

DIFFERENT MECHANISMS FOR SYNTHESIS OF NANOWIRES AND THEIR APPLICATIONS

Abstract:

The role of one-dimensional nanostructures has gained immense importance in recent times. These types of nanowires and nanorods are used in probe microscopy, nano electronics, quantum devices and mesoscopic devices. This review compares the various methods used to synthesize such nanowires such as vapor-liquid-solid growth mechanism, oxide assisted nucleation and carbothermal reduction. The different nanowires thus formed were characterized by selected area electron diffraction (SAED), energy dispersed X-ray spectrometry (EDX), X-ray photoemission spectra (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM and HRTEM). The nanowires formed ranged from diameter of 10 nm to 100 nm, while the length is typically about 10 to 100 μm . The elemental composition of these nanowires will also be compared.

IN the study by Liang et al [1] of the Chinese Academy of Sciences, amorphous silica (SiO_x) nanowires were synthesized and it was seen that the growth mechanism was similar to that of the vapor-liquid-solid (VLS) growth. Mesoporous silica containing iron nanoparticles were evaporated in the presence of silicon. 5 parts each of Tetraethoxysilane (TEOS) and ethanol were mixed with 4 parts of 0.3M iron-nitrate aqueous solution and 1 part of deionized water. 0.3 parts of concentrated nitric acid was added while constant stirring to obtain a gel. This gel was dried for a week at 90°C to get rid of all water and solvent present in the system and subsequently calcined at 500°C . The mesoporous silica with iron oxide nanoparticles thus formed was then reduced in an argon atmosphere with 9% hydrogen to convert the iron oxide to iron. This silica xerogel and silicon powder were mixed at a molar ratio of 1.1:1 and placed in an alumina boat in a furnace. The furnace, free of oxygen, was heated to 1180°C for 2 hours to get the silica nanowires.

The silica nanowires can be classified according to their morphology. As seen in Figure 1, the nanowires have a straight and smooth curved structure 1(a,b), while other forms like helical 1(c) and braided 1(d) are also evident. The first types of wires, the straight and smoothly curved have an average diameter of 40-50 nm, while the helical and braided nanowires were slightly thinner at 10-25 nm.

It is seen from the EDX spectrum, Figure 2, that the nanowires contain only silicon and

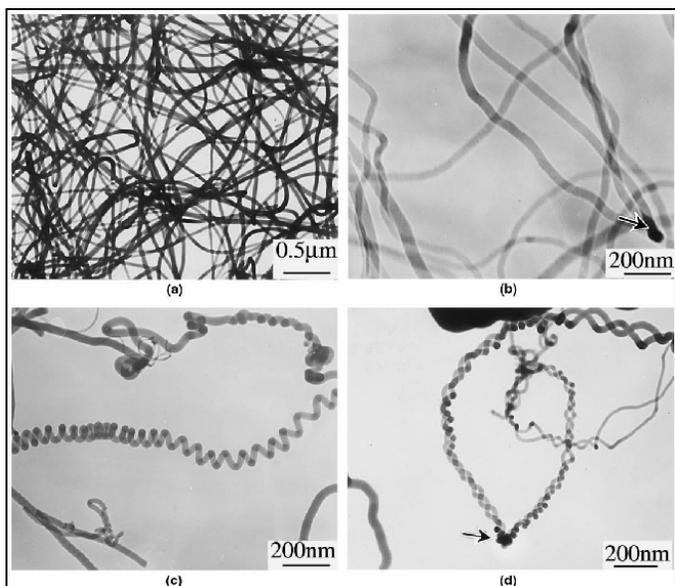


Figure 1. [1] Different Morphologies of Silica Nanowires.

oxygen, with a ratio of 1:1.4. The SAED pattern has a diffuse ring and absence of any spots proves that the wires are amorphous in nature. The high-resolution transmission electron microscopy (HRTEM) pictures of randomly tilted sample nanowires show that there is no crystalline silicon phase. The wires can thus be concluded to consist only of amorphous silica. The nanoparticles attached to the wires (shown by arrows) consisted of silicon, oxygen and iron as evident from the EDX spectra, which has two peaks at 0.5 and 1.8 KeV.

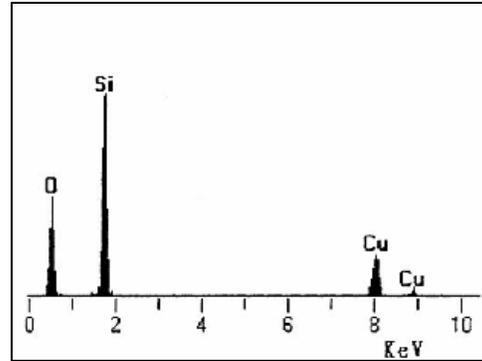


Figure 2 [1] EDX Spectra of Silica Nanowires

The growth mechanism of these silica nanowires can be explained by the VLS model. The spherical nature of the nanoparticle is evidence of presence of a droplet. Although Liang et al do not give enough conclusive proof about the presence of the VLS mechanism, the experimental conditions and the ultimate morphologies agree with the VLS model. The amorphous nature of the nanowires is due to the fact that the temperature of the system is below the eutectic point of FeSi_2 . Therefore when the Si and O atoms supersaturate the Fe-Si-O alloy droplets they form amorphous nanowires instead of recrystallizing to form crystalline nanowires. It is suggested that the different morphologies of the nanowires is a result of vibration of the liquid Fe-Si-O droplets and presence of temperature and concentration gradient.

ANOTHER study by Liang et al [2] explains the formation of silicon carbide nanowires, each surrounded by silicon oxide shells. The core of the wire has diameter of 10-30 nm and are crystalline in nature. The growth process can be explained by carbothermal reduction and VLS process. A dried calcined gel of mesoporous silica containing iron oxide particles was obtained similar to as explained above [1]. This xerogel was then crushed and mixed with activated carbon to get a molar ratio of C:Si equal to 4.1:1. This mixture was heated in a ceramic tube of a furnace at 500°C for 4 h. The furnace was flushed with argon to get rid of any oxygen. While heating the atmosphere in the furnace was controlled at H_2/Ar ratio of 9%. The iron oxide is reduced to iron nanoparticles. The system was then heated to 1400°C for 2 h in presence of argon and then allowed to cool down to room temperature. Light green material was found on the inner wall of the ceramic tube and was characterized by TEM and XRD.

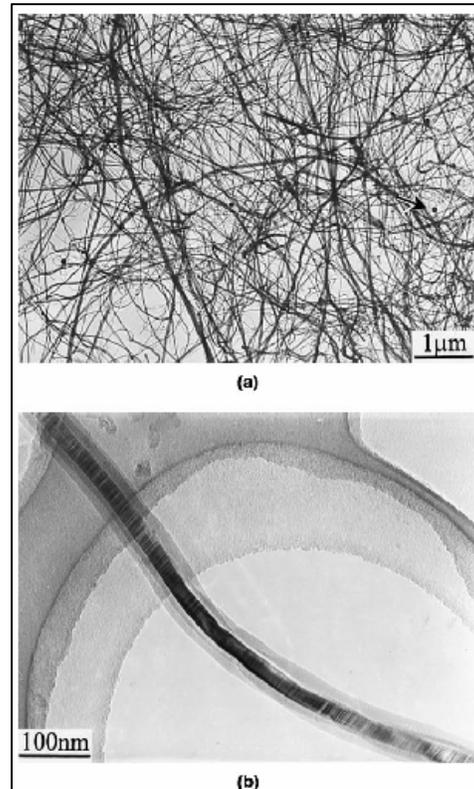


Figure 3 [2] TEM images of SiC nanowires

The TEM image 3(a) showed that the nanowires formed a web-like structure. They had diameters of 20-50 nm and were several microns long. Some nanoparticles attached to the ends of these nanowires can be also seen. A high magnification TEM image 3(b) clearly shows that the nanowires is made up of a core covered by another layer. The XRD pattern 4(a) has three strong peaks at 36° , 60° and 71.5° , which correspond to cubic SiC. A fourth peak at 33.5° arises due to the stacking faults in the core. The nanowires grows in the direction perpendicular to the [111] plane. The EDX spectra 4(b,c) of the nanowires core indicate the presence of only carbon, silica and oxygen while the nanoparticle is seen to contain iron as well. The chemical composition of the wire can be assumed to be 45.56 atomic% silicon, 27.08 atomic% carbon and 27.36 atomic% oxygen. All of the carbon is used up to from silicon carbide (SiC) in the core. The remaining silicon combines with oxygen to form silica ($\text{SiO}_{1.48}$) in the shell.

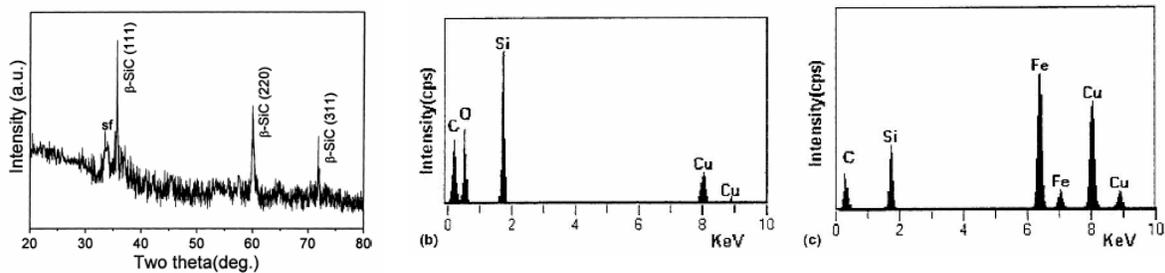


Figure 4 [2] (a) XRD pattern of nanowire and EDX spectra of (b) nanowire core and (c) nanoparticle

The process of formation of wires can be explained in brief as follows. The silica undergoes carbothermal reduction at 1400°C to give silicon monoxide and carbon monoxide. The iron particles in silica xerogel evaporate to form a vapor, which has SiO, CO and Fe. Upon contact with the ceramic tube, nanosize liquid droplets of Fe-Si-C alloy are formed and these form the nuclei point for the formation of the SiC nanowire. As the carbothermal reaction proceeds, SiO and CO concentrations increase. These two then react to give Si and C, which will supersaturate in the liquid alloy to form SiC wires. This is also evident from the fact that no SiC wires were observed on the reactant or source materials, thus their origin is from the reaction between SiO and CO catalyzed by Fe nanoparticles. The melting point of iron is reduced due to the presence of the silica and thus the reaction can be carried out at lower temperatures. The $\text{SiO}_{1.48}$ layer is a result of the reaction between SiO and O_2 . The photoluminescence spectrum of the nanowire shows two peaks at 340 nm and 440 nm. The first peak is suggested to be due to the amorphous SiO_x layer, while the latter blue peak is an effect of the SiC nanorods.

MENG et al [3] report findings of a joint study between the Chinese Academy of Science and the Max Planck Institut (MPI) für Metallforschung. SiC nanowires were synthesized in the exact similar

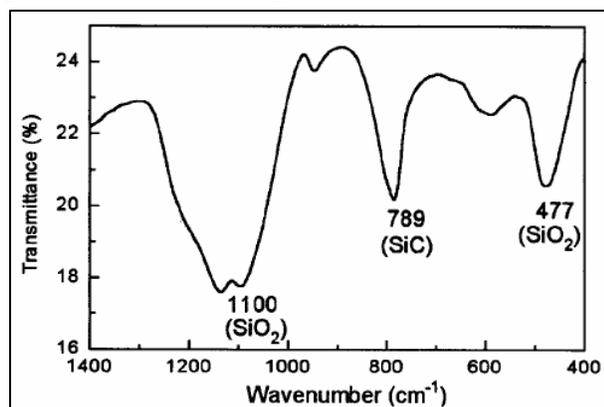


Figure 5 [3] IR spectrum of nanowires with SiC core

manner as Liang et al [2]. In this case too the SiC nanorods had a shell of silica, referred to as silica wrappers. The dimension of the core was 10-25 nm in diameter and 20 μm in length. The wrappers had an outer diameter of 20-70 nm. Although in this case infrared (IR) spectroscopy was used for characterization purposes. The IR spectrum in Figure 5, the absorption band at 789 cm^{-1} corresponding to SiC while SiO_2 has characteristic absorption bands at 477 and 1100 cm^{-1} . The HRTEM and EDX confirm that the nanowire can be divided into the SiC core and the SiO_2 shell.

WU et al [4] synthesized amorphous silica nanowires through the carbothermal reduction process. The reaction takes place between the silicon dioxide and active carbon. The silica nanowires show emission of bright blue light upon excitation and can be used in high-resolution scanning optical microscopy. The growth mechanism was also explained by the VLS model. The experimental procedure consisted of crushing 4 g silica, 250 mg iron nitrate and 4 g active carbons. The were then pressed into circular pellets and calcined in a furnace with alumina tube at 1350°C for 3 h in an inert atmosphere of argon and allowed to cool to room temperature. The resultant white product was characterized by TEM and the composition was studied by XPS.

As shown in Figure 6, three types of wires were observed. These are polyp-shaped 6(a) which had a trunk and branches sticking out of the main backbone. The trunk was seen to be a bunch of nanowires and had an average diameter of 110nm and length of a few hundred microns, while the branches were 60 nm thick and $5\mu\text{m}$ long. The second set of nanowires were amoeba-shaped 6(b) and had a diameter of 70 nm. The third picture shows a very curious shape of nanowires. The nanowires were formed by attachment of nanospheres to form pearl-like chains. The particles vary in size from 60 nm to 100 nm. These were termed as frog-egg-shaped 6(c).

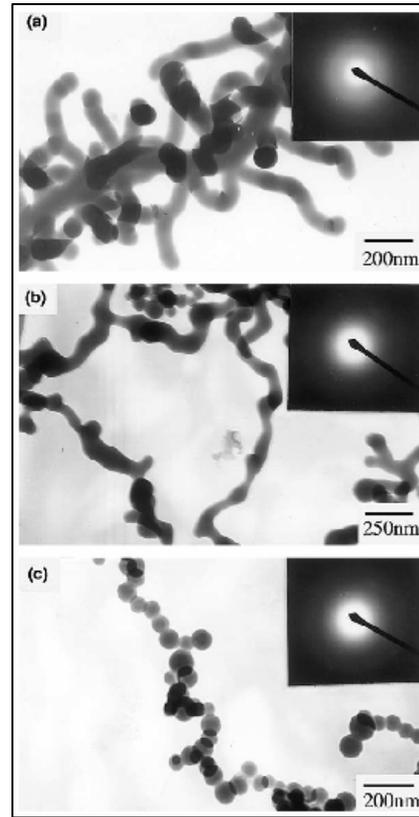


Figure 6 [4] Silica Nanowires

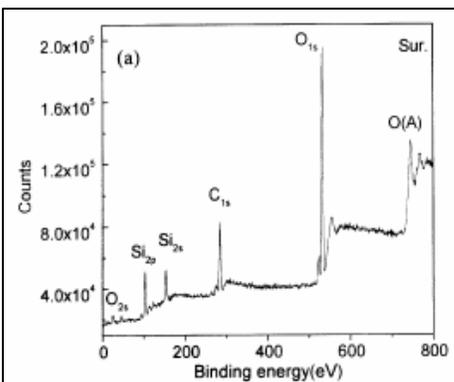


Figure 7 [4] XPS of Silica Nanowires

The nanowires were formed by attachment of nanospheres to form pearl-like chains. The particles vary in size from 60 nm to 100 nm. These were termed as frog-egg-shaped 6(c).

The SAED patterns in Figure 6 indicate that the nanowires are amorphous in nature. The composition of the nanowires was determined by XPS. The spectrum in Figure 7 shows three strong peaks of interest. The Si(2p) peak at 103.35 eV and the O(1s) peak at 532.65 eV correspond the SiO_2 . Quantitative analysis gives a Si:O atomic ratio of 1:2.41. A third peak at 284.65 eV is due to C(1s) and arises due to any residual carbon

present as result of the reaction.

In Figure 8, the photoluminescence spectrum of these wires reveals emission of intense blue light (435 nm) under excitation at 260 nm. In addition to this, ultraviolet (350 nm) and other blue light emissions (420 and 465 nm) are also seen.

The growth process is convincingly explained by the VLS mechanism. The morphology of the wire has spherical nanoparticles, which can be said to form from liquid droplets. Initially carbothermal reduction of silica gives SiO and Si, which reacts with iron to form FeSi₂. This FeSi₂ form liquid droplets, which act as catalytic nucleating points. Finally the vapor of silicon and silicon-monoxide forms nanowires at these nucleation growth centers. The oxidation of SiO and Si to amorphous SiO₂ wires takes place during the cooling step.

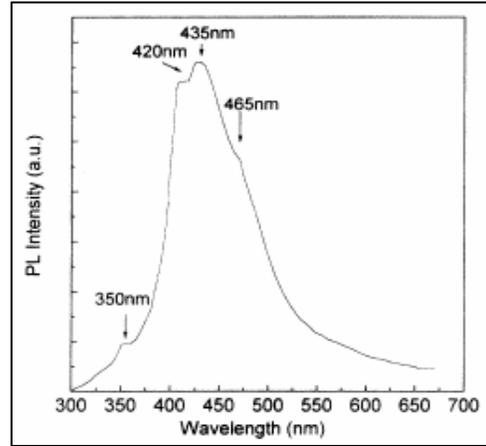


Figure 8 [4] PL spectrum

The different morphologies arise due to the effect of monocentric and polycentric nucleation and its combination with periodic stable and unstable growth. The uniform diameter of the trunk and branches in polyp-shaped nanowires suggests that periodic stable growth took place. The branches are a result of polycentric nucleation because of FeSi₂ nanoparticles. The amoeba-shaped nanowires are a result of monocentric nucleation and instability in growth, which is evident due to the varying diameter. In both these cases the dark black spots are the nucleation sites from where the wires start to grow. The frog-egg shaped nanowires are formed due to deposition of silicon oxide nanoparticles on account of their surface tension. The high reaction temperature is suggested to cause the necks between the adjoining particles.

TANG et al [5] synthesized nanowires of gallium oxide and gallium nitride that were 20-60 nm in diameter and several microns in length. The growth mechanism was seen to be similar to the VLS mechanism in which iron oxide was used as the catalyst.

A solution of ferric nitrate is mixed with alumina and methanol to form a slurry that is dried and baked under vacuum at 150°C. The resultant product, which is the ferric oxide catalyst is then ground into a fine powder. Fumed silica is dried to remove any moisture and carbon dioxide and mixed thoroughly with the ferric oxide catalyst and gallium metal. The powder is then introduced in a furnace at 1200°C under the influence of a constant flow of ammonia for 1 h. After appropriate time the furnace is allowed to cool. During this process the ammonia is replaced by argon gas.

The white product was then studied using XRD and TEM. The XRD results confirm that the crust powder is made up of monoclinic crystalline gallium oxide. Calculations done on the XRD reveal the lattice parameters of $a = 12.25 \text{ \AA}$, $c = 3.10 \text{ \AA}$ and $\beta = 103.72^\circ$. The TEM image in Figure 9 show that the nanowires are straight in nature and have a diameter close to 20-60 nm. The SAED pattern has bright spots, which also confirms that the nanowires are crystalline in nature. The gallium nitride wires are

formed upon introduction of ammonia in the furnace. The diameters of these wires range from 10-50 nm, while they are a few microns long.

The presence of the nearly spherical nanoparticles at the ends of the nanowires suggests that a vapor-liquid-solid (VLS) growth mechanism is present. To prove this, it should be first proved that a liquid is present somewhere in the system. The melting point of iron (1540°C) is far greater than the temperature used for the reaction (1200°C). But the presence of the Si particle reduces the melting point to form liquid alloy of FeSi. Moreover it is known that nanoparticles melt at a lower temperature than the bulk of the same substance. Thus formation of liquid iron (catalyst) droplets is quite possible. The gallium reacts with silica and iron oxide to get gallium monoxide and elemental silicon and iron. This leads to the formation of the liquid Fe-Si droplets that can initiate the vapor-liquid-solid growth to synthesize nanowires. The vapor consists of gallium monoxide and silicon monoxide, which is liberated when silicon reacts with silica. These two gases react in the droplet to form gallium oxide, which upon supersaturating begins to grow as a nanowire.

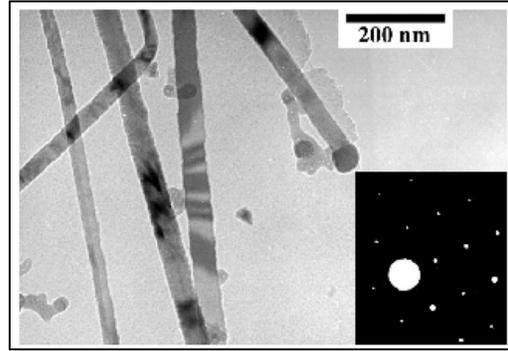


Figure 9 [5] TEM image of Ga_2O_3 nanowire

When ammonia is introduced, it reacts with the gallium monoxide to get gallium nitride. This reaction is also catalyzed by the Fe-Si droplets. Gallium nitride (GaN) nanowires are formed when it starts supersaturating in the droplets.

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HUANG and co-workers [6] give an application of such GaN wires in field effect transistors (FETs). The field effect transistor is a device, which is used to control an electric signal with another signal. It is made up of a source and a drain, which enable passage of the signal to be controlled. The middle portion of the FET is called the gate, which is the controlling signal. The controlling signal can increase or decrease the flow of the electrons (and consequently the electric signal) through the source and the drain.

In this study the GaN nanowires were dispersed onto a conducting silicon substrate. The nanowires were oriented in the direction of flow of current. The two ends of the nanowire were used as the source and the drain, while the silicon substrate served as the gate. The nanowires had an average diameter of 10 nm and lengths up to 10 μm . The measurements were done at room temperature. The gate voltage, V_g , was varied from -8 to 6 volts. It was seen that no current was conducted through the nanowire at V_g of -8 volts, while at V_g equal to 6 volts a maximum of 2000 nA of current flowed through. This can be clearly seen from Figure 10, which is a plot of I_{sd} vs. V_{sd} at different V_g . The subscript 'sd' refers to the current and voltage between the source and the drain. The plot of I_{sd} vs. V_g (Figure 11) indicates

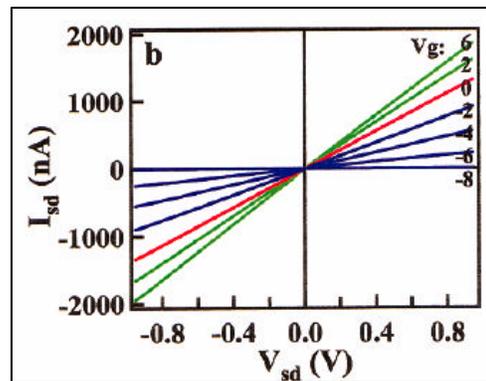


Figure 10 [6] Dependence of I_{sd} on V_{sd}

that the GaN nanowires behave as n-type semiconductors. The n-type behavior in the undoped sample might be due to the nitrogen vacancies and/or oxygen impurities. The electron carrier densities for the nanowires were calculated to be 10^{18} to 10^{19} cm^{-3} . Electron mobilities for these nanowires were seen to range from 150 to 650 cm^2/Vs . Under same conditions GaN thin films reported mobilities of 100-300 cm^2/Vs , while carbon nanotubes FETs had mobilities around 20 cm^2/Vs .

The authors suggest that due to their large carrier mobilities as compared to GaN thin films and carbon nanotubes, n-type GaN nanowires can be coupled with p-type silicon nanowires to build a p-n junction. Such junctions can be used in functional electronic devices. They further predict the use of such nanowires as LEDs when forward biased, logic gates, p-n diodes

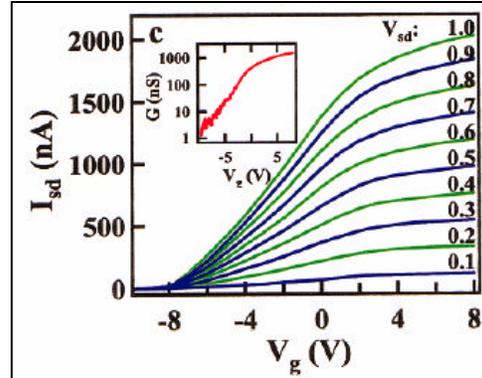


Figure 11 [6] Plot of I_{sd} vs. V_g

ZHANG et al [7] studied formation of silicon nanostructures and silicon nanowires. An alternate mechanism to the conventional VLS, termed as the oxide-assisted nucleation, was proposed to form the nanowires. The system used for the tests consisted of a vapor of silicon oxide. The composition of the gas phase is critical to the formation of the nanowires. The vapor itself contains gas phase silicon oxide clusters, which can be divided into the oxygen-rich clusters, the silicon-rich clusters and silicon monoxide-like structures. These three types can be defined based on a silicon oxide molecule, Si_mO_n . For oxygen-rich clusters, $m = n+2$, while for the silicon rich clusters, $m = n+2$. The silicon monoxide-like clusters were denoted by $(\text{SiO})_n$. It was seen that the silicon-rich clusters had weaker Si-Si and Si-O bonds than the oxygen-rich and monoxide-like clusters. This makes the release of Si atoms from the clusters highly probable.

The plot binding energies and number of oxygen atoms for various combinations of m and n , Figure 12, gives a minimum at the middle, indicating that the favorable atomic ratio of silicon to oxygen in the clusters is 1:1. Density of states (DOS) calculations were further carried out over these favored clusters. The DOS calculations help deduce the effect of the constituent atoms on the formation of the structure, by providing information about the bonding between the atoms, and their reactivity towards other atoms.

The vapor phase silicon oxide clusters interact to form large clusters or deposit on the substrate. This process is controlled by the reactivity of the silicon oxide, which in turn depends on the composition of the silicon oxide clusters. The silicon atoms in the silicon suboxide

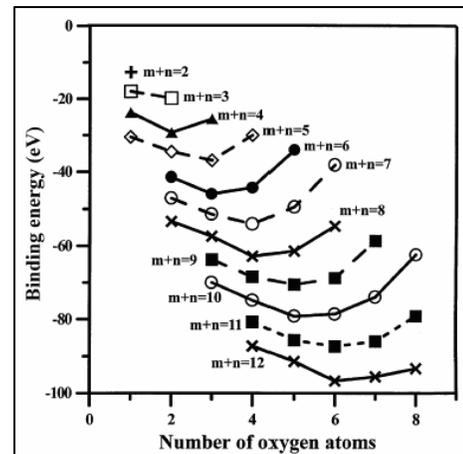


Figure 12 [7] Binding energies of silicon oxide clusters

clusters are highly reactive and readily react with other silicon oxide clusters in the gas phase. In all the clusters it is the silicon atoms, which are the favored sites to form bonds with other atoms. The silicon-rich clusters form a Si-Si bond upon reaction with other silicon oxide clusters, while the oxygen-rich clusters form an Si-O bond. During the synthesis of a silicon nanowire, a fraction of the silicon atoms in the silicon-rich clusters react with the substrate to form strong bonds with the substrate atoms. These strong bonds restrict the movement of the cluster and thus protect the other unreacted silicon atoms. These unreacted silicon atoms are in contact with the vapor and act as nuclei to react with the gas phase silicon oxide clusters. This process carries on to form a silicon nanowire. The oxygen atoms in the silicon-oxide clusters are expelled towards the boundary of the nanowires, where they form a layer of silicon oxide. The oxygen-rich sheath was seen to have less reactivity and this prevents any growth in a direction normal to the silicon wire. Thus if the silicon oxide clusters have a high Si:O ratio (> 1), there is a greater chance to form nuclei of reactive silicon atoms. But the binding energy plot shows that the probability that such clusters are present in the gas phase is very low, the Si:O ratio of 1:1 being the favored type. The silicon wires thus formed were seen to have some crystalline orientation.

Summary:

Nanowires of different compositions can be synthesized by the vapor-liquid-solid (VLS) growth mechanism, the carbothermal reduction mechanism, a combination of these two and by oxide assisted nucleation process. The composition of the nanowires varied from amorphous silicon oxide to crystalline silicon carbide and silicon. Some wires were seen to be made of a core crystalline structure surrounded by a amorphous silica sheath. The nanowires possessed diameters from 10 nm to 60 nm and also had different morphologies. Some of the nanowires were straight and smoothly curved while others had structures which were helical, braided-like polyp-shaped amongst others.

The nanowires can be used in newer electronic nanodevices as well as in mesoscopic physics. Some applications of such nanowires are use in probes for near field scanning optical microscopy, light emitting diodes (LEDs), other diodes and field effect transistors (FETs).

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