “increase the role of technology in enhancing the economic well-being and competitiveness of the United States,” we count on the WTEC study to document for U.S. industry the width and breadth of the technology challenge and opportunities nanotechnology represents.

Also, in order to better pursue our second mission of “developing international science and technology policies that promote U.S. international competitiveness,” we recognize that it is very important to understand the extent of work being undertaken by competitors abroad. The importance of international efforts to commercialize nanotechnology was underscored a few years ago with the announcement by the Ministry of International Trade and Industry in Japan of two 10-year nanotechnology programs: the Atomic Technology Project for $185 million and the Quantum Functional Devices Project for $40 million. The Japanese Science and Technology Agency funds several research institutes on nanoparticles, nanostructures, and related technologies. It is believed that Japanese companies and research institutes are focused more than U.S. companies and researchers on the processing and manufacturing aspects of nanotechnology, including advanced diagnostic instrumentation and applications in microelectronics. We would like this verified. There is also significant work underway in China, Russia, and parts of Europe, especially Germany. We would like to better understand what this entails.

In short, we would like to see a report that would assist U.S. citizens, corporations, and policymakers in understanding and dealing with nanotechnology and its impact on future technology trends and products in the world. We would see this information through its dissemination to U.S. interests supporting our third mission objective, that is, facilitating the rapid commercialization of technology.

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY ACTIVITIES IN NANOTECHNOLOGY

Dr. Robert D. Shull
Group Leader, Magnetic Materials Group, NIST

The National Institute of Standards and Technology (NIST) has been active in the area of nanostructured materials for the last decade, specifically in the topics of magnetism, thermal and mechanical properties, metrology, thermodynamics, thin films, sensors, compositional analysis, sintering, and processes. It has focused on identifying and addressing those topics where key information is missing, where barriers to the application of this new technology exist, and where new standards are necessary. This information is required by U.S. industry if it is to take future advantage of this new class of materials. In order to continue furnishing this assistance to U.S. industry and the scientific community, it is necessary to periodically evaluate R&D activities in nanometer-scale materials outside of the United States. This WTEC report on nanoparticle engineering being sponsored by NIST and many other government funding organizations will provide this update. It is anticipated that this report will also provide the framework for establishing a roadmap for future U.S. research in this area.

The tables and figures on the following pages list the information that NIST would like to obtain from the WTEC report, along with short descriptions of some highlights from previous NIST activity. Included in these highlights are examples of activities designed (1) to develop tools for characterizing materials at the nanometer-size scale, since this size range represents a limit to the applicability of most present equipment; and (2) to focus the broad expertise at NIST on these materials in order to develop an understanding of the physics of the novel properties found in them, since it is not known for many properties whether the new phenomena observed are actually new physics, or are logical extensions of large-scale physics to the nanometer size range. In addition, there has been a significant effort at NIST in the past to identify processing techniques that have the potential to provide large amounts of material, as will be needed for industrial applications. This latter effort was very successful (e.g., development of sol-gel, chemical precipitation, and flame processing techniques, including several patents), so that there should no longer be concern for this new technology of nanometer-scale materials being only a subject of scientific curiosity.

The “Molecular Measuring Machine” being developed at NIST is a good example wherein new metrology is being developed for use with nanometer-scale devices *before* it becomes a barrier to the technology. As devices are made smaller and smaller, the linewidths of chip features become much smaller, which means that the tolerance for alignment of deposition masks becomes smaller. A barrier to the use of nanometer-sized “powders” is the need to find ways to consolidate them without large amounts of coarsening. NIST has recently studied this effect and found that dynamic compaction may be the solution. NIST is now leading the world in giant magnetoresistance (GMR) spin valves (having the largest GMR values for the smallest switching fields, in all three spin valve structures) and in magnetic nanocomposite refrigerants (possessing 4 times the effect of the best low temperature magnetic refrigerant). Finally, the NIST activity on micromagnetic modeling has shown the need in calculational efforts for the development of “standard problems” and a “standard code,” items now being pursued in the micromagnetic community throughout the United States and led by NIST. Ramifications of this finding are now being felt in other calculational activities.

The annual support for NT at NIST amounts to about $4 million per year; $1.0 million is from a direct congressional initiative and the remainder is from other base NIST support.

NIST OBJECTIVES FOR WTEC NANOPARTICLE ENGINEERING REPORT

- Determine Status of Nanometer-Scale Materials, Devices, and Tools
  - Phenomena, Processing, and Characterization
    - a) Summarize Present Knowledge and Understanding (U.S. and non-U.S.)
    - b) Learn of New Developments
    - c) Identify Key Roadblocks
    - d) Identify Key People and Groups Working in the Area
    - e) List Industrial Applications (Actual and Potential)

  (USE: Help Determine a U.S. Roadmap)

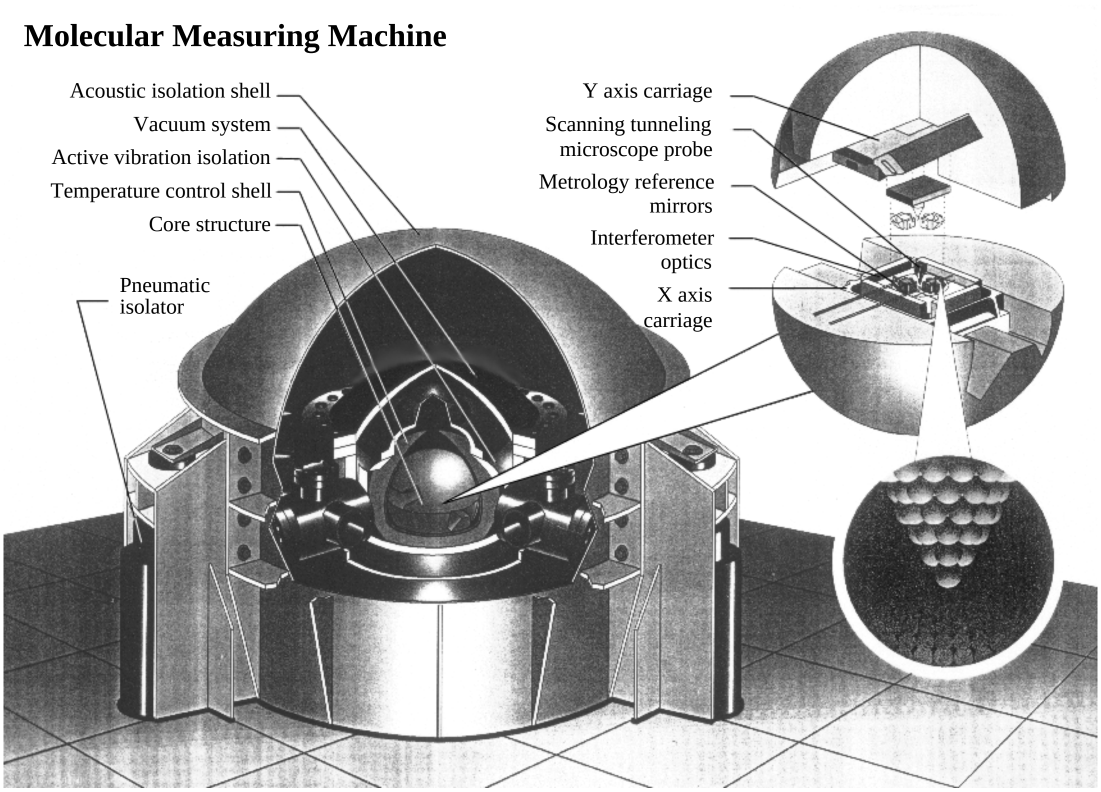
- Assist NIST to Identify Proper Utilization of its Expertise to
    - a) Answer Key Questions
    - b) Address Unknown Areas
    - c) Establish Necessary Databases
    - d) Identify Needed Standards (Hierarchical and Materials)
    - e) Assess Validity of Results (Traceability)
    - f) Promote Technology Transfer to Industry

NIST NANOSTRUCTURED MATERIALS INITIATIVE (FY94-97)

- Synthesis and Processing (Making Things Small)
  - Electrodeposition, Chemical, Vapor, Mechanical Alloying, Consolidation, Composites, Lithography, Templating, Scanning Probe Techniques
- Characterization (at Nanometer Sizes)
  - SANS, Magnetic, Microscopy (Electron, Atomic Force, Magnetic Force), Composition Profiling, Metrology
- Property Measurement (Materials Phenomena at Small Scales)
  - Magnetic, Electrical, Mechanical, Thermal, Chemical, Optical

DEVELOPMENT AND USE OF IMPROVED MEASUREMENT TECHNIQUES

Molecular Measuring Machine



Use for positional metrology (e.g., as needed for industrial mask registration).

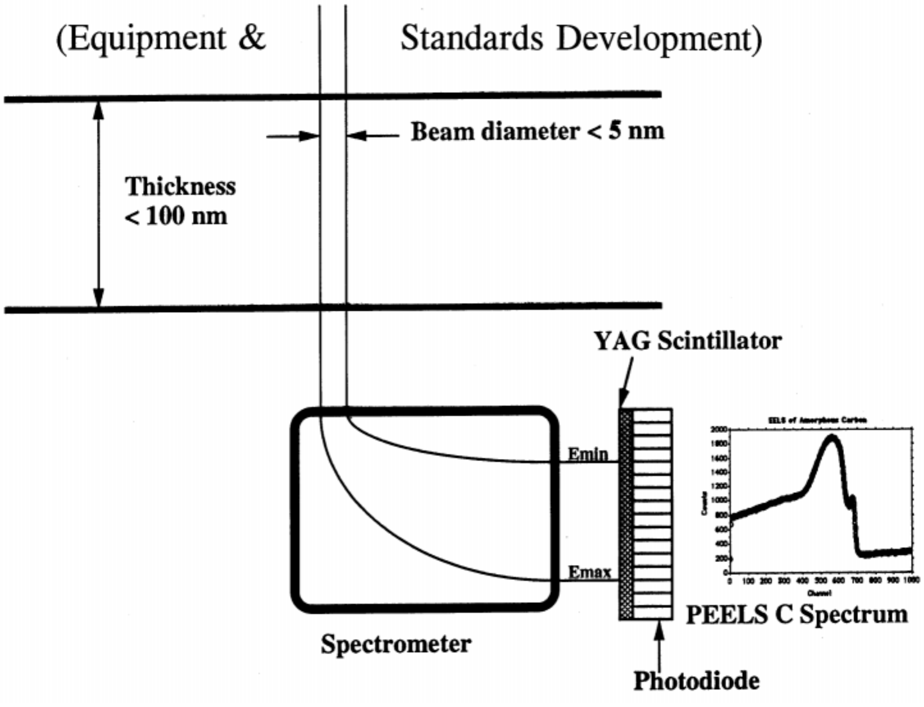
NIST Molecular Measuring Machine — Instrument Status

- All systems working together:

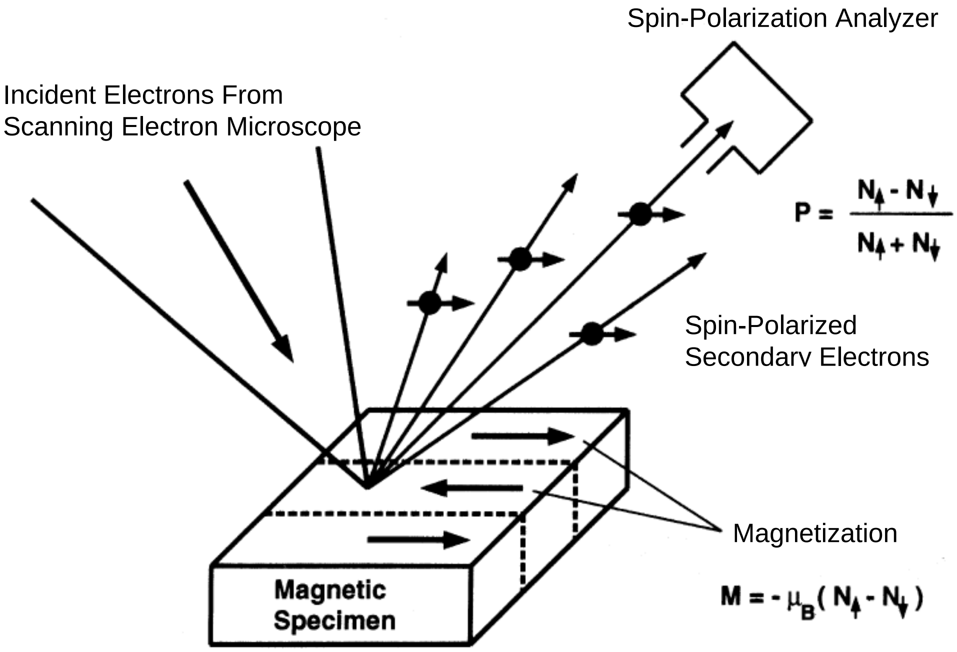
– STM Probe	± 1 nm
– Interferometer	± 100 pm
– SY Motion Generation	50 mm ± 1 µm
	10 µm ± 1 nm
– Z Motion Generation	3 mm ± 0.3 µm
	1.5 µm ± 1 nm
– Temperature Control	± 1 mK
– UHV	10^{-6} Pa
– Vibration Isolation	Passive
– System Control	Closed-loop scanning
– Data Display	

(C. Teague, NIST, private communication)

HIGH RESOLUTION COMPOSITIONAL ANALYSIS

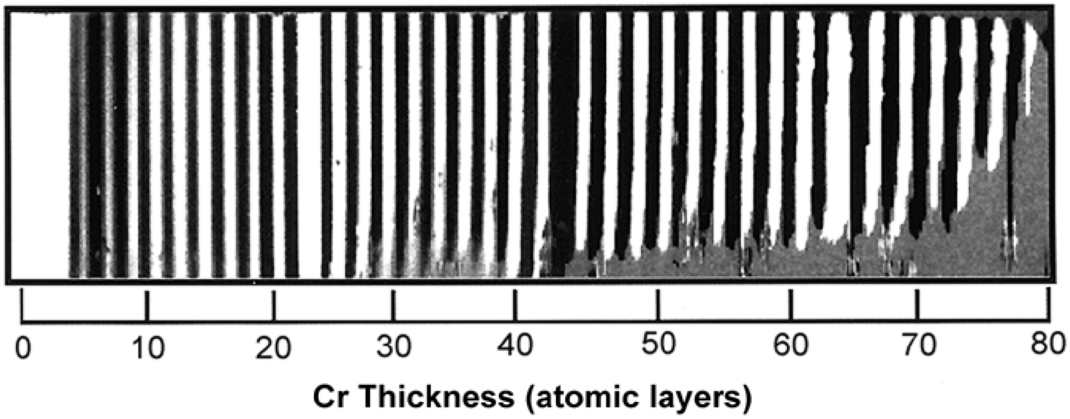


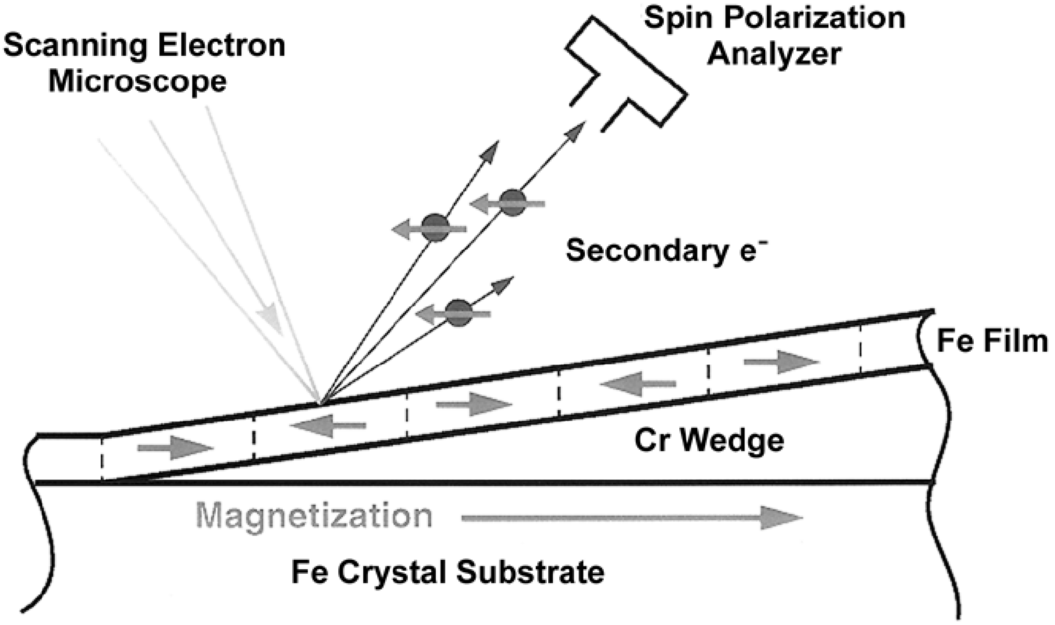
AEM - PEELS Experiment



Scanning Electron Microscopy with Polarization Analysis

Oscillatory Magnetic Exchange Coupling in Fe/Cr/Fe

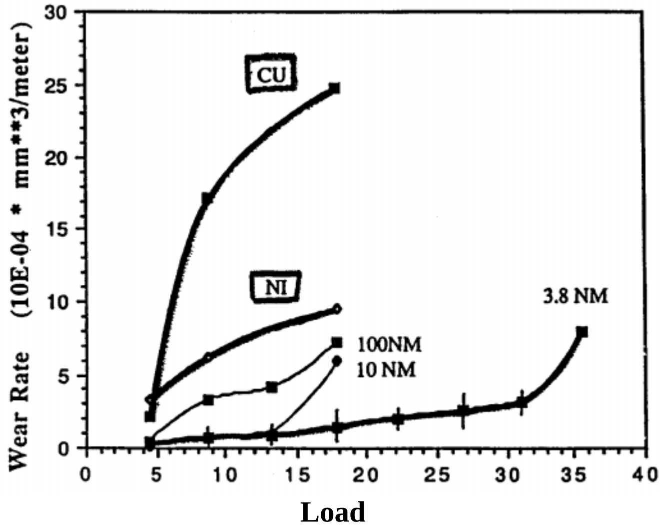




J. Unguris, R.J. Celotta, and D.T. Pierce, *Phys. Rev. Lett.* 67: 140 (1991).

KEY MEASUREMENTS FOR IMPROVED PROPERTY UNDERSTANDING

Effect of layer spacing on wear of Ni-Cu multilayer alloys

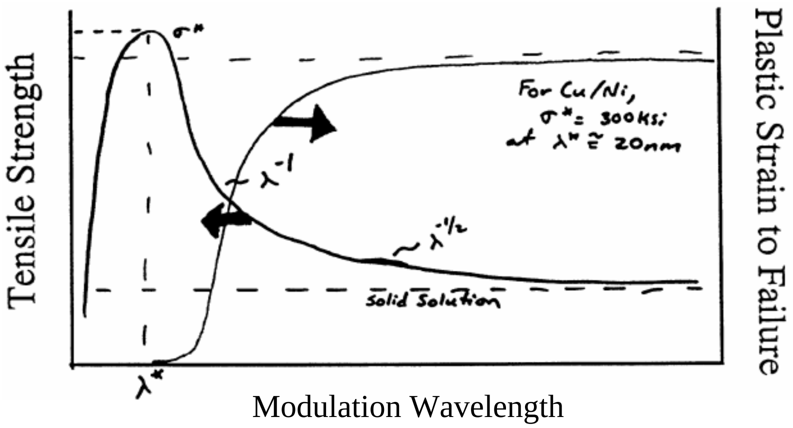


Wear rate as a function of load for a series of electrodeposited Cu-Ni multilayers. The substrate was AISI 52100 steel. Data for electrodeposited nickel and copper is also presented. The wavelength of the multilayers varies from 200 to 7.6 nm.

A.W. Ruff and Zeng-Xiang Wang, *Wear*, **131**, 259 (1989).
A.W. Ruff and D.S. Lashmore, *Wear*, **151**, 245 (1991).

In situ TEM Observation of Deformation and Fracture in Nanoscale Multilayers

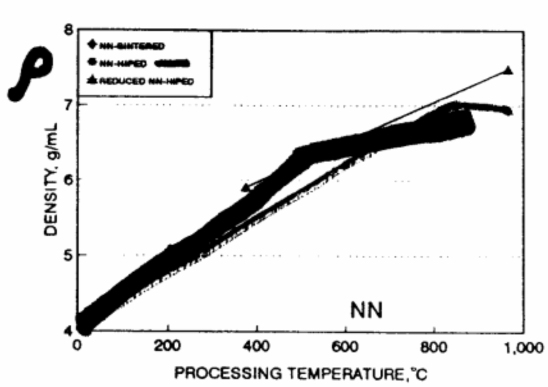
Tim Foecke
Mechanical Properties and Performance Group
Metallurgy Division, NIST



- What are the dislocation generation mechanisms that occur?
- Do dislocations pin at interfaces?
    - Crack tip dislocation emission/interactions?

Powder Consolidation (Nano Fe)

DENSITY VERSUS PROCESSING TEMPERATURE

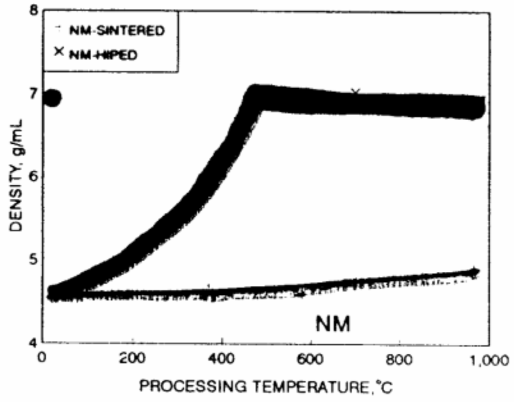


Vapor Condensed

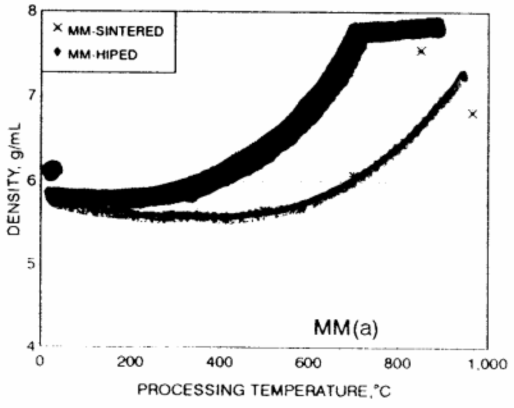
▬ HIP

— Sinter

● Dynamic



Ball Milled



Slow Cooled Liquid → Solid

CONCLUSION: Highest ρ at lowest T (∴ with least grain growth) requires pressure; dynamic compaction is best.

Livne, Munitz, Rawers, and Fields
“Consolidation of Nanoscale Iron Powders”

NISTIR #5990

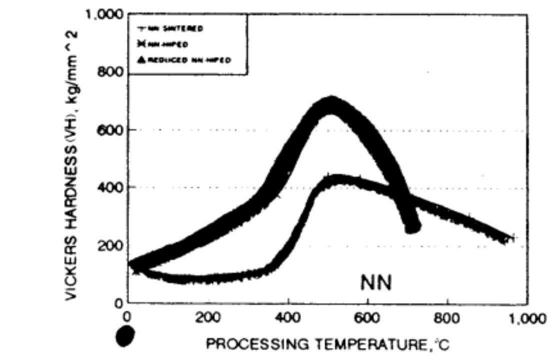
Powder Consolidation (Nano Fe)

HARDNESS VERSUS PROCESSING TEMPERATURE

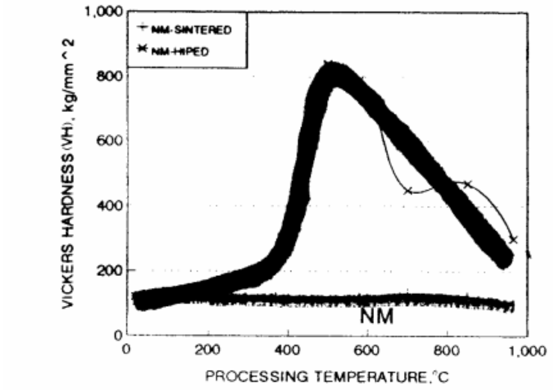
▬ HIP

— Sinter

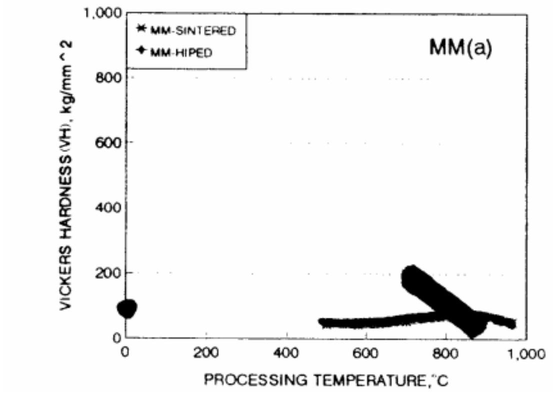
● Dynamic



Vapor Condensed



Ball Milled



Slow Cooled
Liquid → Solid

CONCLUSION: Higher hardnesses (VH) when pressure assisted; VH peak due to competition between densification and grain growth; highest VH via dynamic compaction.

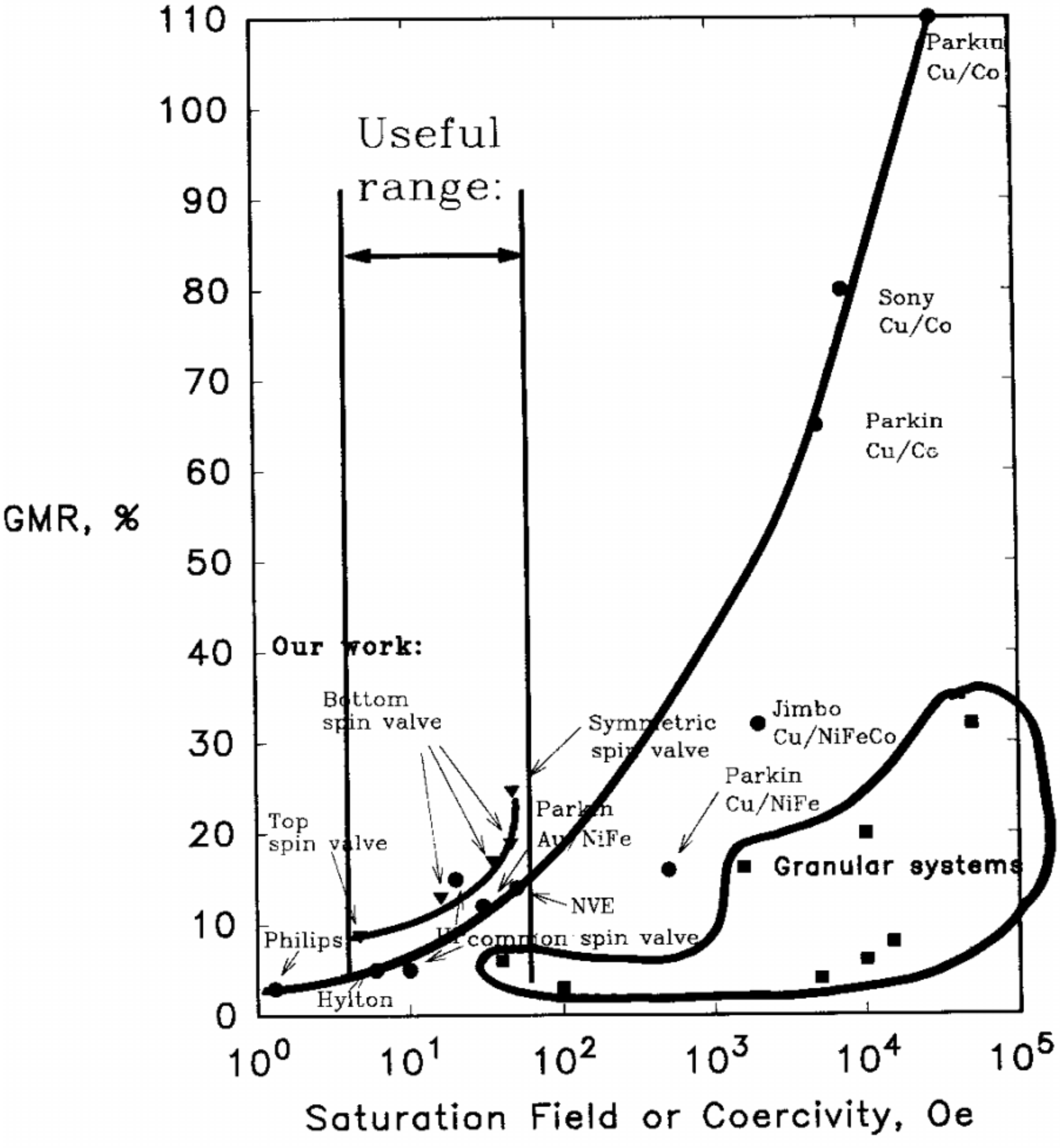
Livne, Munitz, Rawers, and Fields

"Consolidation of Nanoscale Iron Powders"
NISTIR #5990

March 1, 1997

Giant Magnetoresistance (GMR) Spin Valves

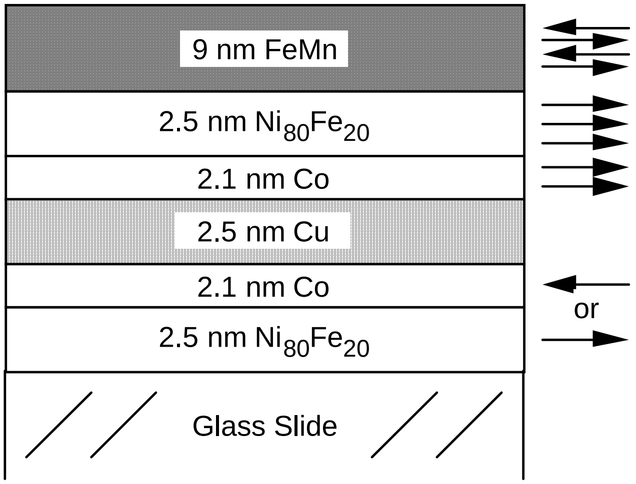
Typical Published Results:



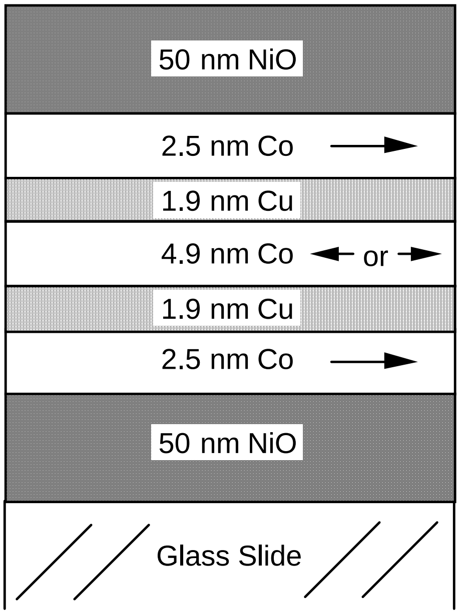
NIST

GMR SPIN VALVE CONFIGURATIONS

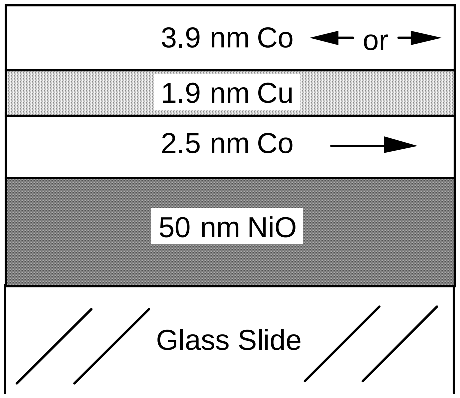
TOP Spin Valve - 11.5%



SYMMETRIC Spin Valve - 23.4%

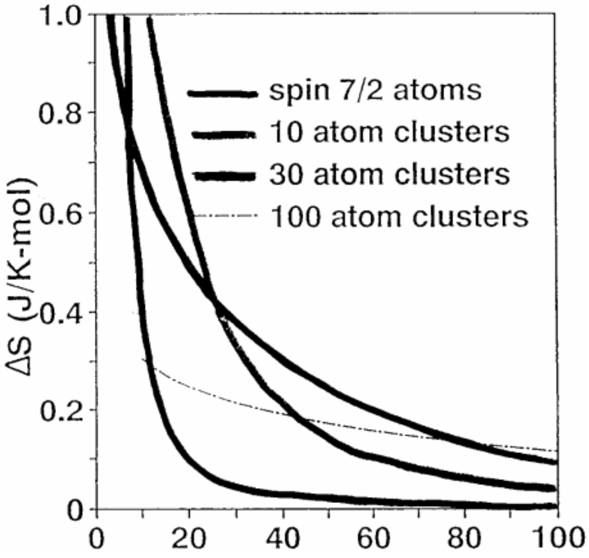


BOTTOM Spin Valve - 17.0%



W. Egelhoff, P. Chen, et al., *J. Appl. Phys.* **79**, 5277 (1966).

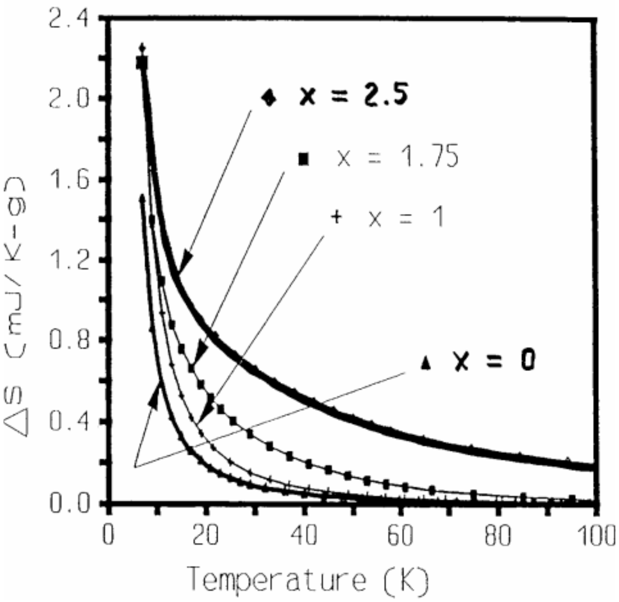
NEW MAGNETIC REFRIGERANTS



TEMP (K)

Calculated entropy change vs temperature for a magnetic field change of 1 tesla for a system of magnetic spins isolated and grouped into clusters as in magnetic nanocomposites. Note the enhancement when clustered. [R.D. McMichael, R.D. Shull, L.J. Swartzendruber, L.H. Bennett, and R.E. Watson, *J. Mag. & Magn. Mater.* **111**, 29 (1992).]

MEASURED MAGNETOCALORIC EFFECT FOR $Gd_3Ga_{5-x}Fe_xO_{12}$ NANOCOMPOSITES



Measured entropy changes (for a field change of 1 tesla) vs temperature for paramagnetic GGG (x = 0) and magnetic nanocomposites GGIC (x > 0) showing enhanced magnetocaloric effects of the nanocomposites. [R.D. Shull, R.D. McMichael, J.J. Ritter, and L.H. Bennett, *MRS Symp. Proc.* **286**, 449 (1993)].

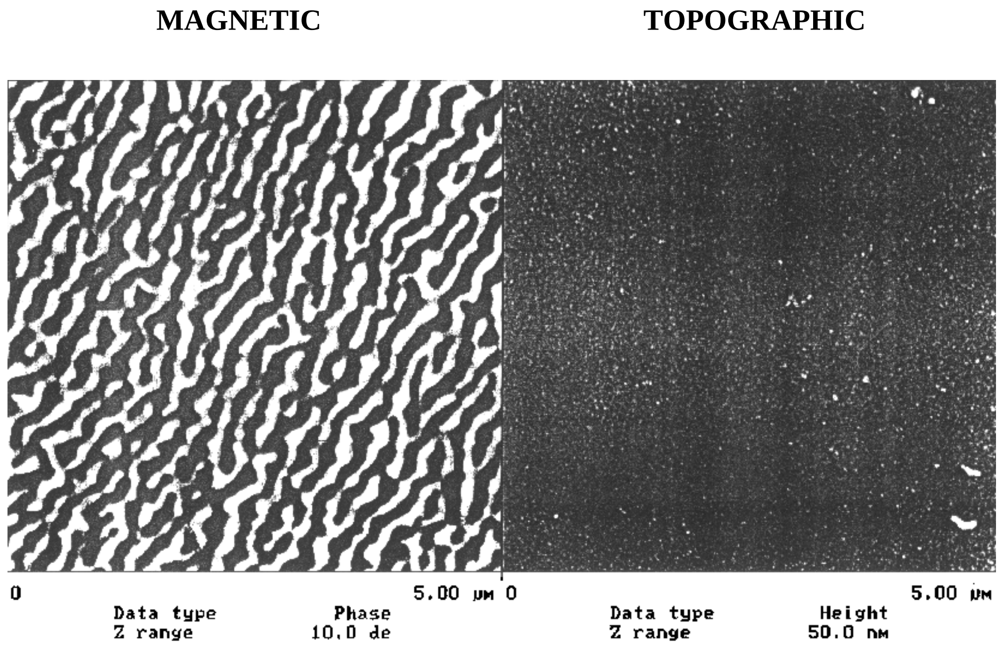
MAGNETIC FORCE MICROSCOPY COUPLED WITH MICROMAGNETIC MODELING

(See illustrations of this NIST work on pp. 55-58)

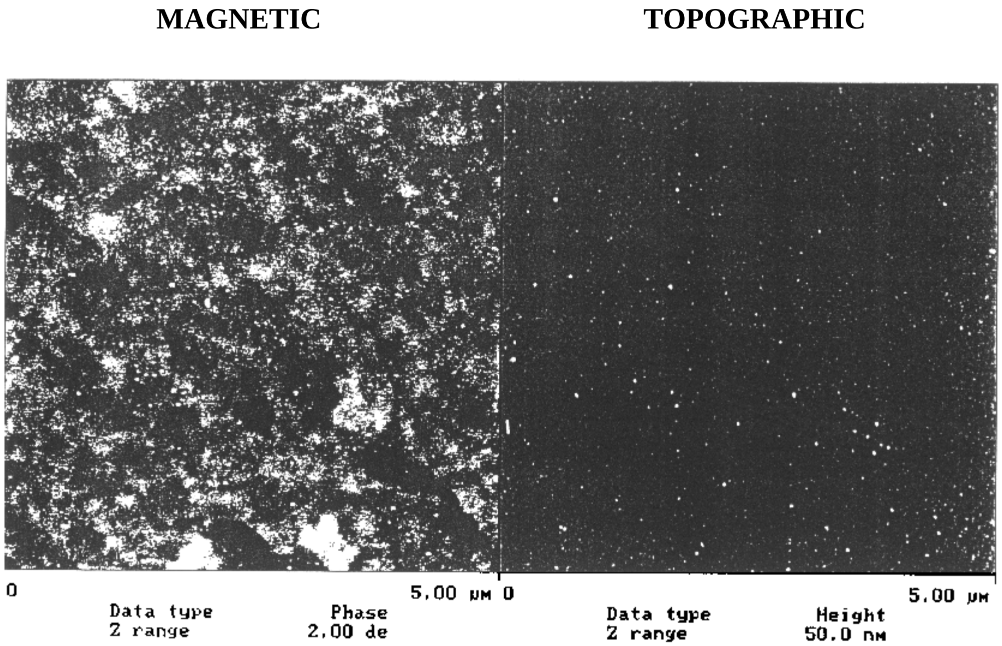
- Loss of domain structure upon size reduction
  (e.g., shown in the results for film thickness effects in thin film Co)
- Different domain patterns for different demagnetizing methods
  (e.g., shown by the elongated domains when an ac technique is used compared to the curved domains obtained by heating thin film Ni above its Curie Point)
- Different stabilities for different domain wall types upon size reduction
  (e.g., Néel walls forming from Block walls, and transverse walls forming from vortex walls)
- Micromagnetic “Standard Problem” and “Standard Code” development
  (see website http://www.ctcms.nist.gov/~rdm/mumag.org.html)

SUMMARY OF NIST INTERESTS IN NANOPARTICLE ENGINEERING

- NIST has identified nanophase materials as an area of particular focus
- It is interested in coordinating activities with those of other research laboratories
- NIST’s role is to assist in accelerating the industrial application of these materials
  - Identify key barriers
  - Provide measurement assistance and leadership
  - Interface closely with industry



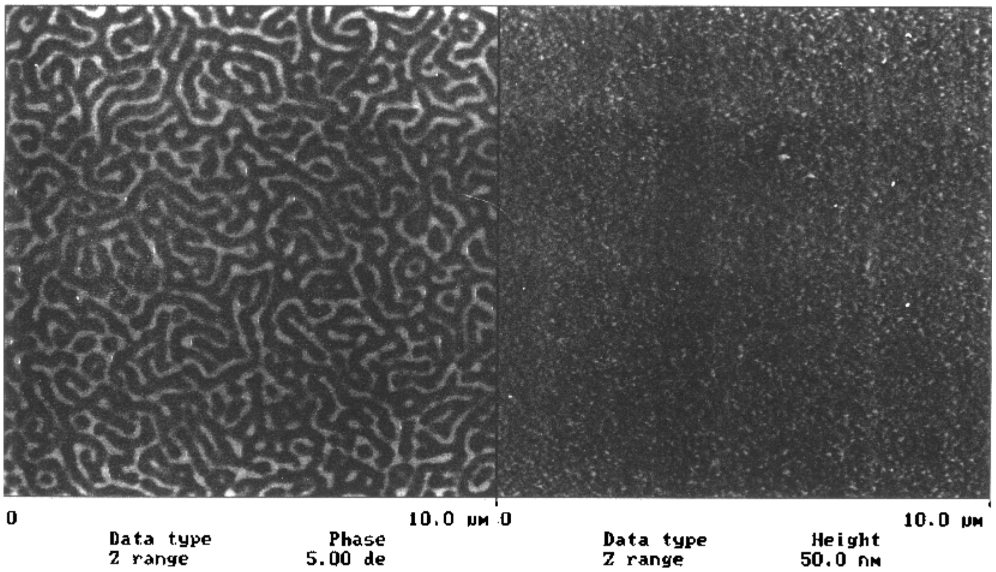
5 µm MFM scan of 200 nm Co film on glass, under a 10 nm protective layer of Au. Magnetic image (left) obtained at a lift height of 25 nm.



As in figure above, but Co film thickness reduced to 20 nm.

MAGNETIC **TOPOGRAPHIC**

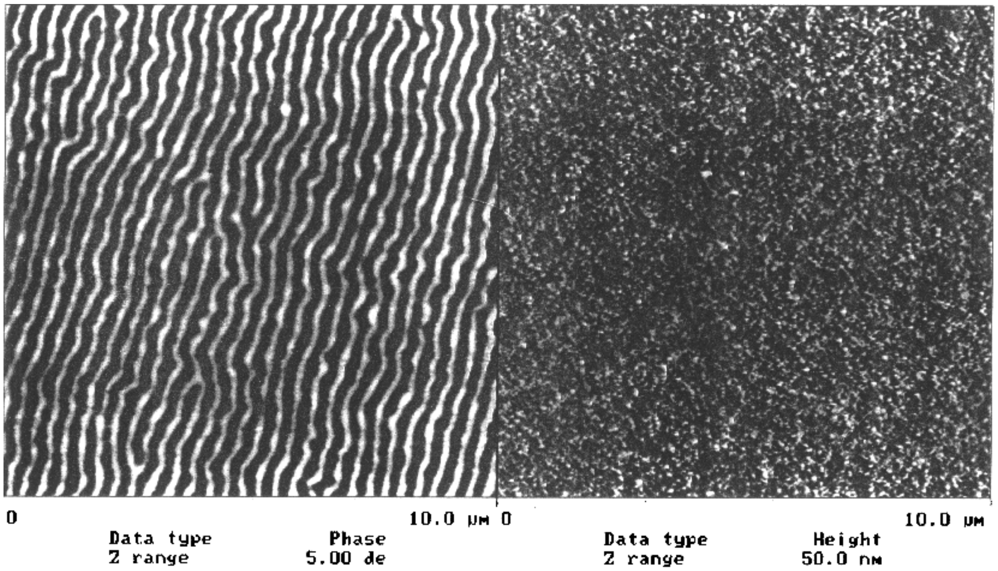
TMAFM Images



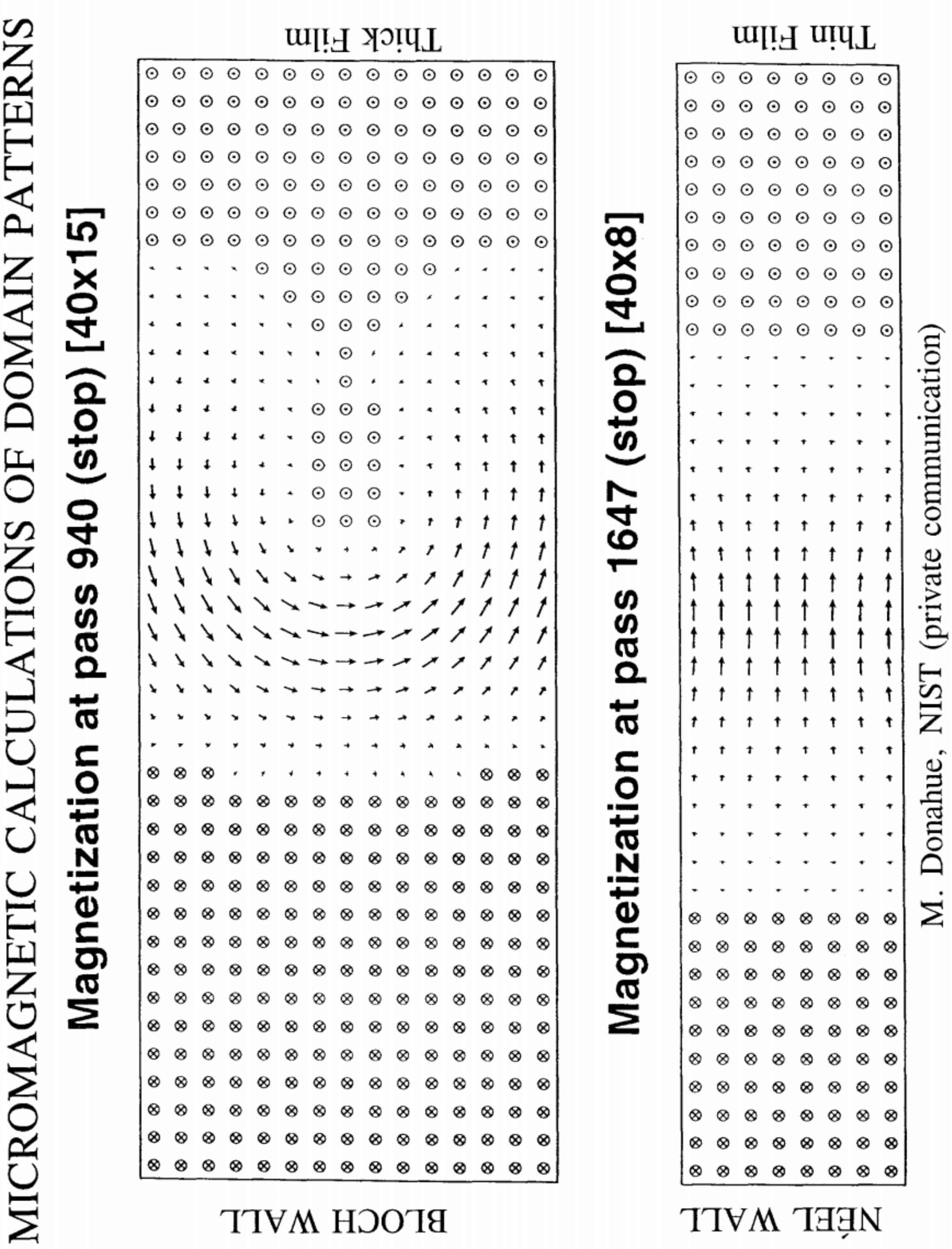
03131257.0f1
3000A Ni on Cu (100) as deposited

MAGNETIC **TOPOGRAPHIC**

TMAFM Images



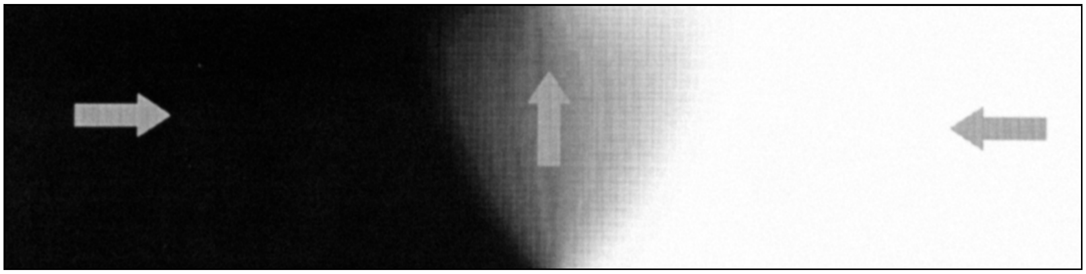
03131334.0f1
3000A Ni on Cu (100) AC demagnetized



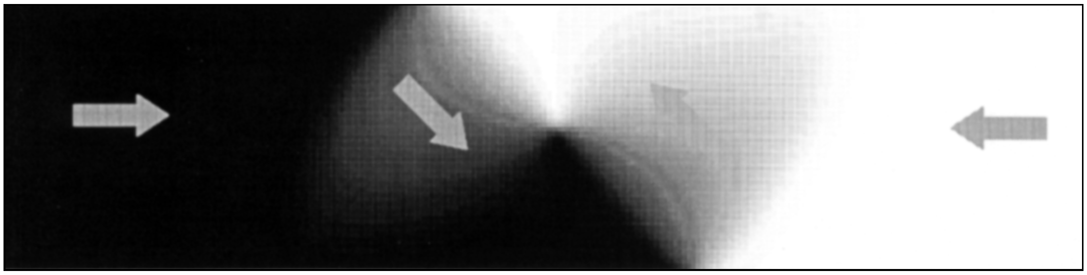
M. Donahue, NIST (private communication)

HEAD TO HEAD DOMAIN WALLS

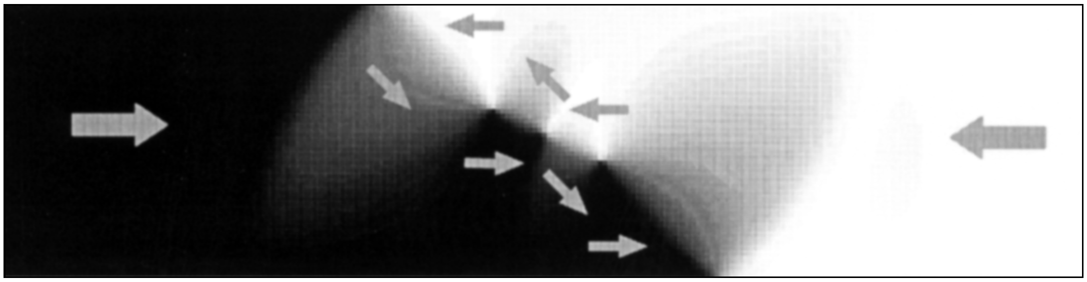
Transverse wall, 250 x 8 nm



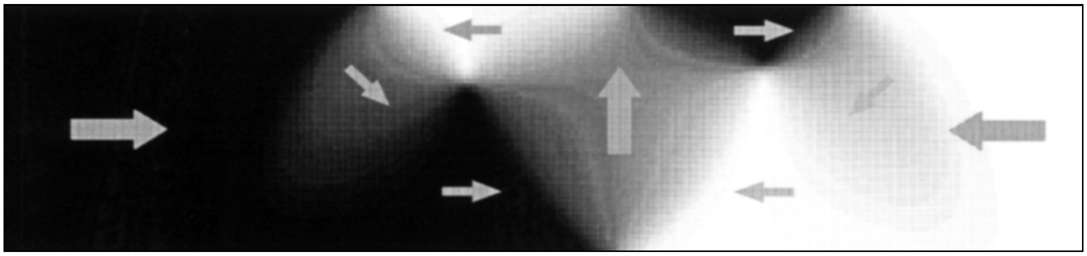
Vortex wall, 250 x 16 nm



Two vortices w/ cross tie, 500 x 16 nm



Two opposing vortices, 250 x 16 nm



R.D. McMichael and M.J. Donahue, “Head to head domain wall structures in thin magnetic strips,” *IEEE Trans. MAG, in press.*

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

(D. Jan and M. Meyyappan)

Nanotechnology Activities at NASA

Dr. Darrell L. Jan
NASA Headquarters

NASA is very excited about the potential for nanotechnologies to provide enhancement or enablement to the NASA mission. There are several areas in which nanotechnology can assist. One obvious area is that of miniaturization of spacecraft systems, such as instrumentation, propulsion, or life support. Reduction in size and mass can yield significant savings in launch costs. NASA has already made significant progress in this area by exploiting advances in microelectronics and MEMS. An example is the Mars Pathfinder mission, with its Sojourner rover, which landed on Mars July 4, 1997. Nanotechnology may enable further advances in miniaturization without loss of measurement accuracy. Miniaturization will also enable more efficient tools and devices for astronaut usage, such as comfortable headmounted information displays, noninvasive physiological monitoring, and wireless communication. Furthermore, the improved material properties enabled by nanostructuring should prove useful to NASA. Applications will be in lightweight structures, hydrogen storage, and chemical processing. In all these applications, a mixture of micro-, nano-, macro-, and meso-scale technologies may be necessary, and the issues related to interfacing and optimizing these mixes need attention.

Information on NASA funding opportunities in these and other areas may be found at http://peer1.idi.usra.edu/ and http://exploration.jsc.nasa.gov.

NASA is funding some theoretical modeling of nanostructures, taking advantage of the considerable computational power available at NASA facilities. NASA Ames has a computational nanotechnology effort in progress addressing physics- and chemistry-related issues in nanofabrication. The motivation for the effort arises from the potential of ultrasmall semiconductor devices (with feature size below 0.1 micron) and carbon nanotube-based electronics for petaflop computing hardware. The device effort focuses on computational quantum device modeling of ultrasmall devices and optical interconnects. Also, the possibility of making switches and three-terminal transistors using carbon nanotubes is being investigated using abinitio quantum chemistry and physics models.

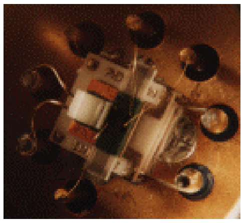
Carbon nanotube-based technology is investigated for producing nanogears and other mechanical systems and as an efficient storage mechanism for hydrogen. The latter application is particularly critical to NASA mission needs since storage and transport of hydrogen is a costly component of many space missions.

Further information may be found at http://science.nas.nasa.gov/Groups/Nanotechnology/.

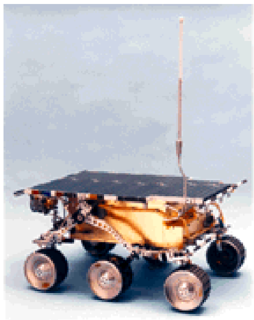
Launch is expensive

- Reduce mass by designing micro-spacecraft or micro-spacecraft systems
  - micro instruments
  - micro propulsion
  - micro landers, rovers
  - micro robotics

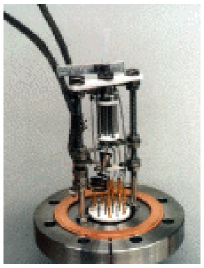
NASA Micro applications



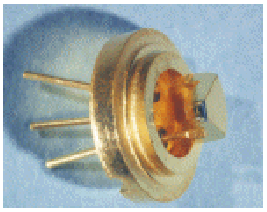
Hygrometer



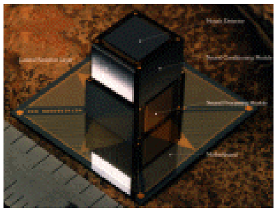
“micro” rover



mass spectrometer

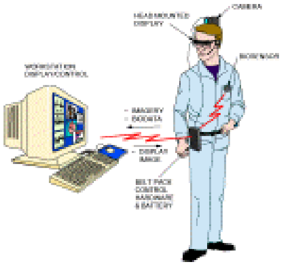


diode laser



neural network

Lightweight Augmented Reality



Improve Human Support

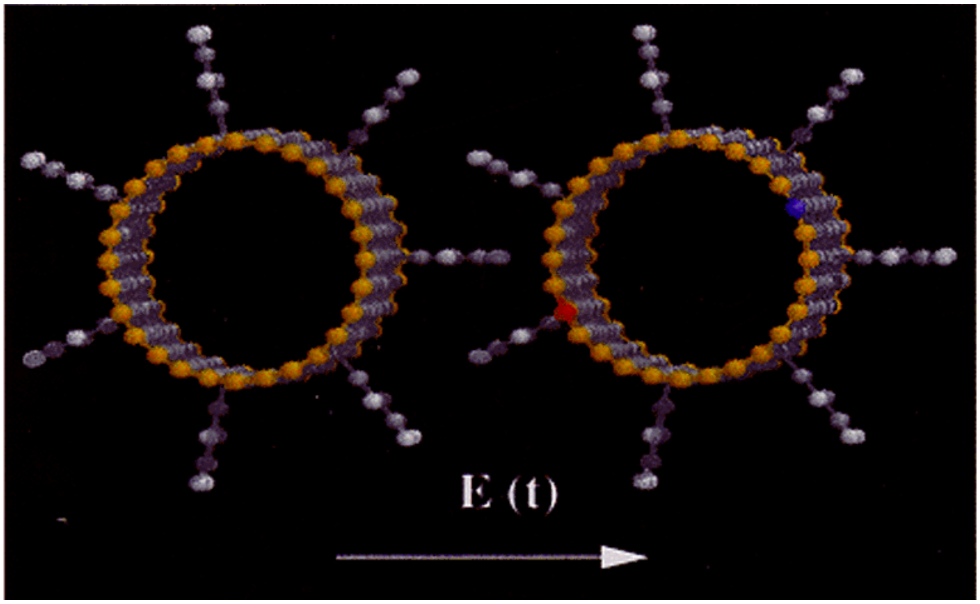
- Biomimetic
  - enzyme removal of CO_2 from air
  - Other air, water, waste treatment
- Nanostructure
  - self-repairing spacesuits, habitats
  - intelligent materials

NASA Ames Work on Nanotechnology

Meyya Meyyappan
NASA Ames Research Center
Space Technology Division
meyya@orbit.arc.nasa.gov

- NASA Interests
  - Petaflop computing — electronics components
  - High performance computers (lightweight and low power consumption)
  - Efficient H_2 fuel storage and transport
- In-house work: Initiated FY97
  - Computational modeling
  - Physics of sub-0.5 µm devices, quantum semiconductor devices, optoelectronics devices
  - Carbon nanotube-based devices

Laser Powered Rotations of Nanotube Gears



Non-linear Equations of Rotational Motion:

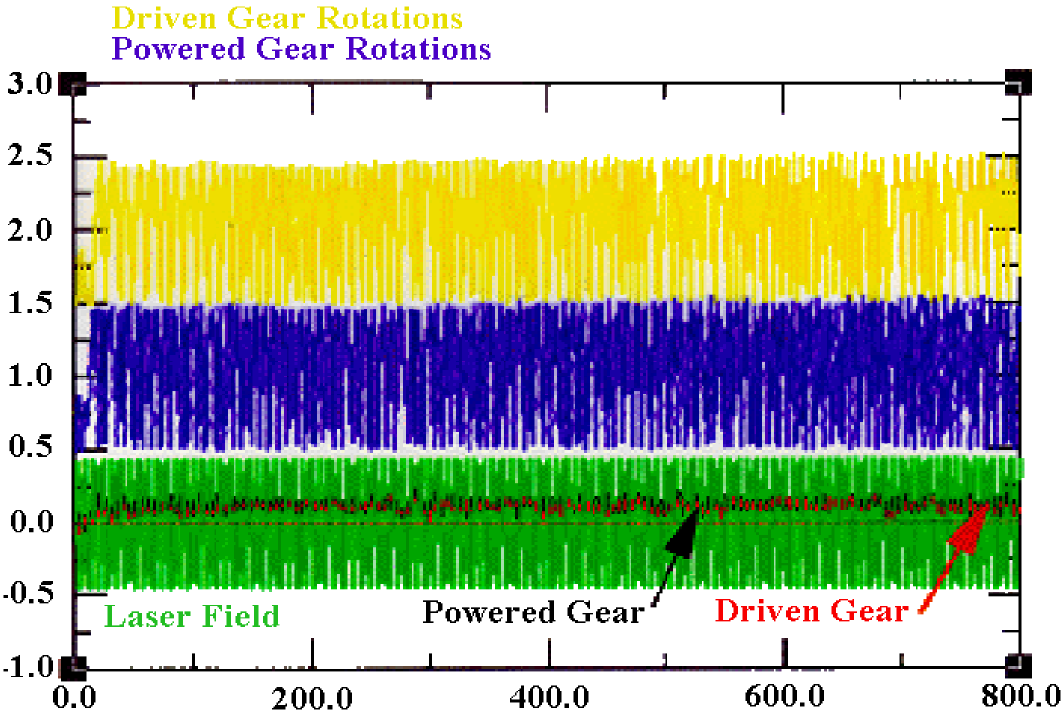
$$\mathrm{I}(t)\frac{dw(t)}{dt} = \mathrm{F}(w,t)Cos(\Omega t + \phi) - \mathrm{D}(w,t)$$

Intrinsic Frequency:

$$\int int = \frac{1}{2\pi}\sqrt{\frac{2qrE_0}{\mathrm{I}_0}}$$

22nd Feb., 1997, D. Srivastava

Rotations of a Nanotube Gear with 130 GHz cw Laser

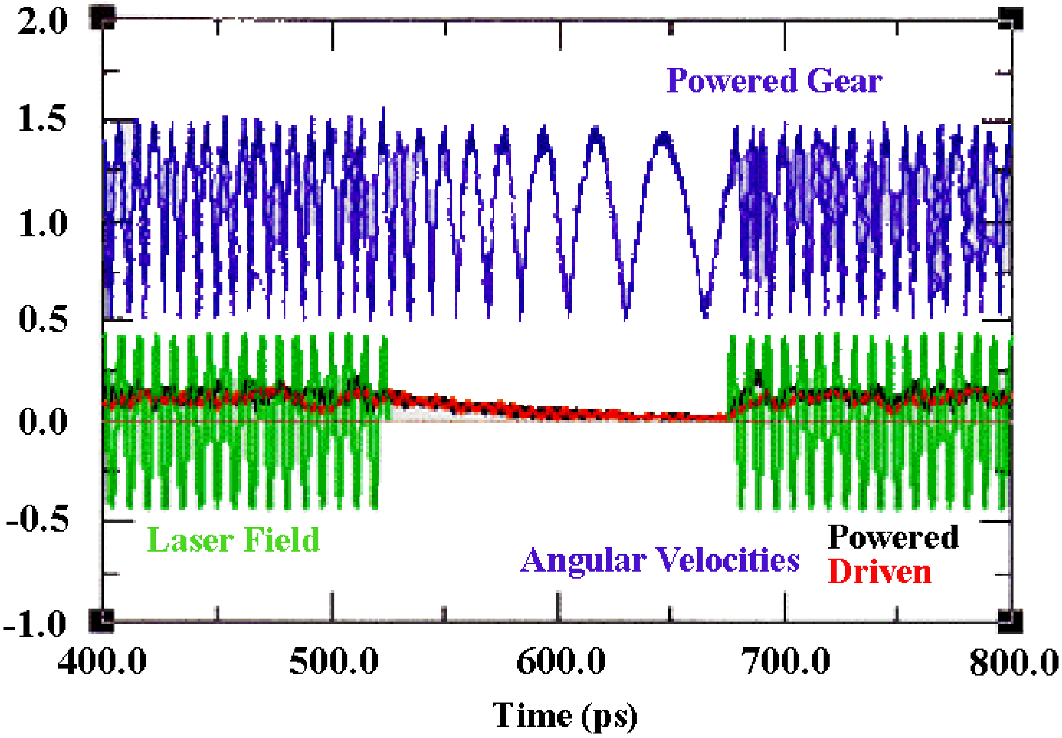


Stable unidirectional rotations up to nanosecond durations

Angular momentum of the driven gear stabilizes the rotations against thermal fluctuations

22nd Feb., 1997, D. Srivastava

Rotations of a Gear with 130 GHz Pulsed Laser

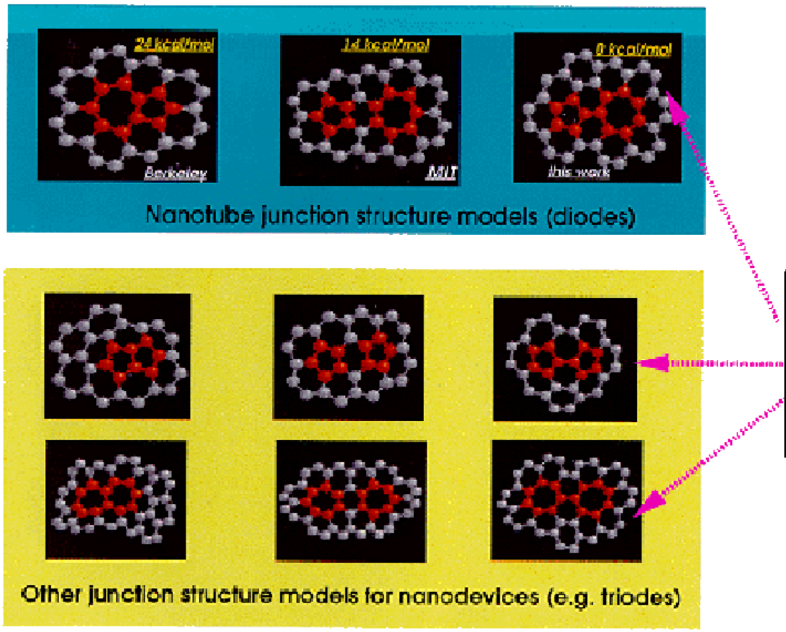


Phase matched switching on/off of a square pulse does not affect the rotational performance of the gear.

In fact, it improves the performance!

22nd Feb., 1997, D. Srivastava

Structural Stability: Our Quantum Chemistry Study



Nanotube junction structure models (diodes)

Other junction structure models for nanodevices (e.g. triodes)

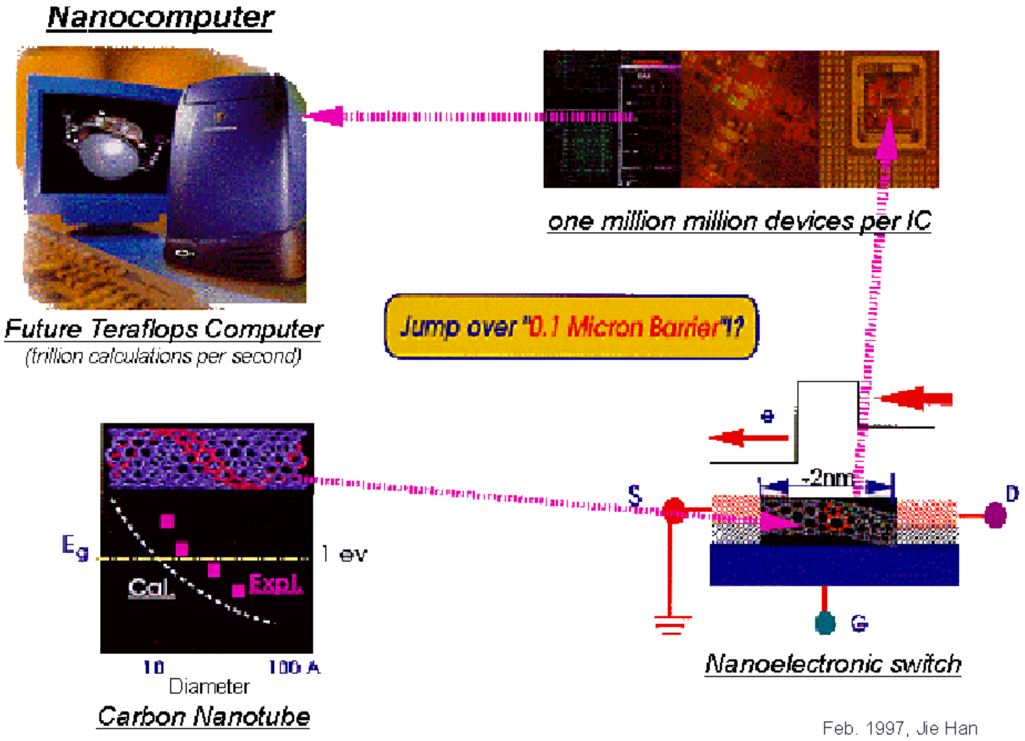
Chemistry

These are much more energetically stable and synthetically accessible than other possible nanostructures.

Feb. 1997, Jie Han

Carbon Nanotube Electronic Devices

Jie Han (NAS) and Richard Jaffe (STC)



Nanocomputer

Future Teraflops Computer

(trillion calculations per second)

one million million devices per IC

Jump over "0.1 Micron Barrier"!?

Carbon Nanotube

Nanoelectronic switch

Feb. 1997, Jie Han

NATIONAL INSTITUTES OF HEALTH NANOTECHNOLOGY ACTIVITIES

Richard Dubois, Dov Jaron
National Center for Research Resources, NIH

The National Institutes of Health (NIH) is a collection of many institutes and a few independent centers; this organization is constantly changing. In the area of nanotechnology at NIH, there are a total of 28 relevant projects supported by 9 institutes and one center. Among these are the National Center for Research Resources, the Cancer Institute, the Dental Institute, and the National Institute for General Medical Sciences. All of these nano-related projects together represent a funding level of roughly $9 million dollars. One NIH institute, the National Institute for Human Genome Research, is the primary supporter of the development of nano chips for sequencing. These are specific projects that we are able to identify; this number is probably a low figure; if the $9 million amount is doubled, it may be closer to the actual scale of NIH research support in the nanotechnology area. Based on a brief review of the FY96 budget, the level of NIH support for this area seems to be going up slightly. The interest in these technologies at NIH appears to be significant.

This is a brief overview of the kind of activities NIH supports related to the present WTEC study. This is based on a search of the database of related projects funded throughout NIH. As a specific example, the National Center for Research Resources supports a Resource Center at the University of Michigan entitled "Center for Neural Communication Technology." David Anderson is the principal investigator and Ken Wise is a coinvestigator. They are developing micro-arrays of electrodes based on the jet film approaches using silicon substrates. They currently have operational electrode arrays of 8 by 8 that make 64 electrodes, each electrode with 4 stimulating or receiving sites; that makes 256 total, so they can put this in the brain and get 256 signals from various neural brain cell areas to monitor brain cell areas in that area. They can incorporate a microchannel using micromachining that allows placement of nanoliter quantities of chemicals in various areas to stimulate and change the environment. We are excited about this project, even though it is fairly small as far as money goes — about $750,000 per year.

It is interesting to note that when we first tried to search this database we used "nanotechnology" as the keyword and didn't get one hit — people don't use that term generally at NIH, at least not when writing their abstracts. But with the keyword "microfabrication," 9 projects came up that account for some $4 million a year, and another 20 projects specifically were using chip technology, accounting for roughly $5 million. The bulk of chip technology projects are with the new National Institute for Human Genome Research and involve DNA sequencing. Other applications include assaying biochemical and sensor development. A brief list (see following viewgraphs) of chip technology uses includes HIV drug resistance determination, a chip for hypothermia, and one for cancer treatment. This latter application is an emerging therapy approach. One interesting application involves a novel approach to delivering aerosols to lungs with a large array of extremely small micro-nozzles. Medical imaging is another important application area, and nano force measurement is another area of real interest. There is a general interest in sensors.

Projects Supported by NIH in FY95

- U. of Michigan Resource Center for Neural Communication Technology —$750,000/yr
- Twenty-eight projects are supported by nine other NIH components — $9 million total

Chip Technology Use

- The bulk of chip technology projects is aimed at genomic sequencing.
- Other applications include assaying biochemical and sensor development.

Breakdown

- Nine projects are broadly identified as using microfabrication techniques — $4 million.
- Twenty projects specifically use chip technology — $5 million.

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
ULTRA ELECTRONICS: ULTRA DENSE, ULTRA FAST COMPUTING COMPONENTS

Gernot Pomrenke
DARPA/ETO

The Ultra Electronics program of the Defense Advanced Research Projects Agency (DARPA) offers a platform for advanced microelectronics research in support of nanoelectronic technologies. The goals of the Ultra Dense, Ultra Fast Computing Components program are to explore and develop material, processing technologies, quantum and conventional devices, and device architectures for a next generation of information processing systems and subsystems. The Ultra program seeks improved speed, density, power, and functionality beyond that achieved by simply scaling transistors. These improvements should manifest themselves in systems operating at room temperature at speeds 10 to 100 times faster than current systems, denser by a factor of 5 to 100, and lower-power by a factor of more than 50.

The initial goals of the Ultra Electronics program were to explore, assess, and benchmark alternative electronic approaches to embedded and stand-alone computing architectures. The program has demonstrated methods for applying novel quantum well electronic devices to improve densities of integrated electronic devices, methods of improving the control of epitaxial deposition to realize these devices, efficacy of resonant tunneling devices with respect to speed and reduced power, and techniques for monolithic and hybrid integration of devices based on gallium arsenide (GaAs), indium phosphide (InP), and silicon. Other achievements include developing nanoprobes to study nanometer material structures and devices with picosecond time resolution.

The subsequent phase has been to develop further the most promising approaches. A specific program thrust includes the design, fabrication, and testing of electronic devices with critical feature sizes well below 0.1 micron. Other thrusts include developing silicon-based nanoelectronics, chemical self-assembly techniques and improved semiconductor processing, and molecular beam epitaxy (MBE) in-situ process control and other fabrication techniques for future quantum device-based electronics. Silicon-germanium-carbon (SiGeC) -based devices are being developed to enable scaled silicon nanoelectronics. Lift-off techniques are being explored to enable combining III-V quantum device and standard CMOS electronics. These approaches will allow nanoelectronics to leverage all the continuing improvements of conventional electronic devices while providing the functional improvements of nanoelectronics. Other aspects of the program focus on developing high speed supercomputer visualization, examining the potential of single-electron devices, exploring nanolithography that targets patterning with critical dimensions below 50 nanometers, and examining fundamental issues associated with molecular electronics. A continuous interest exists to examine nanoelectronic technologies that take nontraditional approaches to enable advanced electronics beyond scaled silicon.

ULTRA Electronics

Ultra Dense Ultra Fast Computing Components/ Nanoelectronics

<u>PROGRAM GOALS</u>: The goal of the program is to explore microelectronics device technologies which will achieve massive computer operations (trillions ops/sec), massive storage (terabits/cm^2), and extremely low power (nanowatts/gate) to enable performance requirements for real-time battlefield analysis, grand challenge problem solving, language processing, and multi-tasking.

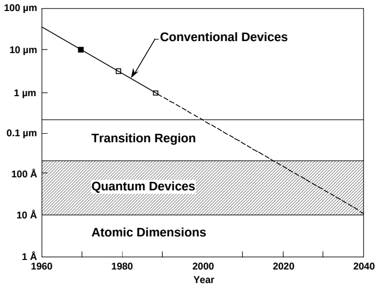
The program investigates materials, processing technologies, quantum and conventional devices, circuits and architecture to develop sub 100 nm room temperature electronic components for speed, density, and power characteristics beyond current silicon transistor scaling trends. Specifically, it demonstrates

- Efficacy of quantum effect devices, molecular and hybrid electronics
- Circuit speeds 10X to 100X faster than conventional approaches
- Device densities with physical or functional compression factors well over a factor of 15, including exploring critical feature sizes well below 100 nm
- Extreme reduction in active power per circuit

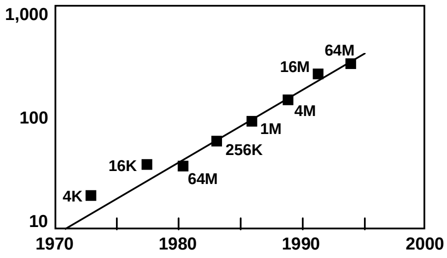
The program seeks innovative approaches and fundamental new strategies which will enable revolutionary advances in the science and technology of ultra small electronic devices to realize computation, signal processing, and storage requirements beyond the next generation military systems.

TRENDS

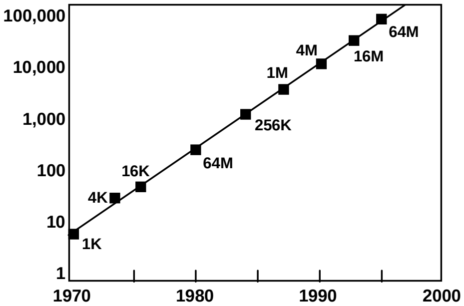
Device Size



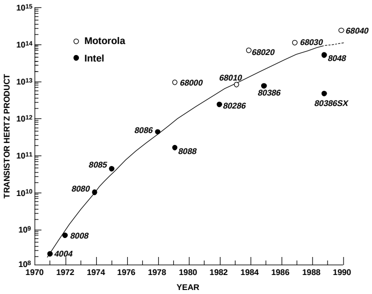
Increasing Chip Size

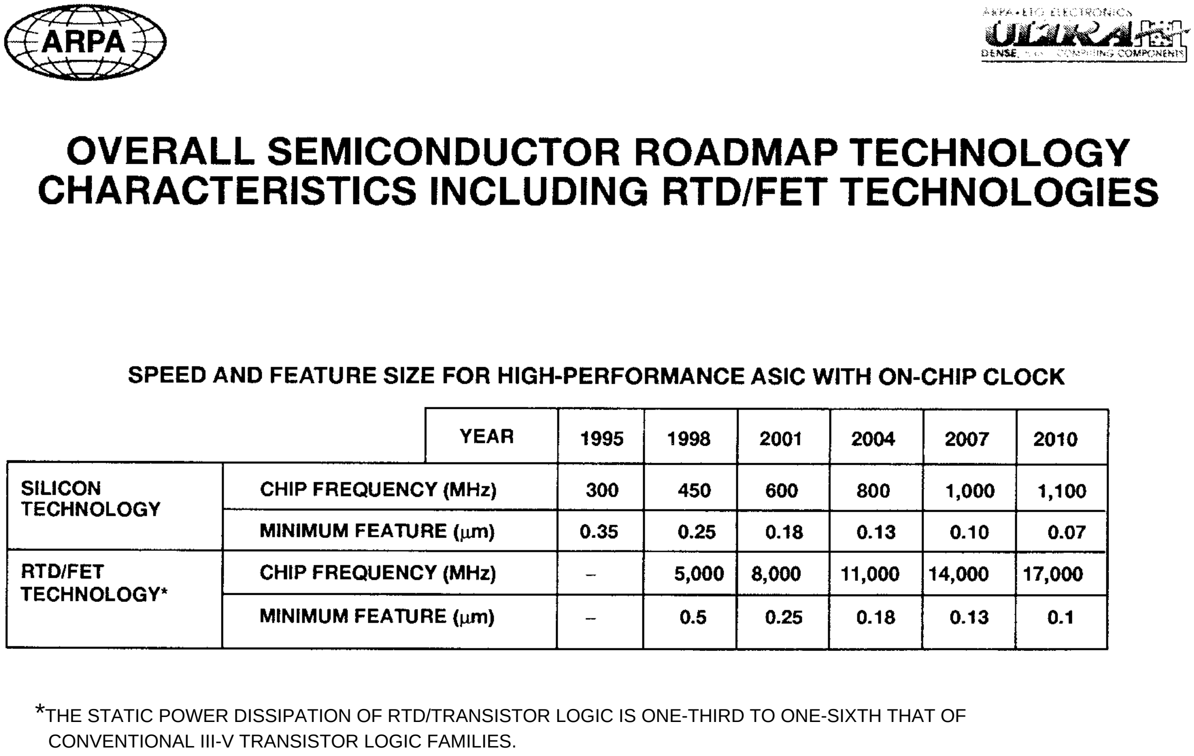


Growth in No. of Transistors/Chip



Functional Throughput of ICs





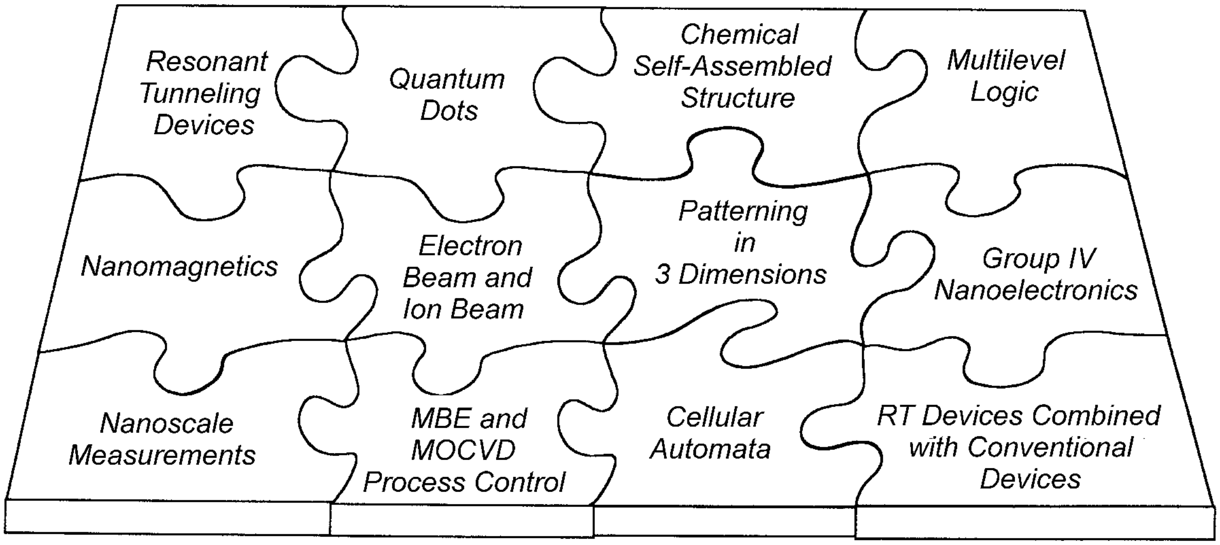
OVERALL SEMICONDUCTOR ROADMAP TECHNOLOGY CHARACTERISTICS INCLUDING RTD/FET TECHNOLOGIES

SPEED AND FEATURE SIZE FOR HIGH-PERFORMANCE ASIC WITH ON-CHIP CLOCK

	YEAR	1995	1998	2001	2004	2007	2010
SILICON TECHNOLOGY	CHIP FREQUENCY (MHz)	300	450	600	800	1,000	1,100
	MINIMUM FEATURE (μm)	0.35	0.25	0.18	0.13	0.10	0.07
RTD/FET TECHNOLOGY*	CHIP FREQUENCY (MHz)	–	5,000	8,000	11,000	14,000	17,000
	MINIMUM FEATURE (μm)	–	0.5	0.25	0.18	0.13	0.1

*THE STATIC POWER DISSIPATION OF RTD/TRANSISTOR LOGIC IS ONE-THIRD TO ONE-SIXTH THAT OF CONVENTIONAL III-V TRANSISTOR LOGIC FAMILIES.

Ultra Electronics Thrusts



Resonant Tunneling Devices

Quantum Dots

Chemical Self-Assembled Structure

Multilevel Logic

Nanomagnetics

Electron Beam and Ion Beam

Patterning in 3 Dimensions

Group IV Nanoelectronics

Nanoscale Measurements

MBE and MOCVD Process Control

Cellular Automata

RT Devices Combined with Conventional Devices

Nanoelectronics

Future Directions

Quantum Circuits and Systems

Q-effect devices combined with conventional devices

Si-based tunneling devices and QMOS circuits

CMOS integration

Hybrid

Demos — ADC, FIFO, high speed electronics for optical networks, processors, nanoprocessors

Massive Memory

Quantum effect

Nanomagnetics and nanoprobes

SET/FET

Devices

Quantum effect (tunneling, QCA, single electron, Q-dots, …)

Molecular electronics / single molecule electronics

Hybrid

Novel (DNA, cellular-biological)

Architecture and Interconnected Systems

RTD-based
Multivalued
Multilevel
Optoelectronics

Materials, Processing, and Characterization

Materials and structures
Growth and process control

- Nanoprobes, proximal probes, and e-beam microcolumns
- Non-photolithography
- Self-assembly

Chemical engineering
Diagnostics

Fundamental Device Physics, Modeling, Computer Visualization, and CAD

BALLISTIC MISSILE DEFENSE ORGANIZATION NANOTECHNOLOGY ACTIVITIES

Guy Hammer
Ballistic Missile Defense Organization (BMDO), Office of Technology Applications

BMDO funds nanotechnology development as part of its research in new materials and the manipulation of materials below 100 nanometers, primarily through its Advanced Technology Development Program. Generally, the BMDO-funded research is in two categories: nanotechnology and supporting technologies. BMDO nanotechnology has potential application in areas such as electronic devices, directed energy, propulsion systems, thermal management, and sensors. In 1996, BMDO published a nanotechnology report, entitled "Nanotechnology: Products for the Material World," as a supplement to the Summer issue of the *BMDO Update* quarterly newsletter; this report describes a number of specific nanotechnology projects that BMDO supports, including R&D in opto- and micro-electronic devices, lithography, and materials:

Electronic Devices

- Use of bacterial masks to make 2 nm quantum boxes for use in thin flat-panel displays (Astralux, Inc.)
- Development of silicon-based superlattice or quantum transistors for use in future large-scale integrated circuits and optoelectronic circuits (NanoDynamics, Inc.)
- Production of giant magnetoresistance (GMR) materials from alternating thin-film layers of ferromagnetic material and nonferrogamnetic conductors for application in magnetic field sensors and nonvolatile memory devices (NonVolatile Electronics and Motorola)
- Development of porous erbium-implanted silicon LEDs for use in long-distance fiberoptic communications (Spire Corp.)
- Several University of Texas (Austin) programs, including growth of SiGeC heterostructures and alloys through ultrahigh-vacuum chemical vapor deposition (UHVCVD), and deposition of quantum wires and dots using scanning tunneling microscopy
- Development of vertical cavity surface-emitting lasers (VCSELs) (Vixel Corp.)

Lithography

- Development of e-beam lithography capable of producing 0.2 µm linewidths, leading to 0.05 µm linewidths, for use in building GMR-based memory cells (NonVolatile Electronics)

Materials

- Production of vapor-grown carbon fibers with diameters down to 200 nm for such applications as electromagnetic shielding and nanostructural reinforcement in rubbers and elastomers (Applied Sciences, Inc.)
- Use of dynamic magnetic compaction to rapidly consolidate material powders using pressures generated from pulsed electromagnetic fields, for application to nanophase materials, among others. This spinoff technology resulted from BMDO railgun research (IAP Research, Inc.)
- Development of Jet Vapor Deposition (JVD™) process that uses sonic jets and inert carrier gases to produce metal, semiconductor, insulator, and organic films controlled at the microstructural level for application in semiconductor manufacturing, turbine blade coatings, and fuel cell components (Jet Process Corp.)
- Development of self-reinforced, rigid-rod polymers (Poly-X™) with high tensile module for use in structural composites, scratch-resistant windows, and electronics packaging (Maxdem, Inc.)

The BMDO nanotechnology report also describes 9 projects in supporting technologies (characterization, modeling and simulation, and process control).

The BMDO Office of Technology Applications welcomes the opportunity to leverage its investment in nanotechnology with others to help facilitate the transfer of this technology to commercial applications for the benefit of all citizens.

CONNECTIONS TO OTHER FIELDS; EDUCATION ISSUES

Gary Poehlein
Directorate for Engineering, NSF

Other Fields

The use of the prefix "nano" on many terms has expanded rapidly in the past several years. One of the drivers for this has been new technical capabilities and knowledge in dealing with materials in the size range between single molecules and a micron and, of course, the enormous commercial potential for new products, especially in the electronics and biotechnology marketplaces. Man-made nanoparticles for a few applications, however, have been produced commercially for many years. Hence, one factor that needs to be considered as work in this area expands rapidly is, how much can be learned from previous research and development in some of the more mature nanofields?

The area of emulsion polymerization and latex technology is one example of a more mature technology. Polymer nanoparticles have been commercially produced for more that 50 years. In the current state of the art it is possible to produce particles in the size range of about 20 nm (maybe slightly smaller in special cases) to more than one micron. The sizes and size distributions can generally be controlled with reasonable precision. It is possible to produce monodisperse latexes good enough to serve as calibration standards, bi- and tri-modal distributions, as well as rather broad continuous distributions. The particles in these systems can have the same or different (and controlled) chemical compositions, morphologies, surface characteristics, and shapes. Major advances in theory, manufacturing methods, and prediction of application performance have strengthened the fundamental knowledge base and thereby accelerated development is this important area.

Connecting workers in the "new nanotechnologies" to those in some of these more mature fields may be of significant benefit to all participants. Some knowledge and well established practices may be transferable, and new insights may flow in both directions.

Education

The development, manufacture, and intelligent utilization of the numerous new products that will flow from the nanotechnology age will require highly skilled human resources. The extensive research activities in industry, national laboratories, and especially universities will play a major role in addressing the need for people with in-depth knowledge who are capable of making contributions at the cutting-edge. Sources of persons who are able to efficiently modify products and processes, manufacture devices, and intelligently utilize nanoproducts could be a more serious problem. Current college courses deal almost exclusively with molecules and macroscale phenomena with nothing in between. Most universities, even some highly recognized research institutions, do not even have a basic course in fundamental surface and colloid science. The question is rather straightforward: How will we prepare science and engineering graduates, at all degree levels, to function effectively with the new and future technologies at the nanoscale? What should be done with basic courses, advanced electives, and equally important, continuing education for persons who enter these new fields? The costs of not dealing with these important issues could be very significant.

CHAPTER 4

SYNTHESIS AND ASSEMBLY

OVERVIEW

Evelyn Hu
University of California at Santa Barbara
WTEC Panel Co-Chair

A basic premise that informs the diverse work on nanostructure synthesis, and a premise of this WTEC study in particular, is that the length scales defining structure and organization determine the fundamental characteristics of the material. Hence, if we can control structures at the level of those length scales, we can control the material. Aksay posits nested levels of structural hierarchy that together yield improved properties in the total material (Aksay et al. 1992): this is a useful framework to employ in a comparative description of the various techniques of synthesis and assembly presented in this study.

Hierarchical organization begins at the nanometer length scale and can comprise the unit cell of a crystalline structure. Succeeding levels of the hierarchy might include the scale of the grain size within a polycrystalline or composite material. We may choose to synthesize the nanoscaled building blocks of our materials through the aerosol techniques described by Friedlander (Wu et al. 1993); the controlled reaction of organo-metallic precursors to form semiconductor "nanocrystals" described by Brus et al. (1995); or the formation of powder particles by gas condensation of metal vapors in a low pressure inert atmosphere described by Schwarz (Wasz et al. 1995). Those building blocks can subsequently be further organized through incorporation into a matrix material (e.g., a polymer) or through compaction of component heterogeneous nanoparticles into a composite whole.

Another approach is to create uniform macroscopic layers of the desired material and, separating materials synthesis from subsequent processing, pattern and "carve out" the desired nanostructures. This is the approach that characterizes the formation of "functional" electronic and optical nanostructures fashioned largely from single crystal semiconductor materials; it requires a battery of pattern formation (such as electron beam lithography) and pattern transfer processes (such as reactive ion etching) that have the requisite spatial resolution to achieve creation of structures at the nanoscale. This particular area of nanostructure formation has tremendous scope, warranting its own separate study. It is a driving issue for the electronics industry and is not a principal theme of this WTEC study. We simply mention here that there are tremendous problems associated with the viability of present techniques for nanometer scale fabrication: some of these issues are addressed through Whitesides' "soft lithographic" techniques (Wang et al. 1997). Based on the study of self-assembling surfaces (e.g., alkylthiols and other biomembrane mimics on gold), soft lithography incorporates an elastomeric stamp that enables multiple-use, rapid pattern transfer, extendible to non-flat surfaces. Soft lithography has been shown to be viable at dimensions < 25 nm (Chou, Krauss, and Renstrom 1996).

Yet another approach, the most potentially powerful one, is the one Aksay describes as pertaining to biogenic materials (Sarikaya and Aksay 1994), in which nanostructural design is achieved through the self-assembly of organics (1-100 nm), which forms the scaffolding for the deposition of inorganic materials. The organic structures form a natural, ordered structure that can in turn catalytically or epitaxially induce growth of specifically oriented inorganic thin films. Ying's work follows this theme, with the use of surfactant-metal interactions to form self-assembled structures. These two themes, self-assembly and the formation of natural templates at the nanoscale for the further nucleation of material, may be key concepts in the controlled engineering of materials from the nanostructure level. For example, zeolite cages or carbon nanotubes could serve as the templates for the nucleation of nanostructured synthesis of metal or semiconductor materials.

"Self-assembly" is a term that arose from and best pertains to biological synthesis of molecules that undergo exquisitely selective binding and obey highly specific rules for self-assembly. Because of these properties, research is now being focused on the specific utilization of such highly ordered, complex biological materials, such as DNA, as the building blocks of more complex, three-dimensional nanostructures (Du, Stollar, and Seeman 1992). Research frontiers that exploit the capacity of biomolecules and cellular systems to undergo self-assembly have been identified in two recent National Research Council (NRC) reports (1994, 1996). The general importance and desirability of this degree of control of composition, size, and structure is so critical to the area of nanostructure synthesis that self-assembly has been an increasing hallmark of the field, whether applied to the synthesis of semiconductor structures or polymers employed as templates for lithography. The term has therefore taken on a spectrum of meanings: in many cases chemical specificity leads to the self-assembled formation of zeolite, mesoporous structures, or carbon nanotubules. The pseudomorphic growth of lattice-mismatched semiconductors and the drive of the system to minimize its free energy leads to the islanded growth of self-assembled quantum dots, as detailed by Petroff (Leonard et al. 1993).

The synthesis techniques discussed in this report span a wide number of applications and different levels of maturity and utilization in manufacturing. The applications in turn dictate different levels of tolerance in the size distribution and control over the component nanostructure, although process and structure control remain important issues even for the more mature technologies, such as those used in powder production (see, for example, Pratsinis and Kodas 1993; also, Table 1 in WTEC 1997, 93). For example, nanostructured thermal barrier coatings offer the advantage of lower thermal conductivity, but the change in thermal conductivity may vary only slightly for an order of magnitude change in the nanostructure dimension (Gell 1997; also p. 126 in Chapter 6 of this volume). However, certain electronic device applications may require a uniformity in the nanostructure size of less than ± 1 nm in order to realize the expected device benefits.

Concerning the diversity of approaches to nanostructure synthesis that are treated in this study, the broad questions are as follows:

- What are the issues of control of the nanostructure formation (level 1 in the hierarchy)? Brus has mentioned the importance of the separation of nucleation from growth process; is this an important strategy to adopt?
- What are the issues of control of compaction/consolidation process (level 2 in hierarchy)?
- Will present nanostructure synthesis techniques be able to evolve to the greater hierarchical (more sophisticated) structures characteristic of biogenic systems? Will we be able to devise economical means of integrating synthesis and consolidation as in biogenic systems — that is, use self-assembled structures to form templates for further growth, etc.?

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SOFT LITHOGRAPHY

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Scientific Drivers

Fabrication of new types of electronic, magnetic, and optical devices currently consists of redesigning existing structures in down-sized versions. We are exploring an alternate strategy that uses "soft lithography" for the fabrication and manufacture of nanostructures. With these techniques we are able to generate patterns with critical dimensions as small as 30 nm. These techniques use transparent, elastomeric polydimethylsiloxane (PDMS) "stamps" with patterned relief on the surface to generate features. The stamps can be prepared by casting prepolymers against masters patterned by conventional lithographic techniques, as well as against other masters of interest.

Several different techniques are known collectively as soft lithography. They are as described below:

- *Near-Field Phase Shift Lithography*. A transparent PDMS phase mask with relief on its surface is placed in conformal contact with a layer of photoresist. Light passing through the stamp is modulated in the near-field. If the relief on the surface of the stamp shifts the phase of light by an odd multiple of π, a node in the intensity is produced. Features with dimensions between 40 and 100 nm are produced in photoresist at each phase edge (Rogers et al. n.d.).
- *Replica Molding*. A PDMS stamp is cast against a conventionally patterned master. Polyurethane is then molded against the secondary PDMS master. In this way, multiple copies can be made without damaging the original master. The technique can replicate features as small as 30 nm (Xia et al. 1997).
- *Micromolding in Capillaries (MIMIC)*. Continuous channels are formed when a PDMS stamp is brought into conformal contact with a solid substrate. Capillary action fills the channels with a polymer precursor. The polymer is cured and the stamp is removed. MIMIC is able to generate features down to 1 µm in size (Kim, Xia and Whitesides 1995; Xia, Kim, and Whitesides 1996).
- *Microtransfer Molding (µTM)*. A PDMS stamp is filled with a prepolymer or ceramic precursor and placed on a substrate. The material is cured and the stamp is removed. The technique generates features as small as 250 nm and is able to generate multilayer systems (Zhao, Xia, and Whitesides 1996).
- *Solvent-assisted Microcontact Molding (SAMIM)*. A small amount of solvent is spread on a patterned PDMS stamp and the stamp is placed on a polymer, such as photoresist. The solvent swells the polymer and causes it to expand to fill the surface relief of the stamp. Features as small as 60 nm have been produced (Kim et al. n.d.).
- *Microcontact Printing (µCP)*. An "ink" of alkanethiols is spread on a patterned PDMS stamp. The stamp is then brought into contact with the substrate, which can range from coinage metals to oxide layers. The thiol ink is transferred to the substrate where it forms a self-assembled monolayer that can act as a resist against etching. Features as small as 300 nm have been made in this way (Kumar and Whitesides 1993).
- Techniques used in other groups include micromachining of silicon for microelectricalmechanical systems (MEMS) (Mehregany et al. 1992), and embossing of thermoplastic with patterned quartz (Chou, Krauss, and Renstrom 1996).

Our techniques require little in capital investment and most can be carried out in ambient laboratory conditions at low cost. Unlike conventional lithography, these techniques are able to generate features on both curved (Jackman, Wilbur, and Whitesides 1995) and reflective substrates and rapidly pattern large areas. A variety of materials have been patterned using the above techniques, including metals and polymers (Joon et al. 1995; St. John and Craighead 1996; Wang et al. 1997). The methods complement and extend existing nanolithographic techniques and provide new routes to high-quality patterns and structures with feature sizes

≥30 nm. There are, however, important unresolved problems such as distortions in the mask and issues such as runout and registration in multilevel fabrication.

Applications of soft lithography in the near future could include simple optical devices, such as polarizers, filters, wire grids, and surface acoustic wave (SAW) devices (Zhao et al. 1996). Longer term goals include working toward optical data storage systems, flat panel displays, and quantum devices. Soft lithographic techniques are currently not competitive with conventional photolithography for multilayer fabrication where there are critical requirements for pattern regularity.

Critical Parameters

Soft lithography appears to be a promising route to nanostructures and nanosystems. Many issues remain to be solved, however, before the techniques can be brought to the market. Some critical parameters are applicable to all the techniques, while others apply only to specific techniques.

Multilevel structures and devices necessitate the ability to accurately place one layer on top of another. High-resolution registration is problematic with elastomeric, distortion-prone materials. Distortion currently limits soft lithographic techniques to the fabrication of single-layer structures and devices. Registration is possible on micron-sized features using a mask aligner. Studies are also underway in our group to quantify the distortion in elastomeric stamps and to limit this distortion by using thick stamps and rigid backings.

The formation and distribution of defects also must be controlled if these techniques are to be used in device fabrication. Defects arise from dust particles, poor adhesion to the substrate and poor release from the stamp, bubbles in the precursor, and contamination from low molecular weight monomers in the stamp. Another problem is the presence of a thin film of polymer under the nanometer-sized features in certain of the soft lithographic methods; microtransfer molding and solvent-assisted embossing often have problems with underlayer control. The presence of the underlayer makes etching and lift-off difficult. Although reactive ion etching can be used to remove thin layers, the time necessary to remove thick layers would damage small features.

The resist used has been a limiting factor in some cases. Phase shift lithography is able to generate features in photoresist more than an order of magnitude smaller than those for which the resist and mask aligner are designed. The resist is, however, only filtered to particles of 40 nm, suggesting that it will be difficult to achieve smaller features consistently with current materials. In microcontact printing where the SAM functions as a resist for etching, the resolution of the grain size of gold in the substrate produced by evaporation (30 nm) limits the edge resolution of the etched area.

Phase-shift lithography has its own set of problems. Features are formed at a phase edge: a mask with a 4 µm period generates two 90 nm lines with a distance of 2 µm between them. Increasing the density of the features is challenging. The fabrication of features such as T-junctions is complex because of the necessity of the phase edge. Integration of large and small features in phase shift lithography is also difficult. The compatibility of these patterning techniques with the production of microelectronic circuitry is starting to be addressed.

The above difficulties are tractable; creativity, however, will be necessary to overcome them.

Bringing Soft Lithography to the Market

Nanostructures are fabricated ordinarily using advanced nanolithographic techniques such as e-beam writing, X-ray lithography, and proximal-probe lithography. These techniques are capable of providing very small features, but their development into methods for generating large areas of nanostructures rapidly and at low cost will require some ingenuity. Conventional techniques are also limited to the formation of two-dimensional structures in a limited number of materials on planar surfaces. The lack of techniques capable of generating and manufacturing nanostructures rapidly and economically represents a limiting step in the area of nanoscience and nanotechnology.

Soft lithography suggests a new conceptual approach to nanomanufacturing: advanced nanolithographic techniques would be used to make masters, and these structures would then be transferred into organic polymers or other materials using procedures such as printing, molding, embossing, or a combination thereof. The techniques could be automated (Xia, Qin, and Whitesides 1996). The ability to make both positive and negative replicas and to modify the dimensions and shapes of features present on elastomeric masters by mechanical deformation adds further flexibility to this methodology (Xia and Whitesides 1997). Currently, our ability to manufacture is limited to devices where small feature size is important but lateral distortions are not: single-level structures such as polarizers and waveguides. The limitations are due to the yet unresolved issues of registration and distortion. Further practical technological uses of these techniques will require further development.

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NANOSTRUCTURED CERAMICS THROUGH SELF-ASSEMBLY

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Opportunity

The length scales defining structure and organization determine the fundamental characteristics of a material. Traditional ceramic materials exhibit organization on two length scales: the atomic scale, e.g., the unit cell of the crystal or the local arrangement of amorphous materials, and the scale of the grain size within the composite, typically much longer length and on the order of micrometers or greater. In biogenic materials, however, we observe a much broader range of organizational length scales: (1) a hierarchical organization always starts at the nanometer length scale, in which case, nanostructural design is the building block of larger scale composite structures; and (2) the nested levels of structural hierarchy appear to yield improved properties for particular functions (Aksay et al. 1994; NAP 1994).

In biogenic systems, nanostructural design is accomplished through the self-assembly of organics. Inorganic structures form via template-assisted self-assembly, where self-assembled organic material (e.g., proteins and/or lipids) form the structural scaffolding for the deposition of inorganic material (Sarikaya and Aksay 1994; Sarikaya and Aksay 1992). Organic materials are organized on length scales of 1-100 nm and used as frameworks for specifically oriented and shaped inorganic crystals (i.e., ceramics such as hydroxyapatite, $CaCO_3$, SiO_2, and Fe_3O_4) (Lowenstam and Weiner 1989; Mann 1993 a and b; Heywood and Mann 1992). In some cases, structurally organized organic surfaces catalytically or epitaxially induce growth of specifically oriented inorganic thin films. Further, nature’s way of mineralization uses environmentally balanced aqueous solution chemistries at temperatures below 100°C. This approach provides an opportunity for the processing of inorganics with nanoscale patterns. Two examples are used to illustrate the potential of this approach.

Template Assisted Nanostructured Ceramic Thin Films

A new class of materials discovered by scientists at Mobil Corporation ideally illustrates the utility of self-assembly in materials design (Kresge et al. 1992; Beck et al. 1992). Silica precursors when mixed with surfactants result in polymerized silica “casts” or “templates” of commonly observed surfactant-water liquid crystals. Three different mesoporous geometries have been reported (Kresge et al. 1992; Beck et al. 1992; McGehee 1994; McGehee et al. 1994; Monnier et al. 1993), each mirroring an underlying surfactant-water mesophase (Figure 4.1). These mesoporous materials are constructed of walls of amorphous silica, only ten or so angstroms thick, organized about a repetitive arrangement of pores up to a hundred angstroms in diameter. The resulting materials are locally amorphous (on atomic length scales) and crystalline on larger (tens to hundreds of angstrom) length scales.

The availability of highly controlled pores on the 10 to 100 Å scale offers opportunities for creating unusual composites, with structures and properties unlike any that have been made to date. However, the effective use of mesoporous silicates requires two critical achievements: (1) controlling the mesophase pore structure and (2) synthesizing large monolithic and mesoporous “building blocks” for the construction of larger, viable composite materials. Although important information exists on some aspects of controlling the mesoporous structure (Kresge at a. 1992; Beck et al. 1992; Huo et al. 1993), large scale structures have not yet been constructed. However, the general outline for fabricating useful composites is known: First, rigid silica (or other ceramic) skeletons form at the surfactant-water interface. This is followed by the removal of the organic phase to yield a ceramic cellular solid containing periodic, 1-10 nm diameter pores. The porous structures may be used as a cellular solid or subsequently infiltrated with secondary phases.

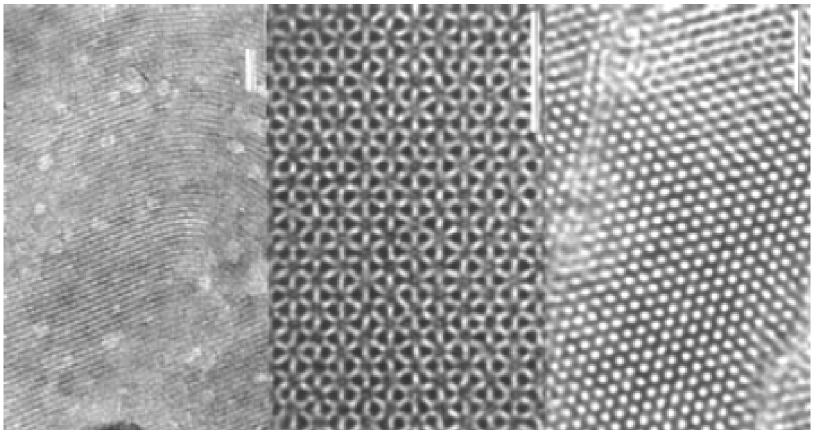
(a) (b) (c)

Fig. 4.1. Transmission electron microscope images of (a) the lamellar morphology, (b) the cubic phase with Ia3d symmetry viewed along its [111] zone axis, and (c) the hexagonal phase viewed along its [001] zone axis of the silica/surfactant nanostructured composites by co-assembly (McGehee 1994; McGehee et al. 1994) (bars = 30 nm).

The synthesis scheme of silica-based mesostructured materials (Kresge et al. 1992; Beck et al. 1992; Monnier et al. 1993; Huo et al. 1993) using supramolecular assemblies of surfactant molecules to template the condensation of inorganic species has now been extended to include a wide variety of transition metal oxides (Antonelli and Ying 1995) and recently, cadmium sulfide and selenide semiconductors (Braun, Osenar, and Strupp 1996). Although the exact mechanism for this type of mineralization is still controversial (Monnier et al. 1993), this technique holds great promise as a synthetic scheme to produce nanostructured materials with novel thermal, electronic, optical, mechanical, and selective molecular transport properties. For any of these applications to be realized, however, what is clearly required is a method by which these nanostructures can be formed into controlled shapes and patterns rather than the microscopic particulates (Aksay et al. 1996; Yang et al. 1996).

Our work (Aksay et al. 1996) has shown that continuous mesoporous silicate films can be grown onto a wide variety of substrates. Of primary concern here is the structure of the first layer of adsorbed surfactant at each of these interfaces. Although the molecular organization and self-assembly of surfactants at interfaces is a widely studied area, little is yet known about the precise structure of adsorbed surfactant layers. Recent work (Manne et al. 1994) has shown that three-dimensional surfactant structures such as cylindrical tubules and spheres can be formed at solid/liquid interfaces. Adsorbed hemi-micellar arrangements are observed on poorly orienting amorphous substrates such as silica, and aligned tubular structures are observed on more strongly orienting crystalline substrates such as mica and graphite. The latter substrates orient adsorbed surfactants via anisotropic attraction (either van der Waals or electrostatic) between the crystalline substrate and the surfactant molecule. The amorphous silica substrate has no preferential orientation for surfactant adsorption.

Figure 4.2 shows in-situ atomic force microscopy (AFM) images of the atomic lattice of mesoscopic films grown on mica and graphite interfaces. The structure of the respective substrates is shown in each insert, with the main image revealing the structure of the mesoscopic silica overlayer growing on each surface. All films are continuous and display distinctly different textures at length scales between 0.5-10 microns.

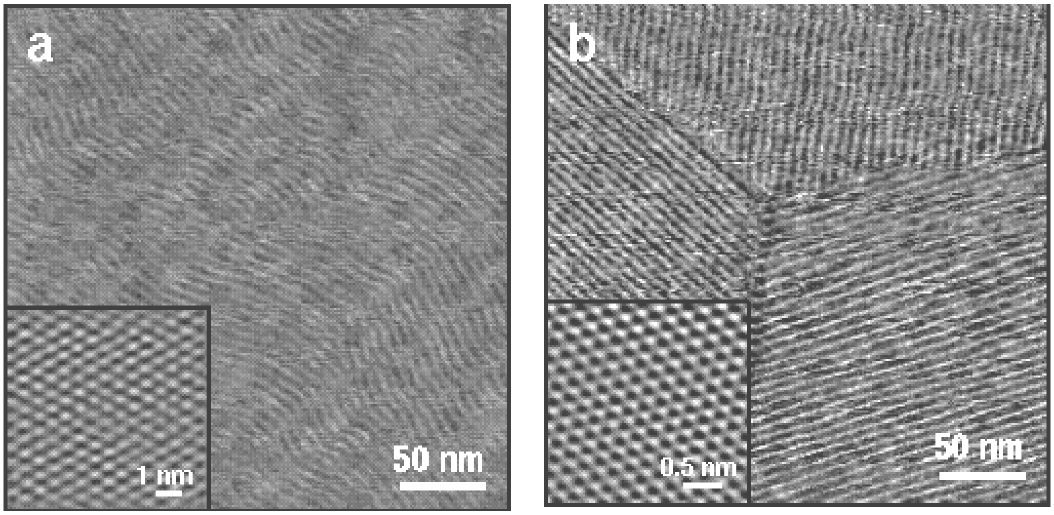

Fig. 4.2. In-situ AFM images of mesostructured films growing on (a) mica and (b) graphite substrates, respectively. AFM images of the substrates used to grow mesoscopic silica films are shown in the insets. (a) and (b) illustrate the periodic mica and graphite atomic lattice onto which CTAC adsorb and orient (Aksay et al. 1996).

Nanoscale Patterning With Block Copolymers

Towards the goal of forming nanostructured composites with periodic patterns, we have also successfully grown amorphous $BaTiO_3$ regio-selectively onto polybutadiene (PB) interdomains within a polystyrene (PS)-polybutadiene-polystyrene triblock copolymer, Kraton D1102® (Shell Chemical Company, Houston, TX) thin film (Figure 4.3). The structure of Kraton was preserved throughout the chemical reactions. $BaTiO_3$, a dielectric and a ferroelectric, was selected as the inorganic phase because it is used extensively in multilayer capacitors, thermistors, and electrooptic devices (Wakino, Mirai, and Tamura 1984; Maurice and Buchanan 1987). Its low temperature (< 100°C) synthesis, an essential requirement for coupling with polymers, is well understood (Slamovich and Aksay 1996).

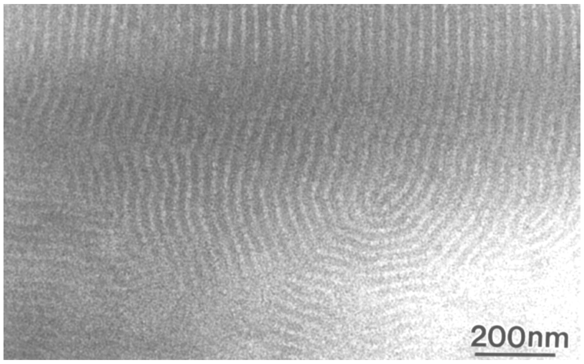

Fig. 4.3. A TEM bright field image of the amorphous barium titanated (dark lines) thin film of Kraton (Lee, Yao, and Aksay 1997).

Unlike the “solid-state micelle” method of Cohen and coworkers (Cummins et al. 1991; Yue and Cohen 1994), our approach allows: (1) the nanodomains in solid films to be chemically functionalized in situ, (2) the inorganic precursors to propagate along template macromolecules within the interdomains in solid films, and (3) the inorganic precursors to grow on the top of the polymerized ceramic precursors.

Conclusions

Similar to the processes observed in the processing of biogenic composites, the architectures generated through self-assembly of surfactants or macromolecules can serve as templates to process ceramics with nanostructural patterns. Two examples given in this summary illustrate the potential of this approach, especially in applications where substrates cannot be exposed to high temperatures. The method is ideal for processing organic/inorganic nanocomposites. However, the removal of the organic yields nanostructured ceramic scaffoldings that can be used to process ceramic/ceramic or ceramic/metal nanocomposites as well.

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SYNTHESIS OF NANOPARTICLES AND THEIR AGGLOMERATES: AEROSOL REACTORS

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Introduction

Aerosol processes are used routinely for the commercial production of ultrafine particles ($d_p < 100$ nm) and materials fabricated from them, and for pilot and laboratory scale production as well. *Aerosol reaction engineering* refers to the design of such processes, with the goal of relating product properties to the material properties of the aerosol precursors and the process conditions. The most important process conditions are usually the aerosol volume concentration (volume of particles per unit volume of gas) and the time/temperature history of the system.

Powdered material produced commercially by aerosol reactors is usually in the form of large agglomerates of particles held together by bonds of varying strength. The smallest, roughly spherical elements are called *primary particles*. These combine to form *aggregates* held together by necks resulting from sintering. *Agglomerates* are undispersed clusters of aggregates held together by weak (van der Waals) forces or binders. Agglomerates can be relatively easily broken down into their aggregate components.

Product properties of interest include primary particle size (and/or size distribution) and substructure (grain boundary, pore size and defect concentrations, and crystalline state). Also of great interest are the properties of the aggregates, including fractal dimension and particle bond energies. Methods have been developed for relating particle size to process conditions and material properties. Commercial technologies for the manufacture of fine particles have been for the most part designed with limited recourse to the principles of particle formation and growth. Requirements for product properties for existing commercial applications are not exceptionally demanding compared with anticipated needs for advanced materials. Commercially produced particles are polydisperse. The individual particles are polycrystalline with grain boundaries, and there may be significant necking between particles. It should be possible to exploit the available theory (and foreseeable advances) to permit significant improvements in product properties while retaining the high throughputs of commercial production methods, without excessive cost increments.

Fine particle formation by aerosol processes almost always takes place by gas-to-particle conversion. Condensable molecules produced by physical or chemical processes self-nucleate to form particles. The nuclei may be as small as a single molecule for refractory materials, but subsequent collision and coalescence leads to the formation of larger particles. Many lab-scale studies have been made to demonstrate novel methods for particle synthesis or to elucidate the mechanisms of particle formation, and there is an extensive literature (included in Selected References section below). Table 4.1 shows some of the more common processes that have been used for fine particle production. The most important full-scale commercial systems are flame reactors used for production of pigments and powdered materials and in the manufacture of optical fibers, and pyrolysis reactors for carbon black manufacture. Nanometer particles are produced in pilot scale evaporation/condensation (EC) generators operated at low pressures, usually a few torr. Commercial and pilot scale reactors are discussed briefly below.

The collision/coalescence mechanism that controls particle formation in the widely used flame reactors is probably important in pilot and laboratory reactors as well. Theoretical analysis of the collision/coalescence mechanism has focused on particles smaller than the mean free path of the gas, the range of interest for nanoparticle synthesis. The basic concepts are discussed at the end of this paper, along with the factors that determine the formation and properties of agglomerates.

Table 4.1
Comparison of Aerosol Processes for Powder Production

	Flame	Evap/Cond Reaction	Laser	Plasma	Hot Wall	Spray Pyrolysis
Max Size, μm	1	0.1-10	1	1	10	0.10-100
Spread	broad	narrow	narrow	broad	narrow	broad
Morphology	solid agglomerates	solid	solid	agglomerates solid	spherical solid	spherical solid, porous hollow
Max T, K	2500	<2000	2000	25,000	2000	1600
Material	oxides	metals and oxides	non-oxides oxides	non-oxides oxides	non-oxides oxides, semi-conductors	non-oxides oxides
Complexity	low	low	medium	high	low	low

From Pratsinis and Kodas (1993)

Aerosol Reactors: Commercial and Pilot Scale

Flame Reactors

The flame reactor is the most widely used for commercial production of inorganic oxide particles by aerosol processes. The aerosol precursor in the form of a vapor is mixed with oxygen fed into a reaction chamber and burned. Inert gases and fuels such as hydrogen or methane may also be present. An important commercial product made this way is pyrogenic silica with silicon tetrachloride vapor as the aerosol precursor. Pyrogenic silica is used as a filler in silicone rubber and in natural and synthetic rubber and to modify the rheological properties of paints, resins, and inks. Annual worldwide silica production in 1991 was an estimated 10^5 tons.

The stoichiometry of the reaction (but not the true chemical reaction steps) can be represented by the equations

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

Since the reaction occurs with water vapor, the process is called flame hydrolysis. The gas leaving the furnace, which contains silica particles, gaseous hydrochloric acid, hydrogen, and a small amount of chlorine, is passed through a series of tubes to provide residence time for agglomeration. The agglomerates are collected in cyclone separators, which may be followed by a bag filter. Flame temperature is varied over the range 1850°F to 2000°F by varying air, hydrogen, and silicon tetrachloride concentrations. At the lower end of the temperature range, the product particle size is smaller and the surface area higher. Nominal particle sizes for the various grades range from 7 to 27 nm, and surface areas range from 100 to 380 m^2/g. The particles form as a result of the collision/coalescence mechanism discussed later.

The flame process is also used in the production of nanoparticles from other vapor aerosol precursors. Examples are alumina and titania, commercial products produced from $AlCl_3$ and $TiCl_4$, respectively. Mixed oxides are produced from a vapor precursor mixture, for example, 99% $SiCl_4$ and 1% $TiCl_4$. Zirconium oxide is also produced on a pilot scale.

In the fabrication of optical fibers, a silica aerosol generated by the oxidation of silicon tetrachloride vapor in argon or helium passes into a quartz tube preform about a meter long, 25 mm o.d., 19 mm i.d. The silica aerosol deposits on the walls of the tube by thermophoresis. Detailed information on the particle size distribution of the aerosol that forms has not been published, but the size range is said to be 20 to 100 nm. Since the particle size is in the free molecule range, the thermophoretic velocity is almost independent of the diameter. The rotating tube is heated by a traversing oxyhydrogen torch, which sinters the deposited silica aerosol to form a surface layer without deforming the substrate tube. In this way, the core or cladding is built up layer by layer. The composition of the individual layers can be varied between torch traverses to produce the desired refractive index gradient in the fiber.

The principal dopant added to the silica for control of the refractive index gradient is germanium dioxide, with germanium tetrachloride vapor as the aerosol precursor. After mounting the preform vertically and heating it above the glass-softening temperature, the 1 m preform is drawn into a 125 μm diameter optical fiber 50 to 100 km long. This product of aerosol processes is of a very high purity capable of transmitting light over long distances with very little attenuation.

Pyrolysis Reactors

Carbon blacks, the oldest manufactured aerosols, are an amorphous form of carbon used in rubber, pigments, and ink. The surface area of the blacks used in rubber goods is in the range 10-150 m^2/g, and the primary particles have an average diameter of 20 to 300 nm. Pigment carbon black particles are smaller, with areas of 300 to 500 m^2/g. Carbon blacks are made by feeding a heavy petroleum oil and air into a reactor, where partial combustion of the oil raises the temperature to 1100-1700^{o}C, causing decomposition of the unburned hydrocarbon. The hot reaction products including carbon black are cooled by a water spray, and the particles are collected by cyclones and bag filters.

Reactors designed to produce higher surface area grades are operated at high gas velocities, temperatures, and turbulence. The reactors have three zones: a mixing zone in which the feedstock is introduced as a spray into a gas/air mixture, a cylindrical reactor where carbon is generated by the chemical reactions and particle formation occurs, and a third zone consisting of a water quench. The mechanisms of particle formation are not well understood but appear to be a combination of nucleation and growth followed by particle collision and coalescence, similar to inorganic oxide particle formation.

Evaporation/Condensation Aerosol Generators

In the evaporation/condensation (EC) generator, a solid material, usually a metal, is evaporated into an inert gas, and the vapor is then cooled by mixing to produce an aerosol. A systematic study of aerosol properties was made in a chamber consisting of a glass cylinder, 0.34 m in diameter and 0.45 m high, fitted with water-cooled stainless steel endplates. Metal samples were placed in an alumina crucible mounted in the chamber and heated by radiation from a graphite heater element. An inert gas, usually argon at 0.5 to 4 torr, was introduced into the chamber and the crucible heated at constant temperature and inert gas pressure. Hot metal vapor from the crucible mixed with cool surrounding inert gas to nucleate and form particles in sizes ranging from about 3-100 nm. The particles were collected by thermophoretic deposition at the top of the chamber. This system was capable of producing a few milligrams of powdered material over a reasonable period of operation; it has served as a prototype for similar systems operated at higher production rates.

The effect of metal vapor pressure on median particle diameter for magnesium and zinc particles was studied at argon pressures of 2.5 and 3.5 torr. The median particle diameter was roughly proportional to the vapor pressure for a given inert gas pressure. Increasing the inert gas pressure significantly increased particle size. An extensive set of samples of aluminum particles and a smaller number of samples of magnesium, zinc, and tin was produced. Electron diffraction showed that in all cases the particles were crystalline. Size distributions for aluminum and other particles were measured and correlated by lognormal size distribution functions. It was concluded that particle size was controlled by particle collision and coalescence processes. More experimental studies are needed using a wider range of materials and operating conditions, with well-controlled geometries and flow regimes. The experimental results need to be analyzed in light of our understanding of aerosol formation processes. While the EC generator operated in the batch mode has a low production rate, it offers the possibility of limiting contamination, since chemical reactions are usually excluded or limited.

The Collision/Coalescence Mechanism of Primary Particle Formation

Industrial flame reactors are operated at high particle concentrations resulting in high rates of particle collision. Particle size is determined by the rates of particle collision and subsequent coalescence. The collision/coalescence mechanism for particle formation is based on a series of steps assumed to proceed as follows:

- A chemical (or physical) process converts the aerosol precursor to condensable molecules.
- The condensable molecules self-nucleate to form a cloud of stable nuclei, which may be single molecules (corresponding to a nucleation process with zero activation energy).
- Stable nuclei collide and, initially, coalesce to form larger particles. The particles may be liquid or solid during the coalescence period.
- Coalescence ceases or slows significantly, leading to the formation of agglomerate structures.
- Coalescence and neck formation may continue for particles within the agglomerate structures.

These processes may go on simultaneously. For example, chemical or physical processes may continue to generate condensable monomer molecules throughout the process of particle formation. In this case, after an initial surge of particle formation, further releases of monomer molecules will deposit on existing particles without generating new particles.

The size of the primary particles depends on the temperature/time history and material properties. At high temperatures and for very small particles, the individual particles grow because particle coalescence occurs almost on contact, resulting in agglomerates of large individual particles, hence small specific surface area. At low temperatures, however, particle coalescence takes place slowly compared to collisions, producing fractal-like agglomerates with a high specific surface area. The two processes, collision and coalescence, can be incorporated in a single theory by including coalescence in the general dynamic equation for the aerosol particle size distribution. The rate of coalescence is introduced into the general dynamic equation by a term for the rate of surface area reduction; the final rate of approach to a spherical shape is proportional to the difference in the areas of the actual particle surface and a sphere with the same volume. A key material property controlling primary particle size is the solid state diffusion coefficient, D, which appears in the proportionality coefficient for the surface area decay. For a given aerosol time-temperature history and volumetric loading of solids, increasing D tends to increase primary particle size. Since solid state diffusion is an activated process, there is a strong temperature effect on particle formation in aerosol reactors.

Nanoparticle Agglomerates and Aerogels

Fractal concepts have been extensively used to characterize agglomerate formation and structure. However, fractal models provide little information on the strength of the bonds that hold particles together in agglomerates. Understanding of particle bond energies and agglomerate rigidity is important to downstream processing of particles and the manufacture of ceramic compacts. Based on experiment, hypotheses have been advanced on the effects of aerosol material properties and process conditions on particle-particle bond energies. In addition, the effects of temperature on the rate of restructuring of agglomerates have been used to estimate the activation energies of particle restructuring for silver and copper agglomerates.

Ceramics and metals made of consolidated nanoparticles may have significantly different and improved properties compared with materials made from coarser-grained powders. Previous studies of the behavior of nanoparticle consolidates have emphasized the importance of individual particle size. Nanoparticles are usually generated as chain aggregates. We have discovered that chains of nanoparticles stretch under tension and contract when the tension is relaxed. Figure 4.4 shows the stretching and contraction of a titania nanoparticle chain aggregate (NCA), initially about 250 nm long, composed of primary particles that are approximately

7 nm. There is reason to believe this behavior is general for morphologically similar aggregates of other transition metal oxide particles. NCA polymer-like behavior may help explain the ductility of nanoparticle ceramic compacts and the ability of carbon black and silica additives to increase the tensile strength and elastic modulus of rubber.

Aerogels are rigid structures composed of nanometer-sized particles with a void fraction up to 99%. In some ways, they can be considered giant aggregates held together by strong chemical bonds. Aerogels are of value for thermal insulation, for catalysis, and as electrode materials. The traditional route to the preparation of aerogels is to fix the particles in the form of a gel from the solution phase. Subsequent drying of the gel by a supercritical expansion leaves the skeleton of the interlinked particles, that is, the aerogel. A disadvantage of this technique is the long preparation time and expensive drying step. Efforts have been made to use an aerosol process to build an aerogel-like structure. Aerosol particles of different materials (carbon, brass, and steel) were generated by laser evaporation at atmospheric pressure; large, low-density agglomerate structures were produced by exposing the aerosol to an electric field.

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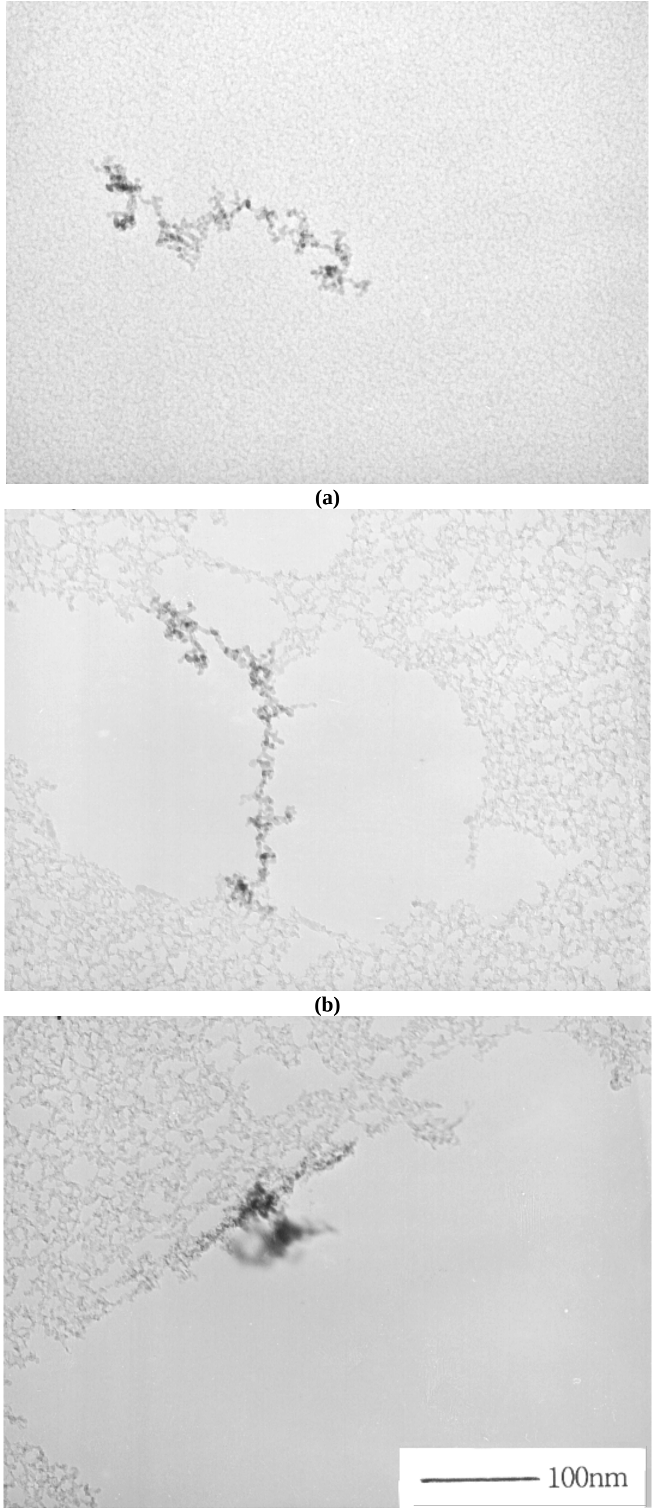

(a)

(b)

(c)

Fig. 4.4. (a) Initial shape of a titania NCA on the carbon film of an electron micrograph grid. (b) Stretched NCA connecting the edges of the carbon film that has partly evaporated in the electron beam. (c) Contracted NCA that is vibrating (seen as a blur) at one edge of the carbon film after disconnecting from the other edge. A portion of the NCA embedded in the film remains in focus. (a), (b), and (c) show the same NCA. The exposure time was about 4 s.

SEMICONDUCTOR NANOCRYSTALS

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Scientific Drivers, Technology, and Critical Questions

Electrical Circuits for Computers

The silicon microelectronics industry is the technological driver of modern society. The industry is built upon two major inventions: the solid state transistor and the photolithographic integrated circuit. The present technology is robust and advancing rapidly, as shown by the amazing improvement in and decrease in cost of simple PCs. Much of this is due to continued miniaturization in both magnetic memory and Si device size. This engineering improvement will continue to an ultimate Si feature size of perhaps 3-6 nm, an order of magnitude smaller in size than the smallest production devices at present. At even smaller sizes, several factors slow progress: basic statistical fluctuations in the power necessary for reliable driving of one device by the next and in the performance of individual transistors, coupled with the optical problem of photolithography on such a small scale. It is likely to be only several decades into the future when Si circuits ultimately reach a practical size limit. However, in approaching the 3-6 nm size, manufacturing and design must evolve, as semiconductors in this size regime are not true bulk materials. Nanocrystal research will thus guide the “ultimate” design principles of photolithographic Si circuits.

Going much smaller towards single-electron and small nanocrystal (“molecule”) devices will require an absolute revolution in all aspects of the industry. Such hypothetical circuits do not appear to violate the fundamental laws of physics and would offer huge performance advances. Today, with slow scanned probe techniques, we can move single atoms and assemble molecular-level devices; however, this is not a realistic manufacturing process. At present we are far from understanding how to carry out a practical engineered “chemical self-assembly” of diverse components to create a circuit approaching the complexity and especially the reliability of modern photolithographic circuits. Just as the photolithographic Si circuit of 1997 could not be imagined in the vacuum tube era of 1937, today we can not envision the circuit of 2057. Major, unexpected inventions and truly novel scientific insights are necessary; it is not simply a question of increasing money for development. The engineering of such circuits would represent a merging of synthetic chemistry and industrial technology. Indeed, academic chemistry is evolving towards fundamental study of very large molecules, self-assembly, and macroscopic matter. Solid state physics is evolving towards new materials with molecular level structure and very large unit cells. The nanometer range is being approached from both ends: top down and bottom up.

In this context, nanocrystals are basic building blocks. Even the most elementary questions are not quantitatively understood: How does charge transfer on and off nanocrystals? What is the influence of the environment? How can the internal electron-hole kinetics and the charge transfer be controlled by surface passivation, with both inorganic and organic species? Can we entirely eliminate surface states? Can we find ways to make crystalline nanocrystals of uniform shape, size, and surface stoichiometry? Can we find ways to assemble nanocrystals of different materials and electronegativities? What role does the difference in dielectric constants play? In a material with high internal interface area, can long-term stability while carrying current approach the stability of bulk semiconductors?

Solar Cells, Displays, and New Materials

In the next century, the question of global warming due to carbon dioxide in the atmosphere is likely to become critical as increased industrialization in the third world causes accelerated warming. Direct conversion of sunlight into electricity would require large-area, inexpensive, environmentally benign solar cell designs that could be integrated into building construction. The O’Regan-Gratzel liquid junction, thin film solar cell is composed of intimate, percolating networks of liquid electrolyte and partially fused titanium dioxide 10 nm particles (O'Regan and Gratzel 1991). Photoexcited charge separation occurs at the interface between the two phases. This cell represents a new design in solar cells and is very efficient, despite the fact it is made from inexpensive, poor electrical quality oxide semiconductor nanocrystals presently manufactured in huge quantities for the ceramic and paint industries. Can a liquid junction device be as inherently stable as an all solid state device? How do we understand charge transport through such as device when the diffusing carrier interacts with both the electrolyte and titanium dioxide? This device offers a glimpse of what novel designs might be possible; can we learn from this device to optimize other applications?

Nanocrystals have higher electron affinities than organic polymers such as PPV, which are used as hole conductors in organic displays. Moreover, nanocrystal affinities are size-tunable, and when used as luminescence centers for electron-hole recombination in electroluminescent displays, the emission color is also size-tunable. Thus, in the construction of inexpensive flat panel displays, layers of neat passivated nanocrystals make good electron transport layers, and the resulting hybrid organic/nanocrystal device can emit a range of colors (Dabbousi et al. 1995; Colvin, Schlamp, and Alivisatos 1994). Can we learn to optimize transport, and can we achieve a fundamental understanding of junctions between nanocrystal layers and organic layers?

Monodisperse nanocrystals can self-assemble into three-dimensional "supercrystals" that structurally resemble naturally occurring gem opals. The optical and electrical properties of such organized nanocrystal solids could be tuned through nanocrystal size, through the inter-nanocrystal coupling as controlled by surface passivation, and by doping via material in the interstitial spaces. Can we learn to make a wide variety of such materials?

Present Scientific Understanding and Synthetic Abilities

Work over the past decade has lead to an understanding of the evolution from molecules to bulk solids, at least in outline form, for individual nanocrystals, as shown in Fig. 4.5 (Brus et al. 1995).

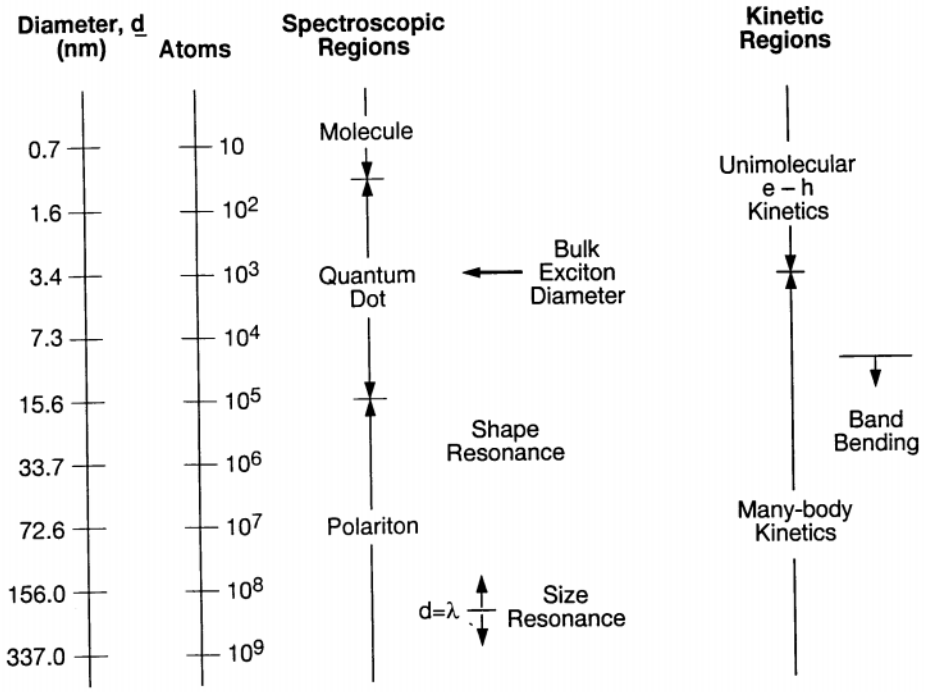

Fig. 4.5. Schematic size regimes for semiconductor nanocrystals.

In spectroscopic properties, there are three physical regimes: molecular, quantum dot (or nanocrystal), and polariton. Small clusters of some tens of atoms are molecules — the bulk unit cell is not present. In the nanocrystal regime, the unit cell is present, yet the electronic states are strongly quantum-confined in three dimensions. The excited electronic states and the band gap variation with size can be quantitatively calculated with advanced theory. In the polariton regime, the interaction with the electromagnetic field becomes strong and can be described by Mie theory.

In kinetic properties, there are two limiting regimes: unimolecular kinetics in small nanocrystals, and many-body kinetics in large nanocrystals. In small nanocrystals, the electrical field of a moving charge exits the nanocrystal and interacts with the local environment: this is essentially a molecular property (Brus 1996). In the absence of a moving charge, nanocrystals are intrinsic dielectric particles. (In bulk semiconductor transport, the physics is entirely internal; the fields of moving carriers terminate on ionized donor atoms.) Also, monolayer surface passivation with a higher band gap material can eliminate most nanocrystal surface states, while still allowing efficient electron transfer on and off the particle. In the CdSe system, organometallic synthesis has achieved the ability to make nearly uniform nanocrystals (Murray, Norris, and Bawendi 1993). An equivalently good synthesis for Si nanocrystals does not exist.

The ability to do single nanocrystal luminescence spectroscopy should accelerate our efforts to rigorously understand the physics (Nirmal et al. 1996). Nanocrystals are highly polarizable molecules, some thousands of atoms in size; in the electronic properties, every atom counts. Real samples have a wide distribution of shapes and surface structures; thus, the ability to examine properties one nanocrystal at a time is quite useful. Figure 4.6 shows room temperature luminescence from single CdSe nanocrystals. The luminescence is intermittent; the nanocrystal appears to "blink" on and off on a time scale of minutes. Such blinking is incoherent from one nanocrystal to the next and was averaged out in prior hole-burning and size-selective photoluminescence ensemble studies. The blinking is slowed down by surface passivation with ZnS and has been tentatively attributed to photoionization. The single molecule method is quite powerful for such complex systems.

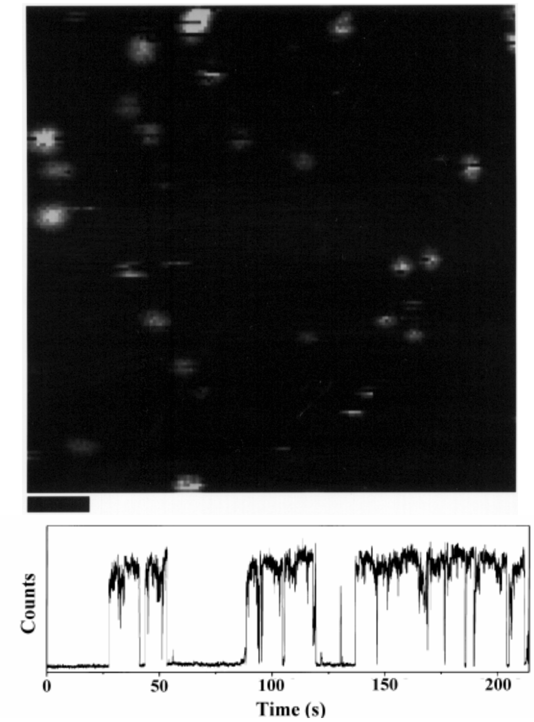

Fig.4.6. Scanning luminescence image of single CdSe nanocrystals (top); time trace of single nanocrystal luminescence under quasi-cw excitation (bottom) (Nirmal et al. 1996).

In the past five years, we have begun to understand the size dependence of indirect gap materials such as Si. The remarkably high photoluminescence quantum yield of Si nanocrystals and porous Si thin films can be traced to the size dependence of Auger nonradiative recombination. Small silicon nanocrystals remain indirect gap-like in all essential properties. They do not become partially direct gap-like, as was initially conjectured when the quantum properties of porous Si films were first discovered.

Just recently, systematic study of solid-solid phase transitions in nanocrystals has lead to the realization that nanocrystals in six-coordinate, dense structural phases, which are only theromodyanmically stable at high pressure, may be metastable at STP (Brus, Harkless, and Stillinger 1996). These phases have completely different optical and electrical properties than the normal sp3 hybridized phases. This opens up the possibility of an expanded inventory of possible nanocrystal materials in the future; to achieve this, novel synthetic methods are required (Brus 1997).

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STORAGE OF HYDROGEN IN POWDERS WITH NANOSIZED CRYSTALLINE DOMAINS

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Abstract

The term “nanostructured materials” is being used in the literature to denote different materials prepared by two different techniques: (1) by the gas condensation of vapors in a partial vacuum, and (2) by mechanical alloying, a high energy ball-milling technique. We discuss the origin of this confusion and propose a differentiating nomenclature. We then discuss the use of particles with nanosized structures for the storage of hydrogen.

Comment on Nomenclature

The terms “nanoparticles” and “nanostructures” are now commonly used to denote a variety of products, sometimes having quite different properties. This creates an unnecessary confusion. The term “nanoparticle” appeared in the literature around 1982 in connection with powder particles having physical dimensions of one to ten nanometers in diameter. These particles were prepared by H. Gleiter and co-workers by the gas condensation of metal vapors in a low-pressure inert atmosphere. These particles were then condensed and consolidated into small solids, and the products were called “nanostructured” materials. The structure of such a material, as revealed by a transmission electron microscope, consists of nanosized crystalline domains separated by sharp grain boundaries. The grain boundary thickness is on the order of one atom diameter, whereas the crystalline domains have a very low dislocation density.

In 1983, Koch and coworkers showed that binary amorphous alloy powders could be prepared by ball milling a binary mixture of elemental powders. Later, Schwarz and coworkers showed that to obtain an amorphous alloy powder, the two elemental powders must have a large negative heat of mixing in the liquid state; if the heat of mixing is positive, then the product is a crystalline powder. In both cases, the particle sizes were about 30 microns in diameter. The X-ray diffraction pattern of the heavily deformed powder had very broad diffraction peaks, indicating that the various crystalline domains that were diffracting coherently within each powder particle had very small dimensions, on the order of nanometers. Thus, the powder prepared by mechanical alloying (MA) was simply termed “nanocrystalline.” This denomination does not distinguish between powders prepared by MA and by gas condensation. In the MA powder, the crystalline domains within each particle are separated by wide amorphous-like transition regions having a very high dislocation density. These transition regions are often called grain boundaries, even though they are usually as wide as the crystalline regions. The transition regions diffract X-rays incoherently as an amorphous structure would, whereas the crystalline domains diffract coherently.

Since the diffracted intensity from the amorphous-like regions is very weak, the overall shape of the X-ray diffraction pattern from a heavily deformed MA powder is quite similar to that obtained from a true nanostructured powder prepared “a la Gleiter.” It is clear, however, that the structure of the two so-called “nanostructures” are quite different and thus the properties might also be different. It is thus advisable to denote the structures prepared by the gas condensation method as “nanostructures” (as originally used by Gleiter) and the powders obtained by MA as “heavily deformed.” A post-annealing treatment can be used to annihilate the high-density dislocation tangles in the mechanically alloyed powders and thus recover a more perfect crystalline structure; however, the annealing usually leads to grain growth.

Scientific Drivers and Advantages of Fine Microstructures in the Storage Of Hydrogen

Hydrogen presents one of the best alternatives to petroleum as an energy carrier. It is nonpolluting (burning hydrogen in a fuel cell causes no CO_2 emissions) and can be easily produced from renewable energy sources. However, the development of a hydrogen-based economy is contingent on the development of safe and cost-effective hydrogen storage systems. Of the known methods for hydrogen storage (cryogenic liquid, compressed gas, and metal hydrides), metal hydrides offer the best compromise weighing both safety and cost. The metal hydride systems of current industrial interest have been classified as AB_5 (e.g., $LaNi_5$), AB (e.g., FeTi), A_2B (e.g., Mg_2Ni), and AB_2 (e.g., ZrV_2). The hydrogen storage capacity, the number of times the storage can be done reversibly, and the kinetics of hydrogen absorption/desorption are intimately linked to the alloy microstructure. Powder particles having nanostructured features have some definite advantages.

Critical Parameters in the Performance of the Hydrogen Storage Material

Of primary importance in the hydrogen storage by metal hydrides is the pressure “plateau” at which the material reversibly absorbs/desorbs large quantities of hydrogen. For many applications, the plateau pressure should be close to ambient pressure because this allows the use of lightweight storage containers. The plateau pressure can be tailored to a specific application through alloying. For example, the plateau pressure of $LaNi_5$ can be lowered by the addition of a few percent tin (Wasz et al. 1995). The next important consideration is a fast kinetics of absorption/desorption, and this can be achieved by refining the microstructure.

Magnesium is an excellent hydrogen storage medium since it can store about 7.7 wt. % hydrogen, more than any other metal or alloy. However, the absorption/desorption of hydrogen in magnesium is very slow, and a catalyst is needed to accelerate the reaction. Figure 4.7 shows the microstructure of a Mg-11.3 at % Ni alloy that we are investigating for storing hydrogen gas. At this composition, the alloy is a two-phase mixture of pure magnesium (majority dark phase) and Mg_2Ni (small light inclusions). Most of the hydrogen is stored in the low density magnesium phase. The small Mg_2Ni inclusions catalyze the decomposition of the molecular hydrogen, increasing significantly the hydrogen absorption/desorption kinetics. The catalyst is quite effective since it is finely divided and is in intimate contact with the pure magnesium phase.

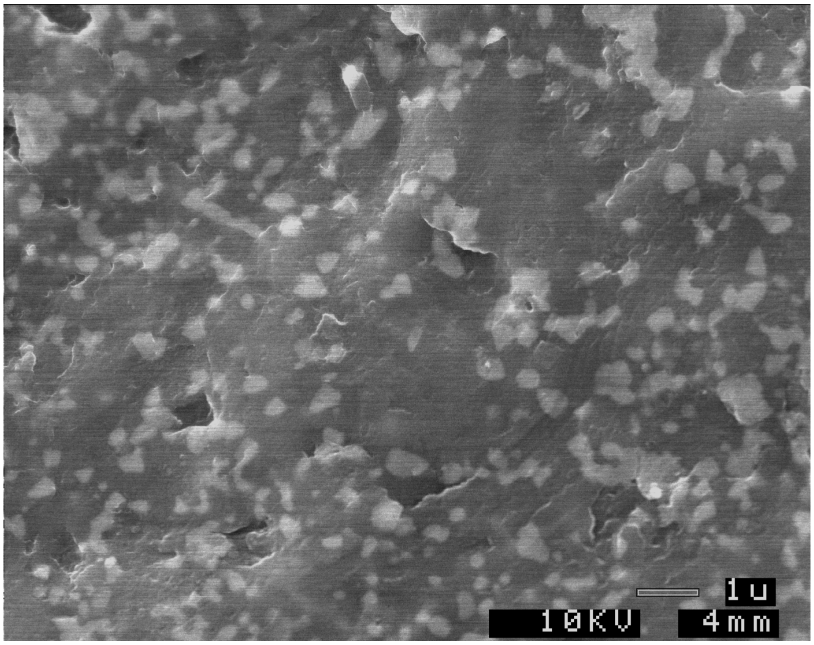

Figure 4.7. Scanning electron micrograph of a Mg-11.3 at. % Ni particle used for hydrogen storage.

Figure 4.8 shows the hydrogen absorption/desorption characteristics of this alloy. The first plateau corresponds to the absorption of hydrogen into pure magnesium, and the second plateau denotes the absorption of hydrogen into the Mg_2Ni phase. The absorption/desorption on hydrogen into this alloy is very fast (comparable to that of $LaNi_5$), and it is clear that microstructure plays an important role in the performance of the material. Another advantage of the fine microstructure is that the alloy powder does not comminute as the result of repeated charging-discharging with hydrogen. The synthesis of the powder particles shown in Fig. 4.7 is accomplished by mechanically alloying a mixture of elemental Mg and Ni powders, followed by a annealing treatment. Other catalysts being studied include FeTi and $LaNi_5$.

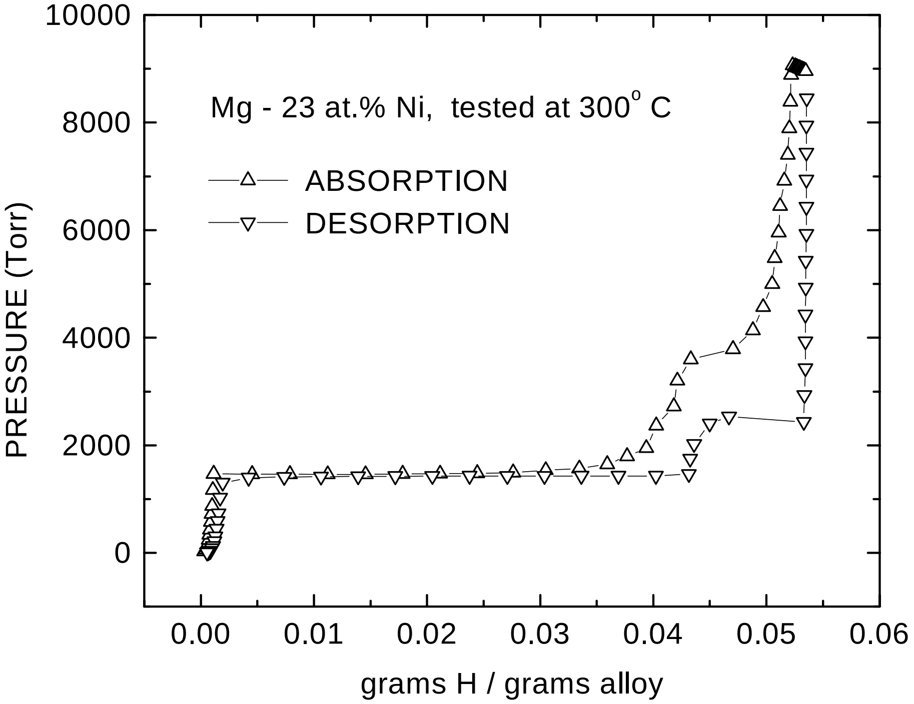

Fig. 4.8. Hydrogen absorption/desorption characteristics.

Possibilities to Bring the Synthesis Techniques to the Market

Alloy powders with nanosized crystalline domains will most likely play an increasingly important role in the storage of hydrogen. There are two main advantages of the MA method in the synthesis of these powders:

- MA can be used to alloy elements having vastly different melting temperatures, which cannot be easily done by conventional techniques such as arc melting.
- MA is a mature powder synthesis technique, and the method can be easily scaled from the laboratory (5 to 50 gram powder batches) to industry (20 kg to 20 ton powder batches).

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NANOSTRUCTURE PROCESSING OF ADVANCED CATALYTIC MATERIALS

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Introduction

Heterogeneous catalysis has had a major impact on chemicals and fuels production, environmental protection and remediation, and processing of consumer products and advanced materials. A survey of U.S. industries revealed that the annual revenue from chemical and fuel production topped all other industrial sectors at $210 billion (MIT 1990). Bennet et al.’s survey (1988) showed that over 60% of the 63 major products and 90% of the 34 process innovations from 1930-80 involved catalysis, illustrating the critical role of this field in the fuel and chemical industry. The significance of catalytic processes can be further demonstrated by the value of their products, which amounted to $1 trillion in the United States alone in 1989 (Cusumano 1992). Improvement in catalytic activity and selectivity holds the key to developing more efficient catalytic processes. Ability to tailor catalytic materials with desired microstructure and active component dispersion can bring about significant advances in the field of catalysis. This can be accomplished through nanostructure processing of materials.

Nanostructure processing offers new capabilities of manipulating materials microstructure and compositional variation on the nanometer scale. Two classes of nanostructured materials are being developed through multidisciplinary research efforts: nanocrystalline and nonporous materials.

Nanocrystalline Materials

The first class of nanostructured systems, nanocrystalline materials, involves crystallites of 1-10 nm in dimension (Gleiter 1989; Siegel 1991). Due to their fine grain sizes, ultrahigh surface-to-volume ratio can be achieved readily in nanocrystalline materials. The large number of atoms located at the edges and on the surfaces of nanocrystallites provide active sites for catalyzing surface reactions. Nanocrystallites further possess unique hybrid properties characteristic of neither the molecular nor the bulk solid state limits. Nanocrystalline processing offers a practical way of retaining the results of property manipulation on the atomic or molecular level, producing novel materials with unique size-dependent behavior, including quantum confinement effects, superparamagnetism, greater microstructural uniformity for better mechanical reliability, and high ductility and superplasticity for advanced ceramics. Over the past decade, research on nanocrystalline materials has been greatly accelerated by the advances in our ability to manipulate structures on the molecular or atomic level. However, most of the studies have been directed towards the synthesis, characterization, and application of these systems as structural and optical/electronic materials. As catalysts, nanometer-sized active clusters have been examined for a long time, but they are mainly limited to supported metal systems. Direct synthesis and successful stabilization of nanocrystalline metallic and ceramic materials have only recently been investigated in detail for some catalytic applications (Trudeau and Ying 1996). It would be particularly fruitful to exploit the nanocrystalline systems for their size-dependent effects in structure-sensitive reactions, whereby the catalytic activity depends not only on the number of active sites, but also on the crystal structure, interatomic spacing, and crystallite size of the catalytic material.

A recent study on nanocrystalline cerium oxide-based catalysts demonstrated several unique features of nanocrystalline processing (Ying and Tschöpe 1996). By inert gas condensation of Ce clusters followed by controlled post-oxidation, it is possible to achieve highly non-stoichiometric CeO_{2-x} (Tschöpe and Ying 1994). The unusually high oxygen vacancy concentration possessed and retained by these nanocrystallites is associated with active superoxide surface species. Compared to the conventional high surface area CeO_2, nanocrystalline CeO_{2-x} enabled catalytic activation at a significantly lower temperature for SO_2 reduction and CO oxidation, and demonstrated superior poisoning resistance (Tschöpe et al. 1995). Nanocrystalline processing further allowed ultrahigh dispersion of components, such as that demonstrated in $Cu\text{-}CeO_{2-x}$ nanocomposites (Tschöpe, Ying, and Chiang 1995). Unique chemical and electronic synergistic effects can be obtained from such homogeneously dispersed multicomponent systems, useful towards promoting catalytic activity, especially when they are thermally stable under the reaction conditions.

Future research and development efforts in nanocrystalline materials should be directed towards improved powder processing that will minimize grain growth and loss of surface area in heat treatment. To greatly expand the commercial market for such new materials in catalysis, methods for cost-effective large-scale production of nanocrystals have to be developed, with advanced reactor design, without compromising grain size distribution, and with excellent control on particle agglomeration. There is a great deal of opportunity in synthesizing doped and multicomponent nanocrystalline materials to improve substantially the catalytic activity and selectivity of existing catalysts. Such endeavors are particularly fruitful when a fundamental approach is adopted, whereby the design of the catalyst composition and microstructure is targeted towards solving the bottleneck of specific reactions (i.e., the reactant adsorption, surface reaction, or product desorption step in the reaction mechanism scheme). There is value in pursuing research directed towards attaining a better understanding of the structure-property relationships in the area of catalytic materials. In this important arena, nanocrystalline processing will not only serve to improve the performance in critical catalytic processes but also help establish a superior knowledge base concerning the effects of structural manipulation on the generic catalytic characteristics for the major classes of catalytic reactions.

Nanoporous Materials

The second class of nanostructured systems, nonporous materials, is characterized by the molecular assembly of structures consisting of nanometer-sized cavities or pores. Conventional porous structures with long-range crystalline order are typically limited to aluminosilicates (e.g., zeolites) and phosphates with pore openings of less than 15 Å. The inflexibility in the composition and pore size of such materials does not address the needs of the variety of catalytic reactions and gas adsorption applications that exist in chemical industries. Ability to process nanoporous materials with greater control in compositional and pore structure variation will open up tremendous opportunities in advancing catalysis and separation technologies.

In 1992, Mobil researchers reported that a family of aluminosilicates (termed M41S) with pores larger than 20 Å could be synthesized in an ordered packing through a liquid crystal route (Kresge et al. 1992; Beck et al. 1992). Of particular interest is MCM-41, which has hexagonally-packed cylindrical pore channels containing surface areas greater than 1200 m^2/g and uniform pore sizes that can be tailored from 20 to 100 Å in diameter, making for attractive heterogeneous catalysts, catalyst supports, and nanocomposite host materials for a wide range of novel applications (Wu and Bein 1994; Bowes et al. 1996; Sayari 1996; Brinker 1996). The ability to synthesize these materials and to control the structural characteristics on a mesoscopic scale stems from the unique synthesis route of using surfactant solutions to template the inorganic precursors into a continuous solid framework. The formation of mesoporous materials with a variety of crystallographically well-defined frameworks (Huo et al. 1996) has been made possible via a generalized "liquid-crystal templating" (LCT) mechanism (Huo et al. 1994; Chen et al. 1993).

To create materials with superior structural and surface chemical properties, much work has been done to expand upon the LCT synthesis to include non-aluminum metal dopants within the silicate MCM-41 framework (Tanev et al. 1994; Corma et al. 1994), and to derive non-siliceous MCM-41-types of mesostructures (Huo et al. 1994; Braun et al. 1996). The ability to introduce compositional variation into the supramolecular templating of nanoporous structures will present exciting opportunities for attaining a great variety of molecular sieves well beyond the current synthetic flexibility of the zeolitic systems. For example, transition metal oxides play an important role as industrial catalysts in petrochemical production, pollution control, and pharmaceutical and fine chemical syntheses, but they are typically available with relatively low surface areas and poorly-defined pore structures. Improved performance can be achieved by developing transition metal oxide materials with the highly desirable microstructural characteristics of MCM-41. A number of non-siliceous M41S-like materials have been reported for the oxides of such transition metals as antimony, iron, molybdenum, tin, and vanadium; however, these mesostructured materials collapsed upon surfactant removal and did not yield mesoporous molecular sieves (Huo et al. 1994; Stein et al. 1995; Janauer et al. 1996; Ulagappan and Rao 1996). These attempts at synthesizing transition metal oxide mesostructures were based on the LCT mechanism involving Coulombic charge interplay between charged surfactant head groups, metal precursor species, and counterions in solution.

To successfully synthesize transition metal oxide mesoporous materials, it is critical to establish a strong interaction between the surfactant head groups and the inorganic precursor prior to micellar self-assembly (Antonelli and Ying 1996c). Based on this idea, our laboratory has created new organometallic compounds that consist of transition metal alkoxides ligated with a variety of surfactants through covalent bonding. This precursor design proves to be ideal for creating transition metal oxides with a hexagonally packed cylindrical mesoporous structure. The resulting family of transition metal oxides, termed TMS or tech molecular sieves, is characterized by uniform pore diameters that can be flexibly altered through varying the surfactant chain lengths and through the addition of swelling agents (Antonelli and Ying 1995, 1996a, and 1996b; Antonelli, Nakahira, and Ying 1996). Consequently, we are able to achieve transition metal oxides with surface areas in excess of 600 m^2/g and pore sizes tailored in the range of 20-100 Å. These uniformly large pore openings overcome the configurational diffusion limitations of zeolitic systems. The transition metal-based composition further offers the fundamental chemical flexibility of tailoring mixed oxidation states, electronic interaction, surface modification, and thermal stability.

A wide variety of reactions and processes will profit from the dual microstructural and chemical functionalities of the TMS family of molecular sieves. For example, zirconium oxide-based TMS materials (Wong et al. 1997) could serve as acid catalysts for isoparaffin-olefin alkylation that provides for higher octane number reformulated gasoline blends. The ability to tailor chemical composition and pore sizes may offer significant advantages in controlling surface acidity, catalytic activity, product selectivity, and coking behavior in alkylation catalysis. When developed as solid acid catalysts, TMS materials will serve to reduce the usage of hazardous liquid hydrofluoric and sulfuric acid catalysts in commercial alkylation operations.

Important future directions for the development of nanoporous materials include extending the supramolecular templating synthesis beyond the pore diameter range of 20-100 Å to benefit processes (e.g., enzyme catalysis, bioseparation, and biosensing) that require substrates with uniform distribution of ultralarge pores. Systematic bridging of the microporous and mesoporous range, particularly with tailored pore dimensions of 5-15 Å, would be very useful in overcoming the current limitations with existing zeolitic pore structures for selective petrochemical and fine chemical processing. Such pore size tailoring would be especially useful when attained simultaneously with compositional flexibility. Advanced design of catalytically active sites will call for the ability to ultimately control (1) the concentration of different components in mixed oxides while retaining a well-ordered microstructure, (2) the degree and homogeneity of dispersion of different components and dopants, and (3) the stability of the surface dispersion. Addressing these issues will enable us to tailor the surface chemistry of the active species, the coordination chemistry of the dopants and minor components, and the chemical/electronic interaction between the different components, in the context of a desirable porous microstructure.

Research on the synthesis of advanced nanoporous materials would be most fruitful when targeted towards specific catalytic and separation applications of interest. In particular, mesoporous materials offer unique opportunities not only to provide shape and size selectivity for molecules too large to react within the framework of conventional microporous zeolitic structures, but also to serve as stable catalytic supports for fixating bulky organometallic catalytic complexes. The latter constitute novel heterogeneous catalyst systems that have the advantage over homogeneous catalysts of ease of handling and separation in continuous operations, while retaining the high activity and selectivity associated with designed organometallic ligands. Finally, nanoporous materials can be very useful when processed with desired morphology (Aksay et al. 1996; Yang et al. 1996) and crystal size. They may be used as membranes and sensors, for example, operating on the principle of separation via molecular sieving effects. They may also serve as host matrices for quantum dots and wires in novel optical, electronic, and magnetic devices.

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CHAPTER 5

BULK BEHAVIOR

OVERVIEW

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WTEC Panel

The bulk behavior session of the May 8-9, 1997 WTEC workshop addressed the unique properties of nanostructured bulk materials; that is, bulk materials with nanoscale grain sizes and/or multiphase dimensions. The properties represented by the four speakers comprise mechanical properties of structural materials (Kear and Froes) and magnetic properties (Hadjipanayis and Ramanan). Speakers in other sessions also addressed some aspects of nanostructured bulk materials, such as structural ceramics (Ying, Chapter 4) and hydrogen storage materials (Schwarz, Chapter 4). In the field of nanostructured materials for potential structural applications, there are a number of other important efforts in the United States:

- fundamental studies of the mechanical properties of nanocrystalline materials
  - J.R. Weertman, Northwestern University
  - W.W. Milligan, Michigan Technological University
  - J.A. Eastman, Argonne National Laboratory
  - C.C. Koch, North Carolina State University
- ferrous nanocrystalline alloys
  - E.J. Lavernia, University of California, Irvine
  - J.C. Rawers, U.S. Bur. of Mines, Albany Research Ctr.
  - K.E. Gonsalves, University of Connecticut
- aluminum-base nanocrystalline alloys
  - G.J. Shiflet, University of Virginia
- intermetallic nanocrystalline alloys
  - E. Ma, Louisiana State University
  - B. Fultz, California Institute of Technology
  - C.C. Koch, North Carolina State University
- superplastic nanocrystalline materials
  - K. Mukherjee, University of California, Davis
  - R. Raj, Cornell University
  - M. Mayo, Pennsylvania State University
- nanocrystalline structural ceramics
  - M. Mayo, Pennsylvania State University
  - L. Shaw, University of Connecticut
  - D.L. Bourell, University of Texas

Other important efforts in the area of nanostructured magnetic materials research in the United States include

- S.A. Majetich, Carnegie Mellon University
- R.F. Ziolo, Xerox
- A.E. Berkowitz, University of California,
- L. Tackacs, University of Maryland, Baltimore County Campus
- R.D. Schull, NIST

San Diego

NANOSTRUCTURED BULK MATERIALS: SYNTHESIS, PROCESSING, PROPERTIES, AND PERFORMANCE

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Introduction

Two different approaches to the fabrication of bulk nanostructured materials are being pursued today: (1) a powder processing route, wherein nanoparticles of the desired material are first synthesized by some convenient chemical or physical method and then consolidated by pressure-less or pressure-assisted sintering, and (2) a spray forming route, wherein nanoparticle synthesis, heating (or melting), and consolidation are combined into a single operation.

Both approaches have their scientific challenges, which must be addressed and overcome. In powder processing, it is essential to synthesize nanoparticles that are nonagglomerated and preferably monodispersed, since these powder characteristics facilitate low temperature sintering, which is a prerequisite for mitigating grain coarsening during the sintering process. When the source material is nanocomposite in nature, such as a ceramic/metal (cermet) powder, liquid phase sintering at high temperatures is required, in which case grain growth inhibitors are essential in order to avoid significant coarsening of the nanodispersed ceramic phase.

In spray forming, the grain coarsening problem is virtually eliminated, and there is little opportunity for contamination of the product material when the entire operation is conducted in a controlled atmosphere of inert gas at low pressure. For these reasons, this approach is now gaining favor. A challenge is the high degree of control of processing parameters needed to achieve a theoretically dense structure. Much of today's research, therefore, is focused on the development of process diagnostic tools, typically nonintrusive laser spectroscopy methods, for elucidating the mechanisms involved in the transformation of the chemical precursor directly into a nanostructured bulk material. Such diagnostics studies are being complemented by extensive work on process modeling. The ultimate goal of these efforts is to develop a computer-integrated process for the production of fully consolidated nanostructured bulk materials, starting from inexpensive chemical precursors.

The following are examples of materials systems that have been produced by these two fundamentally different processing routes.

Nanostructured WC/Co and WC/Co/Diamond

Nanostructured WC/Co is the material of choice for cutting tools, drill bits, and wear parts. Typically, this material is produced by mechanical mixing of powders of the constituent phases, followed by cold compaction and liquid phase sintering. This limits the attainable structural scale of the composite material to about 0.3 microns, so-called "micrograined" WC/Co. Recently, a new chemical process, called Spray Conversion Processing, has been introduced, which is capable of synthesizing "nanograined" WC/Co. The new process involves (1) preparation of an aqueous solution mixture of salts of the constituent elements, (2) spray drying of the starting solution to form an homogeneous precursor powder, and (3) fluid bed conversion (reduction and carburization) of the precursor powder to the desired nanocomposite powder. Using this process, Nanodyne, Inc., is producing industrial-scale quantities of nanophase WC/Co powders, with compositions extending over the range of commercial interest from 3-30 wt% Co. Major advances are also being made in the fabrication of high performance nanostructured sintered parts.

For several years, Rutgers University has been conducting research on the preparation and consolidation of nanophase WC/Co powders. Concurrently, a tribology group at Stevens Institute of Technology has been evaluating the material's friction and wear properties. Highlights of this collaborative effort include (1) synthesis of WC/Co powders with WC grain size controllable down to about 50 nm, (2) densification of powder compacts by liquid phase sintering in vacuum or hydrogen, (3) mitigation of WC grain growth during liquid phase sintering by the use of potent grain growth inhibitor carbide phases, such as VC or Cr_3C_2, (4) demonstration of hardness in fully sintered nanograined WC/Co (with inhibitor carbide phase) that is twice that of conventional micrograined material, and (5) confirmation of enhanced wear resistance and cutting performance in sintered materials of high hardness.

In tests performed on VC-doped nanophase WC/Co materials, the measured hardness increases with VC concentration up to a maximum of 2190 VHN at 0.8 wt.% VC. These data correlate with a reduced mean free path for the cobalt binder phase (i.e., reduced WC grain size), as determined by magnetic coercivity measurements and transmission electron microscopy. This is striking evidence for the potency of VC as a WC grain growth inhibitor in liquid phase sintering of nanophase WC/Co alloys. Recent measurements show that nanograined materials possess superior hardness at all compositions, without sacrificing fracture resistance.

More recently, the research has shifted towards the synthesis of WC/Co/diamond nanocomposites. Such materials are being produced by chemical vapor infiltration (CVI) of partially sintered nanophase WC/Co with graphitic carbon, followed by high pressure/high temperature (HPHT) conversion of the carbon to diamond. In the critical CVI step of the process, the kinetics of the carbon decomposition may be controlled to develop either a uniform or graded carbon distribution throughout the porous WC/Co preform. After HPHT consolidation, these two types of carbon-infiltrated structures transform into their corresponding triphasic WC/Co/diamond nanocomposites. A functionally-graded superhard material, comprising a nanophase WC/Co core and a diamond-enriched surface, combines high strength and toughness with superior wear resistance, making it an attractive candidate material for applications in percussion tools and roller cone bits.

Nanostructured Ceramics

Silicon-base ceramics, such as SiC and Si_3N_4, are useful materials for many engineering applications like highly stressed components in heat engines, grinding wheels, and wear parts, because of their excellent high temperature mechanical strength and good oxidation resistance. Silicon carbide is also useful because of its favorable electrical resistance (heating elements) and thermal conductivity (substrate materials). A limitation of today’s processing of these materials is the very high sintering temperatures and pressures needed to consolidate powders, which is a consequence of their covalent bonding. Sintering aids can be used, but they frequently degrade properties. An alternative approach is to take advantage of the lower sintering temperatures characteristic of nanostructured powders. This approach is being adopted by many research groups.

Inert Gas Condensation (IGC) is the most versatile process in use today for synthesizing experimental quantities of nanostructured powders. A feature of the process is its ability to generate non-agglomerated nanopowders, which are sinterable at relatively low temperatures. In IGC processing, an evaporative source is used to generate the powder particles, which are convectively transported to and collected on a cold substrate. The nanoparticles develop in a thermalizing zone just above the evaporative source, due to interactions between the hot vapor species and the much colder inert gas atoms (typically 1-20 mbar pressure) in the chamber. Ceramic powders are usually produced by a two-stage process: evaporation of a metal source, or preferably a metal suboxide of high vapor pressure, followed by slow oxidation to develop the desired n-ceramic powder particles.

Recently, we have modified a conventional IGC processing unit for the purpose of synthesizing nanophase ceramic powders from metalorganic precursors. In this new chemical vapor condensation (CVC) process, the original evaporative heating source is replaced by a hot-wall tubular reactor, which decomposes the precursor/carrier gas to form a continuous stream of clusters or nanoparticles exiting from the reactor tube. Critical to the success of the hot-wall CVC process are (1) a low concentration of precursor in the carrier gas, (2) rapid expansion of the gas stream through the uniformly heated tubular reactor, (3) rapid quenching of the gas phase nucleated clusters or nanoparticles as they exit from the reactor tube, and (4) a low pressure in the reaction chamber.

The hot-wall CVC process has been used to synthesize nanophase powders of a variety of ceramic materials, which cannot easily be produced by the IGC process because of their high melting points and/or low vapor pressures. Examples are nanophase SiC_xN_y powders, for which there are many suitable metalorganic precursors, such as hexamethyl-dilazane (HMDS). In a particular case, the actual composition of the resulting powder is strongly influenced by the choice of carrier gas. Thus, HMDS/H_2O, HMDS/H_2 and HMDS/NH_3 give ceramic nanopowders with compositions close to SiO_2, SiC, and Si_3N_4, respectively.

From our experience with the synthesis of nanoparticle powders by the hot-wall CVC process, it was realized that the key to the high-rate production of powder is the efficient pyrolysis of the precursor/carrier gas stream in the hot zone of the reactor. This can be accomplished by replacing the hot-wall reactor with a combustion-flame reactor. The much higher temperature of the combustion flame ensures a much higher rate of decomposition of the precursor compound. Gases such as hydrogen, methane, or acetylene burned in oxygen may be used to generate a steady state combustion flame. The flame extends a few millimeters out of the burner and uniformly over the entire face, and it provides an intense heat source with a short residence time (fraction of a second) for effective thermal decomposition and reaction of the precursor/carrier gas stream. The burner is capable of operating at pressures as low as 5-25 mbar, which is in the optimum range for the synthesis of non-agglomerated nanoparticles. A variety of nanophase oxide ceramic powders have been produced by the combustion-flame CVC process, including SiO_2, TiO_2, and SnO_2. For high powder production rates, the flat-flame combustor is placed in contact with a rapidly rotating copper chill. On the other hand, when operating in the spray forming mode, a heated substrate is placed in front of the burner so that the superheated nanoparticles sinter as fast as they arrive at the moderately heated substrate. Relatively high deposition rates of fully sintered material over large areas can be realized by this means. Using two or more flat-flame combustors, nanomultilayers with compositionally modulated or continuously graded structures can be produced.

Scientific Issues

Powder processing

1. Establish the mechanism involved in grain growth inhibition during liquid phase sintering of WC/Co powder compacts.
2. Having established a new mechanism of displacement reaction processing in the amorphous state for tungsten-base precursors, determine the mechanism involved in the transformation of an amorphous tungsten oxide to an amorphous tungsten carbide. This is a promising route to the synthesis of nanophase WC powders at temperatures as low as ~400^{o}C.
3. Determine the influence of volume fraction of diamond phase on the abrasive wear properties and fracture toughness of both homogeneous and functionally graded WC/Co/diamond nanocomposites.

Spray forming

1. Establish the relationship between processing parameters and properties of nanophase spray-deposited materials.
2. When operating in the multilayer spray deposition mode, characterize the interface structure between the dissimilar phases, determine the internal stress distribution in the nano-multilayered structure, and evaluate properties.
3. Determine the heat transfer properties of nano-multilayered ceramics, consisting of alternating layers of nanoporous and dense material, and investigate their effectiveness as thermal barrier coatings.

COST-AFFORDABLE NANOSTRUCTURED MATERIALS

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Introduction

The nanostructured materials program at the University of Idaho is designed to produce nanostructured materials with enhanced mechanical and physical properties in a cost-effective fashion. The program can be conveniently split up into four segments: (1) nanostructured materials production, (2) compaction, (3) characterization, and (4) testing.

The Program

I. Production

A. Plasma Processing (Dr. P.R. Taylor). A non-transferred arc thermal plasma reactor has been designed, built, and operated to vaporize coarse metal powders. Quenching is performed using a supersonic nozzle, and the powders are collected in a filter system that can be sealed and dismantled in a glove box. Experiments have been performed to generate nanometer-sized copper and iron. Handling the fine powders without oxidation is very difficult, and recent experiments have been performed to evaluate improvements in materials handling.

B. Combustion Synthesis (Dr. S. Bhaduri). The “combustion synthesis” process utilizes oxidizers (e.g., metal salts) and fuels (typically organic compounds). When properly controlled, high temperatures can be generated by the exothermicity of reduction-oxidation (redox) reactions between decomposition products of the oxidizer and the fuel. Because of the fast heating and cooling, there is nucleation of crystallites but little growth, resulting in nanocrystalline ceramics. The following are the important features of this process:

1. It is a versatile process leading to the synthesis of single-phase, solid solutions, and composites as well as complex compound oxide phases.
2. It uses cheap raw materials.
3. It is a scaleable and a high production rate process.
4. The products are of high purity and loosely agglomerated, resulting in high sinterability. Examples of materials include n-α-Al_2O_3, n-spinel, n-ZrO_2, etc.

C. Mechanical Alloying (Dr. O.N. Senkov). Mechanical alloying (MA’ing), a high-energy ball milling process, has been used to produce nanostructured powders.

1. Low-cost nanostructured titanium powders have been produced by reduction reactions from titanium tetrachloride (replacement reaction with Mg) and titanium dioxide (replacement reaction with hydrides of light metals, such as CaH_2).
2. Amorphous powders have been synthesized by MA’ing pre-alloyed gas atomized powders of TiAl-based alloys in order to produce nanocrystalline compacts after hot isostatic pressing (HIP’ing).
3. Nanocrystalline composite powders have been produced by MA’ing of blended elemental powders of TiH_2, Ti, Al, Si, and B. Titanium aluminide – titanium silicide and titanium – titanium diboride nanocrystalline composite powders have been produced and characterized.
4. The effect of replacing titanium with titanium hydride in the MA process has been investigated, including effects on contamination and the scale of the microstructure.

D. Supercritical Fluid (Dr. C. Wai and Dr. E.G. Baburaj). The production of nanostructured particles or their films depends upon the substantial change in solubility of a solute in a solvent, at the supercritical point (temperature and pressure) of the solvent. For example, carbon dioxide, which is a good solvent for dissolving organometallic compounds, becomes a supercritical fluid at relatively low temperature and pressure (31°C and 73 atmosphere). Thus, metal or oxide particles can be produced from organometallic compounds dissolved in supercritical carbon dioxide. We have produced Cu films by hydrogen reduction of an organo-copper compound dissolved in supercritical carbon dioxide, and have made SnO_2 particles by heating an organo-tin compound dissolved in supercritical carbon dioxide.

II. Compaction

A. Press and Sinter (Dr. S. Bhaduri). The powders produced by the combustion synthesis process were heat-treated at various temperatures to examine the extent of grain growth. It was determined that the grains remained less than 100 nm at temperatures less than 1200^{o}C because of microstructural tailoring. The powders were cold isostatically pressed at about 300 MPa and were glass encapsulated and hot isostatically pressed at temperatures between 1000°C and 1200°C with pressure levels of about 175 MPa, which led to very dense samples (>95%).

B. Hot Isostatic Pressing (Dr. F.H. [Sam] Froes). Although the fine temperature exposure experienced during hot isostatic pressing is extreme, it has been shown that nanograins can be retained in alloys such as TiAl by low temperature HIP’ing while achieving full density. With nanostructured material, full density can be achieved at 700°C compared to 1100°C for material with micron-sized grains.

III. Characterization (Dr. O.N. Senkov)

A. DTA, SEM, TEM, and EDS
B. Micro-hardness
C. Thermal stability of the nanocrystalline HIP’d Ti Al-based compacts
D. Thermal stability of the nanocrystalline intermetallic-ceramic powders

IV. Testing (Dr. R. Stephens)

Testing of nanostructured materials will commence on small-scale test specimens in the near future.

In other activity, the superplastic forming behavior of nanostructured TiAl has been studied in a cooperative program with Professor A. Mukherjee’s group at University of California, Davis.

This program is predominantly funded by the Idaho State Board of Education.

NANOSTRUCTURED MAGNETIC MATERIALS

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Introduction

During the last several years, interest in the study of nanostructured materials has been increasing at an accelerating rate, stimulated by recent advances in materials synthesis and characterization techniques and the realization that these materials exhibit many unique and interesting physical and chemical properties with a number of potential technological applications. As never before, magnetic materials are the key to the future of the storage industry. The recent development of thin film heads, the demand for higher density of information storage, and the emergence of completely new technologies call for entirely new types of magnetic materials with much higher magnetization and coercivity, H_c.

For the last 12 years, our group has been actively involved in the study of nanostructured magnetic materials, including nanoparticles, thin films/multilayers, and nanocrystalline and nanocomposite magnets.

Magnetic Nanoparticles

Magnetic nanoparticles show a variety of unusual magnetic behaviors when compared to the bulk materials, mostly due to surface/interface effects, including symmetry breaking, electronic environment/charge transfer, and magnetic interactions. Furthermore, since nanophase particles can be as much as 50% surface material, they represent surface and interfacial material in bulk quantities, thus the new magnetism that may develop should be of practical value.

In collaboration with Kansas State University, we have been studying the magnetic and structural properties of ultrafine magnetic particles made by several techniques, including vapor deposition, sputtering, and chemical synthesis. We have prepared nearly spherical and magnetically hard Fe, Co, and Fe(Co)-B-based particles in the size of 7-20 nm that possess an effective anisotropy and coercivity one to two orders of magnitude higher than in the bulk materials (Fig. 5.1). We have shown that the highest coercivities are obtained in passivated particles that have a *core/shell* morphology with a metallic core surrounded by a $\gamma Fe_2O_3/Fe_3O_4$ (or berthollide) oxide shell consisting of small grains. The high coercivity of the ultrafine particles cannot be explained by any of the existing models of magnetization reversal. Most of these models are based on single-phase, uniform ellipsoidal particles without magnetic shells surrounding them and without any particle interactions taken into account. The large coercivities have been attributed to an exchange interaction between the core and shell moments at the interface. This interaction also leads to an anomalous temperature dependence of coercivity and to shifted hysteresis loops in field-cooled samples and is known as *unidirectional exchange anisotropy*, proposed originally by Meiklejohn and Bean. Our studies have shown clearly that a large core/shell interface interaction must be taken into consideration in order to model and fit the data of temperature dependence of coercivity.

We have ample evidence to believe that the core/shell morphology is also present in the magnetic granules of Fe/SiO_2 films. Our studies and those of others showed consistently higher coercivities in particles embedded in an SiO_2 rather than a BN matrix (Figs. 5.2 and 5.3). Our latest Mössbauer data in $Fe_{30}(SiO_2)_{70}$ and $Fe_{30}(BN)_{70}$ granular solids showed that the magnetic granules in the above matrices are not pure Fe particles as was expected, but rather a mixture of crystalline Fe and Fe-Si in SiO_2 and amorphous Fe-B in BN (explaining thus the lower coercivities in the latter because of the lower anisotropy of Fe-B). However, the Mössbauer data consistently show the presence of an Fe-Si-O phase in the Fe/SiO_2 films with higher H_c.

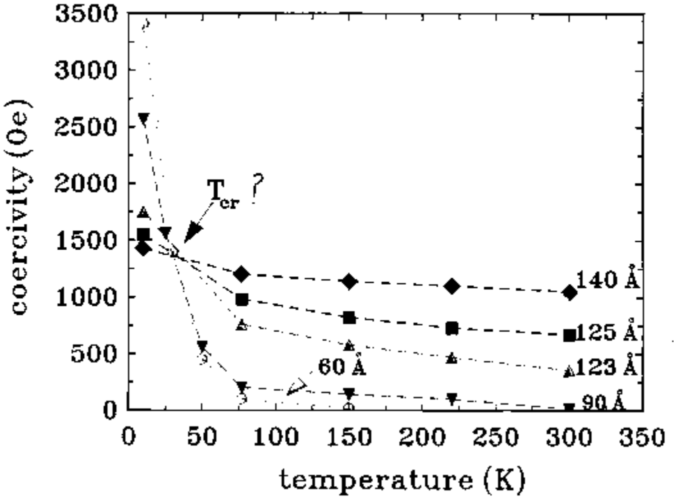

Fig. 5.1. The temperature dependence of the coercivity in passivated Fe particles.

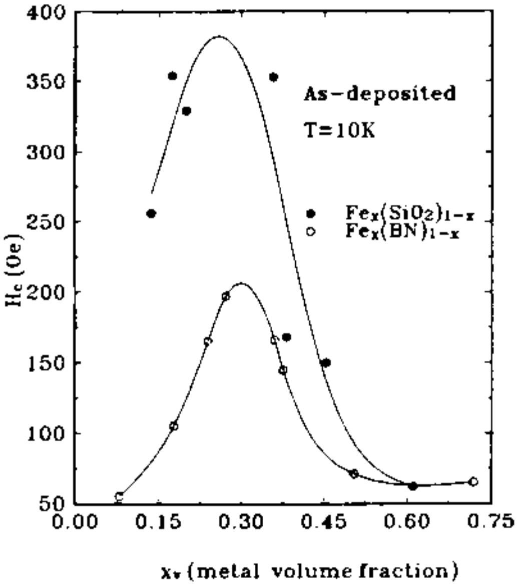

Fig. 5.2. The dependence of the coercivity on the metal volume fraction.

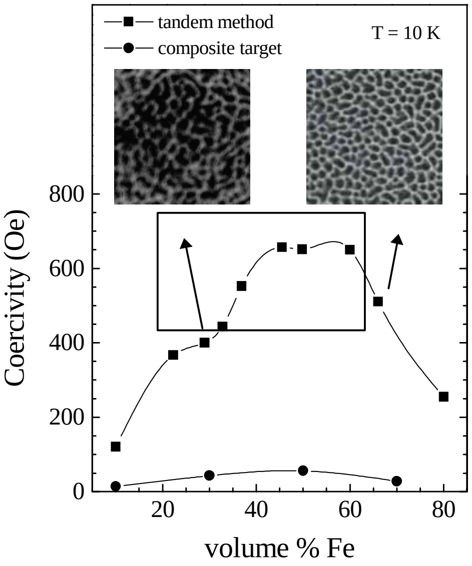

Fig. 5.3. Coercivity versus Fe content in Fe/SiO_2 granular solids.

The theme that has evolved from our past work on the magnetic hysteresis behavior of small magnetic particles is that their high coercivity is due to both size and surface/interface effects, with the latter being predominant. However, it is rather difficult to separate the two effects in particles prepared by either vapor deposition or sputtering, because it is difficult to prepare pure (single phase) particles with either of these techniques. In the former, the particles must be passivated to be protected from oxidation, while in the latter (as discussed above), there is often significant alloying of Fe with Si and B.

In the last few years we have been developing a technique that would allow us to fabricate pure particles separately but in the same chamber where sputtering takes place. We have now constructed and used successfully three particle guns (one uses a resistive heater, the second uses spark erosion, and the third uses sputtering) to make nanoparticles (Figs. 5.4-5.6). This upgraded capability allows us to make composite films with pure or treated uniform magnetic nanoparticles of any material in any matrix by using simultaneous particle deposition and sputtering with a rotating substrate. We strongly believe that this development gives a significant boost to our research efforts in nanoparticles and will lead us to future discoveries of other unique materials and magnetic phenomena.

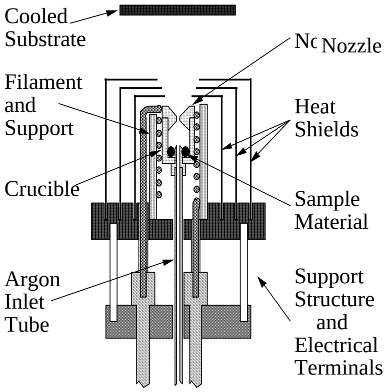

Fig. 5.4. Particle gun based on evaporation.

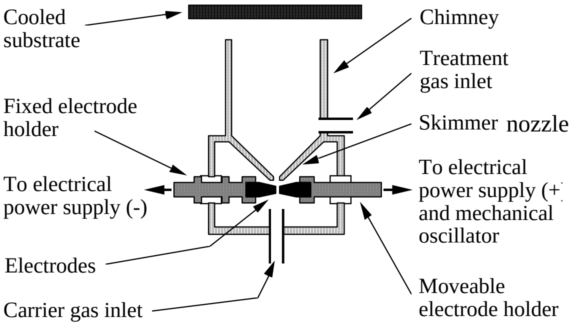

Fig. 5.5. Particle gun based on spark erosion.

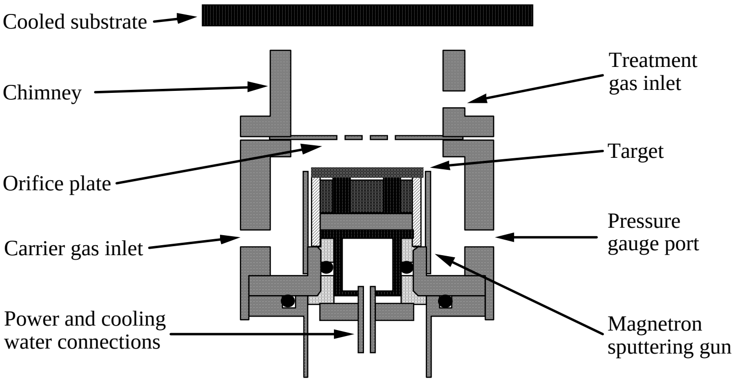

Fig. 5.6. Particle gun based on high pressure sputtering.

We have already undertaken a comprehensive and systematic study that will allow us to better understand intrinsic size effects, surface/interface effects, and the effects of intra- and inter-particle interactions on the magnetic properties of nanoparticles made by vapor deposition, first making pure particles, which we can later treat to modify their surfaces. We have also started preparing nanoparticles of rare earth metals and intermetallic compounds with high anisotropy, which have not yet been studied and are expected to show interesting and unique properties. This information is expected to be of great importance to magnetic recording media, since the drive for higher density media requires isolated particles with size below 10 nm and coercivity greater than 3 kOe. Transition metals and their alloys have a low anisotropy and become superparamagnetic below this size. We believe that the results of these studies will stimulate more theoretical research in this field that would help us better understand the magnetic properties and especially the hysteresis behavior of nanoparticles.

Nanocomposite Permanent Magnets

Nanocomposite magnets consisting of a uniform mixture of exchange coupled magnetically hard and soft phases have been extensively investigated in recent years because of their useful hard magnetic properties. High energy products and relatively high coercivities can be developed in these nanocomposite magnets. Among the advantages of these magnets are the high reduced remanence, m_r (= M_r/M_s), and low material cost due to the reduction in the content of the expensive hard magnetic phase. A small grain size (10-20 nm) and a uniform mixture of the two phases is a prerequisite for exchange coupling. This coupling leads to a smooth hysteresis loop in which the individual character of the constituent phases is concealed (Fig. 5.7). The challenge of preparing a suitable microstructure is most conveniently handled through non-equilibrium metallurgical techniques such as melt-spinning, mechanical alloying, and sputter deposition.

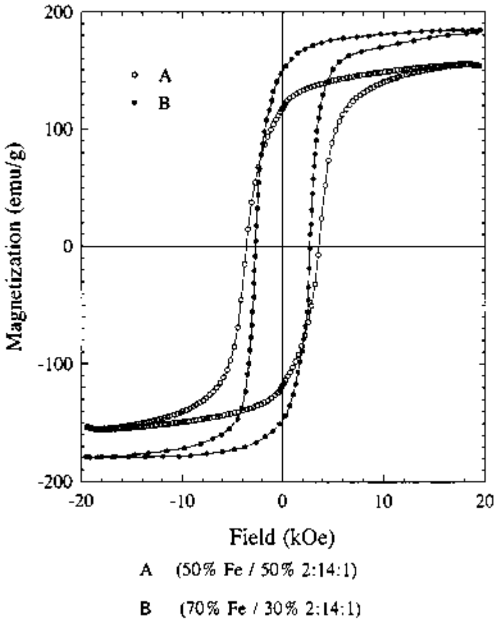

Fig. 5.7. Hysteresis loops of Fe-rich Nd-Fe-B magnets.

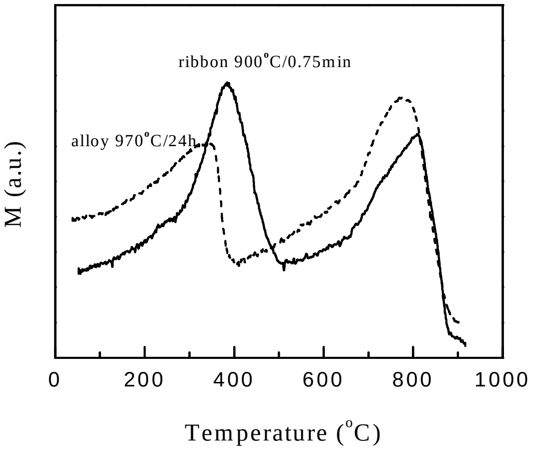

Fig. 5.8. M vs T in $Sm_2Fe_{17}Ga_2C_x$ magnets consisting of $2:17:C_x$ + α-Fe phases.

Over the last several years, we have investigated different systems including $Nd_2(Fe\text{-}Co)_{14}B$, $Pr_2(Fe\text{-}Co)_{14}B$, and $Sm_2(Fe\text{-}Co)_{17}C_x$. Melt-spun ribbons with off-stoichiometric compositions were used to ensure a microstructure consisting of a fine mixture of hard (2:14:1, $2:17:C_x$) and soft (α-(Fe-Co)) phases. We have studied the magnetic properties of these systems including their magnetization, coercivity, remanence, and Curie temperature and spin reorientation temperature as a function of the size and amount of the soft phase. The coercivity of the samples was found to decrease with the amount of soft phase, but the reduced remanence increased with values greater than 0.7. In addition, the Curie temperature of the hard phase was found to be affected by the presence of the higher T_c soft phase (Fig. 5.8).

Properties obtained so far in this type of magnet are inferior to those predicted by existing models, mainly because of the larger grain size of both phases and their non-uniform distribution. Additional studies are needed to find ways to correct these problems. Full exploitation of these effects should be observed in multilayers consisting of alternate stacks of soft and hard phases; however, very few such studies have been reported in thin films and multilayers because of the difficulties involved in preparing such structures with texture.

Thin Films/Multilayers

In the past few years, magnetic studies in nanostructured materials have focused on the interaction between the electron charges and magnetic spins. These studies have already led to discoveries of new and unique phenomena that are neither observable in traditional bulk materials nor explainable using classical theories.

Examples include giant magnetoresistance (GMR) in multilayers and metallic granular solids, spin valves, spin injection in ferromagnet/insulator/ferromagnet sandwiches, etc. Currently in our lab we have three projects in the area of thin films: (1) Fe-O films, bilayers/multilayers, (2) magnetostrictive materials, and (3) nanocrystalline R-Co-M films for magnetic recording.

Fe-O Films

The studies on Fe-O films were designed to clarify whether the large increase of the coercivity and its observed anomalous temperature behavior in small passivated Fe (Co) particles are due to the presence of a particular oxide or are generic to all types of oxides. It is impossible to have good control of the stoichiometry and the thickness of the oxide shell by the conventional evaporation method of preparation. Typically, the oxide passivation layer was about 20 Å and was comprised of a mixture of all major oxides. In the last two years we started a comprehensive program on the fabrication and characterization of thin Fe-O films by reactive sputtering. The goal was to learn how to deposit single phase Fe-O films with controlled stoichiometry and thickness. This will enable us to prepare exchange-coupled Fe/Fe-O bilayers, which will be used to study how the properties of Fe films are affected by the presence of an exchange-coupled oxide layer with particular stoichiometry and thickness.

By increasing the amount of O_2 during deposition, films with increased extent of oxidation were formed. It was found that the stoichiometry goes through the following sequence: α-Fe, amorphous/nanocrystalline film, α-Fe + FeO, off-stoichiometric Fe_xO, FeO + Fe_3O_4, single-phase Fe_3O_4, Fe_3O_4 + γ-Fe_2O_3, Fe_3O_4 +α-Fe_2O_3 and single-phase α-Fe_2O_3.

The most interesting result was the observation of anomalous ferromagnetic type behavior in off-stoichiometric Fe_xO and single-phase α-Fe_2O_3 films. These two oxides are well established to be antiferromagnetic in bulk. Extensive magnetic, structural, and Mössbauer studies revealed that the reason for the strong magnetic behavior in Fe_xO films was the presence of clusters of Fe^{3+} ions tetrahedrally coordinated in an fcc closed packed oxygen matrix. In the case of α-Fe_2O_3 films, the unusual magnetic properties were found to be a consequence of the presence of a significant amount of uncompensated surface moments.

Studies on the thickness dependence of stoichiometry and magnetic properties of Fe-O films are currently underway. Future studies will include exchange-coupled bilayers/multilayers with a particular type of Fe-oxide.

Magnetostrictive Materials

Magnetostrictive materials have been of great scientific and technological importance for many years. The magnetostrictive phenomenon refers to the deformation of a material in a magnetic field. In 1975, the discovery of new magnetostrictive materials, for example, Terfenol-D ($Tb_{0.3}Dy_{0.7}Fe_2$), with enhanced performance and interesting physics renewed interest in magnetostriction.

In the present high technology era, a great need exists for microsystems capable of performing functions that are not fulfilled by existing integrated electronic circuits. In many cases, magnetostrictive films could allow such functions to be readily obtained. For example, in the first class of applications, they could constitute the driving elements of micro-actuators (micro-robots, -pumps or -motors), which are in high demand by industry. A second class of applications would involve the magnetic control of elastic properties or reciprocally the stress/strain dependence of magnetic permeability, to develop various electronic devices like a resonator with magnetically adjustable frequency and stress-controlled inductance.

In all of these applications, the system efficiency depends critically on the relative change in length (λ=$\Delta l/l$) as a function of the applied field. Values of $\Delta l/l$ on the order of 200 x 10^{-6} with a field smaller than 200 Oe are desired. This is not possible with existing materials, which require saturation fields of tens of kOe. These stringent requirements demand new materials or materials with improved structures. Nanostructured materials are potential candidates that can lead to the desired properties through atomic engineering. Such properties can be obtained in amorphous or nanocrystalline alloys with reduced anisotropy and in multilayers with alternate stacks of high magnetostrictive materials and soft magnetic materials that are exchange coupled. Research on magnetostriction in nanostructured materials is currently being carried out mostly in Europe and Japan. There is very little work done in the United States. If this trend continues, the United States will become totally dependent on foreign sources for this highly valued technology. On the other hand, since present studies on high magnetostrictive materials are at an embryonic stage, we expect our efforts to have an immediate and enormous reward.

With the recent advances in deposition techniques and our current understanding of nanostructured materials, it is quite feasible that giant magnetostriction with small anisotropy (and therefore a small saturation field) can be obtained in nanostructured materials. Our preliminary results on amorphous $Tb_{33}Fe_{67}/Fe_{80}B_{20}$ multilayers (Fig. 5.9) have already shown very promising results with high transverse magnetostriction of 600 x 10^{-6} obtained with a small external field around 2 kOe.

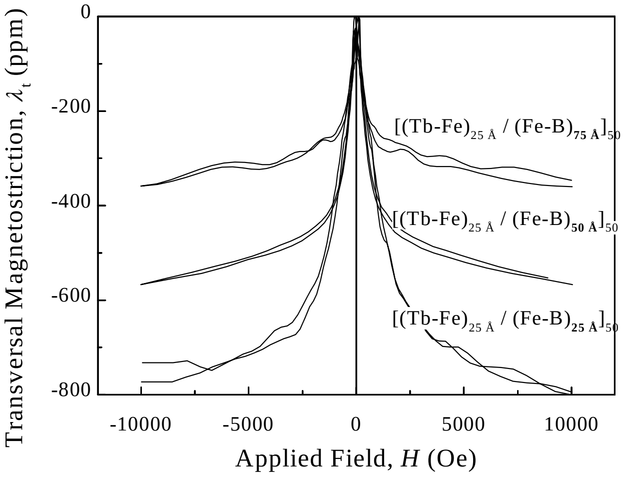

Fig. 5.9. Magnetostriction in Tb-Fe/Fe-B multilayers.

Acknowledgements

This work is supported by NSF-DMR and the U.S. Army Research Office.

List of Other Similar Activities in the United States

1. Magnetic Nanoparticles

- Berkowitz (University of California at San Diego, La Jolla)
- Chien (Johns Hopkins)
- Majetich (Carnegie Mellon University)
- Awschalom (University of California at Santa Barbara)

2. Nanocomposite Magnets

- Magnequench International
- Sellmyer (University of Nebraska)

3. Magnetostrictive Materials

- Walser (University of Texas)
- Wutting (University of Maryland)
- O’Handley (MIT)

NANOCRYSTALLINE SOFT MAGNETIC ALLOYS FOR APPLICATION IN ELECTRICAL AND ELECTRONIC DEVICES

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Introduction

Nanocrystalline soft magnetic materials are derived from crystallizing amorphous ribbons of specific families of (Fe,B)-based alloy chemistries. This new class of materials is characterized by 10-25 nm sized grains of a (bcc) α-(Fe,X) phase consuming 70-80% of the total volume, homogeneously dispersed in an amorphous matrix. The Japanese have pioneered and developed the work on these materials, especially in so far as the impact on major industrial applications is concerned.

As a result of research to date, two families of alloys show the best performance characteristics and have emerged as the leading candidates for reduction to application: Fe-Cu-Nb-B-Si (the "*Finemet*" family) and Fe-Zr-(Cu)-B-(Si) (the "*Nanoperm*" family). The Finemet family is characterized by an optimum grain size of about 15 nm, provides a saturation induction of about 1.2 T, and exhibits very good properties at high frequencies, comparable to some of the best Co-based amorphous materials. On the other hand, the grain sizes consistent with optimum performance are larger, around about 25 nm, in the Nanoperm family. The distinguishing feature of the Nanoperm family of alloys is the very low energy loss exhibited at low frequencies (60 Hz), offering the potential for application in electrical power distribution transformers.

The nanocrystalline materials are obtained by crystallizing precursors cast as amorphous alloy ribbons. The amorphous alloys typically crystallize in two stages: a magnetically desirable bcc-(Fe,X) phase appears first, followed by a boride phase, the presence of which is deleterious to good, soft magnetic behavior. In the optimized chemistries, the separation between the two crystallization events is large (~150 K), so that crystallizing heat treatments may be conducted above the temperature for the first event, while safely avoiding the onset of the other.

The excellent soft magnetic properties noted from these materials — extremely low coercivities, high permeabilities, low energy losses, etc. — has triggered major interest and research activity in both the academic/research community and the industrial community. Additionally, these Fe-based materials have potential as lower cost alternatives to the costly Co-based amorphous materials in many applications. Application of these materials in cores of transformers in switched-mode power supplies, chokes, ISDNs, etc., are already well on their way to commercialization. Other applications in high accuracy current transformers, ground fault interrupters, etc., are being investigated. The applications of these materials that have the greatest cost and performance impact, and yet are the most challenging, is in cores of transformers for electrical power distribution. This is the application that needs to be facilitated through additional work on nanocrystalline soft magnetic alloys.

Why Should These Materials be Studied and What are the Necessary Studies?

Alloy-Chemistry-Related Issues

The soft ferromagnetic behavior in these materials arises from a spatial averaging of the magnetic anisotropy of the aggregate of randomly oriented nanosized particles. Concurrently, the saturation magnetostriction of the materials is also reduced to near zero values.

Consequent to the low, averaged anisotropy, the ferromagnetic exchange length in these materials is estimated to be about 35 nm. In the Finemet family, the nanosized phase is α-(Fe,Si), with about 18 at % Si and possibly some Nb. In the Nanoperm family, an α-(Fe, Zr) phase is obtained, with the Zr content not well established and possibly with some B. It is now widely accepted that the ferromagnetic grain boundary (amorphous) phase facilitates the coupling between the nanosized bcc grains. Absent this phase, the considerably weaker magnetic bcc nanophase particles are decoupled, leading to rather poor magnetic characteristics in the material.

Clearly, the optimized grain size and the fractional volume coverage of the nanosized phase (which, in turn, is related to the width of the grain boundary region) intimately govern the efficiency of the spatial averaging of the anisotropy essential for the soft magnetic behavior in these materials.

- The nature and extent of the grain boundary phase, and a desired chemistry for this phase, need to be well defined and established.
- The development of a computer simulation model to correlate the nanophase grain size with the net volume-averaged anisotropy is highly desirable in this field of materials science.
  - Alloy compositions could be chosen to fine-tune (and, perhaps, fit) a preselected, desired value for the anisotropy in the grains.
  - For a given alloy, heat treatment windows for optimal grain size distribution can be developed. This is essential for any large-scale commercial application for these materials.

There is evidence to indicate that the presence of Cu aids in profuse nucleation, and the heavier elements such as Nb and Zr act as growth inhibitors. The precise mechanism of this nanocrystallization behavior is not yet well established. In addition, the reason that Cu is essential only in Nb containing alloys is not explained.

- Most of the alloy research in this area has proceeded via “hit or miss” attempts at mixing elements from the periodic table to the essential elements Fe and B. A complete explanation of the mechanism for the rejection of the solute elements into the matrix phase is critical to a well-directed and -focused optimization of alloys suited for commercial applications.
  - Such a focused alloy development effort is essential for a rapid deployment of these materials in commercial/industrial applications.
  - Since material cost is the significant driver in today’s applications choices, a well-informed, cost-efficient choice of the constituent alloy elements is made possible.

Processing-Related Issues

Rapid solidification using melt spinning is the technique employed to prepare the precursor amorphous alloys. Without question, this should be the chosen route for manufacturing large quantities of nanocrystalline alloys. However, even though large quantities (about 3 metric tons per hour in continuous production) of amorphous Fe-B-Si ribbons are now produced commercially, the state of knowledge is still in its infancy about cost-efficient casting of the nanocrystalline alloys and, in particular, the Nanoperm family of alloys, in commercially interesting quantities.

The Finemet family of alloys, with their good performance at high frequencies, will be primarily targeted for applications requiring a few tens of grams per core. Available state of knowledge in batch casting is expected to be sufficient for the production of commercially viable quantities of these alloys.

In contrast, large scale, continuous production of the Nanoperm family of alloys *has* to be addressed. There are two reasons for this: (1) This family of alloys, with demonstrated low loss characteristics at line frequencies, has a great potential for application in cores of transformers for electrical power distribution; and, (2) saturation induction levels of about 1.7 T may be attained in Fe-Zr-B nanocrystalline alloy systems, as opposed to the 1.55 T typically attained in the commercially available Fe-B-Si amorphous alloys. Given that Fe-3%Si grain-oriented electrical steel saturates at about 2 T, the larger core sizes necessitated by a lower saturation induction level have been a deterrent to a much wider use of amorphous materials in transformers. The promise of the combination of low loss and high saturation induction available from the Nanoperm type of alloys makes them very attractive for application in large transformers. From available information, it seems safe to say that the Japanese, at best, are able to produce about 5 kg of 30 mm wide material at a time.

- A systematic study aimed at deriving an optimum combination of casting parameters is necessary. The combination of all of the well-known key casting parameters should be addressed.
  - Since there are elements with a low solubility or near insolubility with Fe in the alloy chemistry, because of the presence of Zr or Nb, delivery of a *clean, homogeneous melt* to the casting wheel is of paramount importance. The optimization of casting parameters is not a trivial problem.

AlliedSignal, Inc., in the United States is the leading producer of amorphous metal products in the world and has clear technology leadership in melt spinning. There has been no interest on the part of AlliedSignal to undertake the large investments in time and resources necessary to define the manufacturing process for the Nanoperm family of alloys.

- The study suggested above is needed to supply device manufacturers, such as ABB in the United States, with high-quality materials for evaluation. Successful technical and potential market evaluations by the end user should prompt material manufacturers to accept delivery of the developed knowledge base and address scale-up-related issues.

Application-Related Issues

It is well known that Fe-based amorphous materials tend to embrittle following the necessary heat treatments to optimize their performance. The material manufacturer has learned to optimize the alloys and casting processes to help alleviate this problem related to handling of the materials. The industrial end user, too, has established a large background of experience in cutting, shearing, and handling procedures to minimize breakage and loss of material during the course of processing it for the application.

The nanocrystalline alloy materials discussed here are generally more brittle and more difficult to handle than annealed amorphous alloy ribbons. In the case of small cores (such as those prepared from the Finemet family of alloys), the anneal to obtain the nanocrystalline phase, which embrittles the material, is conducted after the core has been manufactured. The processed core is then not handled. This is not a viable alternative in the case of manufacturing larger cores for distribution transformers.

- The applicability of the existing knowledge base on the handling and processing of brittle materials in larger devices should be confirmed. Any necessary improvements should be defined and implemented.

As an unavoidable consequence of rapid solidification, the materials are confined to ribbon shapes with maximum thicknesses of about 25 µm. Therefore, it is expected that nanocrystalline soft magnetic materials will find their use only in wound core designs for distribution transformers covering the smaller ratings (up to 50 kVA). This, however, is still a sizable market, covering about 1 to 1.5 million transformers per year in the United States alone.

The Technical Community in the United States Must Address These Materials

Since most of the materials development has been carried out in Japan, and since related broad chemistry patents are held by Japanese firms, the U.S. companies have, in general, ignored these materials. There is no known significant activity, even in the U.S. academic community, perhaps due to the absence of supply of material from local sources. A considerable amount of research on these materials, albeit from a “pure science” perspective, is being conducted in Europe and Japan.

With the increase in the number of electronic devices in everyday lives, nanocrystalline soft materials are now finding their way into devices in the marketplace. Soon, with increased emphasis on energy conservation, these materials will have to be considered in the design of larger transformers. With a well conceived and directed effort, a U.S. source for these materials can be established, and such a source is necessary if the U.S. industry is to take full advantage of the benefits indicated in these materials.

The Finemet family of alloys is marketed by Hitachi Special Metals of Japan, Vacuumschmelze GmbH of Germany, and Imphy (a subsidiary of Usinor Sacilor) of France. They all make and sell small cores for many of the “specialty” applications at high frequencies, and others mentioned previously.

The Nanoperm alloys have been developed by Alps Electric Co. of Japan and are more recent than the Finemet family. Alps Electric has been working with Japanese end users to explore the use of nanocrystalline Fe-Zr-B alloys in various applications.

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CHAPTER 6

DISPERSIONS AND COATINGS

OVERVIEW

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Eastman Kodak Company
WTEC Panel

Areas of critical importance in dispersions and coatings for nanoparticle systems include (1) preparation of the dispersions; (2) stabilization of the dispersed phase; (3) scaleup and control of the process; and (4) preparation of subsequent nanoparticle coatings. U.S. involvement in the area of dispersion preparation includes work in lasers, single electron transistors, photoresists, oxide systems, photographic emulsions, inks, magnetic recording materials, fillers, and paper coatings.

Preparing materials in the nanosize range normally makes use of liquid phase precipitation and sol-gel formation as wet chemical methods. Hybrid chemical/physical methods include both spray pyrolysis and flame hydrolysis. There are also numerous physical methods such as mechanical size reduction (which includes media mills and high shear agitation in presence of media) and physical vapor phase separation.

Described within this chapter is work at Lucent Technologies (Bell Labs) by P. Wiltzius. He discusses sol-gel processing where a concentrated colloidal dispersion is chemically converted into a gel. After drying such a dispersion, a glass or ceramic product is obtained. Such a process, when properly controlled, can lead to a variety of shapes — particles, fibers, thin films, tubes as plates — that are stable. Wiltzius describes a silica casting process yielding tubes of one meter or more in length. He also describes polymer dispersed liquid crystals for cellular phones and hand-held computers, and chemical mechanical polishing for semiconductor applications.

Another preparation described within this chapter is physical vapor synthesis. Such work, reported by R. Brotzman from Nanophase Technologies, utilizes vaporized metal particles in the presence of a reactive gas to yield 25 nm nanocrystalline metal oxides. These resulting powders have high purity, spherical morphology, and controlled aggregation. Applications are numerous, including assembled ceramic composites, coatings, and dispersed systems for cosmetics, inks, and specialty applications in electronics and industrial catalysts.

Integral to the success of dispersion preparation is the scaleup and control of the process. In Chapter 4 S.K. Friedlander of UCLA describes in detail various aspects of aerosol reactors. Commercial and pilot scale activities in these areas include flame reactors for the production of pyrogenic silica where worldwide production in 1991 reached 100,000 tons. Friedlander describes pyrolysis reactors for preparing carbon black particles in the 20 to 300 nm range. With evaporation/condensation aerosol generators, a metal is evaporated into an inert gas, and then the vapor is systematically cooled to produce 3-100 nm particles. Such a process, although batch size limited, has the benefits of producing fairly pure materials.

B. Kear of Rutgers University describes in Chapter 5 a three-step process for preparing tungsten/carbon/cobalt powders. The first step is where tungsten and cobalt are prepared as aqueous solutions;

secondly, spray drying of these solutions produces powders; then these powders are reduced in a fluidized bed to nanophase material. Such a process has good scalabilty and compositional range.

In all the cited processes for production/dispersion of nanoparticles there remains a need to

1. control nucleation and grain growth
2. establish conditions for controlling the process for high reproducibility
3. determine process/product relationships that lead to continuous uniformity
4. characterize the interfacial properties between the continuous and dispersed phases, regardless of composition
5. develop process models to scale systems effectively and shorten cycle time to manufacturing

In this chapter, M. Gell of the University of Connecticut describes issues in coating nanostructural materials. Availability and reproducibility of starting materials are critical. The deposition process for creating the coated layer requires careful control of the process parameters so as to achieve critical nanostructured properties of increased hardness, adherence, and strength for systems such as cobalt/tungsten/carbon coatings and erosion-resistant layers with polymer matrix composites. High temperature, crack-resistant coatings require oxygen-impermeable layers. Also, advanced thermal barrier coatings will need nanostructures with reduced conductivity.

Accordingly, preparation of nanoparticle dispersions and subsequent deposition in coatings will require careful attention to raw material uniformity, process control for generating the particles, and stabilization of the nanosize dispersion to prevent agglomeration. These will be a few of the challenges facing the technical community in the future.

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DISPERSIONS AND COATINGS

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Introduction

This paper focuses on several dispersions that are of active scientific and/or technological interest in the Research Area at Bell Laboratories/Lucent Technologies. There are numerous other important dispersions, many of which are discussed by other WTEC workshop participants. These are photographic emulsions, inks, paper coatings, magnetic recording materials, pigments, and fillers.

Sol-Gel Processing

During sol-gel processing a concentrated dispersion of colloids is chemically converted into a gel body. Subsequent drying and sintering leads to the final glass or ceramic product. This method has the potential of producing controlled structures of a variety of shapes, e.g., small particles, fibers, thin films, tubes, and plates. This method can be economical, and the processing is done at low temperatures.

A state-of-the-art colloidal silica casting process has been developed at Lucent Technologies that reproducibly yields tubes of pure silica with lengths of more than 1 meter. These tubes are used as overcladding material for optical fiber preforms. Fiber drawn from these preforms meets the standards for loss, strength, and dimensions.

There were several major technical challenges: achieving sufficient purity of starting materials; removal of refractory particles that lead to breakage during the fiber drawing process; and achieving very tight dimensional tolerances. A particularly difficult problem was the development of procedures for drying the gel bodies that avoid cracking due to stresses.

A successful sol casting, drying, purification, and sintering process has been developed that produces large overcladding tubes for fabrication of optical fiber preforms. The process uses a low-surface-area fumed silica dispersed in a basic aqueous solution. The sol is stable against gelation at high pH and can be centrifuged to remove large impurities. The sol is then cast into a mold after a hydrolyzable ester is added to reduce the pH slowly and start the gelation. The gel body is removed from the mold and dried over several days. Final heat treatment involves several steps: (1) pyrolysis of organics; (2) treatment in reactive halogen atmosphere to purify the body; and (3) sintering in He at temperatures approaching 1500°C.

The above technique allows production of large tubes equivalent to those made by drawing from synthetic silica boules and other shapes, with significant process and cost advantages. Sol-gel processing is also being evaluated for thin film processing in silicon VLSI and “silicon optical bench” (waveguide) applications.

Colloids as Model Systems

Polymer and silica colloidal spheres suspended in solvents have been used as model systems to study the interactions between the colloids and their phase diagrams. Of interest are two-dimensional (2D) and three-dimensional (3D) suspensions and the influence that flat or modulated planes have on the structures that form.

The structure and properties of 2D and 3D assemblies of colloid particles are of intrinsic interest; in addition, the detailed particle real-space and time information obtained from these model systems is valuable for the fundamental understanding of phase transitions of ordinary “atomic” scale matter. In many instances a colloidal suspension can be used as a surrogate for studying the equilibrium properties of an atomic system because a suspension of submicron monodisperse colloid spheres in a solvent has a well-defined temperature by virtue of collisions between the colloid spheres and the solvent molecules. The interaction potential between the colloid spheres can be changed by adjusting their charge.

Recent scientific achievements include the elucidation of the liquid-hexatic-solid phase transition in 2D, the phases of charged spheres confined between walls, phases of binary systems (two different size spheres), the measurement of the interaction potential between colloids, the structure of hard-sphere glasses, and template-directed colloidal crystallization.

Colloidal crystals have been proposed as optical limiters and switches. Further interesting optical materials that could be made by self-assembly of colloidal particles include filters, waveguides, amplifiers, and modulators or photonic band gap components.

There are several groups in the United States working on all aspects of this field: University of Colorado, Boulder; University of Pennsylvania, University of Chicago, Princeton University, Clarkson University, University of Delaware, University of Pittsburgh, and Bell Labs.

Polymer-Dispersed Liquid Crystals

Reflective displays are needed for portable products such as cellular phones, communicators, personal digital assistants, and hand-held computers. Incorporating displays that are reflective enough to be used without a backlight greatly reduces both the weight and power consumption of these products. The reflective displays currently used in portable devices are usually twisted or supertwisted nematic liquid crystal. One drawback of these displays is that the reflected light is attenuated by several passages through polarizers, resulting in a dull “black-on-gray” display rather than a bright “black-on-white” display.

A promising new technology for producing brighter displays is based on polymer dispersed liquid crystals (PDLCs), which are made of micron-sized liquid crystal droplets trapped in a polymer matrix sandwiched between glass plates. If no electric field is applied, the orientation of the liquid crystal is determined by the droplet shape and is random between neighboring droplets. In this state, the PDLC material will appear milky white and opaque, since light is strongly scattered as it passes through droplets of different orientation. By applying an electric field, one can orient all of the liquid crystals in the same direction, causing the material to become transparent. Thus, if a black backing is used in the display, the regions where the electric field is applied will appear dark. Since this technology requires no polarizers, PDLCs can be used to make reflective displays with a brightness and contrast similar to black ink on white paper. Moreover, these displays are simpler to assemble than twisted nematic displays, since they do not require alignment layers.

Several groups in the United States (Kent State, University of Pennsylvania, Bell Labs) have recently made advances in understanding the dependence of the electro-optical performance on droplet structure and size and how to reproducibly achieve the desired microstructure through better processing control. It was also discovered that surface interactions at the droplet walls have a profound effect on contrast and brightness and can be manipulated to yield PDLCs that require very low switching voltages.

A technologically related to PDLCs are nematic curvilinear aligned phase (NCAP) materials, where the liquid crystal is encapsulated in a polymer film by encapsulation or emulsification. Raychem Corporation has products that use NCAP technology.

Chemical Mechanical Polishing

In chemical mechanical polishing (CMP), colloidal dispersions are not part of the end product, but rather play a crucial role during processing. Tight control and thorough understanding of the process is intimately linked to the yield and quality of the product.

As integrated circuits become more and more complex with increasing layers of metallization and interlayer dielectrics, VLSI manufacturing needs tools to planarize the wafers between the deposition and processing steps. Over the past few years it has become clear that the method of choice will be CMP. During this process the wafer is pressed against a polishing pad, and the presence of silica, alumina, ceria, or zirconia colloidal slurries leads to the desired planarization. Factors that influence the effectiveness are, among others, the particle size and shape of the colloids, and their surface chemistry and stability.

Currently, vapor deposited silica is used as the interlayer dielectric material; in the near future, materials with lower dielectric constants will be implemented. Choices are fluorinated SiO_2, porous SiO_2, and polymers. How to planarize these materials is the subject of current investigation.

CMP is an integral part of the semiconductor industry roadmaps and is expected to play a crucial role in back-end wafer processing. All the major integrated circuit manufacturers have efforts in developing CMP. There has been strong publication and patent activity over the past three years (> 180 U.S. patents in CMP since 1984, with more than half of all patents issued since 1993). Several conferences, workshops, and symposia per year are devoted to the subject. There has also been a significant increase in patents by Japanese companies in the past year.

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NANOPARTICLE DISPERSIONS

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Scientific Drivers

Nanophase Technologies Corporation (NTC) was spun off from Argonne National Laboratory in 1989 and is devoted to the commercialization of nanophase materials. NTC technology is based on gas phase condensation (GPC) techniques for synthesizing inorganic and metallic powders invented by R.W. Siegel et al. (1994; patented by ARCH Development Corporation and assigned to NTC). The basis of GPC is the evolution of a physical vapor from the evaporation of elemental or reacted material followed by immediate condensation and reaction of the vapor into small nanometer particles (Siegel and Eastman 1989). To maintain nanometer-sized particles and weak agglomeration, the aerosol is rapidly cooled and diluted to prevent extensive sintering (to form hard agglomerates) and coalescence growth (aggregates).

Early GPC processes employed natural convection flow current for streaming an elemental reactant into the reactive/condensation chamber. Natural convection of an inert gas at low pressure (e.g., helium at 5 - 50 torr) draws condensed crystallites out of the evaporation/condensation region to the (thermophoretic) collection device. Natural convection is established and limited by a temperature gradient between the hot (e.g., 1500°C) evaporation source and the cold (e.g., -200°C) particle collection device. Although an increase in heating drives natural convection faster, the flow rate is insufficient to overcome the concomitant increase in metal evaporation rate (vapor pressure increases exponentially with temperature). As a result, crystallites become larger and aggregate. In addition to the limitations of natural convection, oxidation of metal crystallites into metal-oxide ceramics must occur in a separate processing step. This type of oxidation process is not conducive to commercial-scale production, and in fact, oxidation is often incomplete (Parker and Siegel 1990).

NTC has developed and patented (Parker et al. 1996) a production system using forced convection flow in order to (1) allow control of the particle/gas stream by eliminating the ill-defined flow pattern of natural convection, (2) speed particle transport from the particle growth region to increase metal vapor generation, and (3) complete reaction of metal crystallites to form oxides and nitrides. The process employs a transferred arc to produce metal vapor in conjunction with forced gas flow; the high cooling rate of the plasma tail flame allows the formation of nanocrystals (typically ca. 8-30 nm) that weakly aggregate into submicron particles. The process produces commercial quantities of nanosized inorganic powders that are spheroidal and have narrow particle size distribution.

Economic Drivers

The NTC process reduced the cost of powder from thousands of dollars per gram to dollars per pound while maintaining the high quality observed in laboratory scale powders. Yet marketing efforts revealed only a modest opportunity for application in industry. The lack of market acceptance of nanocrystalline powders for bulk use is largely attributed to the relatively high expense involved in synthesizing and handling these materials, which must compete with conventional materials at nearly one-tenth the cost.

NTC is today a market-driven company that tries to provide what the buyer wants versus a marketing company than sells what it already makes. Four markets are targeted: electronics, structural ceramics and composites, cosmetics, and industrial catalysts. Table 6.1 shows near- and long-term applications being pursued in collaborative relationships with marquee customers in the identified markets. In many applications, dispersed nanocrystalline powders are required.

Critical Parameters

Although every dispersion application is unique, the powder surface must always be rendered compatible with the dispersing fluid. If a coating is employed, individual powders should be coated with a minimal layer of material without causing aggregation and agglomeration. Additionally, in the cosmetics and skin care market, NTC titania must be chemically passivated and photostabilized by introducing surface impurity traps to force recombination of photogenerated excitons (Solomon and Hawthorne 1983).

Table 6.1
Applications for Nanoparticle Dispersions

Market	Near-Term Applications	Longer-Term Applications
Electronics	Abrasives for semiconductor polishing	High performance electrodes
	Anti-radiation coatings for computer and TV monitors	High-refractive-index polymers for optical communications
Structural Ceramics and Composites	Abrasion-resistant polymers for oil drilling sensors	RF-transparent components
	Ceramic components for continuous steel casting	Ceramic armor
	Ceramic mechanical seals	
Cosmetics and Skin Care	Topical health-care products	
	Transparent UV blockers	
	Colorants for cosmetics	
Industrial Catalysts		Chemical-process catalysts

NTC developed a coating process that encapsulates nanocrystalline particles with a durable coating not removed by subsequent processing to ensure that the particle size distribution generated by the GPC process is preserved after coating. Until patents are issued, details of coating chemistry and processing remain proprietary. The coating may be engineered to allow dispersion of nanoparticles in organic fluids with dielectric constants ranging from 2 to 20 as well as water, and steric stabilizers or specific chemical groups can be incorporated into the coating to affect greater dispersion stability or specific (targeted) chemical reactivity, respectively.

Bringing GPC Products to the Market

Examples of two dispersion products are given. NTC sells titanium dioxide dispersions for use in the cosmetics and skin care market as physical sunscreen ingredients. Sunscreen formulations are transparent with measured SPF values greater than 15 at 3 wt % titania and 20 at 5 wt % titania.

Abrasion-resistant polymers for oil drilling sensors are in field testing. Laboratory wear testing demonstrates that NTC coated Al_2O_3 covalently incorporated into an epoxy formulation using targeted chemical reactivity at 30 wt % provides nearly 4 times more wear resistance than 80 - 83 wt % filled epoxy and 19 times more wear resistance than 46.5 wt % filled elastomer-modified epoxy, which are the best commercial materials. The NTC coated Al_2O_3/epoxy dispersion is also the only material than can be processed by filament winding techniques.

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NANOSTRUCTURED COATINGS

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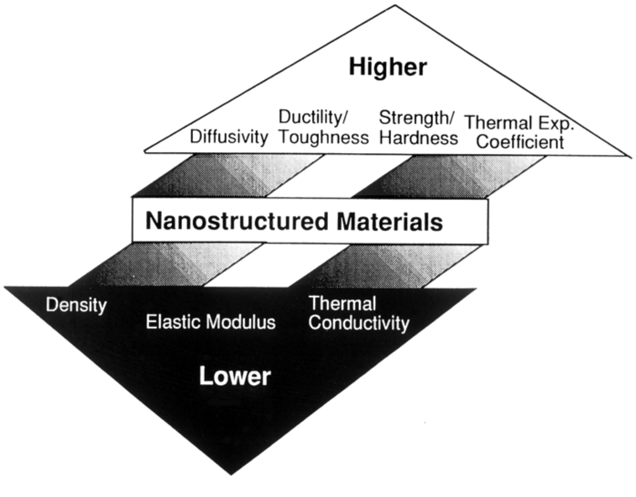
Nanostructured materials and coatings offer the potential for significant improvements in engineering properties based on improvements in physical and mechanical properties resulting from reducing microstructural features by factors of 100 to 1000 times compared to current engineering materials. The potential benefits include higher hardness and strength in metals and cermets resulting from reduced grain size and slip distance, respectively. In ceramics, higher hardness and toughness may be accomplished with reduced defect size and enhanced grain boundary stress relaxation, even at ambient temperature. Diffusivity is greatly increased, associated with a larger volume of grain boundaries. Thermal conductivity may be reduced because of enhanced phonon scattering from grain boundaries and other nanoscale features.

In engineering materials, there is usually a toughness tradeoff with strength and hardness. The possibility exists that this tradeoff will occur at higher levels for ceramics and cermets. This is believed to be the explanation for improved wear and abrasion resistance of monostructured WC-Co. Fischer has shown that the wear track is much smoother and narrower in nanostructured WC-Co. This has important implications for a wide variety of wear-, erosion-, and abrasion-resistant coating applications.

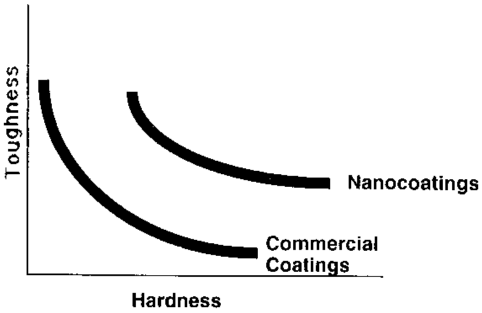
Thermal barrier coatings (TBCs) are used extensively in gas turbine applications to insulate superalloy turbine blades and vanes from the hot gas stream. There is a need for thermal barrier coatings with improved durability and performance. In thermal sprayed TBCs, failure of the coating occurs by spallation in the ceramic “splat” boundaries near the ceramic-to-metal interface. It should be possible to strengthen the boundaries by refining the structure to the nanoscale. In addition, it may be possible to develop TBCs with improved performance, by reducing thermal conductivity resulting from enhanced phonon scattering at grain boundaries. Both of these concepts are being evaluated in a recently awarded Office of Naval Research contract to the University of Connecticut.

The coatings industry is a major industry in the United States and worldwide. Coatings are needed to prevent wear, erosion, and corrosion, and to provide thermal insulation. For both commercial and military applications there is a need for coatings with improved durability and performance. Nanostructured coatings show promise based on initial laboratory trials. Durability improvements of 3 to 5 times can be projected for a number of coating applications. It will be necessary to demonstrate the technical and economic viability of these coatings on a commercial scale. To accomplish demonstration and implementation of this technology in a timely, cost-effective manner, a disciplined concurrent engineering approach is recommended.

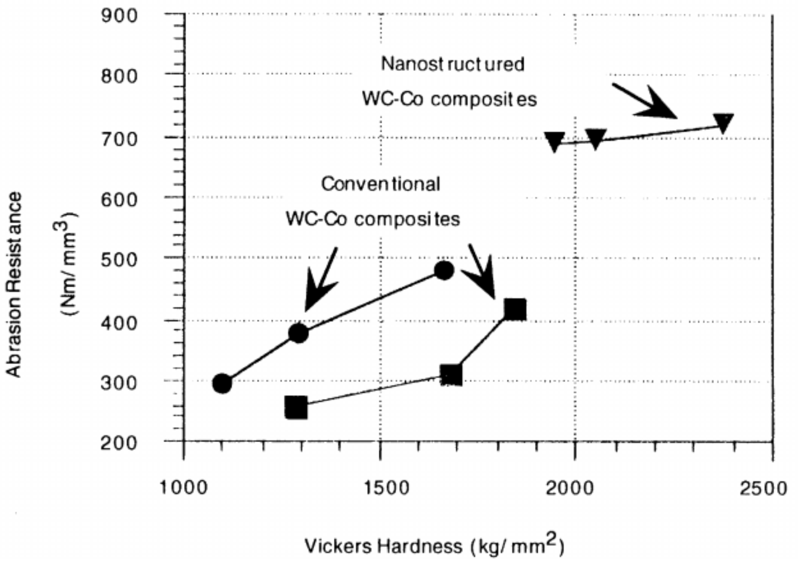
Nanostructured Materials — Potential Benefits



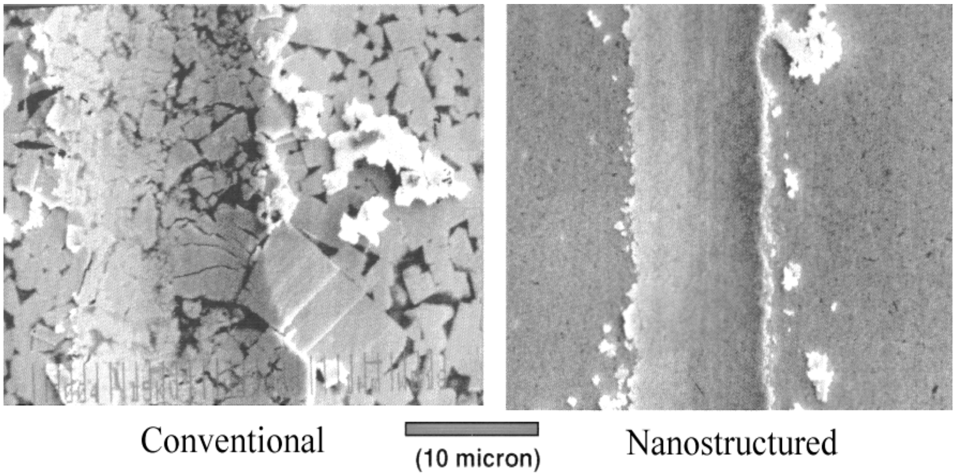
Increased Hardness and Toughness



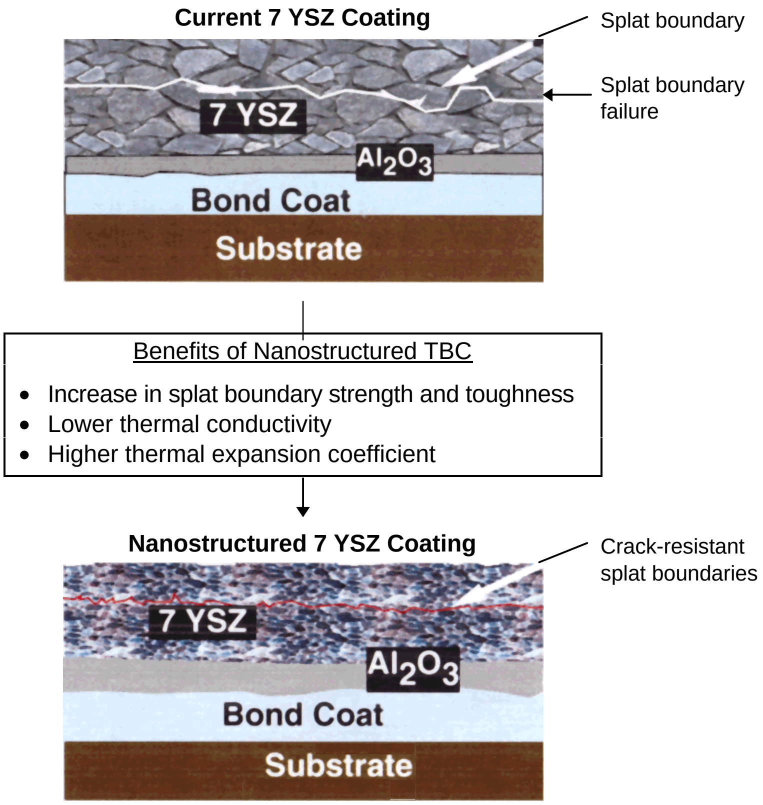
Wear Resistance of Conventional and Nanostructured WC-Co Composites



Wear Surface Morphology of Conventional and Nanostructured WC-Co Composites



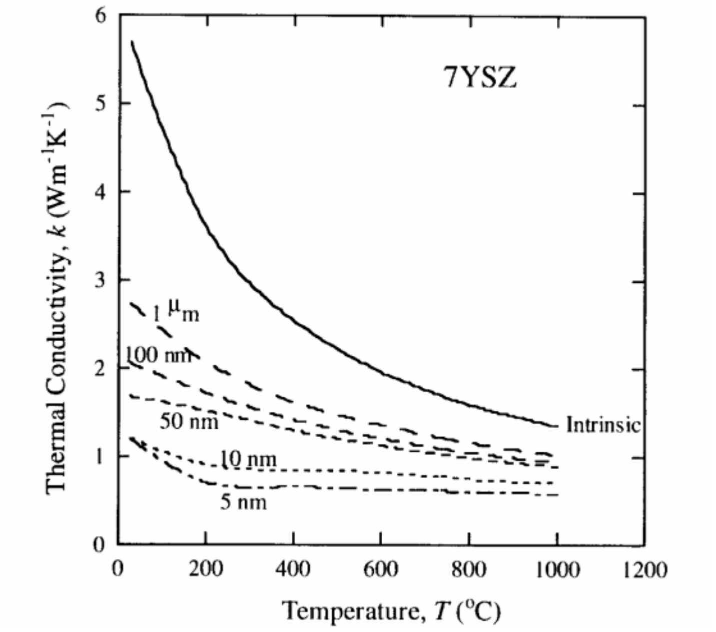
Improvements Afforded by Nanostructured TBCs



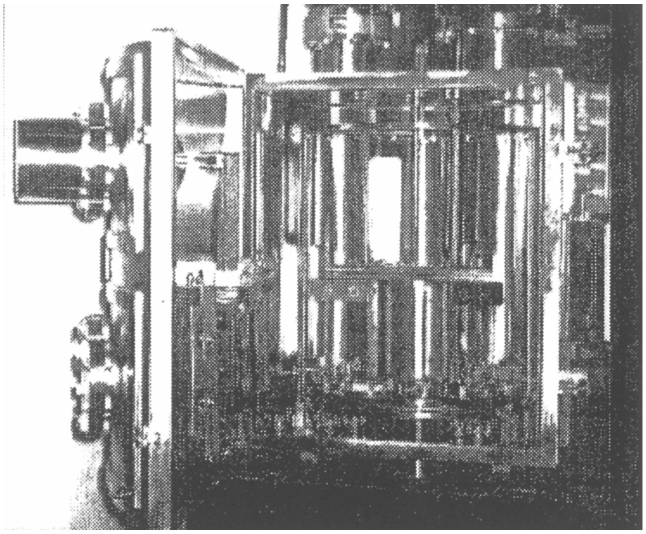
Benefits of Nanostructured TBC

- Increase in splat boundary strength and toughness
- Lower thermal conductivity
- Higher thermal expansion coefficient

Calculated Thermal Conductivity of 7 YSZ as a Function of Temperature and Grain Diameter



Nanostructured Materials — Processing Methods



Sputtering Chamber

- Magnetron Sputtering
- Electron Beam Vapor Deposition
- Cathodic Arc
- Plasma Spray
- Laser Deposition
- Chemical Vapor Deposition
- Jet Process
- Gas Phase Synthesis
- Chemical Synthesis
- Sol-Gel
- Electroplating

Critical Issues for Manufacturability

- Materials Availability
- Materials Reproducibility
- Process Reproducibility
- Materials and Manufacturing Cost

Critical Control Parameters

- Selection of deposition process(es)
- Choice of processing parameters for compositional and microstructural control
- Selection of materials and deposition parameters for interface control in multilayered structures
- Selection of materials and deposition parameters to enhance thermal stability

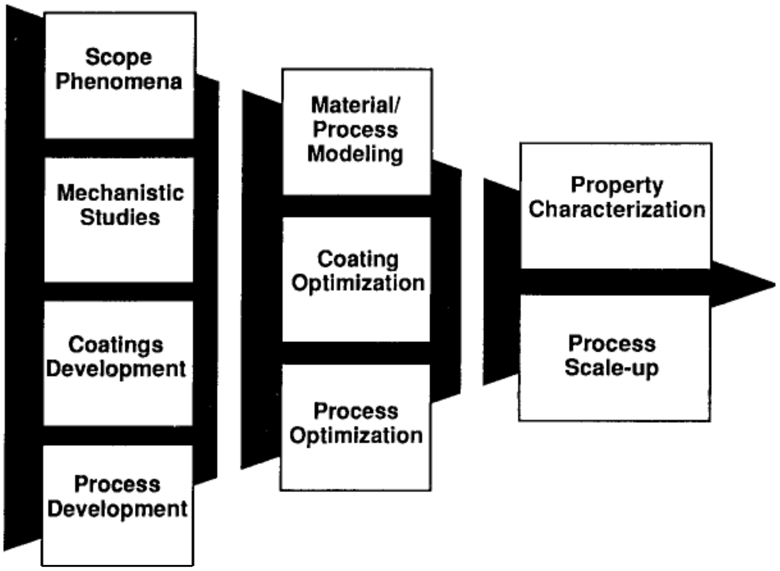
Barriers to Progress

- Materials availability
- Multi-lot properties data
- Thermal stability
- Cost-effectiveness

Approaches to Overcome Barriers

- Establishment and substantiation of scientific drivers
- Applications-driven research
- Disciplined concurrent engineering

Nanostructured Materials — Coating Technology Plan



Coating Applications

- Wear Resistance
- Erosion Resistance
- Oxidation Resistance
- Crack Resistance
- Thermal Barriers

Research

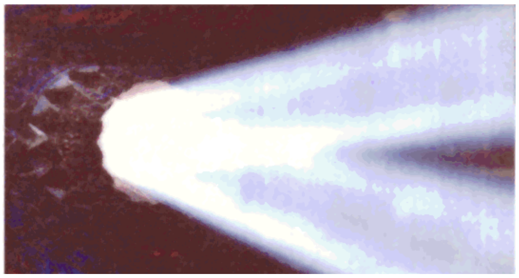
Exploratory Development

Advanced Development

Technology Application

Nanostructured Materials — Gas Turbine Engine Materials Requirements

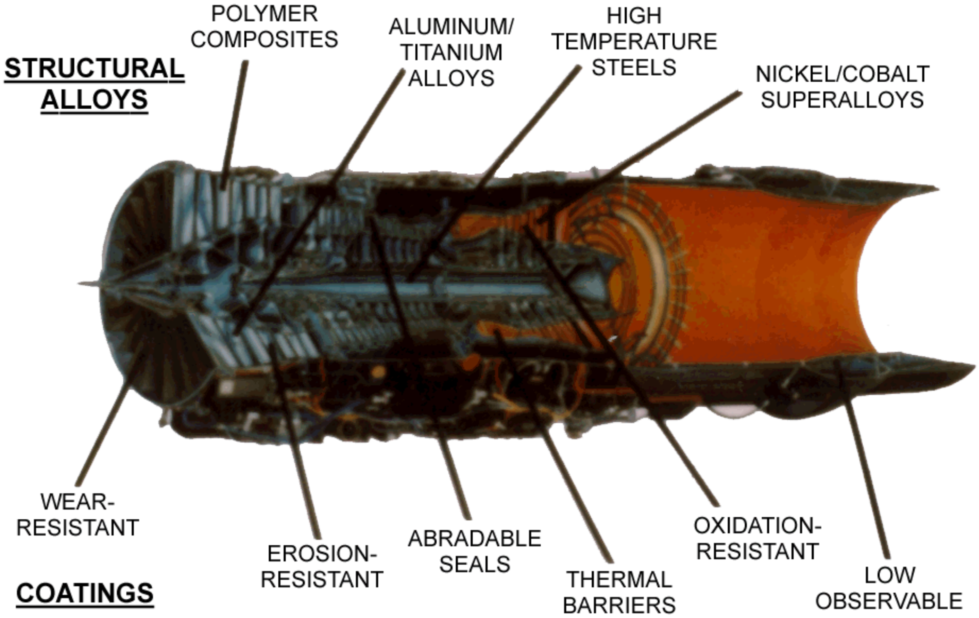
- Increased Strength
- Reduced Density
- Higher Temperature Capability
- Engineering Ductility/Toughness
- Lower Cost



Thrust-Vectoring P&W F100 Engine

High-Speed Civil Transport

Nanostructured Materials — Gas Turbine Engine Applications



Nanostructured Materials — Coatings Opportunities

Coating Programs	Critical Nanostructure Property	Component/Engine Benefit
• Co-WC wear-resistant coating	• Increased hardness	• 5X life
• Erosion/moisture-resistant coating for polymer matrix composites	• Increased hardness • Increased adherence	• 5X life • Higher design allowable
• High temperature, crack-resistant coating	• Increased strength • Interface crack blunting • Oxygen impermeable layer	• 3X life
• Advanced thermal barrier coating	• Reduced conductivity	• +2% thrust/weight • -1% fuel consumption

Nanostructured Materials — Technology Assessment

Technology Assessment

- Quantum improvement in variety of properties
  - Hardness/strength
  - Strength and toughness
  - Thermal conductivity
- Properties generated on subscale specimens for simple alloys/ceramics

Nanomaterials Technology Requirements

- Applications-driven cost/benefit/risk analysis
- Synthesis of engineering alloys
- Generation of engineering properties
- Demonstration of cost-effective manufacturing feasibility
- Some early successes

CHAPTER 7

HIGH SURFACE AREA MATERIALS

OVERVIEW

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Fabricating nanostructured materials and characterizing the effect of nanostructure on the properties of such materials are areas of increasing importance in understanding, creating, and improving materials for applications that require high surface areas. High surface areas can be attained (1) by creating materials such as small particles or clusters where the surface-to-volume ratio of each particle is high, or (2) by creating materials where the void (pores) surface area is high compared to the amount of bulk support material. Materials such as highly dispersed supported metal catalysts and gas phase clusters tend to fall into the first category, whereas microporous (nanometer-pored) materials such as zeolites, high surface area inorganic oxides, porous carbons, and amorphous silicas fall into the second category.

Industrial areas where high surface area materials are critical include the following (Aksay, p. 79; Friedlander, p. 83; Schwartz, p. 93; Ying, p. 96; Brotzman, p. 122; Chianelli, p. 133; Stucky, p. 140; Dresselhaus, p. 169):[1]

- materials for adsorption/separation processes such as H_2O, H_2S, CO_2 removal; gas storage of H_2 and CH_4; and gas separations such as O_2/N_2 and H_2/HCs
- catalysts for many petroleum processing applications
- thermal barrier materials
- ion exchange processes such as radioisotope separation
- certain construction industry materials where bonding and strengthening is dependent on the surface area of the constituents

It is difficult to predict the areas where nanoscale high surface area materials may have the greatest future impact, but some signs point to possibilities of substantial advancement in the areas of adsorption/separations, particularly in gas storage (Schwartz, p. 93; Dresselhaus, p. 169; Baker, p. 172) and separations, and also in novel chemical catalysis using nanoscale catalyst particles (Brus, p. 89; Chianelli, p. 133; Stucky, p. 140; Goddard, p. 197).

One typical objective of nanoscale catalyst research is to produce a material with exceedingly high selectivity at high yield in the reaction product or product slate, that is, chemicals by design, with the option of altering the product by changing the surface functionality or composition at the nanoscale. For instance, new catalysts with increasing specificity are now being fabricated in which only one or two spatial dimensions are of nanometer size (Chianelli, p. 133; Stuckey, p. 140).

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[1] References are to the authors contributing to this proceedings and the beginning page numbers of their papers. Further references on specific subjects may be found in the individual papers.

A second objective is to discover nanoscale materials or structures with exceedingly high storage capacity per unit volume and weight for gases such as H_2 or CH_4, which would then be more economic for use either as a combustion fuel or as the means to power fuel cells for ultralow-emission vehicles or for electric power generation (Schwartz, p. 93; Dresselhaus, p. 169; Baker, p. 172).

A third objective is to fabricate molecular sieving membranes using inorganic crystalline materials such as zeolites (Aksay, p. 79; Stuckey, p. 140). For molecular sieving membranes, one critical challenge rests on discovering ways to create large-scale, thin, nearly defect-free membranes.

The choice of approach is strongly dependent on the particular application or process of interest, whether it be highly specific catalytic chemistry, sorption for storage or trapping of gaseous species, or nanoscale control of one or more dimensions. Many different approaches are now being investigated for synthesizing nanoscale particles (Whitesides, p. 76; Aksay, p. 79; Friedlander, p. 83; Schwartz, p. 93; Ying, p. 96; Froes, p. 105; Brotzman, p. 122; Chianelli, p. 133). Some approaches start by attempting to tailor the structural composition and size by building up materials atom-by-atom; some use controlled crystal growth; some start from bulk materials and use procedures such as cryomilling to produce nanoscale particles that can then be examined.

Synthesis techniques include the following, many of which are described or alluded to in this proceedings report: aerosol reactor synthesis of metal oxides; metal vaporization and condensation reactors; micelle template synthesis of crystalline structures such as zeolites; arc vaporization of graphite for producing fullerenes, carbon nanotubes, and carbon nanoparticles; "graphite"-coated magnetic materials; catalyzed hydrocarbon decomposition to produce highly porous high surface area carbon such as activated aerosols and graphite fibers; and self-assembly of nanoscale structures.

Before generation and utilization of high surface area nanoscale materials can become commonplace, at least two major challenges must be faced. One challenge is to control the critical dimensions of the nanoscale structure over long times and varying conditions. In nanoscale catalyst materials the critical chemical selectivity is likely to be intimately associated with the local environment around what may be called the active site. This suggests that the size, type, and geometry of the atoms making up the active site will play a critical role in defining the conditions under which this active site will be able to carry out its designed function. Fabrication of materials with exactly the same structure and composition at each active site has been and will continue to be a major challenge to materials and catalytic scientists.

Another challenge is to control the thermal and chemical stability of the fabricated nanostructure. It is generally accepted that the smaller the nanostructure (active site), the more likely the structure is to move, aggregate, decompose, or in some way change its shape, composition, or morphology upon exposure to thermal and/or chemical cycling. Identifying windows of stable operation in which the specific structure or material will be able to retain the desired (and designed) behavior is critical for commercial applications. On the other hand, the driving force for investigating nanostructured materials is the fact that they typically exhibit unique properties that are expected to open windows of opportunity previously inaccessible with existing materials.

It should be pointed out that biophysics and biological sciences are having an increasingly important impact in nanoscience and nanotechnology themes (Jelinski, p. 161). For example, atmospheric nanoparticles may play an important role in photocatalytic and thermal production of atmospheric pollutants (Chianelli, p. 133). Atmospheric aerosols in heavily polluted areas have the potential to accelerate ozone formation reactions. Furthermore, because they are respirable, they could represent a health hazard.

Finally, studies of biomineralization, in which an organic substance (usually protein or peptide or lipid) interacts with an inorganic phase (e.g., calcium carbonate or hydroxyapatite) have led to the bioinspired synthesis of composite materials. The structure and porosity of the inorganic phase is controlled by templating with an organic surfactant, vesicular arrays, or liquid crystalline materials. Micelle-templated synthesis has produced ceramics with 20-100 Å pore dimensions (Ying, p. 96), which may be useful as catalysts, absorbents, for gas/liquid separations, and thermal and acoustic insulation. Their high selectivity makes them valuable for biochemical and pharmaceutical separations.

SYNTHESIS, FUNDAMENTAL PROPERTIES AND APPLICATIONS OF NANOCRYSTALS, SHEETS, AND FULLERENES BASED ON LAYERED TRANSITION METAL CHALCOGENIDES

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Introduction

As demonstrated in this workshop, the science of nanoparticles and nanophase materials has blossomed over the past fifteen years and is providing the seeds for new applications in optoelectronic and chemical technologies. Nanoparticles based on layered transition metal chalcogenides (LTMCs) have been important in the field of catalysis and lubrication, but it has been only recently recognized that these materials appear as morphological analogs of fullerenes exhibiting structures described as inorganic fullerenes, nested inorganic fullerenes, single sheets, folded sheets, and nanocrystals. Reports of these structures and synthetic approaches to them now regularly appear in the literature, but relatively little has been reported on their fundamental properties and the chemical origins of the structures.

Layered transition metal chalcogenides have found a remarkably diverse set of applications. MoS_2 and WS_2 catalysts have been used for the removal of sulfur and nitrogen from petroleum feedstocks for over 50 years (Weiser and Landa 1973; Daage and Chianelli 1994). MoS_2 is used as a lubricant additive (Fleishauer 1987). TiS_2 and MoS_2 can act as cathodes in lithium nonaqueous batteries (Whittingham 1976; Tributsch 1981) and have interesting and useful intercalation chemistry (Whittingham and Jacobson 1982). WS_2, WSe_2, TiS_2, MoS_2, $MoSe_2$, and $MoTe_2$ are all semiconductors with unusual properties and potential electronic applications (Wilson and Yoffe 1969).

Most of these unusual and useful properties arise from the highly anisotropic physical properties that are due to weak binding between layers where a layer consists of a monolayer of metal atoms clad by covalently-bonded chalcogen atoms. For example, weak binding between layers leads to the useful lubrication properties. Weak bonding between layers also leads to nearly two-dimensional confinement of optically excited electrons and holes, which in turn leads to excitonic optical absorption peaks that can be observed at room temperature. The variety of transition metals (Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W) that exist in layered structures, coupled with the choice of chalcogen (S, Se, Te) leads to a rich variability in the physics and chemistry.

Synthesis of Layered Transition Metal Chalcogenides

LTMCs with different nanoscale structure have been synthesized recently by a variety of approaches. Tenne and collaborators (1992) reported the gas-phase synthesis of fullerene-like structures of WS_2 and of fullerenes and nested fullerenes of MoS_2 (Feldman et al. 1995). Persans and others (Lu et al. 1990; Persans et al. 1990; Chianelli et al. 1995; Roxlo et al. 1987) have reported on the preparation and optical characterization of crystalline nanoparticles prepared by intercalation and ultrasonic fragmentation of bulk crystals. Divigalpitiya, Frindt, and Morrison (1989; 1990; 1991) have reported the synthesis and preliminary characterization of composites based on single sheets of MoS_2. Wilcoxon and collaborators have reported the growth of MoS_2 nanoparticles using micelle techniques (Wilcoxon et al. 1995; Wilcoxon and Samara 1995; Parsapour and Wilcoxon 1996). These structures are related to one another and to the well-known “poorly-crystalline” and “rag-like” layered transition metal sulfides (Chianelli 1982; 1984; Chianelli et al. 1985).

Recently, synthesis of these materials has focused on high temperature methods that occur above 650°C. These methods involve such techniques as growth from the gas phase in which MoO_3 in the vapor phase is reacted with H_2S in a carrier gas producing nested fullerenes and nanotubes designated as inorganic fullerenes (Feldman et al. 1995). These methods suffer from the difficulty of producing large amounts of materials.

A general method for preparing the transition metal dichalcogenides at or near ambient temperatures was reported by Chianelli and Dines (1978). The materials thus produced have physical properties significantly different from those produced at higher temperatures. By appropriate adjustment of parameters, poorly crystalline or amorphous powders, gels, glasses, or homogeneous dispersions of chalcogenides can be prepared. Additionally, normally crystalline compounds can be prepared, and because the preparations take place below 400°C, portions of the transition metal-sulfur phase diagrams not previously studied are accessible.

Folding in the Layered Transition Metal Chalcogenides

A consequence of the two-dimensional macromolecular nature of MoS_2 and other layered transition metal chalcogenides such as WS_2 and ReS_2 is the existence of highly folded and disordered structures. These structures have been recognized for a long time. “Rag” and “tubular” structures were first reported by Chianelli et al. (1979) and were studied for their usefulness as catalytic materials.

Figure 7.1 shows folded and disordered sheets of MoS_2. Rolled sheets of MoS_2 can also be seen which at lower magnification give the appearance of “crystalline needles.” These are undoubtedly nanotubes, as has been reported recently (Remskar et al. 1996). Interest in these structures has been renewed with the development and importance of carbon fullerenes and the discovery of large inorganic fullerene structures (M.S. and G. Dresselhaus 1995). Figure 7.2 shows some of the many forms which have been prepared using high temperature methods and which are currently under study for potential application.

Fig. 7.1. Folded and disordered sheets of MoS_2 (Chianelli et al. 1979, 1105).

Potential Use of Layered Transition Metal Chalcogenides as Micromachine Components

Recently, transition metal trichalcogenides have been synthesized at high temperatures in a variety of shapes. The trichalcogenides such as $NbSe_3$, TiS_3, and others have layered as well as chain-like structures (Trumbore and ter Haar 1989). These objects exhibit unusual morphologies at larger than atomic scales; Figure 7.3 shows an example. Morphologies observed include “wheels,” “tubes,” “rods,” and numerous other shapes.

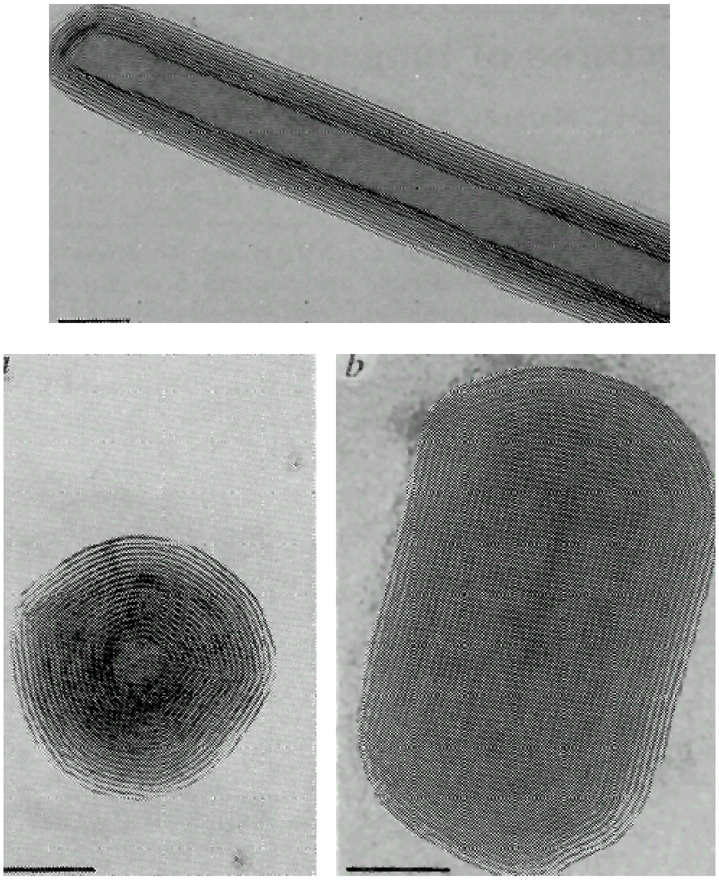

Fig. 7.2. Tungsten disulfide forms (Tenne et al. 1992, 444).

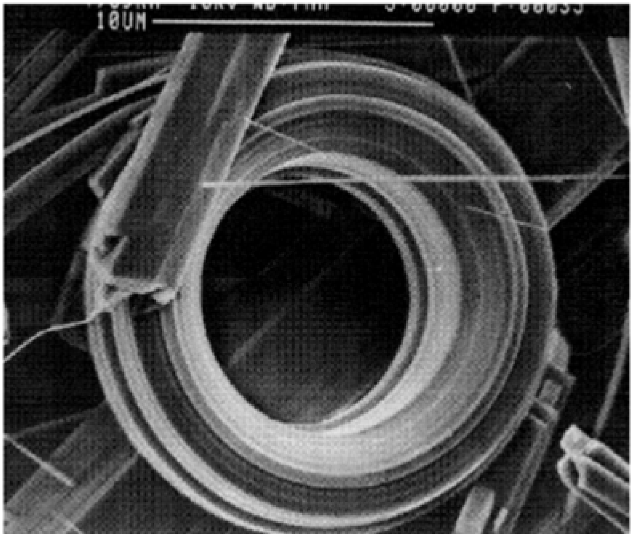

Fig. 7.3. Structure of trichalcogenides — $NbSe_3$ shown (Trumbore and ter Haar 1989, 490).

The ability to synthesize shapes such as these from materials that can be metals, magnets, semiconductors, and insulators have led to speculation regarding the construction of micromachines. For example, the "wheel" shown above if magnetic might be incorporated into a microelectric motor. In another example, a microbattery might be constructed based on the intercalating abilities of the LTMC. Fabrication seems feasible, but reproducible synthesis in large uniform quantities remains a problem; however, possibilities for micromachine devices seem extensive.

Nature of Folding in Layered Transition Metal Chalcogenides

It has been suggested that folded and disordered MoS_2 structures are similar in nature to large fullerene structures. The cause of the ability of MoS_2 and related compounds to form these structures remains unclear and is the subject of intense study. The study of these materials has been hindered by the inability to synthesize large quantities of the material. This situation is similar to early days of research in carbon fullerenes, which progressed slowly until improved synthetic methods led to larger quantities being available. Speculation on the cause of folding and curvature in these falls into three categories:

1. The ability of stoichiometric LTMC layers and chains to "bend"; this is clearly the case in materials such as TiS_2 that are observed to fold and bend during intercalation reactions (the dynamic bending and folding that occurs during these reactions is also seen to "anneal" after the reaction, returning the material to an ordered crystalline state).
2. The existence of alternate coordination and therefore stoichiometry in analogy to carbon-based fullerenes; this has been suggested but not proven.
3. Stoichiometric variation within the material allowing building of closed rings, etc.; this maybe the case in more complex LTMCs such as cylindrite ($FePb_3Sn_4Sb_2S_{14}$) (Salyer and ter Haar 1996).

Nanoparticulate Heterogeneous Catalysts

Heterogeneous catalysts used in the petroleum refining and chemical industries are obvious examples of widely applied nanoparticles. Traditionally, industry has relied successfully on empirical methods for synthesizing these materials but has not applied understanding of nanoparticles to make further improvements. MoS_2 may be used as an example to show how understanding of nanoparticles is leading to improvement of catalytic activity and selectivity.

Catalysts based on MoS_2 have been widely used in the petroleum refining industry since before World War II. Usually the MoS_2 is mixed with a second component such as Co or Ni to improve activity (Weiser and Landa 1973). These very successful catalysts were largely discovered and developed empirically; recently, much progress has been made in understanding their catalytic properties from a nanoparticulate point of view (Chianelli, Daage, and Ledoux 1994).

Several issues have become clear and are probably generally applicable to other heterogeneous catalysts:

1. Commercial catalysts, because they are made at relatively low temperatures, appear in a highly folded and disordered form such as described above. *This is disadvantageous*. Maximum activity is obtained on catalysts that are well crystallized, and a major unrealized challenge is to make nanocrystals of these materials in a commercializable form. Microcrystals are easily made at higher temperatures, but commercial catalysts are cheaply made in large quantities in a supported form.

2. In the case of MoS_2, the selectivity of the reaction is determined by the "stack height" of the crystallites, as indicated in Figure 7.4.

   The industrially important hydrodesulfurization (HDS) reaction indicated in Figure 7.5 occurs along two pathways that take place on different parts of the crystal.

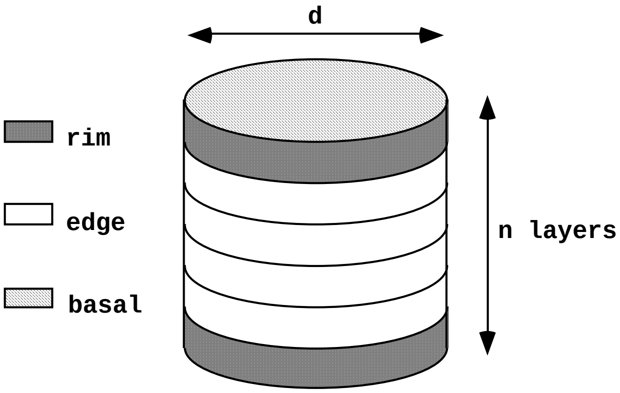

Fig. 7.4. Stack height of crystallites.

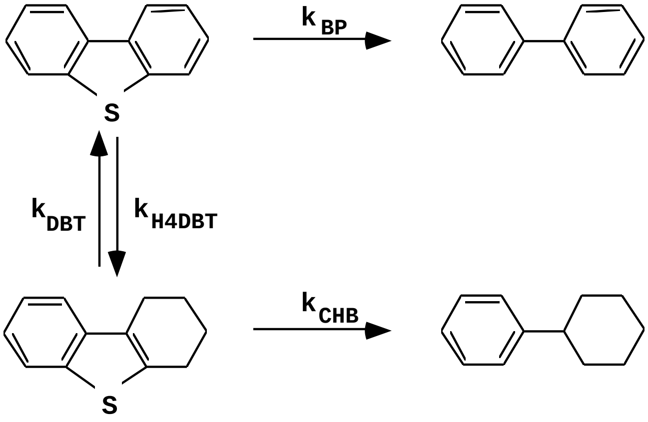

Fig. 7.5. HDS reaction.

The first pathway leading to cyclohexylbenzene occurs only on the "rim" sites, and the second pathway leading to biphenyl occurs on the "rim" and "edge" sites. Thus, the aspect ratio of the nanoparticles must be controlled to control the selectivity of the reaction, and the diameter of the crystallite must be made as small as possible to maximize the activity. All this must be accomplished with as much crystalline order as possible being retained.

3. Working catalysts are "promoted" with a second metal such as Co or Ni. This metal usually occurs as a second component such as Co_9S_8 that interacts at the MoS_2 edge plane and can form an interface with it. It is at this interface that the promotion effect occurs by setting up an interaction at the junction of the two materials. A high resolution electron micrograph of such an interaction is shown in Figure 7.6.

It is a further challenge to synthesize these complex nanophase materials in an optimum form in commercial quantities.

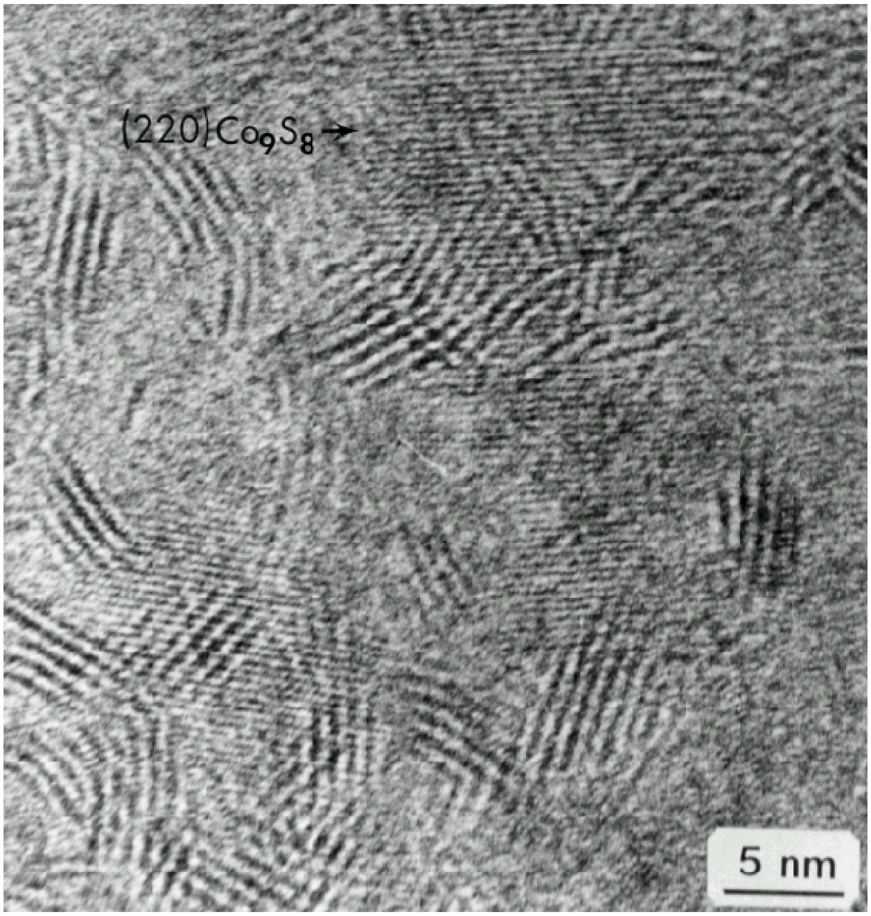

Fig. 7.6. Nanoparticles of MoS_2 and Co_9S_8 at a “catalytic junction” (Fuentes 1992, 232).

The Structure and Potential Role of Atmospheric Nanoparticles in Photocatalytic and Thermal Production of Atmospheric Pollutants

Nanoparticles are now being recognized as playing a potentially important role in the complex physical and chemical processes that occur above heavily polluted cities (Yacaman and Chianelli 1997). Atmospheric aerosols occurring in these areas are found to be complex materials that have the potential to accelerate important ozone-forming reactions both photocatalytically and thermocatalytically. In addition, because the particles are respirable, they represent a considerable health hazard. The aerosols consist of two intermixed components: the first consists of amorphous carbonaceous materials of variable composition with “fullerene-like” materials dispersed throughout; the second is an inorganic material consisting of nanoparticles of oxides and sulfides “supported” on clay minerals. This inorganic component has all of the characteristics of an airborne photocatalyst. Nanoparticles of Fe_20_3, MnO_2, and FeS_2 have demonstrated catalytic properties, particularly when occurring in the nanoparticle range as they do in the subject aerosol materials. These materials have band-gaps that occur in the broad solar spectrum, enhancing the photocatalytic adsorption of solar radiation beyond that of the wider band-gap aluminosilicate and titanate materials that also occur in the aerosols. In addition, the materials are acidic and probably are coated with moisture when suspended in air, further enhancing the catalytic ability to crack hydrocarbons and create free radicals. Though this area is just being studied, nanoparticles appear to play an important but as yet undetermined environmental role.

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HIGH SURFACE AREA MATERIALS

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Scientific Drivers

High surface area (300-2,000 m^2/g) materials technology is directed primarily towards the creation of inexpensive low bulk volume/area media for applications that require rapid and responsive sampling, selective separations, high throughput catalytic processing, enhanced chemical activity (Klabunde et al. 1996 a and b), or 3-D packaging of supported or entrained nanoscopic structured species (Hornyak et al. 1997; Leon et al. 1995; Blake et al. 1996). High surface areas provide a mechanism to achieve detection sensitivities that are in the range of parts per billion on a short time scale or to rapidly sample and chemically process large volumes of reactants. Control of pore or surface structure at the nanostructure level (<1 Å) makes it possible to modify separation or catalytic process selectivities by several orders of magnitude. Promising technological areas in this category are chiral active surfaces for pharmaceutical separations and enantiamorph synthesis (Cao et al. 1992); ordered magnetic high surface area materials for oxygen separation; and optically transparent (Schacht et al. 1996; Huo, Feng, et al. 1997; Belcher, Zaremba, et al. 1996) high surface area monoliths (films, spheres, fibers) for chemical sensor applications (Dunbar et al. 1996; Dickinson et al. 1996).

A second important materials technology category for high surface area materials is in the nanostructured modification or design of bulk properties, usually by a synthetic route that accesses metastable phases and kinetically stable intermediates. Here, high surface area interfaces are useful in creating the necessary interface properties for processible composites, designing thermal transport in low density packaging, and determining chemical and mechanical integrity.

In both categories, a key challenge is processing the high surface areas into forms or shapes appropriate for the desired applications. Appropriate forms include thin films (Yan et al. 1992; Aksay et al. 1996; Yang and Ozin 1996; Dunbar et al. 1996; Tolbert, Schäffer, et al. 1997), fibers (Dickinson et al. 1996; Narang et al. 1996; Huo, Zhao, et al. 1997), hard spheres for chromatographic and catalytic fluid bed reactions (Huo, Feng, et al. 1997), and macroscale patterned structures for pattern recognition in optical sensor pattern recognition applications. Hierarchical structure design based on a nanoscale molecular assembly approach that incorporates multi-dimensional control of function and properties on a space and or time basis is an exciting goal in this area that has important ramifications for materials technology in general (Sarikaya and Aksay 1994; Belcher, Wu, et al. 1996; Schacht et al. 1996; Belcher, Zaremba, et al. 1996).

The nanostructure control parameters typically required for the first category of the above applications are comparable to those of enzymes in biocatalysis. Key figure-of-merit variables include the following: (1) molecular recognition parameters, (2) transition state lifetimes, (3) sorption and desorption rates, (4) ability to functionalize the surface, (5) chemical and mechanical stability; (6) defined defect structure, and (7) interface chemistry and structure from both a synthesis and composite property perspective. In porous media, dimensional resolution and definition of structure are optimally at a few percent of the diameter of the pore diameter. Fractional void spaces in porous media are typically desired in the range of 0.9 with pore volumes from 0.6 to 2.7 cc/g. Three-dimensional patterning and periodicity give the best surface area/volume dimensionality, optimum useful access space, and nanoscale control of structure and properties.

Critical Parameters for Synthesis

High surface area materials are always metastable phases in the sense that they are created by interrupting the kinetics of single-phase assembly. Lower free energy states are invariably accessible; they are created through use of interfaces, including supercritical phases, liquid-liquid, liquid-solid, or even solid-solid interfaces. At the nanostructure level the topology of the created surface is defined by a form of molecular imprinting (Davis et al. 1996; Stucky et al. 1996) that can be achieved using either single molecules or organized arrays of molecules. The nature of the high surface area materials that are created then depends on the relative kinetics and thermodynamics of (1) the polymerization of the species that makes up the final surface, (2) the interface interactions of these species with the molecules that are responsible for creating the ultimate high surface area and surface nanostructure, and (3) the intra-molecular interactions of these molecules. Low-cost synthesis and processing are sought; rapid 3-D assembly of the final high surface area structure is desirable.

Accurate nanoscale assembly therefore always requires the ability to control the kinetics of the surface assembly relative to its “molecular imprinting” definition. On the negative side, this has limited the ability to isolate nanostructured, periodic surfaces having a single composition or a monodispersed pore size. Defect control is always tenuous, and there has been only limited success with creation of designed high surface area macroscale morphologies with monodispersed porosity, such as thin films, beads, fibers, or even millimeter-sized single crystals. On the positive side, if kinetic control of the different interface and assembly processes can be achieved, it is a powerful tool towards fine-tuning over a broad range nanoscale composition, surface area, surface morphology, void space, pore volume, and functionality.

The dimensionality of high surface area porous materials is evolving from the microscale (3-15 Å) domain obtained by the single molecule structure direction used in zeolite and molecular sieve synthesis into the mesoscale (15-150 Å) dimensions of the mesoporous materials (Kresge et al. 1992; Beck et al. 1992; Schüth et al. 1993; Huo et al. 1994). However, progress has been slow in generating monodispersed, high surface area, 3-D periodic arrays of pores and cages above the 10 nm region. In addition, bridging the nanoscale-macroscale (millimeter to centimeter) dimensions in porous material synthesis has to this point meant sacrificing short range nanoscale order to get longer range control of the structure. This is an area that should receive and is receiving considerable attention.

Mechanical and chemical stability are limiting factors for high surface area materials in general and for large pore systems in particular. One way to deal with this is by post-treatment. A second approach is through the use of block copolymer synthesis to create large pores and pore walls with thicknesses of 6 nm or greater (Zhao et al. 1998). An important problem for redox catalytic applications is hydrothermal stability of transition metal defects introduced either by functionalization of the support or by incorporation into the surface during synthesis. Defects, in any case, play an important role in both structure and function; while they can be and are introduced for certain applications, their chemistry and structure are poorly understood.

The synthesis and processing of nanoscale-patterned macroscale shapes and forms of 3-D periodic porous materials is one of the more challenging and exciting recent developments in the field. The synthesis space for this is kinetically controlled and vast, but once defined is simple and can lead to straightforward processing parameters. For example, the simultaneous but independent synthetic definition of hierarchical structure on different length scales can be achieved by multiprocess assembly using emulsion hydrodynamics and surfactants, a route that is highly desirable from a commercial processing perspective. An important area that is being addressed is maximizing access to the interior of these micron-millimeter or larger size continuous structures so that high/space flow velocities for sorbents and reactants and products are possible. The synthesis methodology for creating new cubic and hexagonal mesoporous phases with 3-D access (Huo et al. 1995; Huo et al. 1996), along with spatial pore alignment by applied magnetic (Firouzi et al. 1997; Tolbert, Firouzi, et al. 1997) or electric fields for high surface area mesoporous silica has been demonstrated, making it possible to create highly accessible pore configurations. Quantification of the synthesis conditions, mapping out the pore and cage structures, functionalization, defect chemistry, and diffusion processes with these materials all are essential to successful future applications of the materials.

Commercial Considerations

Commercial applications of high surface area materials already are in the multibillion dollar range; primary contributions to this economic basis are air separation, petroleum and petrochemical processing, environmental cleanup, chemical sensing, fine chemical catalysis, packaging, and chemical separation applications. Economic incentives for development and application of high surface area materials are expected to substantially increase in view of increasing environmental stress, their role as important components of chemical sensors, potential applications in biotechnology, and increasing energy and agricultural consumption demands.

Control of the nanostructure and the nanostructure interface in composite phases can be expected to provide breakthroughs in a number of applications: parallel processing where high density image processing coupled with high space velocity or turnover is required; applications involving pattern recognition, biomaterials synthesis, and design; biotechnology applications; development of small lapel-worn toxic agent detectors for military and environmentally precarious environments; and in general, chemical sensing technology where highly selective, sensitive, rapid detection is required. Breakthroughs are less likely in current bulk processing applications, particularly in the historically more mature air separation, petroleum, and petrochemical industries. The cost of reconfiguring present technologies and plants operating at a relatively high efficiency is a formidable barrier. Nevertheless, the magnitude of the economic impact generated by even small improvements in many of these areas is so substantial that nanostructure-directed modification of the present approaches is still being and will continue to be sought.

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CHAPTER 8

DEVICES

OVERVIEW

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Motorola
WTEC Panel

The complexity of integrated circuits has increased by miniaturization according to scaling rules that preserve chip speed and power dissipation. It is anticipated that by the year 2005 critical dimensions of 50 nm will be required (e.g., for the 16 Gbit DRAM). At those dimensions, normal scaling of conventional MOSFETs will no longer improve performance at the same rate unless the operating temperature is significantly reduced or drastic new technologies are developed.

The trend in gate length reduction has followed an exponential rule since before 1980 and continues today; following this rule, feature sizes will shrink to about 100 nm by the year 2002. The difficulty arises from the fact that gate oxide thickness scales with the gate length. For example, when the gate length is reduced from 250 nm to 150 nm, the corresponding oxide thickness scales from 4 nm to 3 nm. Such scaling maintains roughly constant power dissipation and chip speed over successive generations. However, when the thickness falls below 2 nm, tunnel current can be greater than the channel current, and the gate will no longer control channel charge. The approximate number of electrons in a 1 Gbit DRAM transistor scales to slightly more than 100 and will reach a value of about 20 in a 4 Gbit transistor. Subsequent generations of transistors that follow the same scaling trend will have current-voltage characteristics that are uniquely different from conventional saturating characteristics today. When the number of electrons is sufficiently small, thermal fluctuations can blur the distinction between on and off states.

Post-MOSFET ULSI technology will likely be one in which the basic MOSFET building blocks are replaced by nanoscale devices that exhibit quantum effects. Issues of size and composition control become extremely critical in the case of single-electron devices. In such devices, changes in current with voltage occur in steps rather than continuously. For room temperature operation, the device size must be less than 5 nm for such behavior to become observable and potentially usable. It is not presently clear how such devices will be fabricated. So far, fabrication of room temperature devices has been accomplished using a scanning tunnel microscope tip. Room temperature operation has also been achieved in a polysilicon channel in which quantum size defects embedded in grain boundaries exhibited coulomb blockade effects.

In addition to the requirement for extreme uniformity of composition and thickness in crystalline nanoscale transistors, it will be necessary to control the number and location of individual dopants and defects to a resolution of one atom. Because of this difficulty, there is much interest in fabricating single-electron transistors (SETs) by molecular self-assembly. Here, the critical requirements involve the molecular orientation and chemisorption energy, molecular structure, and corresponding energy band structure. The concept of energy band analagous offsets and absolute reference levels in molecular structures will be an important topic of investigation in this emerging field.

Table 8.1 summarizes the drivers for and main issues in the development of nanoscale devices.

Table 8.1
Critical Issues in Development of Nanoscale Devices

Drivers	
barriers to silicon scaling	quantum electric fields interconnects reliability
need for increasingly dense memory	scaling
fabrication cost reduction	process simplification
flexible displays	polymer emitters & transistors
health industry	biosensor arrays
Research Issues (these become manufacturing issues later)	
critical dimension control	tunnel barriers energy level separation control of size effects threshold control operating temperature
impurity control	doping background stray charge in SETs
interconnects	electromigration time constant
single electron circuits	requirement for unique architecture
monomolecular layers	electrical properties optical properties reactivity to process environment
arrays for biosensors	DNA segmentation for hybridization
self-aligned fabrication	
self-assembled fabrication	molecular or crystalline conduction in single molecules synthesis of molecules
carbon-based nanostructures	electronic and optical properties deterministic structural control
accurate models	molecular “HOMO-LUMO” engineering nonoptimum structures with defects prediction of measurables defect density in self-assembled monolayers (SAMs) S-K atom number distribution
Manufacturing Issues	
soft lithography	defect control runout and dimension control multilayer registration

ORGANIC NANOSTRUCTURE DEVICES

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Scientific Drivers

A primary motivation for the extensive research over the last several years concentrating on the growth and physics of organic thin film nanostructures is their very real potential for use in applications that are not accessible to more conventional, inorganic semiconductors. The recent demonstration of efficient electroluminescence from organic thin film devices promises to transform the flat panel display industry (Tang and VanSlyke 1987; Burrows and Forrest 1994; Burroughes et al. 1990), with the potential of replacing liquid crystal displays with an entirely new generation of efficient, emissive, full color flat panels based on light-emitting organic devices. In more recent developments, organic thin films are showing promise for use as thin film transistors (TFTs) (Dodabalapur et al. 1995; Garnier et al. 1990; Garnier et al. 1997), which might eventually replace amorphous or polysilicon TFTs currently used in the back planes of active matrix liquid crystal displays (AMLCD). These new developments also must be placed in the context of long efforts and progress that has been directed at employing organic thin films for solar energy conversion (Wohrle and Meissner 1991; Tang 1986) and in sensors of various kinds. Finally, vacuum-deposited OMCs have also been proposed as materials with large second or third order optical nonlinearities (Lam et al. 1991; Agranovich et al. 1995; Maruyama et al. 1995; Fang et al. 1993; Leegwater and Mukamel 1992; Wang and Mukamel 1994; Dubovsky and Mukamel 1992; Mukamel et al. 1994), or large χ (Burroughes et al. 1990). There are, in addition, many, somewhat less conventional uses of organic thin films deposited in vacuum, including waveguides and optical couplers (Zang et al. 1991; Zang and Forrest 1992; Taylor et al. 1997), organic/inorganic photodetectors (So and Forrest 1989; Forrest et al. 1982), and lasers.

The primary attraction of organic molecular nanostructures is their potential low cost and the extreme flexibility that the device engineer has in choosing a material whose properties have been specifically tailored to meet the needs of a particular application. The materials are easily integrated with conventional semiconductor devices, thereby providing additional functionality to existing photonic circuits and components.

The potentials of organic molecular nanostructures, however, must be balanced against the problems that have traditionally impeded acceptance of organics for use in active electronic or optoelectronic device applications, including unstable device characteristics; sensitivity to adverse environments (e.g., temperature, humidity, oxygen, etc.); non-ideal metal/organic contacts; and lack of reproducibility of material composition, purity, and fabrication conditions.

It is clear that the ultrahigh vacuum environment characteristic of organic thin film deposition processes can provide the necessary material purity and structural and chemical reproducibility necessary in modern, high performance optoelectronic device applications. While the costs and complexities associated with ultrahigh vacuum (UHV) deposition processes may offset the attractive (but possibly misleading) “simplicity” often attributed to organic-based devices, it is clear that the performance advantages of such structures outweigh these apparent disadvantages. Furthermore, while purity and structural precision are key to the ultimate success of all optoelectronic device technologies, it is not clear how sophisticated the deposition system must be to achieve acceptable device performance. At this point, vacuum deposition serves as the most powerful tool for investigating the detailed growth and physical characteristics of organic nanostructure devices, and hence will ultimately be able to address questions regarding the need for UHV in the production of practical display, transistor, NLO, or other molecular organic thin film device applications.

Recent Progress in Organic Nanostructure Devices

As a background for understanding the current status of organic nanostructures R&D, below is a compilation of some of the best results for organic thin film devices reported to date:

1. *Solar Cells* (Tang 1986; Forrest and So 1988): Highest power conversion efficiency for bilayer organic cells: 1-2%. Challenges that remain include insufficient efficiency to be practical. Also, stability of the devices is inadequate for power generation applications.

2. *Organic Light-Emitting Devices (OLEDs)* (Tang and Van Slyke 1987; Burrows and Forrest 1994; Burrows et al. 1996; Dodabalapur et al. 1994; Tang et al. 1989): These devices are positioning themselves to replace LCDs in several display applications. Some performance characteristics include high brightness (1,000 times brighter than CRT elements) and high efficiency (1-3%). Full color has been demonstrated, but saturated color is not obtainable at all corners of the color palate (R, G, and B), and stability of the devices exceeds 10,000 hrs at video brightness.

   Several challenges yet remain before widespread acceptance of OLEDs will occur. These include the ability to make fully color tunable devices at low cost and to manufacture very thin structures with an acceptable yield. While the operational lifetime of some devices (particularly green emitters) is quite good, other colors (e.g., red) do not have the same high performance and stability attributes. However, there are numerous groups worldwide pursuing OLED technology, and Pioneer intends to bring out a display based on OLEDs in early 1998.

3. *Organic Thin Film Transistors* (Dodabalapur et al. 1995; Garnier et al. 1990; de Leeuw et al. 1997; Dodabalapur, Torsi, and Katz 1995; Lin et al. 1997, 143): Remarkable progress in TFTs based on organic materials has been made in the last couple of years. In particular, pentacene-based organic transistors have resulted in channel mobilities equal to that of amorphous Si (~1 cm^2/V-s), threshold voltages V_T~0V, and on/off current ratios ~ 10^6, albeit not necessarily all on the same device. In addition, circuits consisting of 10 to 20 polymer-based TFTs have also recently been reported (de Leeuw et al. 1997). These results represent major breakthroughs in organic electronics, although many challenges remain. Nevertheless, significant economic drivers exist for ultralow-cost electronics for identification cards, low density memories, display backplanes, etc., which may provide the driving force necessary to bring these devices into widespread use.

These are only three examples of where organic nanostructures are finding application due to the advanced state of their development. As in the case of all immature technologies, there are still significant barriers to their adoption in the commercial world. However, for the first time, active organic nanostructures appear to be on the verge of transforming a large number of optical and electronic applications.

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FUNCTIONAL NANOSTRUCTURES

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Scientific Drivers

The direction of modern technological innovation is clear — smaller, cheaper, faster, smarter. These issues are strongly interelated, and they cut across the broad spectrum of U.S. industries: chemical, measurement, communications, and computation. At the present time, the size scale of electronic technology is significantly below 1 micron, with the current generation of integrated circuits incorporating 0.35 micron features, and the generation of devices scheduled for release at the end of 1998 based on 0.25 micron features. During the past 24 years, the number of transistors integrated onto a single chip has increased by a factor of 16,000, or by a factor of four every 3.4 years. This phenomenal exponential increase in circuit capability is now known as Moore’s Law, and it has been at the foundation of the great success enjoyed by many of this country’s largest and most profitable companies. Compared to the ENIAC, which was first powered up fifty years ago, the present generation of microprocessors can compute 60,000 times as fast while using just .0001 of the power with very much greater reliability.

Many times in the past two decades the end of Moore’s law of scaling has been forecast, with the predicted limiting factors being the increasing complexity of the integrated circuits or the inability of optical lithography to scale to dimensions smaller than the wavelength of light. So far, ingenious engineering and the commitment of significant resources have been able to overcome these limitations by utilizing increasingly sophisticated computer algorithms to aid in the design of the circuits and by applying various optical and chemical tricks to lithography. However, as feature sizes in electronic circuits move into the nanometer size regime, fundamental physics limitations begin to emerge. These limitations include rather obvious issues, such as the impossibility of requiring a fraction of an electron to continue the scaling of a device into the nanometer size range, as well as more enigmatic quantum mechanical issues such as size quantization that opens up significant gaps between allowed energy levels and the ease of electron tunneling through ultrathin insulating barriers.

Thus, if the capabilities of electronic devices are to continue scaling exponentially after the year 2010, which is as far as the Semiconductor Industry Association Roadmap forecasts, there will have to be dramatic changes in device design and operating principles. At this point, one must inquire if absolute limits of electronic circuitry exist. After all, if semiconductor technology is already near those limits, then it makes most sense for industrial organizations to concentrate on software considerations in order to increase the performance and value of their products. However, a simple analysis supplied by Richard Feynman in *Lectures on Computation* (1996) shows how to estimate the ultimate performance of a Boolean logic computing machine that is limited only by fundamental physical constants and the laws of thermodynamics. This analysis shows that it is physically possible to perform calculations one billion times faster than a present generation microprocessor while expending only one watt of power. Thus, the age of electronic computers has not yet even begun. There are clearly huge rewards in store for pushing into the nanometer size range and learning how to harness quantum phenomena as the operating basis for electronic, optical, magnetic, and chemical technologies.

Critical Parameters

The critical parameters for the successful introduction of any significantly new product to the market are performance and cost. A new technology must either offer a substantial performance improvement (by perhaps an order of magnitude) at the same cost, or offer the same performance at a greatly reduced cost (by a factor of three) in order to replace an entrenched technology and the infrastructure that exists to support it. Functional nanostructures offer the potential of both performance and cost enhancements, and therefore their market potential is enormous. However, a huge amount of research in nanoscience must precede the successful introduction of nanotechnology, and there will certainly be a significant transition period where both classical and quantum circuitry will be present in the same systems and will have to be compatible.

In terms of performance issues, nanostructures offer the potential for enormous increases in information storage capacity and computational throughput, just because of their packing density and the short information transit times from site to site. They offer greatly decreased voltage and power requirements for all types of optical sources, from high performance communications lasers to general illumination. In order to deliver these benefits, functional nanostructures will have to be fabricated in huge quantities with extremely uniform and controlled size, shape, and composition distributions to optimize their properties for a particular application. They will have to be assembled into larger structures with ever increasing complexity, hierarchy, and functionality. Utilizing the types of subtractive processes used today to create microstructures will be far too costly to manufacture nanostructures. Moore’s second law states that the cost of building fabrication facilities (or fabs) for electronic circuits based on lithography and subtractive processes increases by a factor of two every generation. The present generation of logic and memory chips are being built in billion dollar fabs, which means that a fab line for true nanostructures made by current strategies would cost many tens or even hundreds of billions of dollars to construct. On the other hand, additive processes, such as chemical synthesis and self-assembly or guided-assembly techniques, hold the promise of making nanostructures very inexpensively and appear to be necessary for the successful development of nanotechnology.

Thus, from the viewpoint of both performance and cost, nanostructures should revolutionize several industries in the next century.

Bringing Functional Nanostructures to the Market

Functional nanostructures will be first introduced to the market gradually over the next decade. The first applications will be passive nanostructures, such as phosphors, pigments, and photographic emulsions, which are not addressed individually but do respond to an external stimulus based on their properties as individual entities. In fact, in the next couple of years such passive applications of nanostructures will account for several billion dollars in revenues for U.S. companies as they are introduced as improvements in existing products rather than as completely new technologies. Nanostructures will be in general use by ordinary people in the industrialized nations on a daily basis by 2001. In most cases, only a very few corporate technologists will know about their use, since they will be held by their companies as trade secrets and proprietary intellectual property. The general public will see dramatic improvements in familiar products that they purchase, but they will not know about and companies will not advertise these first applications of passive functional nanostructures. This is an unfortunate result of increasingly stiff competition and short product life-cycles, because the importance of nanostructures to the economy will not be widely known or understood by the public or the government. In many cases, academic scientists and the research agencies that fund them will have to take it on faith that the results of their work are having a major impact on the economy, even though it cannot be measured directly, and that nanotechnology is indeed a vibrant field in industry, even though there are few publications and patents.

For active nanostructures, those that will be specifically addressed individually in creating the output of a device, the appearance in the market will be much later and will require the combined research efforts of a large and interactive community. Examples of such applications include

- using nanocrystalline active regions in LEDs and lasers to lower threshold currents, lower operating powers, and improve optical output
- using nanostructures in the gate region of FET-like devices to create new semipermanent memory devices and multilevel logic devices
- ultimately, using nanostructures in the fabrication of single-electron transistors or even electrostatically coupled cellular automata

This is where the most visible research will be and where little return on investment will occur for at least the next decade. In academic and governmental circles, the primary attraction will be the intellectual challenge of understanding quantum effects and attempting to express them at ordinary temperatures. There will be repeated cycles of enthusiasm as new discoveries are made and dejection as the time scales for these discoveries to reach the market appear to lengthen (even though they may be in the market already because of the stealth approach being taken by manufacturers). The primary issue for funding agencies will be to provide a substantial and predictable level of funding for the long term, and not to respond to short-term pressures to switch all funding into the latest hot area. In industrial laboratories, the balance will be between the near-term bottom line of the company and the promise of substantial profits to be made by applications of active nanostructures. The major difficulties and slow progress will dissuade some major companies from investing in this area, but there will be a new wave of innovation and invention from small companies, with the creation of a few new giant corporations and the disappearance of a few of the old ones. This is because the use of additive processes for making nanostructures should be cheap enough to allow smaller companies to play seriously in this new arena.

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SI-BASED NANODEVICES

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Silicon is currently the material most heavily used in the semiconductor industry, in particular in logic and memory applications. The devices made thereof are in most of the cases metal oxide semiconductor field-effect transistors (MOSFETs), with the exception of a few applications that still use bipolar transistors. As device scaling continues, the active parts of the devices are inevitably going to be measured in hundreds of nanometers or less.

In the past 15 years, there has been an increasing interest in exploring physical phenomena such as resonant tunneling, Coulomb blockade, ballistic transport, and quantized conductance, to name a few. Most of these studies have been conducted on III-V-based materials or on metal/oxide/metal configurations. Many striking observations have been made in these material systems, but so far these remain of limited use. Therefore, there is a clear tendency to explore the possibility of combining Si technology with these interesting physical phenomena in order to come up with a new breed of devices that maybe useful in the future. Furthermore, the fact that the bandgap of Si is indirect has limited the use of Si in optoelectronic applications. However, the use of heterostructures and nanoparticles may help alleviate this limitation, which would pave the way to the full integration of optoelectronics with digital logic and memory devices.

In response to the above needs, there has been a great deal of emphasis in the past few years on examining nanodevices in Si and in Si-based heterostructures. Three main directions have been taken by various groups interested in this field.

The first direction is to shrink the size of conducting Si islands to the limit where their associated capacitance is so small that the charging energy of the Si islands is higher than the thermal broadening. That design is based on SOI MOSFET processing steps, except for the step needed to form the ultrasmall island, which relies on electron beam lithography and repetitive oxidation. Several groups worldwide (mostly in Japan) have demonstrated working devices that clearly exhibit the Coulomb blockade manifested in current steps as a function of transistor bias. The remaining questions are related to the manufacturability of such devices, their potential integration in standard CMOS, or their use in stand-alone applications.

The second direction is to resort to Si-based heterojunctions to build resonant tunneling and modulation-doped structures, and many other structures that have been previously demonstrated only in III-V-based heterostructures. The most heavily studied material system in this direction is that of strained Si/SiGe, which allows the creation of Si electron quantum wells cladded between SiGe barriers. Modifications can be achieved by adding C to the alloy. More exotic heterostructures involve metals or metal alloys. In strained Si/SiGe, which leaves Si quantum wells under tensile strain, the electron transport properties are modified and allow for investigation of many interesting phenomena that rely on long electron mean-free paths. A novel effect was recently discovered that leads to pronounced negative differential conductance in such devices. Possible memory applications may be based on this effect.

In addition, the fact that Si and Ge are grown under strain, caused by the lattice mismatch, allows for the growth of Ge islands embedded in a matrix of Si. The tendency to island is a result of the strain and the consequent Stranski-Kastranov growth mode. Together with the growth of Si/Ge atomic layer superlattices, such devices may hold promise for novel optical sources. Preliminary results indicate that the luminescence from such structures is already orders of magnitude stronger than in bulk Si.

The third direction is that of creating Si or Ge nanocrystals embedded in the SiO_2 gate dielectric. Presence of such nanocrystals in an otherwise standard MOSFET process allows for a shift in threshold voltage due to charging and discharging these nanocrystals through the gate tunneling currents. Such an effect holds promise to be useful in future memory applications and is currently under investigation by various groups.

FUNCTIONAL MOLECULAR STRUCTURES AND DEVICES

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Within the last few years it has become possible to microfabricate matter on an unprecedented scale. Advances in nanofabrication technology now allow creation of electronic structures that exhibit manifest quantum and single-electron effects. However, proposed solid state device implementations at this level suffer from three problems:

1. *Critical dimensional control difficulties.* For instance, electron devices that operate in this range must operate by tunneling, since a barrier (heterostructure, oxide, or otherwise) is a prerequisite for isolation in a 3-terminal device that can exhibit gain. However, electron tunneling is exponentially sensitive to atomic-layer fluctuations in the tunneling barriers, resulting in device characteristic variations unacceptable for large scale integration. Similar effects also occur for the position of energy states, either size-quantized or charge-quantized.
2. *Reduced operating temperatures.* Device embodiments utilizing discrete electron charging (SETs) suffer from reduced operating temperatures for room temperature operation; 1 nm or less size junctions are required, dimensions that imply severe tunnel barrier and size fluctuation problems for solid state or metal embodiments.
3. *Interconnection and alignment problems*. None of the current nanofabrication approaches to solid state device implementation addresses these problems.

The generic properties of a technology that addresses the critical problems can be detailed:

- the key innovation will be the one that solves the interconnect problem
- the fabrication technology must be predominantly self-aligned, perhaps non-lithographic and self-limiting
- scaling to the atomic level and room temperature operation are desirable

Beyond ULSI, the ultimate device technology (if it exists), independent of device embodiment, must solve the interconnection problem and will be predominantly self-aligned. A technology-dependent issue is where existing ULSI will usefully end (from recent work, it is reasonable that this will occur in the 0.1 micron regime); scaling to just the 100s of Å level may not be cost-effective, as the increase in performance is marginal compared to the development costs of the technology. Thus, identifying an atomic-scale device technology seems the only approach worth the investment.

Conventional contemporary personal-sized computers utilize ca. 10^8 microfabricated devices per instrument with a coverage of ca. 10^7 uniquely addressable transistors per cm^2. Extension of microelectronics beyond these limits requires the exploration of nonconventional electronic structures that scale far beyond these limits. For example, if devices were to be based upon single molecules, using routine chemical syntheses one could prepare 6×10^{23} (Avogadro's number) devices in a single reaction flask, hence, more devices than are presently in use by all the computational systems combined, worldwide. Equally attractive is the fact that self-assembled monolayers can permit thermodynamically-driven ordering of $\sim 10^{14}$ molecules/cm^2, although unique addressing of such structures in a conventional manner is not presently conceivable. Thus, molecular-based systems can offer distinct advantages in density, uniformity, and potential fabrication cost.

The self-aligned spontaneous assembly of chemically synthesized interconnects, active devices, and circuits is a revolutionary approach for spontaneously assembling atomic scale electronics (Reed 1995). It attacks the interconnection and critical dimension control problems in one step and is implicitly atomic in scale. Concurrently, the approach utilizes an inherently self-aligned batch processing technique that addresses the ultimate fabrication limitations of conventional ULSI.

At this point, efforts worldwide are concentrated on obtaining charge transport in and the measurement of the conductance of single organic molecules. Previous measurements have been done on molecular systems by scanning tunneling microscopes (Bumm et al. 1996; Dorogi et al. 1995; Andres et al. 1996; Nejoh 1996) in an attempt to yield detailed direct measurements of molecule conductance. Preliminary results have been reported (Reed et al. 1997) of single molecule conductance in a self-assembled structure, an important first step in creating self-assembled molecular devices. Future work should concentrate on the creation of active device structures with conducting segments (based on π-conjugated oligomers such as oligo[phenylene ethynylene]s) with transport barriers (such as CH_2 [methylene] units), to create the analogues of heterojunction bandgap-engineered devices.

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WHITHER NANOTECHNOLOGY?[1]

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Introduction

A new manufacturing technology looms on the horizon: molecular nanotechnology (http://nano.xerox.com/nano). Its roots date back to a 1959 talk by Richard Feynman (http://nano.xerox.com/nanotech/feynman.html) in which he said, "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big."

In the last few years the idea that we should be able to economically arrange atoms in most of the ways permitted by physical law has gained fairly general acceptance. This can be viewed as simply the culmination of a centuries-old trend: the basic objectives of manufacturing are lower cost, greater precision, and greater flexibility in what can be manufactured: as the decades have gone by, we've gotten better and better at it. The limit of low cost is set by the cost of the raw materials and energy involved in manufacture, the limit of precision is the ability to get every atom where we want it, and the limit of flexibility is the ability to arrange atoms in whatever patterns are permitted by physical law. While it seems unlikely that we will ever completely reach these limits, the objective of molecular nanotechnology is to approach them. Manufacturing costs should be low — a dollar a pound or less — almost regardless of what is being manufactured. Almost every atom should be in the right place — while background radiation limits this, error rates of a single atom out of place among many tens of billions seem feasible in properly designed structures under "normal" conditions. And finally, we should be able to make most of the stable structures that are consistent with physical law. As structures become less stable they become more difficult and arguably impossible to make, but this still leaves a vast space of possible structures that are beyond the reach of current methods. In addition, some structures might be stable if only we could make them, but all intermediate states would be unstable. Drexler, for example, has argued that the molecular equivalent of a stone arch (http://www.asiapac.com/EnginesOfCreation/EOC_References.html#0025) would be unstable unless all its pieces were in place. The final result would be stable, but all synthetic pathways leading to this result would have to pass through an unstable state, making synthesis impossible.

While the broad objective has gained acceptance, as a community we have still not agreed on how best to proceed, nor on what this future technology will look like, nor on how long it will take to develop. The purpose of this paper is not primarily to focus on specific technical approaches, but to ask, "What do we need to do, as a community, to speed the development of this new technology?"

The Goal

Before going further we need to make sure we are in broad agreement about the goal. Molecular nanotechnology should, by definition, permit us to manufacture (among other things) molecular computers with mole quantities of switches, connected in the intricate patterns required by today's complex computers, at a cost of perhaps a dollar a pound (or less). Today's computer — if we weigh the thin layer on top of a computer chip — costs tens of millions of dollars per pound. This thin layer, only a few microns thick, contains almost all the complexity of the modern computer. The rest of the wafer is mere sand, dragged along as a convenient mounting platform for the active region but doing little else. Viewed in this light, lithography falls woefully short of the cost goal.

Molecular nanotechnology should let us extend this very thin and complex layer into three dimensions while greatly shrinking the size of the switches. It should let us position dopant atoms at specific lattice sites

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[1] This rough draft was written over a few days for the May 8-9 WTEC workshop on nanotechnology.

(chosen by design to optimize device function) while simultaneously keeping the manufacturing costs as low as the manufacturing costs of a piece of wood.

Besides computers, molecular nanotechnology should let us make inexpensive materials with a strength-to-weight ratio similar to that of diamond. These would have wide ranging applications in structural and load bearing applications. Manufactured with precisely the desired shape and structured at the molecular scale to optimize material properties, we should be able to make a jet, a rocket, a car or even a chair that would, by today's standards, be remarkably light, strong, and cheap.

The objective of molecular nanotechnology is not simply to provide a few new products nor to greatly enhance the performance of some select high-tech devices, but to replace essentially the entire existing manufacturing base with a new, radically less expensive, radically more precise, and radically more flexible way of making products. The aim is not simply to replace today's lithographic fabrication facilities to let us make better computers, but also to replace the assembly lines for cars, televisions, telephones, books, bookcases, airplanes, tractors, etc. The objective is a pervasive change in manufacturing, a change that will leave virtually no product untouched.

It Will Take a Lot of Work

It seems likely that the development of such a capability will require (a) time and (b) resources. The development of nuclear weapons took billions of dollars and a very focused development project. The Apollo program likewise took a focused effort over many years and billions of dollars in money and vast amounts of creative talent. The development of the computer industry, while following a very different pattern (private versus governmental, incremental "pay as you go" versus large up-front funding), also involved major funding and many years.

It is too early to say exactly what pattern the development of molecular nanotechnology will follow, but it is not too early to say that it is likely to require major resources. Whoever makes the decision to commit those resources is unlikely to do so unless there is a clear picture of both the goal and how to achieve it.

Suppose a hypothetical funder came to the research community today and said, "Molecular nanotechnology has a very high payoff, and I wish to start a major new program in the area. What should I do? What should I fund?" The answer, today, would be a chorus of voices tugging in all directions.

Perhaps our hypothetical funder would fund all the different approaches. This was the basic strategy used to develop nuclear weapons. But that was a war-time effort motivated by panic and the fear of annihilation. A more likely scenario is that our hypothetical funder would say, "You are all saying different things — I won't fund a major new project until at least some substantial fraction of you have reached agreement about what to do."

What, then, is the key to developing molecular nanotechnology? Developing agreement about what it is and how to achieve it. How can we develop agreement? As a first step we must explicitly pursue research into the question, "What would a molecular manufacturing system look like?"

Self Replication and Low Cost

Take the issue of manufacturing cost. This is a primary objective of molecular nanotechnology. One way to keep manufacturing costs down would be to develop self replicating manufacturing systems (http://nano.xerox.com/nanotech/selfRep.html). The development of self replicating systems seems like a daunting task, so it is natural to ask if there are alternative ways of achieving the cost objective. To date, no alternative of similar effectiveness has been proposed. As noted earlier, lithography is perhaps seven orders of magnitude too expensive. Other approaches fall short in terms of the range of things they can make, or in terms of the precision with which they can make them. Bulk chemicals are produced today at relatively low cost, but the range of molecular structures that can be made this way is very limited. Lithography can make a great many patterns on a surface, but not with molecular precision. While self assembly is a powerful approach, the direct manufacture of (for example) a diamond rocket by self assembly seems implausible (while self assembly is likely to be important if not crucial in developing nanotechnology, it can still only make an extremely small fraction of what is possible).

It would seem that either (a) we will develop artificial self replicating systems or (b) we will not. If we do, then we can address the issue of manufacturing cost. If we do not, we must seek an alternative — and no alternative of similar effectiveness has yet been proposed.

It is worth noting that we already have self replicating systems of the biological variety. Such systems can already make desirable materials. Wood, for example, is relatively low cost and provides a reasonable strength to weight ratio. Using a programmable protein synthesizer (a.k.a. a ribosome), these self replicating cells can synthesize many compounds. Biological approaches, though, can make but an infinitesimal drop in the vast ocean of the possible. Shall we turn our backs on that ocean? Diamond semiconductors, materials that resist high temperature, structural materials with the strength to weight ratio of diamond, and a host of other examples do not seem to fall within the range of structures that biological systems can directly make.

If we pursue artificial self replicating systems, what do they look like? What are the principles on which they are based? How complex will they be? These and other questions must be systematically addressed, with a confidence and at a level of detail that lets us base major investments on the answers. (While the author has written several articles about self replicating manufacturing systems (http://nano.xerox.com/nanotech/selfRep.html) and has no doubt that they will play an essential role in future molecular manufacturing systems, the point here is that individual conclusions, regardless of how sound, aren't enough. Some substantial portion of the research community must address the issues and reach at least rough agreement about the answers).

If self replication is the right approach and we fail to pursue it, we'll make no further progress. If it's the wrong approach we must develop an alternative. No plausible alternative has been proposed which could simultaneously achieve the three objectives given above: low cost, molecular precision, and great flexibility in what can be made. Investigations to date strongly support the feasibility of programmable self replicating systems. The obvious strategy is to investigate this approach in greater depth.

Molecular Modeling

If we wish to accomplish that which is new, we must at some point discuss what we have not (yet) done. If what must be done is relatively complex (a self replicating system, for example), then we must be prepared to spend substantial time and effort discussing things that have not been made and will not be made for many years.

At the same time, we must take steps to insure that our discussions of what hasn't been done remain focused and do not drift into abstract errors and vague generalities.

Fortunately, we have a tool at hand for dealing with this: molecular modeling (http://nano.xerox.com/nanotech/compNano.html). We know the laws of physics, and we do not expect them to be substantially in error as we apply them to molecular systems under "reasonable" conditions. The applicability of Schrodinger's equation to molecular machines is unlikely to change in the next several decades. We do not need, nor do we expect, any major revolutions in physical law. Our goal and our desire is to develop molecular machines that are feasible with respect to known and well understood physical law. While physical experiments let us explore a tiny fraction of what is possible, they cannot let us investigate what we do not yet know how to make.

Molecular modeling can be used to probe systems that have already been built (allowing us to check the accuracy of the models), systems that might soon be built (letting us inexpensively explore alternatives) or systems that won’t be built for many years (again letting us inexpensively explore alternatives, but on a longer time horizon).

If the key to progress is developing a shared understanding of the approach or approaches which are worth pursuing, as well as some shared vision of the goal; and if the goal cannot be achieved without many years of work, then we must adopt a disciplined method of analyzing the alternative ways of achieving the objective. Molecular modeling is a major component of that discipline.

Modeling an Assembler

To sharpen the focus on this idea of modeling future molecular machines with present molecular modeling methods, let us consider the design of an assembler (http://nano.xerox.com/nanotech/nano4/merklePaper.html). Such a device is able to make copies of itself — hence achieving low cost — and can be programmed to build a wide range of useful structures. The term “assembler” actually encompasses a rather large family of possible designs. For our purposes, we wish to consider the simplest assembler able to achieve certain core objectives: make a copy of itself, and make a wide range of hydrocarbon structures (including diamond and graphite) under program control.

If we are to build an assembler, than at some point we must completely specify it: we must specify the location and element type of every atom. Interestingly enough, it should be possible to design and model such an assembler using computational chemistry software and computing hardware that are either presently available or could reasonably be developed in the near future (a few years). Molecular mechanics and dynamics models would be used to analyze the behavior of the mechanical components, while *ab initio* quantum chemistry models would be used to analyze the reactions involved (e.g., the making and breaking of chemical bonds). Some potential energy functions (such as Brenner’s potential) are able to model bond formation and bond breaking. They would be used to do molecular dynamics on the chemical reactions where they were applicable.

Some of the reactions that will likely be involved in the synthesis of diamond have already been modeled. One example is the hydrogen abstraction tool (http://nano.xerox.com/nanotech/Habs/Habs.html), which has been modeled by several groups using both *ab initio* and molecular dynamics methods. Other components have been proposed, discussed, and modeled in varying levels of detail. This process can clearly be extended.

It is useful to emphasize that a design for an assembler is not the same as having an assembler. An assembler can build another assembler, but this presupposes the prior existence of an assembler. We must still build the first one using existing technology. This presents a separate design challenge — but a design challenge that can also be addressed by molecular modeling.

The Alternatives

If we are to develop molecular nanotechnology, it would seem that one of the significant tasks is to systematically investigate the various ways of achieving its basic objectives. Is this a reasonable course of action? Again, using self replication as an example, we need to ask: what are the available alternatives? To date, the only proposals for molecular manufacturing systems involve self replication. The obvious approach is to analyze in greater depth the proposals that have been advanced. If we hesitate to pursue this approach then we should explicitly seek alternatives and then analyze them to see if they are as effective at achieving the desired objectives.

If molecular nanotechnology is feasible within the existing framework of physical law — and that seems to be the predominant opinion — then unless (a) we expect physical law will change or (b) we expect molecular manufacturing systems will be easily developed without great effort, then the obvious strategy is to (c) begin the patient task of exploring the space of possibilities, winnowing out the approaches that either don’t work or fail to achieve one (or more) of the objectives, and focus on the approaches that look like they should work. And when we’ve explored the possibilities, studied the alternatives, determined what is possible and rejected what is impossible — when we can see a clear path from where we are today to where we wish to be in the future — then we can begin in earnest.

CHAPTER 9

BIOLOGICAL, CARBON, AND THEORY ISSUES

OVERVIEW

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Biological Aspects

Biology, biophysics, and biomolecules are themes that run through much of the current research on nanoparticles, nanostructured materials, and nanodevices. The structure of the WTEC nanotechnologies study acknowledges and emphasizes the need for interdisciplinary research, especially as it applies to the bio-related aspects of nanotechnology; therefore biological aspects of the study are discussed below within the organizational structure of the entire study.

The relationship between the biological sciences and nanotechnology spans across the missions of a number of federal agencies. For example, NASA is interested in the biomimetic and/or enzymatic removal of carbon dioxide from air, in self-repairing spacesuits and habitats, and in electronic “nose” or sensor technology that can detect adverse chemicals. DOD is interested in biosensors as well, particularly for biological and chemical warfare agents. NSF has programs in molecular self-assembly, in the use of polynucleotide chains as templates for quantum dots, and in oligonucleotide arrays for gene analysis. Biological applications are one of the fastest growing areas of research in NSF’s National Nanofabrication Users’ Network (NNUN). Biomedical research sponsored by NIH offers a rich opportunity for nanotechnology research. For example, NIH sponsors the University of Michigan’s center for neural communications technology, a number of chip technology projects aimed at genomic sequencing, projects involving biosensor development, and projects that involve the measurement of nanoforces and the synthesis of nanocomposites based on bones and teeth.

The complementary interests of the federal agencies illustrated by these examples suggest that it may be fruitful to develop interagency joint proposals to coordinate the funding of nanotechnology research, especially as it pertains to the biological sciences.

Nanotechnology Building Blocks

Synthesis

Modern biotechnology now makes it possible to tap the synthetic machinery of biological systems to produce highly regular materials that might not occur in nature, and/or materials with enhanced properties. Examples include non-native protein polymers with precisely controlled molecular weights, poly(hydroxyalkanoates) that are produced in microbes and plants, and polysaccharides with unusual functionalization (Tirrell et al. 1994; 1995). Furthermore, improved chemistries and separations technologies make it possible to produce unusual DNA and RNA polymers and to obtain purified lipids. These molecules of biological or quasi-biological origin are attractive candidates for building up precisely controlled and complex three-dimensional nanostructures because they usually undergo exquisitely selective binding and obey highly specific rules for self-assembly. These positive qualities notwithstanding, it is important to keep in mind that many biomolecules are fairly nonrobust, and techniques will be required to overcome this problem.

Seeman and coworkers (p. 177[1]) have been investigating the ability of DNA molecules to form complex three-dimensional objects, with the goal of forming 2-D and 3-D periodic structures with defined topologies. DNA is ideal for building molecular nanotechnology objects, as it offers synthetic control, predictability of interactions, and well-controlled "sticky ends" that assemble in highly specific fashion. Furthermore, the existence of stable branched DNA molecules permits complex and interlocking shapes to be formed. Using such technology, a number of topologies have been prepared, including cubes (Chen and Seeman 1991), truncated octahedra (Zhang and Seeman 1994), and Borromean rings (Mao, Sun, and Seeman 1997). The Friedlander work (p. 83) on the synthesis of nanoparticles and their aggregation describes nanochains as a new type of polymer. See the section below, Consolidated Materials and Parts, which describes "biological bar magnets," which are simply nanochains.

Role of Nanoparticles in Health and Pollution

Although beyond the scope of this review, it is important to keep in mind the potential role of atmospheric nanoparticles in photocatalytic and thermal production of atmospheric pollutants (Chianelli p. 133). Atmospheric aerosols in heavily polluted areas have the potential to accelerate ozone formation reactions; furthermore, because they are respirable, they could represent a health hazard.

These aerosols generally contain two major components; one is composed of amorphous carbon that has fullerene-like particles dispersed in it. The second is inorganic and consists of oxides and sulfides supported on clay minerals. In particular, the iron oxide, manganese oxide, and iron sulfide nanoparticles have band-gaps that could enhance the photocatalytic adsorption of solar radiation. In addition, these materials are acidic and may be coated with water, which would enhance their catalytic ability to crack hydrocarbons and create free radicals (Chianelli p. 133). At present this is an underexplored area of research that bears scrutiny.

Assembly

Research frontiers that exploit the capacity of biomolecules and cellular systems to undergo self-assembly have been identified in two recent National Research Council reports (NRC 1994; 1996). Examples of self-assembled systems include monolayers and multilayers, biocompatible layers, decorated membranes, organized structures such as microtubules and drug-delivery systems, biomineralization, and the intracellular assembly of CdSe semiconductors and chains of magnetite.

Biological materials undergo self-assembly in a hierarchical manner, beginning with monomer molecules (e.g., nucleotides and nucleosides, amino acids, lipids), which form polymers (e.g., DNA, RNA, proteins, polysaccharides), then assemblies (e.g., membranes, organelles), and finally cells, organs, organisms, and even populations (Rousseau and Jelinski 1991). Consequently, biological materials assemble on a very broad range of organizational length scales, and in both hierarchical and nested manners (Aksay p. 79).

Research stemming from the study of self-assembling surfaces (e.g., alkylthiols and other biomembrane mimics on gold) led to the discovery of "stamping" (Kumar and Whitesides 1993). This method, in which an elastomeric stamp is used for rapid pattern transfer, has now been driven to < 100 nanometer scales and extended to non-flat surfaces and is called "soft lithography." The exciting and far-reaching applications made possible by soft lithography are described in Chapter 4 (Whitesides, p. 76).

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Self-assembled organic materials such as proteins and/or lipids can be used to form the scaffolding for the deposition of inorganic material to form ceramics such as hydroxyapatite, calcium carbonate, silicon dioxide, and iron oxide. Although the formation of special ceramics is bioinspired, the organic material need not be of

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[1] References with page numbers but not years of publication are to the authors contributing to this report and the beginning page numbers of their papers. Further references on specific subjects may be found in the individual papers.

biological origin. An example of this is the production of template-assisted nanostructured ceramic thin films (Aksay et al. 1996), which is described in Chapter 7, High Surface Area Materials.

A particularly interesting example of bio-inspired self assembly has been described in a recent article by Stupp and coworkers (1997). This work, in which organic “rod-coil” molecules were induced to self-assemble, is significant in that the molecules orient themselves and self-assemble over a wide range of length scales, including mushroom-shaped clusters, sheets of the clusters packed side-by-side, and thick films, where the sheets pack in a head-to-tail fashion. The interplay between hydrophobic and hydrophilic forces is thought to be partially responsible for the controlled assembly.

Dispersions and Coatings

Drug Delivery

Highly porous materials are ideal candidates for controlled drug delivery (Schnur, Price, and Rudolph 1994) and for tissue engineering (Hubbell and Langer 1995). An example of a controlled drug delivery system comes from the area of microtubules. Phospholipid bilayers can be coaxed to self-assemble into long cylindrical tubes with diameters usually below a micron and lengths up to hundreds of microns (Schnur 1993). During synthesis, drugs can be entrained in these nanotubes, and the final product can be used as a controlled delivery system. Tubules prepared from phospholipid bilayers are ideal for such applications because they are biocompatible.

High Surface Area Materials

Ceramics

Fundamental studies of biomineralization, in which an organic substance (usually protein or peptide or lipid) interacts with an inorganic phase (e.g., calcium carbonate or hydroxyapatite) have led to the bioinspired synthesis of composite materials. The structure and porosity of the inorganic phase can be controlled by templating with an organic surfactant, vesicular arrays, or liquid crystalline materials. Micelle-templated synthesis can produce ceramics with 20-100 Å pore dimensions (Ying p. 96). These tailored pores can be used as catalysts and absorbents, and for gas/liquid separations, thermals, and acoustic insulation. Their selectivity makes them very useful for biochemical and pharmaceutical separations. Bioceramics can also be made that are highly compatible with teeth and bone.

An interesting example of an organic/inorganic composite is the new packaging material that has been developed to replace the polystyrene “clam-shell” for fast food products. Composed of potato starch and calcium carbonate, this foam offers the advantages of good thermal insulation properties, light weight, and biodegradability (Stucky 1997).

Functional Nanostructures

Optoelectronic Devices

Biological molecules and assemblies, such as the photochemical reaction center, are capable of capturing light with good quantum efficiency and transforming it into chemical energy. If properly exploited, such assemblies have potential applications as biomolecule information-processing units.

Bacteriorhodopsin, from the purple membrane bacterium *Halobacterium halobium*, is one such system that has been studied extensively and has been commercialized into optical holographic memories (Birge 1995). In the bacterium, the protein bacteriorhodopsin self-assembles into ordered lipid patches. The protein absorbs light and undergoes a cycle involving a complex series of intermediates, resulting in a proton being pumped across the membrane. It was information developed from understanding the basic science behind the way that bacteriorhodopsin works that led to the use of bacteriorhodopsin as a biomolecule information processing unit. To be used for information storage, the protein is placed under nonbiological conditions. It is dispersed and immobilized into a matrix (e.g., collagen or another polymeric substance) and held at liquid nitrogen temperatures. At this low temperature, the protein acts as an optically driven bistable switch. One form, the light-adapted form of bacteriorhodopsin, absorbs light at 570 nm. When irradiated with green light at 77K, it switches to a different stable form that absorbs light at 630 nm. Using light of different colors enables one to read and write images onto these memories. By subtracting one memory from the other, these memories are especially useful for real-time, rapid comparison of images.

Molecular Motors

The molecular motors found in biology provide for bacterial locomotion, as well as for the active transport and delivery of molecules. For example, the bacterial flagellar motor, about 20 nm in diameter, is comprised of a complex assembly of more than 10 different proteins (Imae and Atsumi 1989). The role of the motor is to rotate the helical flagella of the bacterium so that it is able to swim. Chemical energy (in this case, protons or sodium) is transduced into mechanical energy.

Other examples of molecular motors include RNA polymerase (Yin et al. 1995), myosin, and kinesin (Seventh Biophysical Discussions 1995). The fuel that powers these motors is ATP. A number of researchers have proposed schemes by which such motors could be used to deliver molecules, one at a time, for the purpose of the ground-up assembly of nanoscale devices (NRC 1996). It is envisioned that the highways could be actin or tubulin, which would need to be immobilized onto a surface. Myosin or kinesin naturally travel along these highways and could be used to deliver molecular “packages” to a specific assembly site. Needless to say, many details and the ultimate feasibility of this vision need to be worked out.

Other Forms of Biological Transport Using Nanoparticles

In the body, the function of the high density lipoproteins is to transport cholesterol. The ~7.5 nm discoidal lipoprotein assemblies are sandwiched between discs of phospholipids, and stacked, poker-chip style. The lipoproteins stabilize the cholesterol particles and assist in their transport. Current research involves manipulating and fusing the assemblies and particles with an atomic force microscope tip (Sligar p. 181).

Nanoscale Silicon Technology

Up until this point, we have focused almost exclusively on nanoparticles, nanostructured materials, and nanodevices from the point of view of their synthesis from the ground up, i.e., starting with the atoms and molecules and building up to particles and objects. It would be myopic to ignore new advances in silicon nano- and micro-fabrication technology in which structures are formed by subtractive techniques. This is especially true in light of the recent successes in immobilizing biological nanoparticles (e.g., enzymes, antibodies, etc.) on these surfaces, leading to functional devices that can be employed as sensors, nanoelectrodes, prosthetic devices, or nanomachines. The following section briefly highlights selected research activities in this area and focuses on soft lithography, biosensors, medical nanomachines, and nano electrodes and capillaries.

Processing using “stamping” or soft lithography. Whitesides (p. 76) and his coworkers have pioneered the technique of soft lithography, which offers enormous promise for the fabrication of structures in the tens of nanometer scales and larger.

Biosensors. The biotin-avadin coupling reaction and the alkylthiol/gold surface functionalization technique (Allara 1996) have proved to be of major importance in coupling biological elements onto nonbiological surfaces. Once coupled to silicon devices, which can be queried by electrical, optical, or chemical means, these biological assemblies can function as highly specific biosensors. There has been a very large body of work on biosensors, often employing antigen-antibody recognition as the sensing mechanism (bioaffinity sensors), or redox enzymes as the sensing element (biocatalytic sensors).

A particularly interesting example comes from the work of Aizawa and coworkers (1996), who have developed an electron transfer pathway of a modified enzyme by self-assembly in a porous gold-black electrode. This sensor uses glucose oxididase, modified with the conductor ferrocene, to detect glucose in solution.

Medical nanomachines (MEMS devices). MEMS (microelectromechanical) devices, built from silicon technology, consist of integrated parts and can act as miniature machines, cogs, actuators, or free-standing capacitors. When properly configured, these devices could be used for biosensors, neural probes for recording and stimulation, and via telemetry for completely implantable microsystems (Wise 1996).

Nano electrodes/capillaries. In order to make progress in the field of nanoparticles and nanotechnology, it will be necessary to develop characterization and measurement devices. There have been many recent advances in the technology surrounding nano electrodes, microcapillaries, and microfluidics (Hietpas et al. 1996).

Consolidated Materials and Parts

Titanium Nanostructures

The commercially available titanium nanostructures also offer advantages in health-related applications, as they are able to withstand stresses in the body that pure titanium is unable to sustain.

Molecular and Quantum Computation

The smallest possible computer would ideally be able to perform computations on a molecular scale. Even though the computation may be carried out on a molecular scale, the issue becomes one of having enough molecules to obtain sufficient signal-to-noise ratio to read out the answer. Consequently, at least at present, these computations must be carried out in bulk or with extremes in temperature. There have been two recent developments along these lines; both developments are in very nascent stages.

Adleman (1994) has shown how the rules of DNA self-assembly, coupled with polymerase chain reaction (PCR) amplification of DNA, can lead to a molecular computer of sorts. The system was used to solve the Hamiltonian path problem, a classic and difficult (NP complete) mathematical problem that involves finding a path between vertices of a graph. The starting and ending vertices of each edge of the graph were encoded as the first and second halves of a strand of DNA. A solution to the problem (i.e., what is the path between two specific vertices?) was obtained by using PCR primers for the two vertices. Others have extended these ideas and shown how one can make DNA add (Guarnieri et al. 1996). Although these are exciting demonstrations, at present this technology has a number of drawbacks, including the labor and time it takes to analyze the results of the computation and the uncertainties associated with wet chemistry.

Quantum computation offers the possibility of ultrafast computation, but it suffers from the conflict between needing to be able to manipulate quantum degrees of freedom while preventing decoherence from taking over (Gershenfeld and Chuang 1997). Approaches to quantum computation have produced a two-bit quantum computer using a single trapped and cooled ion of beryllium, but they require enormous experimental gymnastics (Monroe et al. 1995). Quantum computing has now been demonstrated on bulk molecules using multiple pulse nuclear magnetic resonance techniques to produce coherences in liquids (Gershenfeld and Chuang 1997).

Biological Bar Magnets

It has been well-documented that a very large number of organisms have the ability to precipitate ferrimagnetic minerals Fe_3O_4 and Fe_3S_4. In addition, linear chains of membrane-bound crystals of magnetite, called magnetosomes, have been found in microorganisms and fish (Kirschvink et al. 1992). For example, the Fe_3O_4 domain size in the organism *A. magnetotactum* is ca. 500 Å, and a chain of 22 of these domains has a magnetic moment of 1.3 x 10^{-15} A/m^2. It is not clear what the biological function of these magnetosomes is, or if or how they could be exploited for non-biological applications. These magnetosomes are an example of the new nanochain form of nanoparticle polymer that is covered by Froes (p. 105).

Carbon

Materials such as carbon nanotubes, fullerenes, nanoparticles, and porous carbon are scientific drivers. They combine one-dimensional properties, such as electronic structures, Coulomb blockade phenomena, and quantum phonon effects, with the mechanical properties of possessing high stiffness yet being bendable (Dresselhaus p. 169).

Nanotubes

Depending upon the method of preparation, nanotubes can be insulators, semiconductors, or conductors. Until recently, nanotubes were produced by methods such as the carbon-arc dischard method, which produced randomly oriented tubes of variable dimensions that were contaminated with carbon particles. However, now Smalley and colleagues (Collins et al. 1997) has prepared all chiral, similar diameter nanotubes. Potential applications include field emission and STM tips, gas storage materials, materials for the manipulation of nanostructures, fillers for conductive plastics, and high power electrochemical capacitors. More recently, Kroto and Walton and colleagues (Terrones et al. 1997) have developed a laser etching method to prepare bundles of aligned carbon nanotubes that are free from contaminating carbon particles. These tubes were produced by pyrolyzing 2-amino-4,6-dichloro-s-triazine on a laser-etched cobalt catalyst on a silicon wafer.

Fullerenes

Polymerized fullerenes, when half-doped with potasium, become superconducting. For example, K_3C_{60} shows isolated phonon modes.

Carbon Nanofibers

Starting with ethylene gas, one can prepare carbon nanofibers that have widths that vary from 2.5 nm to 1 micron and lengths from 5 to 100 microns. Applications include selective absorption agents, molecular sieves, catalyst supports, and electrodes in electronic storage devices. They are especially good for practical hydrogen gas storage systems because the spacings are right; they can store 30 liters per gram of molecular hydrogen. The projection is that the Daimler Benz hydrogen car will be able to travel approximately 5,000 miles on 25 liters of hydrogen fuel (Baker 1997; also p. 172).

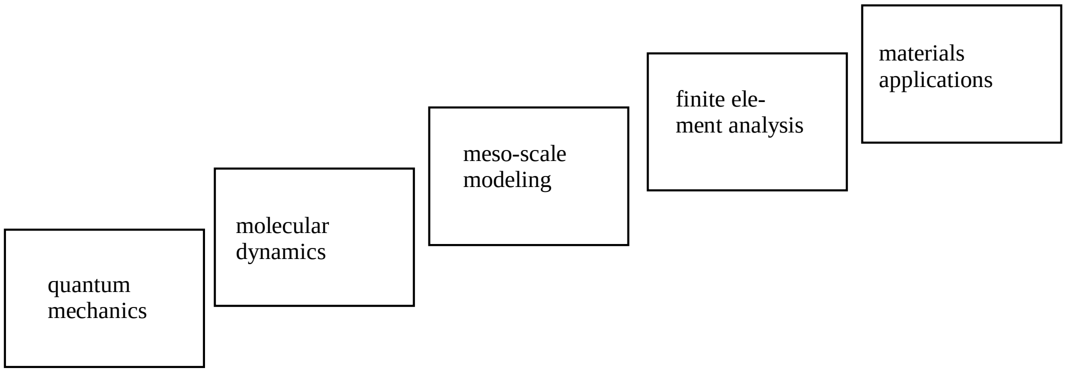
Enabling Technologies

Continued progress in nanotechnology and nanoparticles will require certain enabling technologies. These include (see also Koehler and Vermont pp. 25-29) instrumentation such as optical traps, laser tweezers, and “nano-pokers” to measure femtoNewton forces (Svoboda and Block 1994).

There is also a need to move detection away from the ensemble, to the single molecule scale. This includes driving instrumentation toward single molecule spectroscopy, single spin detection (Rugar et al. 1994), chemical analysis of nanoliter volumes (Hietpas et al. 1996), NMR microcoils, nanoscale electrode arrays, and chemical sensing and detecting technology (McConnell 1996), separations technology, chemical analysis of single cells (Hietpas et al. 1996), new biological transformations, and chemical probes of nanostructures.

Theory

Enhanced computational infrastructure, both hardware and algorithm development, will be required to investigate supramolecular assemblies and to understand interactions that occur over a wide variety of time and length scales. At present we are fairly well-equipped to handle quantum mechanical calculations. At the next level of computational complexity, the current molecular dynamics force fields and atomic charges can handle up to about a million particles and still retain their accuracy. The next scale of complexity, mesoscale modeling, currently requires the use of pseudo atoms. Much more research is required to improve the accuracy of finite element calculations and the modeling of materials applications (Goddard 1997; also p. 197).



There is a critical need for molecular level theory to predict structures, proteins, and dynamics. Especially important are issures of reliability, which means that is is going to be important to operate from first principles.

Mechanisms that encourage the development of theory and computation include the SBIR programs, good coupling between academia and industry, and hardware available through the national NSF centers. Much of the progress in theory and computation is advanced by commercialization.

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CARBON-BASED NANOSTRUCTURES

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Materials Categories

The carbon-based nanostructural materials considered here include fullerenes and related materials, carbon nanotubes, carbon nanoparticles, and porous carbons, including activated carbon fibers and carbon aerogels.

Scientific Drivers

Carbon nanotubes (~1 nm in diameter) are presently the hottest carbon nanostructured material. Single-wall carbon nanotubes, consisting of a cylindrical tube one atomic layer in thickness, are predicted to be either semiconducting or metallic depending on the diameter and chirality of the nanotube. These unusual electronic properties imply novel 1D physics. In addition, single electron (Coulomb blockade) transport phenomena are now being studied in this unique system using nanolithographic techniques. The joining of two dissimilar nanotubes has been predicted to give rise to semiconductor-metal heterojunctions with properties that can be modified by perturbing the junction region, which is of ~1 nm size. Remarkable quantum effects are also predicted and observed for the phonons in carbon nanotubes, also dependent on the diameter and chirality of the nanotubes. Another area of great excitement concerns the elastic properties, especially the extremely high Young's modulus for carbon nanotubes. Applications of carbon nanotubes are under development for displays and for tips for scanning tunneling microscopes and for the manipulation of nanostructures. It is expected that the physical properties of the carbon nanotubes can be significantly modified by intercalation, as for example by using alkali metal dopants, but this is a very new research area, with only a few results now in press.

Fullerenes represent a unique category of cage molecules with a wide range of sizes, shapes, and molecular weights. Most of the effort thus far has gone into the study of C_{60} fullerenes, which can now be prepared to a purity of parts per thousand. Since every C_{60} molecule is like every other one, ignoring ^{12}C and ^{13}C isotope effects, C_{60} provides a unique monodisperse prototype nanostructure assembly with particle size of 0.7 nm. Because of the unique icosahedral symmetry of C_{60}, these molecules provide prototype systems for spectroscopy, optics, and other basic science investigations. Study of the structure and properties of the whole family of fullerene cage molecules, together with their endohedral cousins (formed by insertion of guest species, usually rare earth or transition metals, within the cage) is being pursued worldwide. A few groups are also coating fullerene molecules with one or more layers of alkali metals and alkaline earths and studying their remarkable structures and properties. The intercalation of alkali metals and other species into the crystalline C_{60} lattice alters the structure and leads to large modifications in properties. The special properties of the metallic and superconducting phases thus achieved are of fundamental significance. The new phases associated with polymerization of C_{60} by incident light, pressure, and alkali metal doping are of both scientific and practical interest.

Carbon nanoparticles can be all carbon (such as the so-called carbon onions), or carbon-coated particles consisting of carbon layers wrapped around other materials, usually carbides. Studies of carbon onions have emphasized the basic science of nanostructure growth in carbon systems, while the carbon-coated nanoparticles have combined both basic studies, concerning their growth and structure, with applications, particularly for magnetic nanoparticles. The carbon coating provides a means for stabilizing and separating small particles containing active ingredients with special properties that may, for example, be useful for magnetic information storage.

Porous carbons, such as activated carbon fibers and carbon aerogels, have a high density of pores, with pore sizes < 2 nm. The structure and properties of these nanopores have been investigated both for their scientific interest and for practical applications, utilizing the special properties of high surface area materials. Remarkably high specific surface areas, as high as ~3000 m^2/g, are achievable in these materials.

Critical Control Parameters

The critical control parameters of individual carbon nanotubes are the nanotube diameter and chirality, while the packing density is important for nanotube arrays. Most of the presently used single-wall carbon nanotubes have been synthesized by a pulsed laser vaporization method, pioneered by the Smalley group at Rice University. Their synthesis result of 1996 represents a major breakthrough in the field. There are several oral reports that a catalyzed carbon arc synthesis route also can be used to produce high yields of nanotubes with a diameter distribution similar to those obtained by the Rice group. There are presently many groups worldwide working to develop more efficient synthesis techniques for producing arrays of similar single-wall nanotubes, with a narrow diameter and chirality distribution, at a high production rate, and at a cheap cost. Right now, it is possible through Smalley's recent work to produce significant amounts of (10,10) armchair nanotubes with a small average diameter (~1.3 nm) and a small diameter distribution. Much effort is presently being expended to develop production methods to provide control in the synthesis of armchair nanotubes arrays with different diameters, let alone the controlled synthesis of nanotube arrays with different chiralities. This field is very new, and many groups are now trying to reproduce the sample quality achieved by the Rice group. There is optimism in the community that much progress will be made within the coming year toward improving synthesis capability and properties control for the single-wall nanotubes, by study of the growth conditions, such as temperature, pressure, and kinetics. Computer simulations are being actively employed to improve convergence of the experimental approaches. Considerable effort is also being expended in the study of intercalation as a method for modifying the properties of the nanotubes. Efforts to improve the synthesis of multiwall nanotubes (containing several coaxial single wall nanotubes) continues, with diameters up to ~15 nm defining the nanotube range, and with diameters in the range $15 \leq d \leq 100$ nm defining the nanofiber range where faceting of the individual "tubes" occurs at high heat treatment temperature ($\geq 2500^\circ C$).

The important parameters describing fullerene cage molecules include the number *n* of carbon atoms in the particular fullerene species C_n, and the shape of each of the isomers corresponding to C_n. In the case of the endohedral fullerenes, the number of guest atoms as well as the guest species needs to be controlled, in addition to the mass and isomer type of the fullerene host. In general, the whole gamut of fullerene masses and isomers are formed simultaneously. While some control of the arc discharge conditions (or of other synthesis methods such as laser vaporization or flame methods) can be used to modify the mass and isomer distribution of the synthesis process, most effort has been expended on efficient and sensitive separation methods. These methods are easiest to implement for the lighter fullerenes. Separation according to molecular weight is first accomplished by advanced chromatography methods. Purification of each of the isomers at a given mass value is more difficult, and only limited success has been achieved thus far. Efforts to improve the efficiency of the synthesis process and the purity of C_{60} as a reagent are now largely being carried out in the commercial arena. To a large degree this is also true of C_{70}. Basic research is now being directed toward gaining a fundamental understanding of the growth mechanism and fundamentally new synthesis routes, based, for example, on the building block carbon clusters found in C_{60}. There are also serious efforts by many research groups worldwide to produce larger quantities of higher purity higher fullerenes — C_{70}, C_{76}, C_{84}, etc. — using advanced chromatography, along with other specialized techniques. Many of the same groups are also active in synthesizing, separating, and purifying endohedral fullerenes.

Carbon-coated nanoparticles, produced by arc discharge methods or by laser vaporization techniques, are characterized by their size and shape distribution, the thickness of the carbon coating relative to the particle diameter, and the stoichiometry, crystallinity, and homogeneity of the phase of the enclosed carbide or other constituent. Conditions of temperature, cooling rates, gas transport agents, and other process conditions affect the physical parameters and therefore properties of the nanoparticles. In the case of carbon-coated nanoparticles, basic research on process control, structure, and properties is actively being carried out, mostly

in universities, with some start-up companies working on the improvement of the synthesis process, on scale-up, and on controlling costs.
The parameters characterizing the nanostructure aspects of porous carbons focus on pore size and pore size distribution. Among the various activated carbons, all of which have a large concentration of nanopores, it is the activated carbon fibers that have the smallest pore size distribution. The pore size and its distribution are sensitive to the temperature and pressure of the steam and CO_2 used in the activation process. Carbon aerogels have a much wider range of size distributions, with nanopores found within the small particles in the carbon aerogel chains, and with mesopores and macropores found between the particles and between clusters of particles. The average nanopore size and the nanopore size distribution depend on the precursor materials used in the aerogel synthesis, the carbonization temperature and time, and other process parameters. Steady progress has been made in varying the process conditions to control and vary the diameter distributions of the pores. Activation of carbon aerogels has been demonstrated as a method for adding a high density of nanopores, but this is a new research area that has not yet been widely studied.

Commercialization Considerations

Whereas the quantum aspects of single-wall carbon nanotubes are at an early stage of research, the more general desirable properties of carbon nanotubes are already being exploited commercially. Multiwall carbon nanofibers are presently being used as conductive additives to plastics and in electrochemical capacitor applications. Such commercial applications of nanofibers do not impose severe requirements on uniformity in nanotube diameter and sample homogeneity from one nanotube to another. Carbon fibers in the 1-10 micron range have been produced commercially for several decades. Incremental improvements in the manufacturing process have continued over this time period, leading to enhanced product performance and reliability; however, the relatively high price of the product has restricted the available markets. The same constraints may also apply to the commercialization of carbon nanotubes exhibiting the remarkable and unique 1D properties described above.

Synthesis of C_{60} and C_{70} is now a commercial process, with continuing increases in purity and decreases in cost. As more fullerene applications become commercialized, the demand for C_{60} and C_{70} will increase, and further improvements in the products and reductions in cost are expected. The commercialization of higher fullerenes and endohedral fullerenes is hampered by present limitations on efficient synthesis, separation and purification techniques, and the absence of significant products based on these materials.

Carbon-coated nanoparticles have moved quite rapidly into the commercial sector. Several start-up companies are developing niche proprietary applications and are working on issues of scale-up, reproducibility, reliability, and cost, while basic and applied R&D continue actively in university and industrial laboratories.

Porous carbons have been commercialized for a relatively long period of time for gas adsorption, environmental cleanup, heavy metal and ion separations, and electrical capacitor applications. As control of the pore size distribution has increased and cost has been reduced, these materials have found more applications and markets. Both large companies and start-up companies are involved with these products.

In all carbon nanostructured materials, cost has been a main factor in limiting commercialization, yet it is widely believed that if production volumes increase, costs would decrease markedly, thereby significantly increasing the utilization of the excellent properties of nanostructured carbon.

SYNTHESIS, PROPERTIES AND APPLICATIONS OF GRAPHITE NANOFIBERS

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In recent years, a new type of fibrous carbon material has been developed in our laboratory from the metal catalyzed decomposition of certain hydrocarbons at temperatures ranging from 400 - 800°C (Rodriguez 1993; Rodriguez, Chambers, and Baker 1995). The nanofibers consist of graphite platelets perfectly arranged in various orientations with respect to the fiber axis, giving rise to assorted conformations. One of the most outstanding features of these structures is the presence of large number of edges, which in turn constitute sites readily available for chemical or physical interaction, particularly adsorption. Perhaps one of the most unexpected findings is that such ordered crystalline solids can exhibit high surface areas (300 - 700 m^2/g), where the totality of the surface area is chemically active. From the physical point of view, carbon nanofibers vary from 5 to 100 microns in length and are between 5 to 100 nm in diameter.

From *in-situ* electron microscopy studies it has been possible to determine the sequence of events leading to the formation of carbon nanofibers. The key steps in the process are shown schematically in Figure 9.1. When a hydrocarbon is adsorbed on a metal surface (A) and conditions exist that favor the scission of a carbon-carbon bond in the molecules, then the resulting atomic species may dissolve in the particle (B), diffuse to the rear faces, and ultimately precipitate at the interface (C) to form a carbon nanostructure. The degree of crystalline perfection of the deposited fiber (D) is dictated by the chemical nature of the catalyst particle, the composition of the reactant gas, and the temperature. In this particular case, the graphite platelets are oriented in a “herringbone” arrangement. Surface science studies (Goodman et al. 1980; Nakamura et al. 1989) have revealed that certain faces favor precipitation of carbon in the form of graphite, whereas less ordered carbon will be deposited from other faces (Yang and Chen 1989). By judicious choice of the catalyst, the ratio of the hydrocarbon/hydrogen reactant mixture, and reaction conditions, it is possible to tailor the morphological characteristics, the degree of crystallinity, and the orientation of the precipitated graphite crystallites with regard to the fiber axis. In the “as-grown” condition the graphite layers are separated from one another by a distance of 0.34 nm. This spacing can be increased by introducing selected groups between the layers, a process known as intercalation, thereby generating new types of sophisticated molecular sieves. Such unique structural conformations found in carbon nanofibers opens up numerous possibilities in the fabrication of new materials.

Depending on the crystallographic orientation of the faces that exist at the metal-carbon interface, it is possible to generate nanofibers that consist entirely of graphite platelets or contain a certain fraction of amorphous carbon, i.e., exhibit a duplex structure. Over the past few years we have performed a very comprehensive evaluation of the potential of a number of metals and bimetallics as catalysts for the production of carbon nanostructures. From the data compiled from these experiments it appears that certain nickel- and iron-based alloys are among the most effective catalysts for the reaction (Kim, Rodriguez, and Baker 1992; Rodriguez, Kim, and Baker 1993 a and b; Krushnankutty, Rodriguez, and Baker 1996).

While the “herringbone structures” are frequently found when alloy catalysts are used in the nanofiber process, we have learned that it is possible to tailor this arrangement, and two further conformations are shown in Figure 9.2. Examination of the high resolution electron micrographs clearly indicates that the graphite platelets in these two examples are aligned in directions perpendicular (Fig. 9.2a) and parallel (Fig. 9.2b) to the fiber axis. A more detailed appreciation of these structures can be seen from the respective 3-D models, where the darker geometric shapes represent the metal catalyst particles responsible for generating these conformations. The metal catalyst particles (< 0.4%) can be easily removed by acid treatment, thus producing high purity graphite nanofibers.

The laboratory scale production of carbon nanofibers has been optimized, and it is possible to routinely grow 100 gram quantities in a given experiment. It is estimated that if the method can be successfully scaled up to commercial dimensions, then large quantities of the material could be grown at the relatively low cost of about $2.00/lb., approximately one-tenth of the commercial price of graphite.

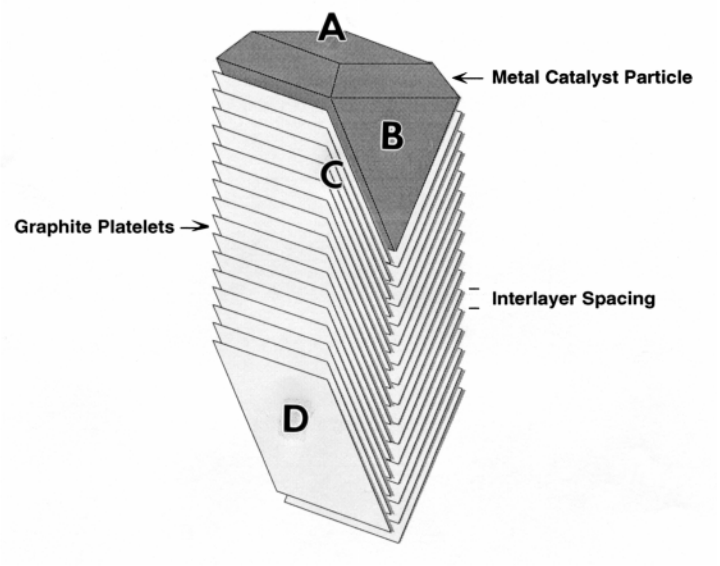
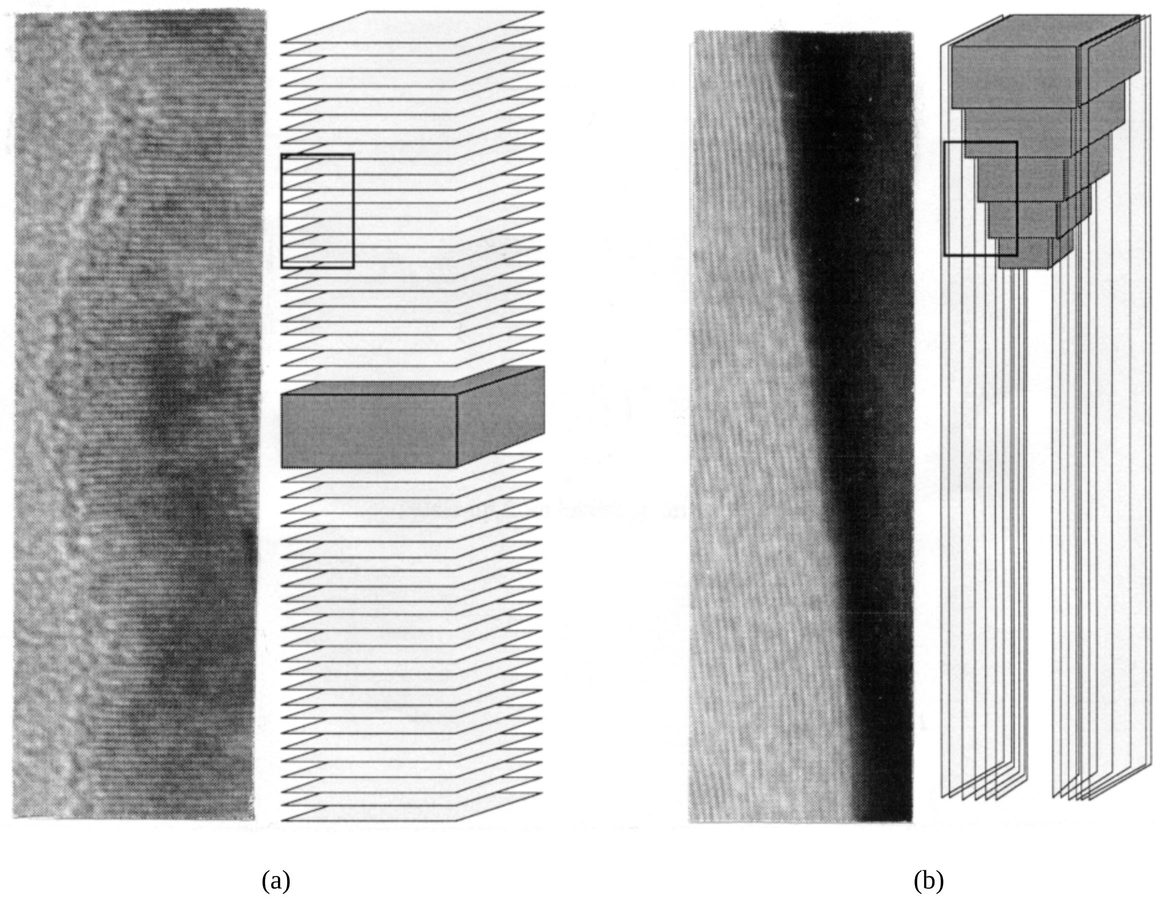


Fig. 9.1. Schematic diagram of a catalytically grown carbon nanofiber.



(a)

(b)

Fig. 9.2. High resolution electron micrographs and schematic representation of carbon nanofibers with their graphite platelets, (a) “perpendicular” and (b) “parallel” to the fiber axis.

Because of the high mechanical strength exhibited by some types of carbon nanofiber structures, the material can be used in liquid phase reactions where it can not only withstand vigorous agitation, but also provide improved transport properties over more conventional adsorbates. Furthermore, because of their size dimensions, separation of the nanofibers from liquid phase reactants and products is a relatively simple task.

Advanced polymeric composites have several advantages (including high specific strength and energy absorption, light weight, styling flexibility, good noise/vibration/harshness characteristics, and excellent corrosion resistance) that make such materials ideal for fabrication of body parts for heavy vehicles. Furthermore, technological advances in processing and materials appear to make advanced composites suitable for high-volume applications; low-pressure fabrication processes such as resin transfer molding could require very low investment costs and, depending on the choice of resin and type of fibers, offer fast cycle times. The high strength-to-weight ratio combined with superior stiffness have made carbon fibers the material of choice for high performance composite structures. For most current applications, composites are manufactured with continuous fibers produced from the thermal decomposition of organic polymer precursors such as cellulose (rayon), polyacrylonitrile (PAN), or pitch (Bacon 1973; Delmonte 1981; Donnet and Bansal 1984; Watt and Perov 1985; Fitzer 1985; Otani 1965; Edie 1990). Carbon fibers have been used to reinforce several matrices, including polymers, metals, and also brittle materials such as carbon and ceramics. When used in the latter application carbon fibers require some form of protective coating to prevent both chemical interaction with the matrix and attack by oxygen during service at high temperature. In high temperature applications a critical factor that can determine the viability of a given fiber/matrix composite is the difference in the thermal expansion coefficients of the two components, which can result in mechanical failure during thermal cycling.

We have focused on modifications in the chemical, physical, and mechanical properties of carbon fibers resulting from the growth of carbon nanofibers on their surfaces. Emphasis was placed on establishing the conditions for optimum growth of carbon nanofibers without concomitant degradation in the mechanical properties of the parent fibers. Using this “whiskerization” procedure, tests demonstrated that it was possible to obtain an improvement of over 4.5 times in the interfacial shear strength of the fibers following deposition of a critical amount of nanofibers (Downs and Baker 1995). In another investigation we showed that incorporation of carbon nanofibers into various epoxy resins had a dramatic impact on the curing reaction; small amounts of the filler tended to retard the process, whereas large amounts of nanofibers exerted the opposite effect. Modifications in curing characteristics were compared with those produced from incorporating carbon black into the same resins, and major enhancements in both the mechanical and electrical properties of the composites were found when large amounts of carbon nanofibers were present in the systems (Yin et al. 1993).

Recent reports have disclosed a rather serious problem associated with several nuclear production and processing facilities in the United States. Over the years, large quantities of low level radioactive waste, some in aqueous solution that also may contain significant amounts of organics, have been accumulating at these sites in various types of storage vessels. These materials have been found to leak from the containers and contaminate the surrounding soil over large areas. Efforts are being mounted to clean up these regions and procedures developed to remove and concentrate heavy metals and radio nuclides, many of which are present in the form of aqueous solutions.

A number of technical approaches have been proposed to overcome this problem. One method utilizes activated carbon as an adsorbent to remove trace quantities of metals. While this form of carbon is very effective for the adsorption of gaseous molecules, its performance in a liquid medium is far from satisfactory. Some success has been achieved by the use of electrochemical deposition on certain metal electrodes. While such a procedure is extremely effective at lowering the concentration of metallic species on a small scale, extension of the concept to a commercially viable scale has been thwarted due to the relatively low surface area of the metallic electrode. One of the major problems when dealing with metal electrode systems is their vulnerability to attack by acid or alkali media. Certain noble metals are exceptions to this rule; however, in these cases expense of the material becomes a prime concern. Because of its unique physical and chemical properties combined with a relatively low cost, graphite appears to offer distinct advantages over metal electrodes, but demineralization of dilute solutions requires the use of carbon electrodes possessing considerably higher surface areas than those presently available.

We are attempting to overcome the shortcomings of active carbon and graphite by using graphite nanofibers. In this investigation, graphitic nanofibers are being employed as the electrode material, in the fabrication of unique types of electrochemical filtration, and in selective collection systems for the removal of heavy metals from liquid phase streams. The electrode consists of graphite nanofibers either in the form of a free-standing interwoven network or grown on a conductive support. When a sufficiently high negative potential is applied to the nanofibers, the metal ions in solution are deposited in the fully reduced state, and over an extended period of time the uniformly deposited film can grow up to several monolayers in thickness. If the reduction potential of a given metal is more negative than that of water (i.e., more negative than -1.05 V vs. Ag/AgCl) then an alternative pathway is available — electrosorption of ions. In this process it is possible to adsorb the contaminant in the cationic state at a more positive potential than its reduction potential. Preliminary studies conducted with graphite nanofibers have indicated that the material exhibits a superior performance for the removal of metal ions from low concentration solutions when used as an electrode in an electrochemical cell over that of graphite felts, metal mesh, and other forms of conductive carbon. Furthermore, by application of a reverse potential, the metal species that are bound on the nanofiber surface can be rapidly released into a more concentrated solution for eventual recovery or disposal.

Failure to create a practical storage system has up to now prevented hydrogen from reaching the commercial forefront as a transportation fuel. The ideal hydrogen storage unit should be lightweight, compact, relatively inexpensive, safe, and reusable without the need for complex regeneration treatments. Four methods are currently being considered for hydrogen storage in commercial applications: (1) pressurized gas storage, (2) liquefied hydrogen, (3) selected metal hydrides, and (4) refrigerated superactivated carbon. While the latter two approaches may offer advantages over the other technologies with regard to cost and safety aspects, they do have their own drawbacks. Metal hydrides are heavy, expensive, and release heat during the hydrogen absorption process. Active carbons are very effective adsorption agents for a variety of gases; however, interactions between the adsorbent and the solid are only of a physical nature, and as such, retention of hydrogen can only be achieved at cryogenic temperatures. It is clear that both storage and controlled release of hydrogen at moderate conditions of temperature and pressure are major issues that must be addressed if this technology is to be exploited on a commercial scale. The ideal solution would be an inexpensive, lightweight material capable of not only absorbing and retaining hydrogen at room temperature and moderate pressures, but also possessing the ability to release the gas at moderate temperatures. One material that fulfills this requirement is graphite nanofiber.

Data obtained in our laboratory has demonstrated that when these structures are pretreated under conditions whereby all adsorbed and absorbed gases are eliminated, then on subsequent exposure to hydrogen at moderate pressures, *they are capable of absorbing and retaining up to 30 liters of molecular hydrogen per gram of carbon at room temperature*. Theoretical calculations made on the hydrogen absorption capacity of single-crystal graphite have indicated that it is possible to store 6.2 liters of molecular hydrogen per gram of graphite as a single flat layer. It is evident from these calculations that the experimentally determined absorption capacity of the material far exceeds that of the theoretical value, which indicates that the process occurs in a multilayer fashion. *It is clear from these data that one could transport molecular hydrogen in a liquid-like state without need for refrigeration or the high volume and weight associated with compressed gas.* The advantages of graphite nanofibers over other materials for hydrogen storage can be summarized as follows:

- The material consists of platelets arranged in a conformation that results in slit-shaped pores, as shown in Fig. 9.3, where the interlayer spacing (3.4 Å) is sufficiently large to allow for the ingress of molecular hydrogen (kinetic diameter 2.9 Å) while restricting the access of other gas molecules such as oxygen and nitrogen. Since the material consists entirely of micropores, the absorption volume is completely utilized, which accounts for the extremely high capacity.
- The presence of delocalized π-electrons within the stacked graphite platelets causes the establishment of a strong interaction between the solid and the gas, which will result in an induced chemisorption. As a consequence, hydrogen can be strongly held at room temperature, and this aspect eliminates the need for cryogenic conditions, one of the requirements of conventional activated carbon.
- When the pressure is reduced below a critical level the molecular hydrogen is released in a reversible manner at room temperature.

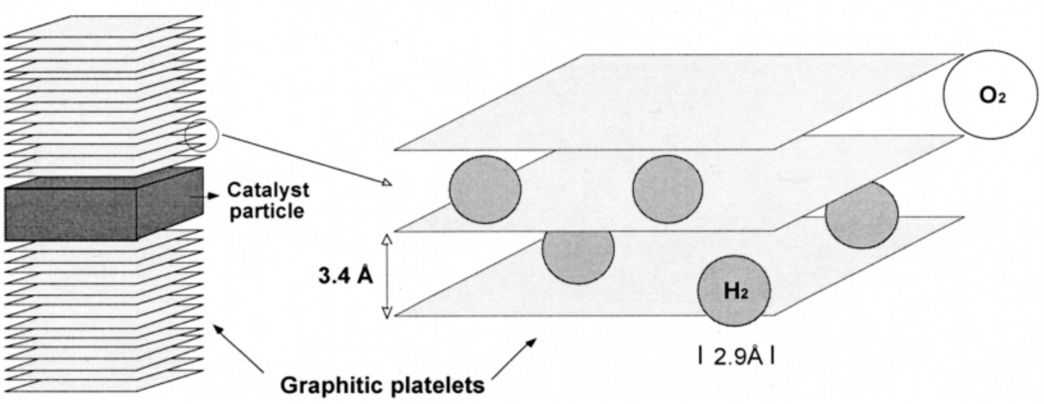


Fig. 9.3. Schematic representation of the structure of a graphite nanofiber and details of the hydrogen absorption process.

Future Requirements

It is clear that for the graphite nanofiber technology to go forward to the commercial arena it will be necessary to devote a significant amount of research effort and funding to the development of a large scale production process. In this endeavor the focus should be placed on a growth procedure that is continuous rather than merely a scaling-up of the current batch method. Control of not only the yield of material but also its physical and chemical properties are essential factors in being able to generate large quantities of graphite nanofibers possessing reproducible characteristics.

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DNA NANOTECHNOLOGY

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Scientific Drivers

Control of structure on the nanometer scale relies on intermolecular interactions whose specificity and geometry can be treated on a predictive basis. With this criterion in mind, DNA is an extremely favorable construction medium: the sticky-ended association of DNA molecules occurs with high specificity, and it results in the formation of double-helical DNA, whose structure is well known. The use of stable branched DNA molecules permits one to make stick figures (Seeman 1982). This strategy is illustrated in Figure 9.4: on the left, we show a stable branched DNA molecule, and on the right we show such a molecule with sticky ends; four of these sticky-ended molecules are shown assembled into a quadrilateral.

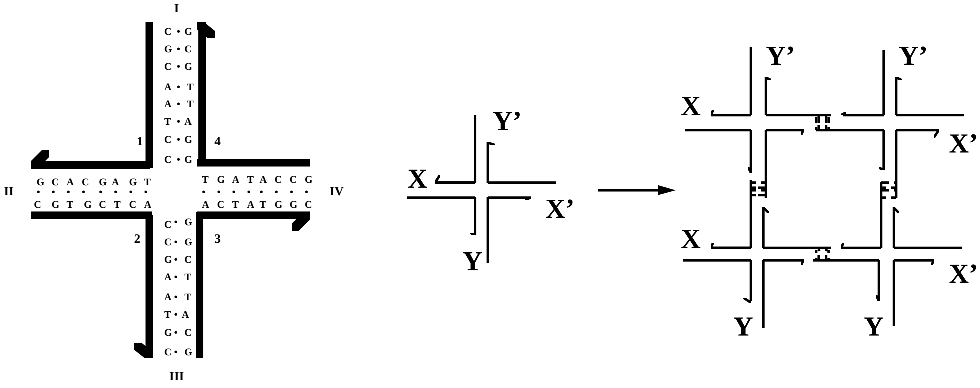

Fig. 9.4. DNA stick figures.

We have used this strategy to construct a covalently closed DNA molecule whose helix axes have the connectivity of a cube (Chen and Seeman 1991). The cube has been fabricated in solution, which is inefficient. Therefore, we have developed a solid-support-based synthetic methodology that is much more effective. We have used this solid-support-based methodology (Zhang and Seeman 1992) to construct a molecule whose helix axes have the connectivity of a truncated octahedron (Zhang and Seeman 1994). Proof of synthesis relies on digesting target polyhedra with restriction endonucleases to generate target catenanes with characteristic electrophoretic mobilities. The cube and truncated octahedron are shown in Figure 9.5.

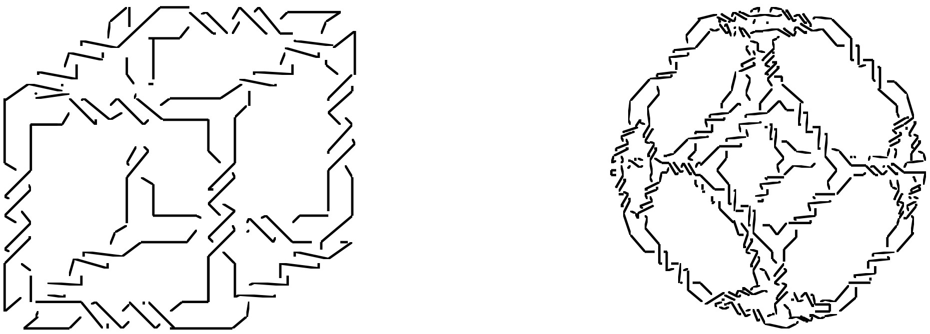

Fig. 9.5. Cube and truncated octahedron.

Our key aim is the formation of prespecified 2-D and 3-D periodic structures with defined topologies. Applications envisioned include nanomechanical devices, scaffolding for assembly of molecular electronic devices, and assembly of macromolecular-scale zeolites that orient macromolecules for diffraction studies.

Critical Parameters

The solid support methodology that has been developed (Zhang and Seeman 1992) appears capable of being used to direct the synthesis of any Platonic, Archimedean, or Catalan polyhedron; however, the construction of a closed object such as a polyhedron is a special case of nanoscale construction, because all of the edges can be specified to be made by the ligation of a finite set of sticky ends. Thus, programmability of sticky ends and a predictable local ligation product (B-DNA in the vicinity of the ligated ends) are sufficient to direct the synthesis of a finite object.

However, the goals enumerated above require the ability to construct periodic matter, which has a further requirement, structural rigidity. The assembly (Fig. 9.4) of four branched junctions into a quadrilateral is predicated on the ability of the junctions to retain their cruciform shape. If the angles between the double helical arms were variable, then a quadrilateral would be only one of many polygons that these molecules could form. In fact, branched junctions are flexible. Whereas the formation of periodic matter entails the same contacts from unit cell to unit cell, flexibility can lead to networks of variable content, and hence can destroy the periodicity of the material. For this reason, we have spent the past several years seeking DNA motifs that are more rigid than branched junctions. We have found that another structure related to recombination intermediates (the branched junction is a recombination intermediate analog) provides a rigid species. This structure is the double crossover molecule (Fu and Seeman 1993). There are five isomeric types for this system, but only the two shown below in Figure 9.6 are stable in small systems.

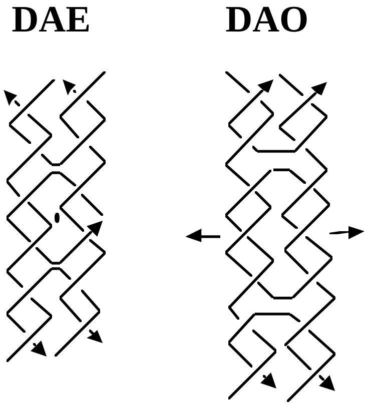

Fig. 9.6. Double crossover molecules.

The double helical domains in the two molecules are antiparallel; they differ in their topologies by the number of half-turns (even/odd) between crossovers. For experimental convenience, we have worked with the DAE molecule. Our assay for stiffness is the lack of cyclization when we oligomerize a molecule containing two complementary sticky ends. Branched junctions cyclize as dimers or trimers, but we have yet to detect cyclization in double crossover molecules (Li et al. 1996), even with species as high as 27-mers. We are in the process of attaching these molecules to the sides of DNA triangles and deltahedra so that we can take advantage of the rigidity of those figures (Li et al. 1996). Figure 9.7 shows a 2-D lattice designed from such triangles and an octahedron whose three double crossover edges span 3-space.

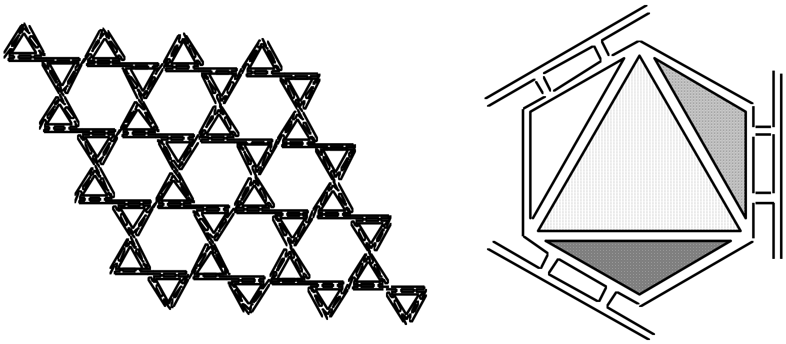

Fig. 9.7. 2-D lattice and octahedron.

Bringing DNA Nanotechnology to the Market

One of the attractive features of products containing DNA is the potential of producing the molecules by biological means, either by cloning or by means of the polymerase chain reaction (PCR). Unfortunately, it is not possible to produce branched species in this way, because reproduction of the strands results in heteroduplex molecules rather than branch reproduction. Nevertheless, there is another approach that might work in this case. Figure 9.8 illustrates a pentagonal dodecahedron in a representation known as a Schlegel diagram, where the central pentagon is closest to the viewer, the outer pentagon furthest from the viewer, and the distorted pentagons at intermediate distances back; this is similar to a polar projection of the Earth, with the North Pole at the center and the South Pole at every point on the circumference. Each edge has been overlaid with two turns of DNA, and an exocyclic arm has been added to each pentagon. The exocyclic arms have been connected together to form a long knotted single strand, whose 5’ and 3’ ends are shown at the top.

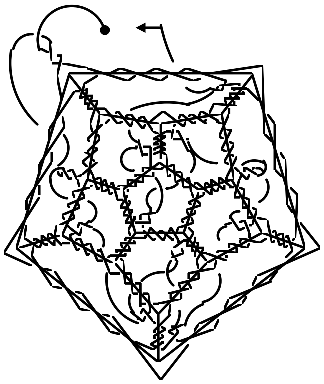

Fig. 9.8. Schlegel diagram of a pentagonal dodecahedron.

The idea is to make the entire structure as a long strand, get it to fold, and then trim off the excess connecting DNA by the use of restriction endonucleases, leaving a DNA polyhedron ready to ligate into periodic matter (Seeman 1991).

It is clear that this is a complicated and somewhat speculative proposal, so we have tried to see how effectively we can get DNA to follow our design in folding. To this end, we have produced trefoil knots with negative nodes from DNA (Mueller, Du, and Seeman 1991) and RNA (Wang, Di Gate, and Seeman 1996). We have also produced trefoil knots with positive nodes (Du, Stollar, and Seeman 1995) and figure-8 knots (Du and Seeman 1992) (with half positive and half negative nodes) from DNA. As a further test of our control of topology, we have recently constructed Borromean rings from DNA (Mao, Sun, and Seeman 1997). These species are shown in Figure 9.9.

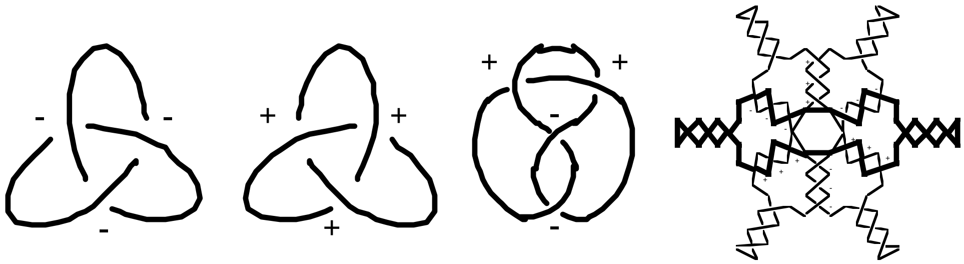

Fig. 9.9. Borromean rings constructed from DNA.

The last issue is the ability to produce DNA products in industrial quantities. DNA synthetic capabilities have increased substantially over the years due to solid-support-based chemistry (Caruthers 1985). There are no obstacles to the production of 100-mers in small quantities (~200 nm). Scale-up may be a more substantial problem. Recently, it has been reported that NeXstar has developed a new methodology for the large-scale production of DNA that combines both solid-support and solution synthetic steps (Liszewski 1997).

Other U.S. Efforts

The only other comparably oriented effort of which we are aware is the one initiated by Donald Bergstrom and colleagues at Purdue (Shi and Bergstrom 1997). They have taken two strands of DNA and hooked them together with rigid organic linkers, which are designed to take the place of the DNA at the bends of conventional DNA branched junctions. When these strands are hybridized, they form a series of cyclic molecules. There is no indication that the rigidity of the organic linkers is able to direct the angle between DNA double helices.

Acknowledgments

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MOLECULAR AND ELECTRONIC NANOSTRUCTURES[2]

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Summary

With goals of creating chains of interdisciplinary research from physics to function and from molecules to mind and of developing leading edge tools for characterization and manipulation of molecular scale structures, the Beckman Institute has fostered research in molecular and electronic nanostructures since its founding. Nanoscale structures and processes explored in the Institute include organic and inorganic self-organizing materials, quantum confined devices and quantum transport in semiconductors, molecular and atomic interactions in gases and on surfaces, synthesis and function in biological molecules, and complexity and coherence in quantum dynamics. These efforts impact physics through improved perspectives on quantum mechanics and complexity, chemistry through improved synthesis and characterization techniques, life sciences through improved understanding and control of biological materials, and technology through improved electronic and photonic materials and devices. We have created world-class laboratories in photonics, genetic engineering, surface chemistry, and advanced electronic, atomic, and optical imaging and lithography. We have developed numerical and theoretical tools to model nanoscale systems using modern developments in quantum transport and density functional theory.

Nanoscale research in the Beckman Institute was combined under the umbrella of the new Molecular and Electronic Nanostructures Main Research Theme (MRT) in 1994. The purpose of the MRT is to coordinate and encourage cross-disciplinary and cross-departmental research. This paper describes the “strategic plan” for the nanostructures MRT. After a brief overview of the nanostructures theme in this section, subsequent sections overview the background, or motivation, of the nanostructures theme, the laboratory and computational resources available to the MRT, and major opportunities in nanostructure research.

The nanostructures MRT has developed in a unique academic environment of cross-departmental communication and collaboration. Common themes, such as process complexity and quantum coherence, and telling contrasts, as between lithographic and self-organizing fabrication, have emerged from this experience. Close interaction between disciplines is essential in pursuit of the difficult and still elusive goals of understanding and controlling the functionality of nanometer scale molecules, processes and devices in biotechnology, chemical dynamics, materials science, and information systems. We are pursuing these goals by integrating our development of computational analysis tools and advanced scanning microscopes with ultrafast photonics and electronics, chemical synthesis, and bioscience. The Molecular and Electronic Nanostructures theme focuses on consultation and collaboration in developing

- experimental imaging, analysis, and synthesis tools
- numerical and theoretical models of quantum systems
- scientific and applications objectives

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In contrast with departmentalized “tool oriented” traditional academic programs, the Molecular and Electronic Nanostructures theme merges work in mechanics, optics, electronics, chemistry, and biochemistry to create a problem-oriented research program. The program focuses on two specific problems: semiconductor nanostructures and self organizing synthesis. We are developing STM (scanning tunneling microscope) lithography, advanced scanning microscopy, chemical self-assembly, and optical and electronic characterization techniques to support these areas. Running through the problem areas are two analysis and development tools: ultrafast dynamical systems and quantum transport-based analysis of complex molecular and electronic systems.

The Molecular and Electronic Nanostructures theme is a model of how cross-disciplinary research programs can have broad and profound impact while remaining focused on excellence in a finite set of laboratory and analytical tasks. By establishing links between artificial and natural nanoscale fabrication, advanced imaging and probe tools, and computational visualization and analysis, we will develop a clear picture of mesoscopic systems and opportunities for their application. Nanostructures are a unique research opportunity from several perspectives. They are both the smallest structures in which artificial structure can be encoded and the largest structures for which nearly complete quantum mechanical models can be developed. They are simultaneously worthy objects of basic scientific research and crucial elements in the continuing development of the information technologies that make advanced research possible. In concert with Beckman Institute research themes in biological intelligence and human-computer interactions, the Molecular and Electronic Nanostructures theme uses unity of purpose and diversity of perspective to achieve understanding of information transfer mechanisms spanning the range from molecular self-assembly to supercomputing.

Background

In 1960, Feynman described “bottomless” opportunities for research and development of smaller and smaller structures based on the microscopic and lithographic resolution of that time. The scanning tunneling microscope and related discoveries and inventions have opened possibilities beyond even Feynman’s vision in the science and engineering of structures on the nanometer scale. Milestone progress has been made in various disciplines. Physics and materials science have achieved an understanding of mesoscopic systems and quantum transport phenomena in solids and solid heterolayers that were unknown before the last decade, the meaning of mechanical engineering has been expanded by the fabrication of springs, turning wheels, and moving pistons on the nanometer scale, and the ever denser integration of electron devices has made 10^6 transistors on a chip a household concept. Chemistry has dealt with nanometer-sized objects (i.e., molecules) all along, but increasingly turns its attention to organizational principles which operate on the supra-molecular length scale.

A broad view of nanostructure research reveals a picture in which mechanics, reaction dynamics, optics, and electronics merge and lose their conventional meaning, and an overlapping interest arises in the corresponding disciplines: physics, chemistry, biochemistry, and mechanical and electrical engineering. Arising from this melting pot of disciplines are three common foci:

1. fabrication and self-assembly tools
2. advanced imaging, visualization, and dynamical probe techniques
3. numerical modeling and analysis tools

The Beckman Institute has fostered major interdisciplinary research in each of these areas. Fabrication of semiconductor nanostructures is the aim of the STM-based Nanolithography Program, and molecular self-assembly in organic and inorganic systems is being developed in several groups from chemical, biological, and mechanistic perspectives. Extensive experimental imaging facilities for scanning tunneling and atomic force microscopy (AFM) have been built and are being extended. The Beckman Institute has developed outstanding facilities for optical and electronic characterization and is developing unique ultrafast and scanning optical probe spectroscopy and microscopy systems.

Powerful computation facilities for scientific visualization and numerical modeling are present in the Institute, including the National Center for Supercomputing Applications and the National Center for Computational Electronics. Computers and computation play a unique role in nanostructure research. Artificial fabrication and imaging of nanoscale systems rely on computer-controlled scanning microscopes and computer-intensive data analysis. Analysis of self-assembling systems and nanostructure dynamics requires detailed computational modeling. Large computational resources and supercomputer applications are necessary to understand the quantum dynamics of nanostructures, and visualization tools are necessary to link these pictures to theoretical ideas and mental images. Of course, modern computers are made of integrated circuits with features approaching nanoscale dimensions. Using such computers, the Molecular and Electronic Nanostructures theme links the bottomless opportunities for spatial and temporal complexity in small structures and the opportunity for explosive growth in computational tools.

The next section of this paper overviews existing Institute resources in nanostructure research. Following this overview, we consider future opportunities and describe six areas of special strength and promise in Beckman Institute nanostructure research:

1. Fabrication and Characterization of Semiconductor Nanostructures
2. Self-Organizing Synthesis in Chemistry and Structural Biology
3. Dynamics of Nanostructures
4. Quantum Transport in Complex Systems
5. Circuit Testbeds
6. Theoretical Biophysics

The final section of this paper presents extremely brief synopses the specific research interests of the faculty participating in the MRT.

Resources

Scanning Tunneling Microscopy

The Beckman Institute houses one of the most advanced STM laboratories in the world. This laboratory is the central facility of the ONR-funded "STM-Based Nanolithography" URI and consists of several UHV-STM chambers that are interconnected to permit sample and tip transport between multiple experimental stations under UHV (ultra-high vacuum) conditions. In addition to the three UHV STMs, there is a full suite of sample preparation and conventional surface analysis tools in this system. Among these are LEED/Auger, residual gas analysis, gas dosing, sample heating and cleaving, ion sputtering, and annealing. The STMs employed in this system were developed at the University of Illinois and have a unique combination of features. They employ an inertial translation scheme for tip/sample approach that eliminates the bulky mechanical components other designs use, resulting in much greater rigidity and insensitivity to mechanical disturbances. The design is also highly thermally compensated, resulting in thermal drift below 1 Å/hour. This design is currently being marketed by two U.S. companies under patent license from the University of Illinois.

A more recent development is the incorporation of an integral coarse translation system in which the STM tip can be inertially translated by several millimeters in any direction. This feature enables alignment of the scan area with prepatterned device structures or molecular beam epitaxy (MBE)-grown heterolayers. Another key feature of this STM is the ability to relocate the same scan area even after the sample has been removed from the STM. This facilitates many important experiments in which the effects of sample treatments outside of the STM can be studied at a previously scanned or patterned region of the surface. A special etching chamber has been incorporated in this system for etching experiments using chlorine or other hazardous gases.

Currently under development is a variable temperature UHV-STM that connects directly to the existing facility for UHV transfers. This instrument will enable studies to be performed over the 1.5-400 K range. At low temperatures, the greatly enhanced spectroscopic resolution of the STM will enable electron wavefunction mapping for the studies of quantum size effects. In addition, by controlling the temperature, it will be possible to control the dynamics of absorbed surface species. This is expected to open new directions in the study of molecules on surfaces.

Also under development is a field ion microscope (FIM) combined with a STM to diagnose and control tip shapes. STM tips are generally prepared with empirical recipes using electrochemical etch solutions. The FIM will allow direct atomic imaging of the tip and will also be used to field evaporate atomic layers until the desired structure is achieved. This is especially important for STM nanolithography experiments in which the tip is operated in field emission. Tips prepared in the FIM will be transferred under UHV to all of the other experimental stations.

Additional commercial STM instruments are also available, including a Nanoscope III for imaging and manipulation of mesoscale biological systems and a suite of Topometrix instruments for surface chemistry characterization.

Atomic Force Microscopy

The Beckman Institute houses a fully operational AFM facility consisting of three instruments capable of standard AFM, lateral force, and non-contact imaging. An upgrade to add capabilities for magnetic force electrical imaging is in progress. The instruments are capable of producing both long range (100 nm) and atomic images in either a liquid or dry environment.

The AFM facility is an integral part of the Beckman Visualization Facility, which also houses instruments for electron, confocal, and light microscopy as well as extensive computational tools. The network linking all of the instruments and computers facilitates the transparent transfer of data from the atomic force microscopes to the computer workstations for further processing, analysis, and finally preparation for presentation.

Photonics

The Beckman Institute maintains laser and computational laboratories to support studies of the photodynamics of molecules, solid-state materials, and quantum confined systems and to develop applications of ultrafast optics in communications, data storage, and polychromatic sensing. Facilities include five femtosecond mode-locked laser systems; a molecular beam spectroscopy system; cryogenic spectroscopy systems; a variety of ion, solid state, and semiconductor laser systems; high speed data acquisition and analysis systems; and computational modeling tools. The photonic systems program has unique capabilities for generating and detecting complex ultrafast optical fields. Using diffractive pulse shapers and interferometric cross-correlators, the capacity has been demonstrated to encode cross-spectrally coherent time domain optical fields to micron spatial resolution and 100 femtosecond temporal resolution over millimeter scale spatial windows and 100 picosecond scale temporal windows. These fields offer an unprecedented opportunity for direct time domain control of quantum dynamical processes. Complex space-time fields can be coded with sufficient degrees of freedom to coherently specify and manipulate the space-time dynamics of molecular and electronic nanostructures.

Under a major grant from the NSF's Optical Science and Engineering Initiative, construction of an integrated STM/ultrafast optical surface studies laboratory began September 1996. Completed in 1997, this laboratory allows programmable terahertz modulation of STM tip-surface interactions and surface nanostructures.

Proteins - Recombinant DNA Technology

State-of-the art facilities for the application of recombinant DNA technology to the understanding of protein, nucleic acid, and lipid functionalities are critical to the synthesis and manipulation of nanoscale biological systems. The Beckman Institute has available the complete suite of capabilities, from computational macromolecular modeling for *de novo* design, DNA-RNA synthesis, site-directed mutagenesis, combinatorial library generation and screening, heterologous expression through fermentation, macromolecule purification, characterization, and assay. Central problems under investigation include construction and characterization of protein-based Coulomb blockade devices, studies of quantum transport in condensed macromolecular arrays, subnanosecond initiation and documentation of protein folding events, *de novo* design of sensors of environmental pollutants and xenobiotic compounds, construction of artificial nanoscale materials for use as blood substitutes, and documentation of macromolecular dynamic modes linked to function.

Computational Electronics

The Beckman Institute hosts the NSF National Center for Computational Electronics (NCCE) which encompasses nationwide more than sixty groups mainly from universities but also from industry and government laboratories. Much of the work of the center is concerned with advanced numerical simulation of electronic transport in semiconductors with a very large fraction of researchers interested in semiconductor nanostructures. Emphasis is placed on the interdisciplinary aspect of computational electronics, and the center includes applied mathematicians, computer scientists, physicists, chemists, and electrical engineers. The topics attacked in the center range from conventional device simulation to standardizing Monte Carlo simulations and to solving difficult eigenvalue problems and problems related to quantum transport.

Beckman faculty associated with the center interact with many other NCCE groups, including groups at Stanford (K. Hess and R. Dutton co-direct NCCE), Notre Dame, NCSU, and Oregon State University, as well as with groups at IBM Watson, AT&T - Murray Hill, groups at NIST and ONR, and many foreign partnerships.

Near Field Scanning Optical Microscopy (NSOM)

Under development at the Beckman Institute is a NSOM facility that will feature a commercial turnkey instrument for general use as well as support the development of a state-of-the-art instrument with the capability of performing spectroscopy on single molecules. NSOM is a relatively new technology that takes the flexibility of optical microscopy down to the nanoscale regime. Although electron and other particle-based microscopies have superior spatial resolution to NSOM, the large number of contrast mechanisms, including (a) opacity, (b) refractive index variations, (c) polarization, (d) light emission (photoluminescence), (e) reflectivity, and (f) spectroscopy, that have been worked out for normal diffraction-limited optical microscopy can be carried over to NSOM but are not available to particle microscopies. Thus, NSOM is well suited for the optical characterization of fabricated mesoscale and nanoscale device structures, as well as comparably-sized biological structures, which opens rich opportunities for interactions with other thematic groups within the Beckman Institute. By establishing such a facility at the “ground floor” of this new field, Beckman researchers will have access to the latest developments and will be able to influence the evolution of commercial NSOM instruments. In addition, the NSOM facility is a near-perfect complement to existing UHV-STM and atomic force microscopic capabilities.

NCSA and Nanostructures

The National Center for Supercomputing Applications (L. Smarr, director) is one of four NSF-supported high performance computing and communications facilities. NCSA has a total staff of two hundred. The Beckman Institute houses the NCSA Applications group and its high performance visualization facilities. NCSA has long had a partnership with Illinois faculty in developing both theoretical simulations and experimental facilities. As a national center it has co-hosted workshops on both topics. The computational facilities at NCSA include state-of-the-art parallel supercomputers such as a Silicon Graphics Power CHALLENGE array, an HP/CONVEX Exemplar, an HP/CONVEX C3, and a Thinking Machines CM-5, as well as networks of high-end workstations. These are all interconnected at high speed and available over the network to both remote users and scientific instruments.

Over the last several years, NCSA and the scanning tunneling microscopy component of the Molecular and Electronic Nanostructures group have developed a distributed computing support structure for STMs that allows for real-time remote control and visualization of STM imaging and nanolithography. This system couples in high-end graphics systems as well as collaborative software and has been demonstrated over continental distances. It allows for restructuring silicon surfaces under remote visual control.

Similarly, NCSA has been a long-time partner with the National Center for Computational Electronics (NCCE), directed by Karl Hess. NCSA has provided both computational facilities as well as training in advanced topics through NCCE. What has emerged in the last five years is a move from the traditional semiclassical approximations of electron transport in semiconductors, appropriate to scales above 500 nanometers, to the emergence of pioneering attempts to model the full set of quantum effects appropriate to nanoelectronic scales. This will begin to allow for the design and simulation of novel new electronic effects not possible in the semiclassical regime.

These two approaches could come together in an interdisciplinary approach at the Beckman Institute to molecular and electronic nanostructures. One can easily imagine the next generation of scaleable supercomputers being powerful enough to perform real-time simulations of the atomic interaction of the STM tip with the underlying substrate. If these simulations were fed back into the loop of the nanolithography, one would have an experimental tool of unprecedented power. Similarly, one can foresee quantum electronic devices created first virtually by full quantum simulations, then created with nanolithographic techniques and measured, comparing the physical device with the predicted features of the virtual device. Because of the difficulty of precisely studying the properties of such tiny devices experimentally, the simulations will probably become an essential part of nanoelectronic design. Computational resources are also vital to the design of chemical and biological nanostructure and the prediction of macromolecular and polymer folding and assembly.

Opportunities in Nanostructure Research

Motivation for a “Molecular and Electronic Nanostructures” main research theme (MRT) arises from scientific and pragmatic considerations. From the scientific point of view, the nanostructure research theme is a sound and exciting approach to the broad Beckman Institute goal of research, which covers “physics to function” and “molecules to mind.” The research goals of the nanostructure theme are to develop basic understanding of physical and chemical processes in molecular nanostructures, mesoscopic semiconductor structures, and macromolecular assemblies and to explore emergent function, dynamics, and structure in these systems. The molecular and electronic nanostructure project includes biochemists, chemists, physicists, electrical engineers, computer scientists, and material scientists working on topics with obscure disciplinary boundaries. For example, nanostructure dynamics occur on such fast time scales that they belong in the realm of optics but they encompass atomic, molecular, and electronic phenomena of interest to physicists, chemists, and electrical engineers. This blending of disciplines attracts us to nanoscale science and forces us to broaden our perspective. From the engineering side, device functionality is the overriding goal. Engineering nanostructure research begins with the idea of using semiconductor or molecular devices in information science. For example, one might use self-organizing synthesis to create dense or 3-D logic or memory arrays. However, experience shows that function is the least predictable result of research. A unique benefit of broad cross-disciplinary research is the diversity of perspective that will allow disparate groups to identify and develop new functions quickly. An example of novel function arising from cross-disciplinary fertilization might be the use of engineering control and information theoretical concepts in the design of self-organizing structures for biological or organic environmental control or sensing systems.

From a pragmatic point of view, the “Beckman experience” of common facilities for cross-disciplinary research has shown that groups pursuing disparate interests often require similar equipment. Chemistry groups use the same scanning microscopy systems to characterize macromolecular arrays as physics and engineering groups use to build and characterize solid state materials and devices. Electrical engineers working on high speed communications and control use the same laser and data acquisition equipment as chemists studying ultrafast reaction dynamics. Even without direct collaboration, shared resources are economically attractive. Imaging and visualization are common interests among groups in the nanostructures area and in the Biological Intelligence and Human-Computer Interface MRTs. Leading edge facilities that resolve the atomic structure of complex molecules (organic, inorganic, or biological) and of materials with complex composition (natural or artificial superlattices) are necessary to guarantee experimental and theoretical progress in many areas of Beckman Institute research. The expectation that coordinated development and application of leading-edge fabrication, characterization, and analysis facilities will simultaneously enable research in a number of areas is a driving force behind the foundation of the Molecular and Electronic Nanostructures theme. Participating researchers master the most advanced tools of their own discipline of engineering or chemical and physical science and contribute tools and perspective to the institute-wide effort to manipulate and characterize the smallest building blocks of complex matter. Imaging, visualization, and characterization tools developed through this collaboration will also be of service to other groups in the institute and around the world.

Interconnections and collaborations between individual research groups in the nanostructure area are dynamic and ongoing. Group membership also varies with topics as they evolve, research matures, and new horizons and frontiers open. We are currently focused on several opportunities based on the expertise of present researchers and on the current assessment of where progress is most likely and necessary. Participating groups maintain their individual identities but collaborate in the use and development of research tools such as imaging, computational and visualization facilities, and dynamical data acquisition and control systems. All groups overlap in developing scientific perspective and technological function. Opportunities in these areas are detailed in the following subsections.

(i) Fabrication and Characterization of Semiconductor Nanostructures

Advanced patterning of materials is central to research on electronic nanostructures. The Beckman Institute contains several unique resources in this area as the focus of the national DOD University Research Initiative for “STM-Based Nanolithography.” This program involves nine faculty members from the Departments of Electrical and Computer Engineering, Physics, and Chemistry in a coordinated effort to develop a quasi-atomic scale lithography based on utilizing the low-energy electron beam from an STM to control surface chemistry on Si, GaAs, and related semiconductors.

The UHV-STM Laboratory headed by Joseph Lyding and John Tucker contains a five-chamber interconnected system designed specifically for atomic-level imaging, pattering, and processing of semiconductor nanostructures. A sixth chamber, currently under construction, will provide liquid-He-temperature spectroscopy and luminescence capabilities for characterizing devices *in situ*. Further analysis is available in the AFM laboratory maintained as a central facility. The adjacent Microelectronics Research Laboratory houses the primary facilities for several collaborating faculty. High-resolution conventional e-beam lithography and gaseous etching facilities are headed by I. Adesida, MBE of III-V layered materials by K.-Y. Cheng, and photo- and electro-luminescence analysis by Steven Bishop. These faculty and their students routinely participate in parallel experiments within their own laboratories and in the Beckman Institute in order to develop the techniques that will eventually be required to grow, fabricate, and test STM-patterned nanostructures entirely within a single UHV environment. Additional capabilities in Si advanced processing of device structures and air-STM exposure of resists are obtained through collaboration with groups outside Illinois (e.g., University of Minnesota). An effort to utilize molecular self-assembly in the development of new e-beam resists is headed by Paul Bohn, tying the STM-based lithography project to extensive research in molecular recognition and synthesis within the Beckman Institute.

To date, the most significant result achieved in the STM-based nanolithography program is the selective removal of hydrogen atoms from atomically clean H-passivated $Si(100)_{2x1}$ surfaces in ultra-high vacuum. The highly-localized STM electron beam has been found to reproducibly eliminate H-atoms from the Si dangling bonds, yielding linewidths of ~15A corresponding to only two atomic dimer rows. This opens the door to a wide variety of nanoscale patterning possibilities on Si, including selective oxidation, nitridation, epitaxy, and doping, which are now beginning to be explored. For future industrial applications, an attractive feature of this technique is that it should be possible to deliver the low-energy electrons by a method other than STM, using e-beam microcolumns or mask exposure systems, for example.

Work on GaAs and other compound semiconductors within this program is based on combining STM lithography with *in situ* gaseous etching, to be performed in side chambers attached to the main UHV system. Recent work done elsewhere has demonstrated that gentle gaseous etching of heated samples can virtually eliminate the surface damage that ordinarily depletes carriers from nanostructures when etching is assisted by plasma ionization. Research in this area is now getting underway by employing more conventional gaseous etching facilities in the microelectronics group in parallel with those on the STM side-chambers in Beckman in order to develop the techniques. A major goal in this direction will be to pattern the 2-dimensional electron gas (2DEG), which forms naturally on the surface of thin InAs epitaxial layers due to Fermi level pinning above the conduction band edge. Since the 2DEG lies on the surface of this material, spectroscopic capabilities of (low-temperature) STM can be used to probe the wavefunctions and energy levels of laterally confined electrons, including aspects of carrier transport on a scale never before realized.

The unique coarse translation capability of the Beckman UHV-STM system is currently used to locate and examine cleaved III-V heterolayers and quantum wells, including state-of-the-art resonant tunneling diodes grown at MIT Lincoln Laboratories and Texas Instruments in addition to structures grown in the microelectronics group. Recent experiments with δ-doped heterolayer interfaces appear to have yielded the first direct images of a 2DEG. This ability to readily locate nanoscale device structures within a macroscopic area of several millimeters while preserving atomic resolution is a major resource for the nanolithography effort, since it provides the capability to modify individual devices that have been pre-patterned by conventional e-beam techniques. In the future, we anticipate that there will be great opportunities to combine this unique atomic-scale STM imaging capability with femtosecond laser spectroscopy in order to help elucidate new areas of electron dynamics and surface chemistry in nanostructures.

(ii) Self Organizing Synthesis — Chemistry and Structural Biology

This effort is parallel to and (see final section) in close collaboration with the solid state nanostructure research and emphasizes the molecular aspects. It seeks to understand the fundamental scientific principles relating to the mechanisms for assembly and function of mesoscale biological structures. Although there have been great advances in the visualization of biological structures at the angstrom scale with X-ray crystallography and nuclear magnetic resonance (NMR) spectroscopy and the direct manipulation at these length scales using recombinant DNA technology, the synthesis, characterization, and structure determination at the mesoscale (10 - 500 mm) is in its infancy. Yet it is at these scales that Nature utilizes macromolecular assemblies for the key processes of life, including nucleic acid synthesis and processing, biopolymer synthesis, energy transduction, and control of cell growth and division. This region is the arena where physics and electrical engineering meet biochemistry. Advances in our ability to visualize and manipulate mesoscale structures will not only provide direct structural input, but also allow utilization of biological macromolecules as the building blocks for composite molecular structures and devices.

Our efforts to date have exploited our combined expertise in rational synthesis of complex molecular architectures, *de novo* gene synthesis routes to protein engineering, and sophisticated surface chemistry and characterization capabilities to pursue the development of structures and devices that have no counterparts in classical device technology. Characterization of natural and designed mesoscale structures makes use of our combined expertise in surface chemistry, electrochemistry, ultrafast photoinitiated electron transfer measurements, and STM, AFM and NSOM probe methodologies. We believe that the case for the study and manipulation of biological macromolecules at interfaces and rational engineering of quantum and chemical transformation is attainable.

1. Construction of chemical and biological mesoscale devices. Research in our joint laboratories over the past few years has resulted in significant advances in the ability to control the assembly of proteins on surfaces and at interfaces. The critical concept in our approach is that the utilization of oriented metalloprotein arrays will allow device functions to be realized that are simply inaccessible to classical device modalities. This key point is germane, as an organizational principle, to implementations of biological macromolecules in smart sensors, distributed signal processing schemes, nanoscale autonomous power systems, and to interfacing with electrooptic semiconductor materials, i.e., to the whole of the problem of nanoscale hybrid devices.

Nature has provided interesting systems with potential application in molecular devices. Indeed, some systems such as bacteriorhodopsin and the photosynthetic reaction center are being actively investigated in many laboratories. However, the systems that nature has provided gratis are most often not ideally suited for a particular application. They are often not assembled into useful superstructures, they have nonexistent or inefficient abilities to recognize neighbors, they have the wrong optical or electrical (i.e., electron transfer) properties, etc. Hence, genetic engineering is a key technology in our efforts. The coupling of recombinant DNA technology with sophisticated surface chemistries, spectroscopic measurements, and controlling technologies for external manipulation of structure offers an excellent opportunity to construct hybrid biomolecular devices in which real control over the function is designed into the device from the first planning steps. The first step in directing the complete three-dimensional control of assembly is one in which structures are assembled with defined orientation in a planar array. This “tethering” must be specific and selective in the control of protein orientation. Our efforts in this arena have resulted in the merging of genetic engineering, chemical synthetic, and bioanalytical methods to provide a unique attachment site at a predefined location on the macromolecular surface with resultant control of orientation. As an initial step, oriented arrays of metalloproteins have been achieved and characterized using both self-assembly and Langmuir-Blodgett fabrication strategies. This approach is useful for selective immobilization and assembly of other protein-based mesoscale assemblies, such as antibody and catalytic enzyme complexes, which will have a major impact on design of sensing and processing methods in diagnostics and industrial procedures.

To support these research goals it is necessary to develop fundamental understanding of the key molecular aspects of assembly, patterning, and control. Ability to simultaneously engineer the binding specificity and the surface attachment site in metalloproteins and other mesoscale systems and to introduce such engineered proteins into planar arrays that can subsequently be interrogated optically is crucial to this effort. We have already demonstrated that genetic engineering techniques can be used to place a unique amino acid residue (typically a cysteine) at an appropriate point to orient the binding site in the desired direction, and the geometric and electronic properties around the prosthetic group have been engineered to introduce a desired *de novo* specificity of molecular recognition and electronic property of the prosthetic group. We are developing specific changes in the metalloprotein properties, which can be coupled efficiently to an external electronic or optical interrogation scheme. As an example, we have generated a “molecular wire” of self-assembled protein monomers for the study of the fundamental properties of charge transport and its regulation through quantum interference pathways.

2. Mesoscale imaging, manipulation, and characterization. The Molecular and Electronic Nanostructures theme offers exciting possibilities for completely novel directions in self-organizing synthesis. Self-organizing synthesis refers to an assembly of units in which the units themselves are single molecules, genetically derived biomolecules, or complex molecular clusters in a predesigned pattern with control over molecular placement, orientation, spacing, and interaction, and in which this control is manifested over supermolecular length scales. Thus, these experiments really seek to marry the exciting advances of the last decade in the areas of scanning probe microscopies for both imaging and pattern delineation (nanolithography), genetic engineering for structural/functional control of biological macromolecules, complex synthetic routes to molecules approaching mesoscopic dimensions, and chemical characterization capabilities that have now evolved to examining samples at the level of a single molecule.

Characterization of these mesoscale assemblies employs techniques at the cutting edge of physics, chemistry, and biochemistry. For example, an understanding of the quantum charge transport in biological energy transducing oligomeric systems is being advanced in our group by the development of pulse and modulation methods for measurement of redox transfer events on the time scale of femtoseconds to milliseconds, over temperature scales from a few degrees Kelvin to ambient, and over pressure ranges from atmospheric to 100,000 psi. Only by having the assay capabilities over these extended decades of scale can a molecular understanding evolve. Likewise, only having a direct interface and contact across multidisciplinary boundaries connects the notion of biological electron transfer with the theories and experiments of semiconductor physics, condensed matter physics, and molecular motion and vibronic coupling.

As exciting as each of these advances is in and of itself, the possibilities which are opened by bringing them together with the right mix of highly creative and motivated investigators, state-of-the-art research facilities, and in an environment that actively promotes investigators sharing ideas across traditional disciplinary lines, are unprecedented. The types of fundamental questions that must be answered to address the experimental vehicles described herein are pertinent to the whole of nanoscale manipulation for fabrication of molecular devices:

- How does one prepare molecules and surface templates such that size/shape and chemical compatibility are maintained?
- How does one configure surface reactivity with size control on the nanometer length scale?
- How does one prepare the macromolecular entities which can be manipulated in these assemblies and yet which retain interesting chemical, electronic, and optical functionality?
- How does one characterize the resulting assemblies in which the important properties are determined as much by the degree of control over molecular spacing, placement, orientation, and interaction, as they are by the properties of the individual molecules themselves?

The research groups of the principal investigators who are brought together, within the context of the Beckman Institute and with strong records of individual accomplishment, are particularly well-suited to tackle these challenges. These include the use of sophisticated modern techniques for the synthesis of mesoscopic molecular entities with exquisite control over structure and function; expertise in the use of scanned probe techniques for the study of interfaces in situ, in particular complex electrochemical interfaces where the properties are determined by the interplay of surface reconstruction; molecular adsorption and solution structuring; and developing and applying novel measurement schemes for the characterization of complex molecular assemblies, in particular composite assemblies in which self-assembled and Langmuir-Blodgett mulitlayers layers are exploited for the external control of molecular transport. This exciting interdisciplinary research initiative in mesoscale synthesis, visualization, manipulation, and characterization is ripe for discovery by a synergistic multi-investigator effort in the Molecular and Electronic Nanostructures Group.

3. Nanolithographic patterns (templates for the controlled assembly of molecular nanostructures). While nanolithographic techniques are well-suited for generating patterns on the submicron size scale, they are unlikely to become the method of choice for the manipulation of matter on the atomic size scale. Chemical synthetic techniques, although capable of generating extremely complex structures on the atomic-molecular level, are ill-suited for manipulating matter on a larger size scale, relying on spontaneous self-assembly as opposed to controlled assembly. A hybrid of the two approaches, however, should be capable of yielding materials whose structures can be controlled on both the atomic-molecular and the submicron size scales.

Nanolithographic patterns are being used as templates for assembling molecular nanostructures in a controlled fashion, thus generating supramolecular arrays whose structures are completely defined on both the atomic-molecular and the submicron size scales. Starting with passivated (protected) surfaces, nanolithography will be employed to generate arrays of points, lines, or polygons having nanoscale dimensions. These patterns, comprised of deprotected substrate surface atoms, will be exposed to large, molecular clusters capable of forming covalent bonds with the deprotected atoms. The dimensions of these clusters will be comparable to the dimensions of the surface patterns such that the patterns will serve as templates for generating ordered assemblies of molecular species. In the simplest case, for example, a square grid pattern could be generated nanolithographically from points whose dimensions allow binding of one and only one molecular cluster at each point. In this fashion, the nanolithographic pattern would serve as a template for the controlled assembly of a square grid of individual molecular clusters. The same approach could, of course, be applied to more complex patterns to generate more complex molecular arrays.

Research is conceptually advancing in three phases. First, passivated surfaces must be developed that can be patterned on the ~1-2 nm size scale to generate reactive surface atoms surrounded by passivated substrate. In chemical terms, the lithographic pattern must be comprised of reactive functional groups in a sterically confined environment of protecting groups. Systems of potential interest include exposed Si atoms on a hydrogen-passivated silicon surface, exposed copper atoms on an oxide-passivated copper surface, exposed Au-OH groups on a gold surface protected with organic molecules, or exposed edges of MoS_2. Exposure would be accomplished by using an STM or AFM, scanning with high tunneling currents or forces, respectively, over the surface. Exposure (deprotection) or etching using STM or AFM has been shown on each of the systems above. This etching occurs either through electron-stimulated desorption (in the case of the STM) or through local heating of the surface by the augmented tip-surface interaction (in the case of the AFM). The etching can be controlled to at least 1 nm in extent and in many cases down to true atomic dimensions. Patterning might also require more than one step. For example, reactive Au-OH patterns might be created on organic-passivated Au(111) surfaces by first forming patterns of exposed Au atoms and then electrochemically performing a one-electron oxidation of the exposed surface. There continue to be reports of preferential etching via SPM-surface interactions of a variety of passivated materials. Al and GaAs have been the subject of recent papers. In concept, almost any passivated material can be etched and deprotected with high spatial resolution using probe microscopy. The etching and exposure steps in this project both require the ability to operate in liquid environments (see below). The capability of operating in an aqueous environment has been developed at Illinois, and extension to nonaqueous environments using inert atmosphere techniques is anticipated.

The second phase of the program involves selection and synthesis of suitably sized and suitably reactive molecular species designed to react with the appropriate functional groups on previously prepared patterned surfaces. Reactive surface hydroxyl groups, for example, are known to be reactive toward metal alkoxides, and polynuclear alkoxides would therefore be appropriate molecular species in this case. Specifically, titanium oxoalkoxide clusters such as $[Ti_{12}O_{16}](OPri)_{16}$ and $[Ti_{16}O_{16}](OEt)_{32}$ display regioselective alkoxide exchange with alcohols and should react in a similar fashion with surface hydroxyls. For exposed metal surface atoms, polynuclear metal-sulfur clusters or large organic phosphines might possess suitable reactivity. For exposed metal sulfide surface atoms, transition metal carbonyl clusters with labile substituents are good candidates.

The final and critical research phase involves devising experimental procedures for assembling the molecular clusters on the patterned surface and examining their structures using SPM-based techniques. In order to avoid problems associated with sample transfer, researchers will perform nanolithography, cluster array assembly, and product analysis in a solution environment. The following sequence of events is envisioned: (a) preparation of a protected surface, for example, by oxidation or self-assembly of organics, (b) immersion into a suitably inert liquid that also serves as a solvent for the molecular clusters to be employed in a subsequent step, (c) deprotection or etching, at which point the exposed area is immediately decorated with the molecular cluster already present in solution, and (d) SPM-analysis using more modest interaction parameters. This protocol could be extended to include a second immersion-deprotection/decoration-analysis sequence involving assembly of a second molecular cluster on the surface, yielding a final product in which two types of molecular clusters are assembled in close proximity to each other. Post-processing, i.e., either thermal, chemical, or photochemical processing of the decorated areas, could follow emersion.

4. Rodcoils and supermolecular assemblies. This research (directed by S. Stupp) focuses on two areas, the self-assembly of organic molecules into nanostructures and the use of supermolecular assemblies as templates to generate nanostructured semiconductors. The self-assembling molecules of interest were synthesized for the first time in a Beckman laboratory and were termed “rodcoils” in the first publications. These molecules are either of oligomeric or polymeric dimensions and contain one molecularly rigid segment covalently bonded to a flexible one in a common molecular backbone. Between 1995 and 1997 this group discovered the self-organization of these structures into superlattices in which aggregates of the rigid parts with dimensions on the order of a few nanometers become dispersed in a specific geometry in a continuum of flexible segments. A hexagonal superlattice has been constructed in which 5 nanometer diameter discs have formed through segregation of the rod-like segments. The nature of the aggregates and of the superlattices is different from those previously known in block copolymers. We believe that this self-organization opens the door to the rational design of nanostructured organic patterns.

In the area of nanostructured semiconductors we are interested in the design and synthesis of amphiphilic block molecules that form ordered assemblies and can bind in selective nanocompartments the precursor ions for inorganic semiconductors. The basic concept is to explore the controlled nucleation and growth of semiconducting solids with nanoscale features produced by the imprint of nonbinding blocks of the amphiphiles. We have discovered one system in which a hexagonal assembly of organic molecules mediates the growth of II-VI semiconducting lattices containing cylindrical holes three nanometers in diameter and arranged periodically in a hexagonal lattice eight nanometers apart.

The synthetic laboratory, the visualization laboratory, the numerical laboratory, and the advanced chemical systems facilities available at the Institute have been critical for the development of this from 1995-7. Addition of electron microscopy to the Institute in the near future will be another important resource.

Future experiments will expand work on self-assembled nanostructures by developing rodcoil molecules in which the aggregates of rigid units will have interesting electronic, and possibly electro-optical, properties. Such structures could generate new sensor technologies or serve as templates to generate nanoscale patterns for electronic devices. There is also the possibility of using our nanostructures as templates to create two-dimensional arrays of special proteins produced in the Sligar group. The development of nanostructures with reasonable electronic conductivities will also allow exploration together with Lyding's group of the potential for further patterning using STM techniques. As the chemical structures are modified we will also develop a parallel computational effort that will use genetic algorithms to make predictions on the stability of molecular aggregates required for the formation of nanostructures

In the area of nanostructured semiconductors formed with supermolecular templates, we will pursue two specific directions. One will be to consider chemical vapor deposition of metals in periodic nanocavities formed in semiconductors and occupied in precursor phases by molecular assemblies. This will allow us to create semiconducting lattices with nanoscale periodic features of various metals. Working in collaboration with Hess and Tucker it may be possible to simulate the band structure of such systems and also to design model devices. The second direction we plan to follow is to explore synthetic methodologies to internalize in semiconducting lattices organic structures with specific functions. For example, we are interested in incorporating within the lattice organic molecules that act easily as electron donors or acceptors and thereby can impact directly on the electronic properties of the semiconductor. The presence of such organic inclusions could mediate the recombination rates of holes and electrons and produce novel semiconducting materials and devices.

5. Structural and dynamic aspects of molecular assemblies. This research (directed by P. Bohn) addresses fundamental aspects of molecular self-organization. In the last decade of this century and beyond, a fundamental thrust in the molecular sciences will be to understand the relationship of structure and function for molecularly engineered architectures. One subset of such structures are nanolayer arrays, in which structural regularity exists over coherence lengths of many hundreds to thousands of molecular diameters in-the-plane, but in which adjacent molecular planes may be completely different. Understanding structure-property relationships in these arrays is a central focus of this research, and Bohn's efforts are centered on exploiting powerful laser spectroscopic techniques coupled with optical phenomena for spatial localization. For example, we are building a near-field scanning optical microscope that will be capable of routinely measuring the spectroscopic properties of isolated single molecules at surfaces (see Existing Resources section).

In a new collaborative venture, Paul Bohn and Jeff Moore are using the unique structural properties of topologically diverse phenylacetylene macrocycles to build assemblies in which long-range ordering opens exciting possibilities for molecular recognition. In these assemblies subtle changes in molecular architecture, e.g., changing the steric bulk of *meta*-substituents, can produce dramatic changes in packing and, thus, in small-molecule binding properties of the supermolecular array. The full power of different structure elucidation tools in the Beckman Institute (STM, LB isotherm measurements) can be brought to bear on nanolayer arrays and provide the input for rational molecular engineering of structural properties on the supermolecular length scale.

Similar ideas are being pursued jointly with Steve Sligar (see Section ii.1 above) to fabricate, manipulate, and characterize two-dimensional assemblies of genetically engineered heme proteins (e.g., cytochromes b5 and c and myoglobin). The chief objective of this work is to develop techniques for making two-dimensional crystals of these materials and to use the unique selectivity of biological macromolecules to make electro-optically addressable devices for sensing, recognition, and separation.

Another project being carried out in collaboration with Lyding and Bishop seeks to understand how self-assembled monolayers (SAMs) of organic nucleophiles can be used for passivation and for resist function at III-V interfaces and how near-field scanning optical microscopy can be used as a parallel exposure tool for nanolithography of these SAM layers. These efforts are focused on developing the chemical principles pertinent to a massively parallel processing scheme, which has spatial capabilities in the nanometer size regime. Such capabilities are crucial for the eventual realization of nanometer-scale quantum electronic devices.

SIMULATIONS AND MODELING FOR THE NANOSCALE

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Scientific Drivers

The everlasting desire to probe and understand natural phenomena with increasing spatial and temporal resolution, coupled with the trend toward device miniaturization and the technological and economical potentials of molecularly designed and nanoscale engineered and fabricated materials structures, motivate increasing research efforts pertaining to these issues.

The properties of materials depend on their chemical composition and on the degree (size) and state, form, dimensionality, and phase (structural, morphological, and thermodynamical) of aggregation. While materials properties are normally listed without reference to their size, it is expected, and indeed found, that their physical and chemical properties exhibit size-dependent evolutionary patterns (SEPs), ranging and bridging the molecular and condensed phase (bulk) regimes. The nature and origins of such SEPs of materials properties, which include structural, electronic, spectral, transport, magnetic, chemical, mechanical, and thermodynamical characteristics, are varied, depending on the cluster or nanostructure size and the pertinent length (or time) scale. Such property-dependent materials characteristics include the following:

- electronic effective wavelength determined by its effective mass
- electronic elastic and inelastic mean free path lengths
- atomic or ionic diffusion lengths
- effective range of interparticle interactions and couplings
- correlation and screening lengths
- distribution of single particle and collective excitations relaxation times
- effective sizes of topological defects, such as dislocation cores and sources
- dimensions of crystalline facets
- surface-to-volume ratio expressed approximately as the inverse of the cluster radius

We reiterate that the relevant operative length scales are materials- and property (functionality)-dependent and should be considered and examined in such context. Thus, for example, novel phenomena are exhibited in semiconductor structures at carrier lengths of tens of nanometers. On the other hand, electron exchange lengths governing cooperative magnetic response are in most magnetic materials on the order of a few lattice spacings requiring structural control of the material on this small scale.

Quantum size effects and consequently dependencies on size and shape occur when the size of a system becomes comparable to the characteristic length scale determining the coherence of the wave functions. Simple considerations show that qualitatively new size-dependent behavior and functionality of metallic systems (such as quantized electronic conductance) are expected to occur mostly for systems where at least one of the spatial dimensions is reduced to a scale of only up to several nanometers, while for semiconductors they may occur for larger systems (10 nm and above, due to small effective masses and large dielectric constants). Interestingly, theoretical studies in our laboratory have predicted, and recent experiments on nanowires have confirmed, that not only the electronic properties (room temperature conductance quantization, magnetotransport, and thermopower), but also the mechanical properties of such systems of reduced dimensions, are modified significantly — that is, plastic deformations of metallic nanowires are characterized by order-of-magnitude larger yield stresses over bulk values.

Naturally, nanoclusters and nanostructures in this size range, and the physical and chemical functional specificity and selectivity that they possess, suggest they are ideal building blocks for two- and three-dimensional assembled superlattice structures. To maintain and utilize the basic and technological advantages offered by the size specificity and selectivity of nanoclusters, it is imperative that theoretical and experimental understanding be gained and implemented of the principles and methodologies of preparation and processing of cluster assembled materials, in macroscopic quantities and with high standards of size, structural, morphological, and shape uniformity.

In the above, new physical and chemical properties and selectivities originating from the size, dimensionality, and degree of aggregation of materials have been outlined. The ability to fabricate such nanostructures, coupled with the emergence and proliferation of proximal probes and atomic-scale simulation techniques, provide the impetus and means for theoretical and experimental investigations of nanometer-scale modifications, manipulations, and assembly of materials structures as components of devices and machine elements.

In particular, understanding the atomic and molecular processes occurring at the interface of two materials when they are brought together, separated, or moved with respect to each other, is central to many technological problems, including adhesion, contact formation, friction, wear, lubrication, nanoindentation, and machining. For example, molecular dynamics computer simulations have predicted the occurrence of an interfacial "jump-to-contact" instability when two materials surfaces are brought to close proximity (about 0.5 nm) leading to formation of nanoscale adhesive junctions whose resistance to shear is the cause of energy dissipation, that is, nanoscale friction and wear. Furthermore, preventing the formation of such junctions requires that the narrow spacing between the approaching surfaces be lubricated (as, for example, in the case of a read/write head and the surface of an ultrahigh-density information storage device) by a very thin lubricating film. It has been found through both theoretical simulations and experiments that the energetic, structural, dynamic, thermodynamic, and rheological properties of molecular lubricating liquids differ greatly under nanoscale confinements from their bulk behavior. For example, such highly confined liquids (globular or chains) organize into layered structures, forming strata parallel to the confining solid surfaces; are capable of supporting load; may undergo dynamic phase changes; and show rheological, and in particular, visco-elastohydrodynamic response characteristics that depend on the degree of confinement, the nature of the interfaces, the strength of bonding to the surfaces, the molecular architecture of the lubricant (straight vs. branched chains), and the shear velocities.

Methodologies and Perspectives

Investigations of nanoscale materials structures present an immense theoretical challenge. Underlying the theoretical difficulties is the reduced (finite) size of the nanostructural components, which is intermediate between the condensed-phase and molecular regimes. This renders inadequate the well-established solid state approaches and methodologies constructed for extended (often translationally invariant) systems. At the same time, such systems are too large for applications of techniques that are most useful in studies of molecular size systems. The atomistic nature of nanoscale materials systems and methods for their manipulation require development of atomistic theoretical approaches for studies pertaining to energetics, structure, stability, thermodynamics, physical properties (optical, phononic, magnetic, and transport), chemical reactivity, and mechanical characteristics (response, deformations, and rheology), as well as for investigations of mechanisms of nanostructure formation (including self-organization and self-assembly) and the response of such materials to external fields (electric, magnetic, optical, and mechanical).

These considerations have led to development of theoretical atomistic simulations and modeling methodologies that allow investigations of the issues mentioned above with refined spatial and temporal resolution. Among the methodologies we note particularly those based on classical and quantum molecular dynamics (MD) simulations, where the appropriate (atomistic) equations of motion for a system of interacting particles are integrated, and the resulting phase-space trajectories are analyzed (numerically as well as in animated form). In classical MD simulations the interatomic interaction potentials are constructed using semi-empirical data and/or fitting to quantum-chemical calculations. More recently first-principles molecular dynamics (FPMD) methods have been implemented, where the interactions are evaluated concurrently with the atomic motions through self-consistent solution of the many-electron Schrödinger equation. Such FPMD techniques extend our capabilities to investigate systems and phenomena involving electronic rearrangements and chemical transformations, as well as allowing studies of electronic spectral and transport properties. Other simulation methodologies include classical and quantum Monte Carlo techniques and methods for structural optimization (simulated annealing and genetic algorithms).

The emergence of atomistic simulations as a principal theoretical methodology in nanoscience (as well as in other disciplines) is correlated with progress in understanding the nature of bonding and cohesion in complex materials, algorithmic advances, and a symbiosis with novel computer architectures that allow simulations of ever larger systems (up to several million atoms) and for longer time periods.

Current methodologies have demonstrated interpretive and predictive capabilities in several areas: atomic and molecular clusters, nanocrystals and their assemblies, nanowires, surface-supported structures, atomic-scale contacts and switches, atomic-scale surface manipulations, thin film growth, transport in reduced dimensions, interfacial systems, nanotribology, lubrication and molecular scale thin film rheology.

It is imperative, however, that future efforts be focused on development of simulation methodologies and algorithms that will allow extension of such studies to longer time scales. Such approaches may include embedding schemes, renormalization techniques, and methods based on variable/adaptable spatial and temporal resolutions. Progress on these issues, which form “grand challenges” in computational materials science, requires focused timely initiative on a national scale. Indeed, several countries have recognized the critical importance of this challenge and have established major initiatives targeted at its resolution. Already, large-scale programs have been established in Japan and in Europe through creation of institutional and multi-institutional focused programs and consortia.

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NANOSCALE THEORY AND SIMULATION:
A Critical Driver for and a Critical Challenge to Commercial Nanotechnology

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Introduction

Nanotechnology is concerned with the structures, properties, and processes involving materials having organizational features on the spatial scale of 1 to 300 nm. This is bigger than simple molecules but smaller than the wavelength of visible light. At these scales there are new phenomena that provide opportunities for new levels of sensing, manipulation, and control. In addition, devices at this scale may lead to dramatically enhanced performance, sensitivity, and reliability with dramatically decreased size, weight, or cost. From the experimental point of view, the fundamental problem in nanoscale technology is that the units are too small to see and manipulate and too large for single-pot synthesis from chemical precursors; consequently, most synthetic nanotechnologies focus on self-assembly of molecules. Most presentations at the May 1997 WTEC workshop focused on the challenges and strategies required to synthesize and copy at the nanoscale and to characterize the systems experimentally.

Another critical challenge in developing successful nanoscale technology is development of reliable simulation tools to guide the design, synthesis, monitoring, and testing of the nanoscale systems. This is critical for nanotechnology because we cannot “see” the consequences of experiments at the nanoscale. Thus we believe that it is essential to build fast computational software that reliably predicts the chemistry and physics (structures and properties) as a function of conditions (temperature, pressure, concentrations) and time. Such software must also predict spectroscopic signatures (IR, Raman, UV, NMR) and properties (density, color, surface tension) that can enable experimentalists to gauge the progress in the reactions and processes.

The difficulty from the theory point is that such systems are too large for standard atomistic approaches — a cube of polyethylene 100 nm on a side contains about 64 million atoms. This requires a level of description coarser than atomic that must still contain the atomistic information responsible for the chemical properties. This nanoscale regime is also referred to as the *mesoscale*; it lies between the molecular or atomistic scale (where it is convenient to describe molecules in terms of a collection of bonded atoms) and the continuum or macroscale (where it is convenient to describe systems as continuous with a finite element mesh basis for a digital description). The relationships between various scales in the hierarchy of materials modeling approaches is illustrated in Figure 9.10.

We do not yet have sufficient fundamental understanding of the theory and methods required to adequately describe the mesoscale regime, just as we do not yet have all the experimental technology and strategies to synthesize, copy, and manipulate nanoscale systems. Predicting the structure, dynamics, and properties of mesoscale systems on the required time scale (minutes or preferably seconds) demands substantial improvements in

- *theory* — we require a better basic understanding of the connection between structure and properties at the mesoscale
- *methods* — we require new algorithms to carry out calculations of mesoscale phenomena
- *graphical representations* — we require improved ways to communicate mesoscale information in appropriate graphical representations where the relevant elements for designing new systems can be visualized and manipulated

Simulation theory and software that meet these requirements are likely to be both drivers toward nanotechnology and challenges to the development of commercially successful nanotechnology.

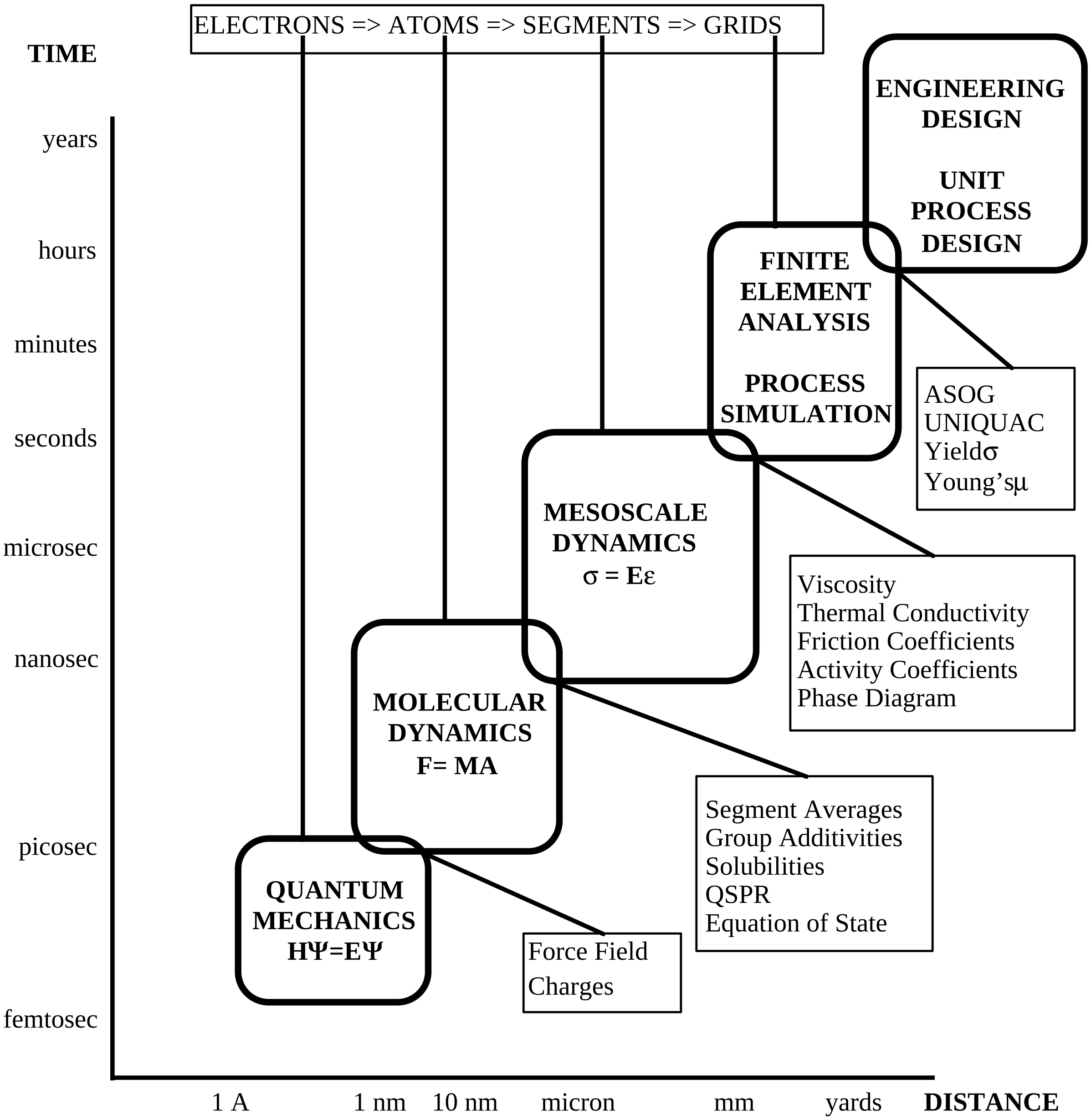

Fig. 9.10. The California Institute of Technology Materials and Process Simulation Center (MSC) hierarchy of materials simulation. It is necessary to predict reliable properties *prior* to synthesis and experiment. The foundation is quantum mechanics (QM). This allows prediction in advance, but it is not practical for time and distance scales of engineering. Thus, it is necessary to extend from QM to engineering design by a succession of scales, where at each scale, the parameters are determined by averaging over the finer scale. This allows first-principles simulations for engineering problems.

The development of these kinds of computational tools for nanotechnology has for several years been a goal of the Materials and Process Simulation Center (MSC) at the California Institute of Technology. Progress has been slow due to a lack of direct funding for this area, which has certainly impeded progress. Recently NASA has established a mechanism for seed funding in this area, which although quite small, has helped significantly.

Computational Nanotechnology: Design, Characterization, Operation, Analysis, and Optimization of Nanoscale Systems

Nanoscale device design involves four stages:

1. predicting the physical and chemical properties of the materials components
2. modeling and characterizing the fabrication and assembly processes
3. analyzing the simulated device under operational conditions
4. controlling and optimizing simulated device operation

The components of a nanoscale device may be in the vapor/gas, liquid, or solid phase (or all three phases may be present and interacting through vapor-liquid, solid-liquid, vapor-solid interfaces) at various stages of fabrication assembly and operation.

Our objectives are to

- develop and validate the computational tools and algorithms required to predict from first principles the materials properties (structural, mechanical, electrical, thermal, rheological, and interface properties) of nanoscale devices as a function of time, pressure, and temperature
- apply these tools to design, characterize, analyze, and optimize devices for various applications
- improve computational performance by porting and optimizing these computational tools into multi-processor environments using emerging parallelization tools
- make these computational tools useful by assembling them into an engineering workbench that allows a designer to construct a nanoscale system on a computer and then test computationally the properties of the resulting system
- aid the iterative design of nanoscale systems by providing graphical analysis tools that allow the engineer to modify parts of the nanostructure and then measure the change in properties

Our goal is to develop accurate, robust, and efficient physics-based and chemistry-based computational and analytical tools and assemble them as a nanoengineering design and simulation workbench, *NanoSim.* These tools should be useful in enhancing the performance, reliability, and affordability of nanoscale devices, making them valuable for use in advanced technology applications.

Research and Development Scope

Challenges that the MSC team is addressing in its work on NanoSim include the design and simulation of the following kinds of nanoscale systems (NSS):

- memory systems with nanoscale elements
- nanoscale chemical sensor arrays (e.g., electronic noses)
- quantum dot arrays
- nanoscale fuel cells
- nanoscale batteries
- nanoscale springs
- vibration isolators
- nanoscale diodes and transistors

Ultimately, these various units would be integrated into nanodevice systems, which may include internal power sources (e.g., nano fuel cells); energy storage (e.g., nano batteries); controllable switches (combining nano memory); and switches controlled by light, heat molecules, electric, and/or magnetic fields, etc.

Elements of the nanoscale systems might include those shown in Table 9.1, and properties that need to be predicted with the NanoSim computational tools include those shown in Table 9.2.

Table 9.1
Elements of Nanoscale Systems

ELEMENTS	EXAMPLES OF ELEMENT TYPES
Chemical Sensors	binding of molecules that cause changes in the • structure (volume) • dipole moment • polarizability • magnetic moment • electronic energy level
Molecular Switches	switching of a two-state system from one to the other state by applying • electric field • laser light • magnetic field • temperature • pressure (and/or stress)
Materials	• carbon nanotubes • dendrimers • diblock, triblock polymers • liquid crystals • semiconductor clusters or surfaces • metal surfaces or clusters • alkanethiols on Au
Substrates (onto which the materials are built)	• electronic materials [Si(100), GaAs(100)] • ceramics and oxides (Al_2O_3, SiC, MgO) • graphite • polymers • metals (e.g., Au)

Nanoscale System Design and Simulations: Electrons to Atoms and Beyond

The nanoscale device design computations involve various levels of theory: quantum mechanics; force field development; massive molecular dynamics on all atoms of large systems; and long term molecular dynamics with semi-rigid systems (high frequency modes fixed).

Quantum Mechanics

It is important to use quantum mechanics to describe systems in which bonds are being broken and formed. Only then can we be sure to obtain accurate barrier heights and bond energies. There are a number of developments that are improving and extending the modern methods of quantum mechanics: generalized valence bond, GVB (Goddard et al. 1973); psuedospectral GVB (PS-GVB) (Greeley et al. 1994; Tannor et al. 1994); multireference configuration interaction, MR-CI (Carter and Goddard 1988); and Gaussian dual space density functional theory, GDS-DFT (Chen et al. 1995). These methods are needed to establish the fundamental parameters for new systems. Given the quantum mechanical results we develop force field (FF) descriptions to predict the structures, energetics, and dynamics of the nanoscale systems. The research requirements in this area are to obtain more accurate descriptions for periodic boundary conditions that include many-body effects and accurate forces sufficiently quickly to be used directly for molecular dynamics (MD) without force fields.

Table 9.2
Properties to be Predicted with NanoSim Computational Tools

PROPERTIES	EXAMPLES
Structural	• internal structure (bond topology, distances, and angles) • morphology • microstructure
Mechanical	• vibrational modes • elastic moduli • yield limits • strength • toughness • temperature and pressure effects on mechanical properties (creep)
Surface	• reconstruction • oxidation • adhesion • friction • wear
Electrical	• chemical potential (for electrons, protons) • band gaps in the bulk and at the surface • Fermi energy pinning by defects and surfaces • electron transfer rates (tunneling through barriers at the surfaces)
Optical	• density of electronic states • polarizability • dielectric constant (frequency dependent) • optical absorption as function of wavelength • quantum dots and lines • nonlinear optical properties (hyperpolarizabilities)
Magnetic	• ferromagnetic and antiferromagnetic coupling parameters • size effects • surface effects
Rheological	• viscosities and flow of fluids in nanoscale regime (anisotropic) • non-Newtonian behavior • flow and transport properties of electro-rheological or magneto-rheological fluids • structure-fluid interactions and their effect on transport properties • time and frequency dependence of the flow properties • gas flow under conditions with mean free path comparable to physical sizes

Force Fields

Despite the progress in first principles electronic structure theory, the calculations remain far too slow for studying the dynamics in nanotechnology applications. Thus, it is essential to replace the electrons with an FF suitable for MD simulations. Most important in atomistic modeling of nanotechnology systems is to use force fields that faithfully represent the structures and properties of real materials. This is necessary because there may be few experimental tests of the predictions in the early years, requiring that the theory be validated and well founded. In recent years, new force field technologies have been developed to achieve such reliability.

The Hessian-biased force field (HBFF) (Dasgupta et al. 1996) combines normal mode eigenstate information from Hartree Fock (HF) theory with eigenvalue information from experiment. This HBFF approach has been used to develop accurate FF for many industrially interesting polymers such as PE (Karasawa et al. 1990), PVDF (Karasawa and Goddard 1992), nylon (Dasgupta et al. n.d.), POM (Dasgupta et al. 1993), and PSiH (Musgrave et al. 1995); ceramics such as Si_3N_4 (Wendel and Goddard 1992) and C_3N_4 (Guo and Goddard 1995); all semiconductors in group IV, III-V, and II-VI systems (Musgrave 1995); and metals such as the face centered cubic (fcc) metals (Li and Goddard 1993; Kimura et al. n.d.).

For rapidly carrying out calculations on new systems it is also useful to have generic force fields suitable for general classes of molecules. Thus the DREIDING FF (Mayo et al. 1990) has proved quite useful for constructing many nanosystems from main group elements (e.g., C, N, O, F, Si, S, P, Cl). The Universal force field (UFF) (Rappé et al. 1992) is defined for any combination of elements from H to Lr (element 103) and is suitable for any inorganic, organometallic, or organic. To obtain the charges required for accurate calculations, we find that charge equilibration (QEq), which is defined for any combination of elements from H to Lr, allows fast but accurate predictions (Rappé and Goddard 1991). Thus, with UFF and QEq one can predict structures for any combination of elements from H to Lr (element 103).

Standard FF uses springs to average over the electrons of quantum mechanics in describing structures and vibrations of molecules. However, there are many systems where the instantaneous response of the electron (polarizability) is essential in describing the properties. Rather than using quantum chemistry to describe polarization effects (which would be too expensive for most simulations), we have found it possible to use pseudoelectrons in the FF to properly describe the polarization for polymers, metals, ceramics, and organometallics (Karasawa and Goddard 1992). We believe that force fields suitable for accurate prediction of the temperature behavior of moduli and other mechanical, dielectric, and optical properties will require use of such pseudoelectrons.

Thus to predict the piezoelectric and dielectric properties (Karasawa and Goddard 1992; 1995) of poly(vinylidene fluoride) (PVDF), we developed the covalent shell model (CSM) (Karasawa and Goddard 1992) in which each atom is described with two particles: one possesses the mass and is connected to the valence springs of the standard FF theory; the other is light (zero mass) and attached only to its nucleus with a spring constant related to the charge and polarizability. These atomic polarizabilities are obtained by fitting to the polarizability tensor from quantum mechanics calculations on model systems.

Massive Molecular Dynamics

Nanosystem simulations may contain explicit descriptions of 1 million to 1 billion atoms. To make such calculations practical has required major improvements in MD methodologies.

The biggest bottleneck obstructing atomic-level simulations on superlarge systems is accurately summing the Coulomb interactions, which decrease slowly with distance and could lead to $N^2/2 = 0.5 \times 10^{16}$ terms for a 100 million particle system. The standard approach to simplifying such calculations for finite systems has been to use nonbond cutoffs with spline smoothing; however, this leads to an enormous nonbond list for one million particles and also leads to errors two orders of magnitude too large. The only reliable previous procedure (Ewald) for summing the Coulomb interactions for a periodic system requires Fourier transforms (Karasawa and Goddard 1989), which scale as $N^{1.5}$, totally impractical for a million atoms.

Because of the need to simulate millions of atoms, we developed methods and optimized parallelized computer programs efficient for high capacity MD (simulation of 10,000 to 10,000,000 atoms for finite molecules or 10,000 to 1,000,000 atoms per unit cell for periodic boundary conditions). There have been a number of important developments:

1. The Cell Multipole Method (CMM) (Ding et al. 1992b), which dramatically reduces the cost of long-range Coulomb and van der Waals interactions while retaining high accuracy. The cost scales linearly with size, allowing atomic-level simulations for million atom systems (Ding et al. 1992b; Lim et al. n.d.; Gao 1997).
2. The Reduced Cell Multipole Method (RCMM) (Ding et al. 1992a), which handles the special difficulties with long-range Coulomb interactions for crystals by combining a reduced unit cell plus CMM for interaction of the unit cell with its adjacent cells. The cost scales linearly with size while retaining high accuracy, allowing simulation of crystals having a million atoms per unit cell (the major use is for models of amorphous and semicrystalline materials).
3. Hierarchical internal coordinates for molecular dynamics, in which some regions (e.g., an alpha helix) are treated as rigid, while others (e.g., an alkane block) are treated with only the torsional degrees of freedom, and others are allowed full Cartesian freedom.
4. The Newton-Euler Inverse Mass Operator (NEIMO) method (Mathiowetz et al. 1994; Vaidehi et al. 1996) for internal coordinate dynamics (e.g., torsions only), which allows the solution of the dynamical equations for internal coordinates without inverting the mass tensor (moment of inertia tensor). The cost of NEIMO is linear in the number of degrees of freedom and small compared to other costs for million atom systems.
5. A semi-rigid body dynamic, MPSim (Gao 1997; Iotov 1997), which allows some units to be treated as rigid bodies, others to be described semi-flexibly (with bonds and angles fixed, but torsions free), and others to be treated semi-rigidly (with torsions fixed relative to each other but allowed to move as a unit, while other parts of the same unit are semi-flexible).
6. A focus has been to develop the algorithms and methods suitable for massively parallel high performance computers and to develop optimal software for exploiting such computer environments (Lim et al. n.d; Gao 1997; Iotov 1997).

The new MPSim program was written and optimized for parallel supercomputers. MPSim is now being used for production simulations on million atom systems using the SGI Power Challenge and HP-Convex systems. These parallel programs scale quite well through 500 processors, as illustrated in Figures 9.11 and 9.12.

Nanoscale System Design and Simulations at the MSC

Examples of nanosystem simulations recently performed at the MSC include the following:

1. structures and binding properties of dendritic polymers; these have substantial potential for the design of tailored hyperbranched structures for use in molecular nanotechnology applications (Miklis et al. 1997)
2. molecular mechanics and molecular dynamics to determine the structure and properties of alkali-doped single-walled nanotubes (Gao et al. 1997b)
3. moduli and pseudo-plasticity of single-wall nanotubes (SWNTs) from accurate force fields, using molecular mechanics (Gao et al. 1997a)
4. molecular dynamics and molecular mechanics simulations of nanomachines (Musgrave et al. 1991; Cagin et al. 1997)
5. QM studies of diamond mechano-synthesis (Walch et al. 1997)
6. development of nanodevice and nanomachine simulation tools in a molecular modeling environment (Che et al. n.d.)
7. incorporation and extension of bond-order-dependent force fields (BOD-FF) for carbon nanotechnology into MPSim, and PolyGraf[3]

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[3] The program utilizes equilibrium and nonequilibrium molecular dynamics techniques while allowing manipulation capabilities suitable for designing nanoscale molecular machines and devices. It has been developed in the Cerius2 commercial MD software using the Software Developers Kit (SDK).

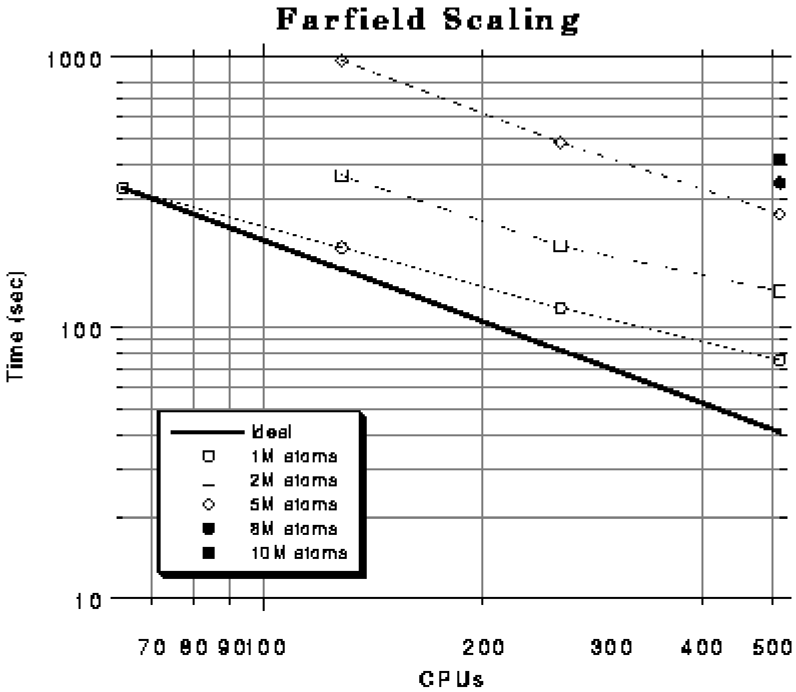

Fig. 9.11. The scaling behavior of massively parallel evaluation of energy and forces using Cell Multipole Method in MPSim as a function of number of CPUs and atoms.

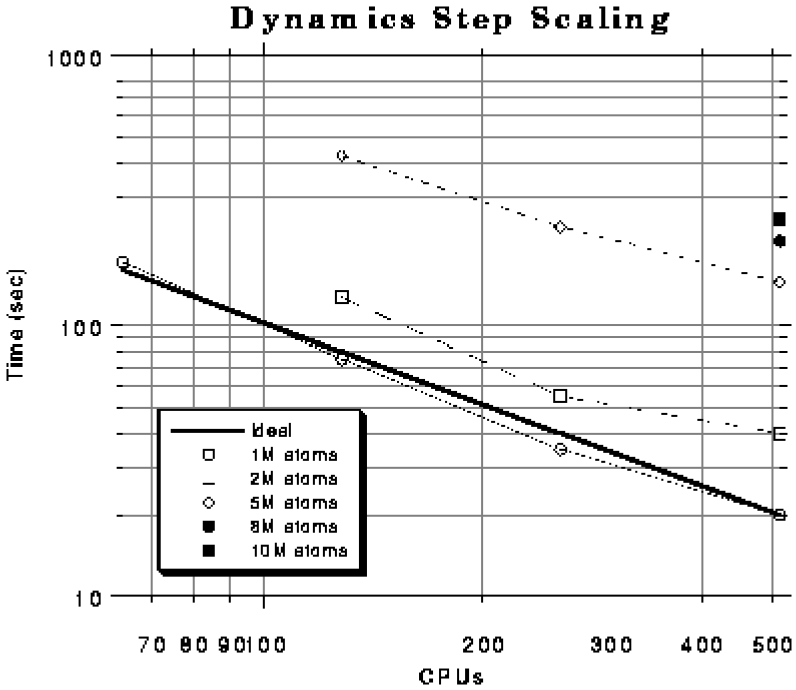

Fig. 9.12. The scaling behavior of molecular dynamics step in MPSim as a function of number of CPUs and atoms.

Recent Developments

Among several new projects related to computational nanotechnology started during 1997 are the following:

1. BOD-FF for description of wear and tribology of microelectricalmechanical systems (MEMS). A key problem is developing BOD-FF with terms to represent long range tube-tube interactions in a continuous manner to address nano and micro tribology problems for nanomechanical and micromechanical devices. The problems of wear and friction are especially important in the design of nano- or micro-mechanical devices for long term space missions. The preliminary results of this investigation will be presented at the American Physical Society March 1998 meeting (Che, Cagin, and Goddard n.d.).
2. Molecular self-assembly. Researchers at the MSC have made substantial progress in investigating the role of molecular self-assembly of Langmuir-Blodgett (LB) films on gold (Gerdy and Goddard 1996) and of corrosion inhibitors (Ramachandran et al. 1996) and wear inhibitors (Jiang et al. 1997) on metals and ceramics. At present, we are investigating the tribology of molecularly thin self-assembled layers and their influence on device operations. These systems involve heterogeneous systems composed of surfaces (mostly hard materials), physisorbed or chemisorbed organic molecularly thin layers on these surfaces and fluid interfaces. Preliminary results of this initiative will be presented at the American Physical Society March 1998 meeting and the ACS 1998 August meeting (Zhou et al. n.d.).
3. Supramolecular assembly of dendritic polymers. We have initiated a subproject to understand the self-assembly of dendrimers on surfaces as possible nano- or microscale sensor applications.
4. Transport properties of carbon nanotubes. Nanotubes as nanoelectronic device components are being studied at several laboratories. An important issue here is the thermal transport properties of the carbon nanotubes. Over the past two years Cagin and Goddard have developed nonequilibrium molecular dynamics techniques to study the transport properties of materials by employing synthetic fields to generate currents and measure the response of materials. Until recently, most of the applications have centered on mass transport and flow properties (Qi et al. n.d.) such as diffusion constants of gases in polymers (Iotov et al. n.d.; Iotov 1997) and viscosity of fluids (metal alloys and hyperbranched organics) (Qi et al. n.d.). Recently we have focused on thermal transport using a synthetic Hamiltonian approach. Next we plan to study the thermal conductivity of nanotubes using nonequilibrium molecular dynamics (NEMD) techniques.

New Initiatives

In addition to continuing the projects listed in the previous section, we have initiated two subprojects:

1. Inherent tribological properties of nanoscale materials. At present, silicon forms the basis of microelectronic and MEMS devices; however, silicon has inherently less desirable wear properties when compared to diamond and polycrystalline diamond (PCD). The promising developments in carbon nanotube synthesis and application make carbon-based materials attractive for device design. Using advanced quantum mechanical techniques, we will investigate the wear phenomena at the electronic level.
2. Failure mechanisms in nanotubes. Using steady state molecular dynamics techniques and BOD-FF, we plan to investigate the yield, fracture, and failure of nanotubes as a function of strain rate and strain profiles. The steady state molecular dynamics technique differs from standard equilibrium molecular dynamics techniques in the sense that the system is not at equilibrium, but it is maintained under a steady state by the presence of various thermodynamic baths. The thermodynamic baths include heat, pressure, and stress for which a constant gradient is maintained.

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GLOSSARY

2DEG	2-dimensional electron gas
ADC	Analog-digital converter
AFM	Atomic force microscopy
AFOSR	Air Force Office of Scientific Research
AMLCD	Active matrix liquid crystal display
AMO	Atomic, molecular, and optical
ARO	Army Research Office
ASME	American Society of Mechanical Engineers
ATP	Adenosine triphosphate
BERAPD	Biomedical Engineering and Research to Aid Persons with Disabilities (NSF)
BES	Basic Energy Sciences office (DOE)
BES	Bioengineering and Environmental Systems (NSF/ENG)
BMDO	Ballistic Missile Defense Organization
BOD-FF	Bond-order-dependent force field
CAD	Computer-assisted design
cermet	Ceramic/metal composite
CHE	Division of Chemistry (NSF/MPS)
CIP	Cold isostatic press
CMOS	Complementary metal-oxide semiconductor
CMP	Chemical mechanical polishing
CMS	Civil and Mechanical Systems division (NSF/ENG)
CRT	Cathode ray tube
CSM	Covalent shell model
CTS	Chemical and Transport Systems division (NSF/ENG)
CVC	Chemical vapor condensation
CVD	Chemical vapor deposition
CVI	Chemical vapor infiltration
DARPA	Defense Advanced Research Projects Agency
DMII	Design, Manufacture, and Industrial Innovation division (NSF/ENG)
DMR	Division of Materials Research (NSF/MPS)
DOC	Department of Commerce
DOD	Department of Defense
DOE	Department of Energy
EC	Evaporation/condensation generators
ECS	Electrical and Communications Systems division (NSF ENG)
ERATO	(Japan) Exploratory Research for Advanced Technology program
ERC	Engineering Research Center on Microelectronics (University of Illinois)
ETO	Education and Training Office (DARPA)
fcc	Face centered cubic (metals)
FET	Field effect transistor
FF	Force field
FIFO	First in - first out

FIM	Field ion microscope
FPMD	First-principles molecular dynamics
GDS-DFT	Gaussian dual space density functional theory
GIC	Graphite intercolated composites
GMR	Giant magnetoresistance
GPC	Gas phase condensation
GPS	Global Positioning System
GVB	Generalized valence bond
HBFF	Hessian-based force field
H_c	Coercivity
HDS	Hydrodesulfurization
HIP('ing)	Hot isostatic press(ing)
HMDS	Hexamethyl-dilazane
HPHT	High pressure/high temperature
i.d.	Inner dimension
IGC	Inert gas condensation
IIA	Individual Investigator Award
IR	Infrared
ISDN	Integrated Services Digital Network
LCD	Liquid crystal display
LCT	Liquid crystal templating
LED	Light-emitting diode
LTMC	Layered transition metal chalcogenide
MA	Mechanical alloying
MBE	Molecular beam epitaxy
mCP	Microcontact printing
MD	Molecular dynamics
MEMS	Microelectromechanical systems
MIMIC	Micromolding in capillaries
MITI	(Japan) Ministry of International Trade and Industry
MOCVD	Metal oxide chemical vapor deposition
MOSFET	Metal oxide semiconductor/field-effect transistor
MR-CI	Multireference configuration interaction
MRSECs	Materials Research Science and Engineering Centers (NSF)
MSC	Materials and Process Simulation Center (California Institute of Technology)
mTM	Microtransfer molding
MURI	Multidisciplinary (university) research initiative, DOD
NASA	National Aeronautic and Space Administration
NCA	Nanoparticle chain aggregate
NCAP	Nematic curvilinear aligned phase material
NCCE	(NSF) National Center for Computational Electronics
NEIMO	Newton-Euler Inverse Mass Operator method for modeling internal coordinate dynamics
NEMD	Nonequilibrium molecular dynamics
NIH	National Institutes of Health
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance

NRC	National Research Council
NRL	Naval Research Laboratory
NSF	National Science Foundation
NSOM	Near-field scanning optical microscopy
NSS	Nanoscale systems
NT	Nanotechnology
o.d.	Outer dimension
OLED	Organic light-emitting device
ONR	Office of Naval Research
PAN	Polyacrylonitrile
PB	Polybutadiene
PBC	Periodic boundary conditions
PCD	Polycrystalline diamond
PCR	Polymerase chain reaction
PDLC	Polymer-dispersed liquid crystals
PDMS	Polydimethylsiloxane
PI	Principal Investigator (also, co-PIs)
POC(s)	Point(s) of contact
PS	Polystyrene
PS-GVB	Psuedospectral generalized valence bond
PVDF	Poly(vinylidene fluoride)
QCA	Quantum cellular automata
QCL	Quantum cascade lasers
Q-dots	Quantum dots
QEq	Charge equilibration
QM	Quantum mechanics/mechanical
RCMM	Reduced cell multipole method
redox	Reduction-oxidation
RGB	Red, green, blue
RTD	Resonant tunneling diode
SAM	Self-assembled monolayer
SAMIM	Solvent-assisted microcontact molding
SAW	Surface acoustic wave device
SEP	Size-dependent evolutionary pattern
SET	Single-electron transistor
SOI	Silicon on insulator
SPD	Superplastic deformation
SROs	Scientific Research Initiatives (DOD)
STA	(Japan) Science and Technology Agency
STM	Scanning tunneling microscope/microscopy
STN	Super twisted nematic
SUNY	State University of New York
SWNT	Single-wall nanotubes
TBC	Thermal barrier coating
TEM	Transmission electron microscope/microscopy
TFT	Thin film transistors

TMS	Tech molecular sieves; family of transition metal oxides
UFF	Universal force field
UHV	Ultrahigh vacuum
UHVCVD	Ultrahigh vacuum chemical vapor deposition
ULSI	Ultra large scale integrated circuit
ULTRA	Ultra Electronics: Ultra Dense, Ultra Fast Computing Components Program (DARPA)
URI	(University) research initiative (see also MURI, DOD initiative)
VC	Vanadium-carbon
VCSELs	Vertical cavity surface-emitting lasers
WC/Co	Tungsten carbide/cobalt
WTEC	World Technology Evaluation Center

Notes

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