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Molten Gallium as a Catalyst for the Large-Scale Growth of Highly Aligned Silica Nanowires

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Abstract: The vapor−liquid−solid (VLS) process is a fundamental mechanism for the growth of nanowires, in which a small size (5−100 nm in diameter), high melting point metal (such as gold and iron) catalyst particle directs the nanowire's growth direction and defines the diameter of the crystalline nanowire. In this article, we show that the large size (5−50 μm in diameter), low melting point gallium droplets can be used as an effective catalyst for the large-scale growth of highly aligned, closely packed silica nanowire bunches. Unlike any previously observed results using gold or iron as catalyst, the gallium-catalyzed VLS growth exhibits many amazing growth phenomena. The silica nanowires tend to grow batch by batch. For each batch, numerous nanowires simultaneously nucleate, grow at nearly the same rate and direction, and simultaneously stop growing. The force between the batches periodically lifts the gallium catalyst upward, forming two different kinds of products on a silicon wafer and alumina substrate. On the silicon wafer, carrot-shaped tubes whose walls are composed of highly aligned silica nanowires with diameters of 15−30 nm and length of 10−40 μm were obtained. On the alumina substrate, cometlike structures composed of highly oriented silica nanowires with diameters of 50−100 nm and length of 10−50 μm were formed. A growth model was proposed. The experimental results expand the VLS mechanism to a broader range.

Introduction

The vapor−liquid−solid (VLS) crystal growth mechanism, proposed by Wagner and Ellis in 1964 for silicon whisker growth,[1,2] has been widely used to guide the growth of various kinds of one-dimensional nanostructures, such as carbon nanotubes,[3,4] nanowires of element semiconductors,[5,6] compound semiconductors,[7,8] and oxides.[9,10] In this mechanism, a liquid eutectic alloy droplet composed of metal catalyst component (such as Au, Fe, etc.) and nanowire material (such as Si, III−V compounds, II−V compounds, etc.) is first formed under the reaction conditions. This liquid droplet serves as a preferential site for absorption of gas-phase reactant and, when supersaturated, the nucleation site for crystallization. Nanowire growth begins after the liquid droplet becomes supersaturated in reactant material and continues as long as the catalyst alloy remains in a liquid state and the reactant is available. During growth, the catalyst droplet alloy directs the nanowire's growth direction and defines the diameter of the crystalline nanowire. Ultimately, the growth terminates when the temperature is below the eutectic temperature of the catalyst alloy or the reactant is no longer available. As a result, the nanowires obtained from the VLS processes typically have the following morphological and microstructural features. First, each nanowire terminates at one end in a solid catalyst nanoparticle with diameter comparable to that of the connected nanowire. Second, the nanowires are single crystal with growth direction mostly along [111]. Finally, the nanowires are usually free-standing, randomly distributed, and tangled together. Recently, a solution−liquid−solid (SLS) crystal-growth mechanism, which is analogous to the VLS mechanism, was developed by Buhro and co-workers to grow III−V semiconductor nanowhiskers in solution.[11] It is interesting that the morphologies and microstructures of the SLS-grown nanowhiskers are very similar to that of the VLS-grown nanowires.

The VLS growth mechanism requires the catalyst alloys to be in the liquid state under nanowire growth temperature to serve as a solvent for effectively absorbing and solving reactants from the vapor phase. The nanowire growth temperature is determined by the eutectic temperature of the alloys, which is usually far below the melting temperature of the metal catalyst. For example, VLS growth of Si nanowires can be carried out at temperature on the order of 400−500 °C using Au (melting

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point, 1064 °C) as the catalyst,[6] because of the low eutectic temperature (363 °C) of the Au−Si alloy. In this regard, the Si nanowires could be grown at a much lower temperature if the low-melting-point metal Ga (melting point 29.78 °C) was used as the solvent, since the Ga−Si phase diagram shows a eutectic point of 29.774 °C at only about 0.006 mol % Si.[12] Ga has already been used as a solvent in the low-temperature synthesis of GaAs and GaP whiskers[13] and GaAs[14] and $Ga(As_{1-x}P_x)$[15] crystals. Recently, Chen et al.[16] used molten Ga as a solvent for exploratory synthesis of ternary silicides crystals. Their results show that, for Si-based compound synthesis, Ga seems particularly good due to (i) its ability to solve Si at a wide range of temperature and (ii) its nonreactivity with Si to form stable solid compound. These two important characteristics are actually the crucial criteria for choosing catalyst in the VLS process.[1,2,5−7] Thus, it is reasonable for us to anticipate the synthesis of one-dimensional Si-based nanostructures, such as Si nanowires, by using molten Ga as the catalyst via a VLS process.

While attempting to grow Si nanowires by using molten Ga as a catalyst and silicon wafer as a Si source, we unintentionally obtained SiO_2 nanowires in a high yield.[17] Surprisingly, these nanowires demonstrate many amazing growth phenomena unlike any previously observed through a conventional VLS growth process. The main findings in our experiment are as follows (see the figures and text below for detail): (i) Large size (5−50 μm in diameter) molten Ga droplets could be used as an effective catalyst for amorphous SiO_2 nanowire growth. (ii) Each Ga droplet could simultaneously catalyze growth of hundreds of thousands of SiO_2 nanowires, and the nucleation occurred continuously during whole growth process. (iii) The SiO_2 nanowires tended to grow batch by batch, and they were highly aligned in both macro- and microscale. These findings are apparently different from the conventional VLS processes described above and, thus, greatly enrich the current VLS growth mechanism. A growth model corresponding to these unique growth phenomena was proposed in this paper.

Experimental Section

The key factor for our synthesis using molten Ga as catalyst is how to obtain small, uniform-sized, and evenly distributed Ga droplets. It is well-known that Ga has the longest temperature range in the liquid phase (from 29.78 to 2403 °C). In addition, small molten Ga droplets tend to agglomerate due to its high surface tension. Thus, it is very difficult to get the desired Ga droplets by using the regular sputter coating and subsequent annealing technique, although it has been successfully used to create nanometer scale Au[10] and Fe[4] catalyst particles. To overcome this problem, we use an indirect method, i.e., thermal decomposition of GaN powders, to get the desirable Ga droplets. Our results showed that by using this indirect manner, Ga droplets with diameters of 5−50 μm were evenly distributed on the nanowire growth substrates.

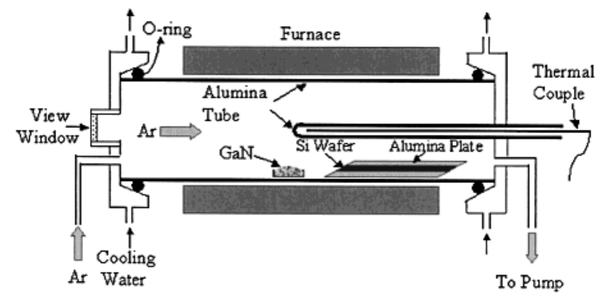

Figure 1. Schematic experimental setup for the growth of SiO_2 nanowires. The GaN powders were placed in an alumina crucible located at the center of an alumina tube. A long silicon wafer stripe (10 × 1 cm^2) is placed on the middle part of a wide alumina plate (10 × 3 cm^2). The temperature range of the SiO_2 nanowire formation region was determined by a in-situ temperature-measuring device.

Materials and Substrates. GaN powders (99.99%) were used as received from Alfa Aesar. Ultrahigh-purity argon (99.999% of purity with O_2 and H_2O contents less than 4 molar ppm and 3.5 molar ppm, respectively) was used as the carrier gas. Substrates of silicon(100) wafers and alumina plates were ultrasonically cleaned in acetone for 30 min before use.

Growth of SiO_2 Nanowires. The experimental setup for SiO_2 nanowires growth is described schematically in Figure 1. In our approach, 1−2 g of GaN powders is placed at the center of an alumina tube that is inserted in a horizontal tube furnace, where the temperature, pressure, and reaction time are controlled. A long silicon wafer stripe (10 × 1 cm^2) is placed on the middle part of a wide alumina plate (10 × 3 cm^2), which is located 10 cm away from the GaN powders at the downstream end of the alumina tube. After evacuation of the alumina tube to $\sim 2 \times 10^{-3}$ Torr, the reaction is conducted at 1150 °C for 5 h under a pressure of 400 Torr and argon gas flow rate of 50 sccm (standard cubic centimeters/minute). At the reaction temperature of 1150 °C, the GaN powders are decomposed into a dense, hot vapor of Ga and N_2. The hot Ga vapor rapidly condenses into small Ga clusters as the Ga species cool through collision with the buffer gas (with the unintentional presence of oxygen in our reaction chamber,[17] there may also exist gallium oxide clusters, such as Ga_2O, in the vapor). The formed Ga clusters are transferred to the downstream end of the alumina tube by the carrier gas and then deposited onto the surface of the silicon wafer and the naked part of the alumina plate in the regions with temperatures <1070 °C. Our results show that Ga droplets with diameters <1 μm can be evenly distributed on the surfaces of the silicon wafer and alumina plate at the early reaction stage; however, the diameters of the Ga droplets increase with the reaction time through continuously accepting the upcoming Ga clusters and are typically in the range of 5−50 μm after 5 h of reaction. The Ga droplets deposited on the silicon wafer etch silicon to form Ga−Si alloy and thus create a dense vapor of Si species around the silicon wafer and alumina plate, which acts as Si source for the growth of SiO_2 nanowires.

During evaporation, the temperature at any point between the tube center and the tube's downstream end was measured in situ by a sheathed thermocouple, allowing us to readily measure the temperature range of the SiO_2 nanowire formation region.

Morphology, Structure, and Composition Characterization. The as-synthesized products are characterized and analyzed by a scanning electron microscope (SEM) (LEO 1530 FEG), transmission electron microscope (TEM) (JEOL 100C at 100 kV and Hitachi HF-2000 FEG at 200kV), and energy-dispersive X-ray spectroscope (EDS) attached to the SEM and TEM. For SEM investigations, the products together with the growth substrates were directly transferred into the SEM chamber, without destroying the location and orientation of the products on the substrates. For TEM studies, some samples were scrapped off from the growth substrates and were directly mounted on Cu folding TEM grids.

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(17) The formation of SiO_2 nanowires is due to the presence of a small amount of oxygen mainly resulted from the inevitable leakage of the vacuum system. The synthesis is conduct in an alumina tube that is sealed by O-ring (see Figure 1 in text for the experimental apparatus). The ultimate vacuum for this configuration is $\sim 2 \times 10^{-3}$ Torr. When the pump is turned off, apparently leakage can be observed through the reading of a high accurate vacuum gauge. The calculated leakage rate for air is about 0.5 sccm.

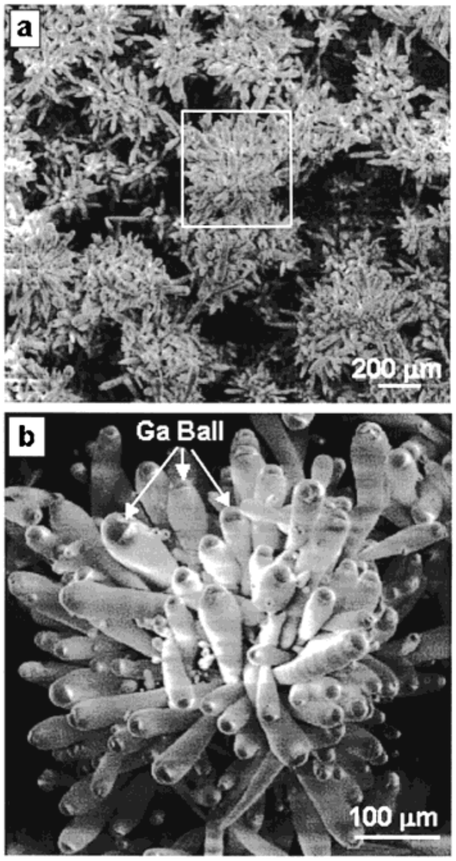

Figure 2. SEM images of the SiO_2 nanowires grown on a silicon wafer: (a) low-magnification SEM image of the as-grown products, showing carrot-shaped rods (CSRs) growing in-groups on the silicon wafer; (b) high-magnification SEM image of the boxed area in (a), showing several tens of CSRs forming a sisallike structure. Note that each CSR has a liquid Ga ball at its tip.

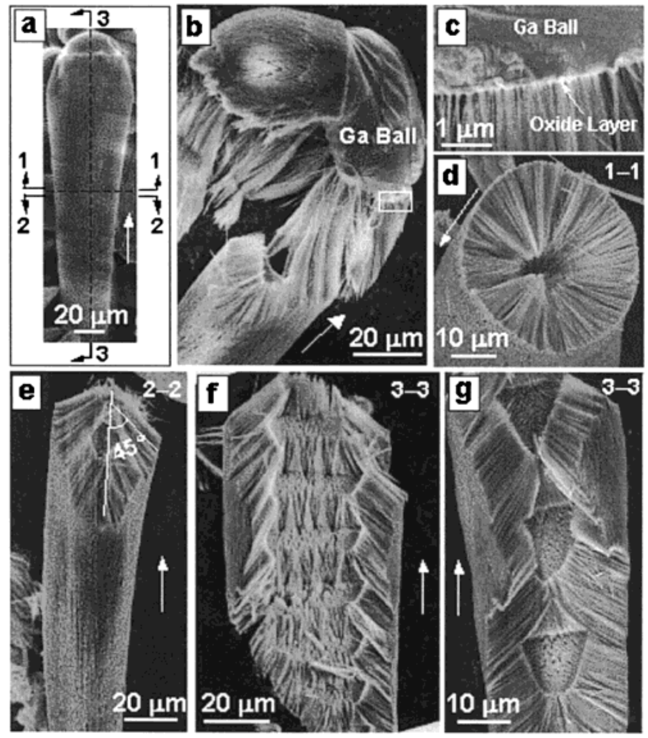

Figure 3. SEM images of the inner structure of the CSRs: (a) an individual CSR used as an example to show the dissection along direction either perpendicular (1−1, 2−2) or parallel (3−3) to its long axis; (b) SEM image of a dissected CSR at its tip region, showing a large quantity of nanowires growing out from the lower hemisphere surface of a Ga ball; (c) high-magnification SEM image from boxed area in (b) with the oxide layer composed of Ga, Si, and O; (d) cross section of a CSR viewed along the 1−1 direction, showing a tubular structure whose wall is composed of closely packed and highly aligned nanowires where the two ends of the nanowires respectively construct the tube's inner and outer walls; (e) cross section of a CSR viewed along the 2−2 direction, displaying an angle of ∼45° between the growth direction of the nanowires and the axis of the tube; (f, g) two cross sections viewed along the 3−3 direction, displaying two kinds of inner structures of the CSRs. The image in (f) shows a continuous central hole with stairlike structure; the image in (g) shows discontinuous upside down bell-like cavities. The white arrows in (a), (b), and (d)−(g) show the growth direction of the CSRs.

Results and Discussion

SEM Results. After the reaction, colorless and transparent products were formed on both the silicon wafer and alumina plate, covering approximately a 4-cm region and temperature range of 850−1000 °C. SEM observations reveal that the products formed on the silicon wafer and alumina plate have different morphology, size, size distribution, and orientation. On the silicon wafer, carrot-shaped rods (CSRs) with diameters of 10−50 μm and lengths of up to ∼1 mm were grown in groups in a high yield (Figure 2a). For each group, several tens of CSRs radially grow upward, forming a sisallike structure (Figure 2b). Each CSR terminates at its top end in a large spherical ball with diameter comparable to that of the connected rod. This corresponds to the morphology of VLS-grown nanowires, suggesting that the growth of the CSRs is likely governed by the VLS mechanism. However, unlike the conventional VLS process, the large terminating balls in our case are still in the liquid state at room temperature.[18] EDS analyses reveal that the balls are liquid Ga covered by a thin oxide layer composed of Ga, O, and a small amount of Si.

To investigate the internal structures of the CSRs, we dissected several CSRs along direction either perpendicular or parallel to their long axes, as that depicted in Figure 3a, and several amazing growth phenomena were then observed.

First, the CSRs are not solid rods; instead, each CSR is composed of numerous, highly aligned, and closely packed nanowires (Figure 3b−g). These nanowires are of uniform diameters (10−30 nm) and lengths (10−40 μm). Quantitative EDS analyses of the nanowires show that the nanowires have a composition close to SiO_2; no other element such as Ga is detected at the 1 at. % sensitivity level of our instrument.

Second, each Ga ball attaches to hundreds of thousands of SiO_2 nanowires that grow out perpendicularly from the surface of the ball's lower hemisphere (Figure 3b); that means, each Ga ball can simultaneously catalyze growth of many SiO_2 nanowires, which is quite different from the conventional VLS processes, in which one catalyst particle usually catalyzes growth of just one nanowire. Both high-magnification SEM image (Figure 3c) and EDS analyses show that the SiO_2 nanowires connect with the molten Ga ball through a thin oxide layer composed of Ga, Si, and O. The function of this oxide layer is to provide Si and O species for the growing SiO_2 nanowires.

Third, the CSRs have a tubular structure; that is, there is a central hole along the long axes of the CSRs (Figure 3d−g). It

(18) The melting point of metal Ga is 29.78 °C, ∼4.78 °C higher than room temperature. The Ga−Si phase diagram shows a eutectic temperature of 29.774 °C at about 0.006 mol % Si. The liquid state of the Ga balls at room temperature may be due to the impurities in the volume.

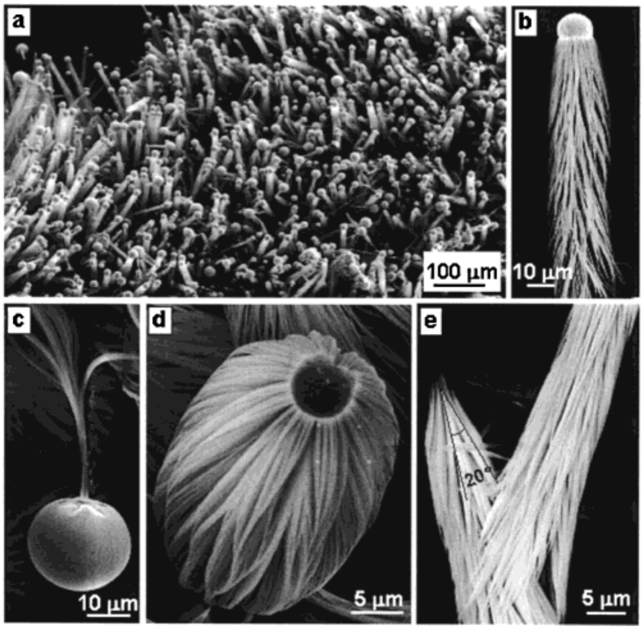

Figure 4. SEM images of the SiO_2 nanowires grown on an alumina substrate: (a) low-magnification SEM image of the as-synthesized products, showing a large quantity of cometlike structures growing perpendicularly from the substrate to form an array; (b) high-magnification SEM image of a cometlike structure, showing that the tail part of the comet is composed of highly oriented SiO_2 nanowires; (c) cherrylike structure; (d) cometlike structure with the Ga ball being removed off, leaving a bowl-shaped cavity at its tip; (e) broken cometlike structure, displaying an angle of $\sim$20° between the growth direction of the nanowires and the axis of the comet.

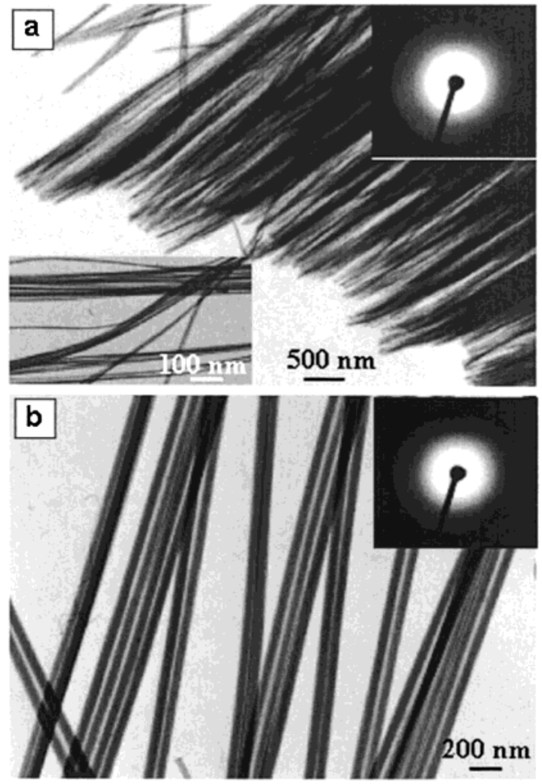

Figure 5. TEM images of the SiO_2 nanowires: (a) bundle of SiO_2 nanowires grown on silicon wafer, showing amorphous (upper right inset) and very thin nanowires with average diameter of $\sim$20 nm (lower left inset); (b) SiO_2 nanowires grown on alumina substrate, showing paired amorphous (inset) and straight nanowires with average diameter of $\sim$60 nm.

is very interesting that the walls of the tubular structures are composed of a large quantity of highly aligned SiO_2 nanowires. The nanowires within the wall arrange at an angle of 30−60° to the axis of the tube, and the two ends of the wires respectively construct the tube's inner and outer walls.[19] The outer wall of the tube is relative smooth, while the inner wall is rough, and it usually exhibits a stairlike structure with almost the same step height of $\sim$10 μm (Figure 3f). Most tubes have a continuous hole running through out their entire lengths (Figure 3f), but in some case like that shown in Figure 3g, the hole is discontinuous and consists of a series of upside down bell-like cavities with almost the same interval between bells. The outer and inner diameters of the tube gradually increase at approximately the same rate from the tube's bottom end to the top end; for an individual tube, the nanowires in it have similar lengths and growth directions, resulting in the thickness of the wall being relatively constant. The regularity of the internal structures of the tubes suggests that the nanowires within a tube grow batch by batch. For each batch, the nanowires simultaneously nucleate, grow at nearly the same rate and direction, and simultaneously stop growing. As will be discussed in depth later, the hole or cavities inside the tube comprise the moving track of the Ga ball, which is periodically lift upward by the nanowires grown batch by batch.

We also investigated the products formed on the alumina plate, and shown in Figure 4a is a typical SEM image. Numerous cometlike structures grow out perpendicularly and separately from the surface of the alumina plate to form a comet array. Both high-magnification SEM image (Figure 4b) and EDS analyses reveal that the tail part of the cometlike structure is composed of a large quantity of oriented SiO_2 nanowires with diameter of 50−100 nm and length of 10−50 μm, while the tip is molten Ga covered with a thin oxide layer. Thus, the products formed on the alumina plate have the same composition as those formed on the silicon wafer. However, detailed SEM studies reveal some differences in morphology and inner structure between these two kinds of products. First, the cometlike structures are much thinner than the CSRs, with typical outer diameters in the range of 5−30 μm and lengths $<$500 μm; the diameters of the molten Ga balls are in the range of 5−20 μm. Second, the SiO_2 nanowires only grow from a small area of the ball's lower hemisphere, resulting in a low wire density in the cometlike structures. In some extreme case, only hundreds of nanowires connect to the ball, forming a cherrylike morphology, as that shown in Figure 4c. In addition, the Ga ball in the cometlike structure can be easily removed, leaving a bowl-shaped cavity on the top of the comet (Figure 4d). Third, no apparent hole or cavity is found in the broken cometlike structures (Figure 4e). Figure 4e also shows that the SiO_2 nanowires in the cometlike structure grow at a sharp angle to the axis, with a value usually less than 30°.

TEM Results. The microstructures of the SiO_2 nanowires were characterized by TEM. Figure 5a,b shows the TEM images of the SiO_2 nanowires grown on the silicon wafer and alumina plate, respectively. Both kinds of nanowires have a uniform diameter along their entire length and a very narrow diameter

(19) Actually, the outer wall of the tubular structure also contains many other wires' tips. These nanowires grow out from the existing nanowires, forming a branch structure. We call such growth manner as "split growth" in the text.

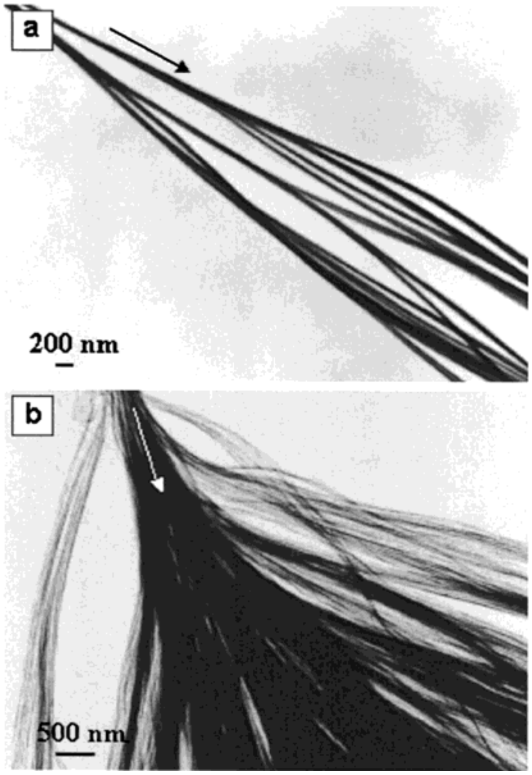

Figure 6. TEM images showing the split growth in the SiO_2 nanowire samples: (a) nanowires grown on alumina substrate, displaying split growth phenomenon; (b) image of the nanowires grown on silicon wafer, showing the amount and volume of the nanowires increasing tens of times within a short distance (~5 μm) through the split growth. The arrows show the nanowires' growth direction.

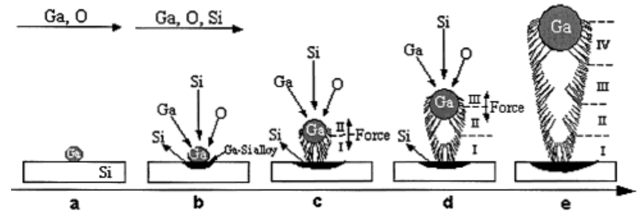

Figure 7. Proposed growth model for CSRs with stairlike inner structures (refer to Figure 3f). (a) The decomposition of GaN powders produces a vapor of Ga that rapidly condenses into liquid Ga clusters. These Ga clusters then deposit onto the surface of the silicon wafer and grow into small Ga balls as the upcoming Ga clusters are absorbed from the vapor. (b) The hot liquid Ga ball etches the silicon wafer to form Ga−Si alloy. The Si in the Ga−Si alloy evaporates into the gas to create a dense vapor of Si species around the silicon wafer region. At this stage, the vapor consists of Ga, O, and Si, and thus, the Ga ball can also absorb Si species from the vapor. (c) When the concentrations of Si and O in the Ga ball are high enough, the Si and O will react to form many SiO_2 nanoparticles on the surface of the lower hemisphere of the Ga ball. These particles act as the nucleation sites, initiating the growth of the first batch (batch I) of the SiO_2 nanowires. The Ga ball is then pushed away from the silicon wafer by the growing SiO_2 nanowires. From this stage, the Ga ball can only absorb Si species from the vapor. As this first batch of nanowires proceeds to grow, a second batch (batch II) of nanowires simultaneously nucleates and grows at nearly the same rate and direction above the first. As growth continues, the newly formed nanowires begin to exert a force on the batch below. Note that split growth proceeds during the entire nanowire growth process. (d) When the force is great enough, the second batch of nanowires will lift the Ga ball upward, thereby detaching the first batch of nanowires from the Ga ball and halting their growth. Since the Ga ball is in the liquid state and the nanowires connect to it though a thin oxide layer, the second batch of nanowires will then sink to the position the first batch initially occupied. A third batch (batch III) of nanowires then nucleates and grows above the second. (e) The process of growth and detachment allows the formation of a tubular structure with regular stairlike inner wall. For this case, the nanowires only grow from a band around the lower hemisphere surface of the Ga ball. If the nanowires also grow from the region below the band, CSRs with a series of upside down bell-like cavities (refer to Figure 3g) will be formed.

distribution. The average diameters of the nanowires shown are ~20 nm for Figure 5a and ~60 nm for Figure 5b, with the later ~3 times thicker than the former. Analysis of images taken from a number of nanowire samples grown on silicon wafer and alumina substrate constantly gave nanowire diameters of 15−30 nm and 50−100 nm, respectively. Detailed TEM studies reveal the following similarities for our two kinds of nanowire samples. First, electron diffraction patterns (insets in Figure 5a,b) and EDS analyses show that the nanowires are pure amorphous SiO_2, which is contradictory to the conventional VLS-grown nanowires that are single crystal. Second, split growth occurs in our SiO_2 nanowires; i.e., one nanowire splits into two branches, and the newly formed branch also splits into two subbranches, and so on (Figure 6a). This growth phenomenon has been observed by Zhu et al.[20] in their cobalt-catalyzed SiO_2 nanofibers. It is interesting that the branches or the subbranches have diameter and growth direction similar to their parent one. This split growth occurs quickly and severely for the nanowires grown on the silicon wafers, resulting in the amount and volume of the nanowires increase dramatically within a short distance (Figure 6b). We believe that the split growth phenomenon is responsible for the formation of the compact tubular structures shown in Figure 2.

Growth Model. The above SEM and TEM results indicate that the low melting point metal Ga can serve as an effective catalyst for the growth of amorphous SiO_2 nanowires via a VLS process. Many interesting growth phenomena and results, which have never been seen in the conventional VLS process, were observed in our experiment. Our results unambiguously indicate that molten Ga has different catalytic behaviors for nanowire growth from the commonly used metal catalysts such as Au and Fe. However, the conventional VLS growth mechanism is still suitable to account for the unique growth phenomena reported here. On the basis of the VLS growth mechanism and the SEM and TEM results described above, a growth model is proposed for CSRs with stairlike inner structures (refer to Figure 3f) grown on the silicon wafer, as that depicted in Figure 7.

For a better understanding of this growth model, the following aspects are addressed:

First, nanowire growth of similar composition was observed on both the silicon wafer and the remote alumina plate. This couples with the fact that the SiO_2 nanowires are catalyzed by a Ga ball that is not in contact with the growth substrates suggest that the nanowire growth is governed by a VLS process, in which Si is fed from the vapor phase. The Si vapor is generated from etching of the silicon wafer by the hot liquid Ga (Figure 7b). Indeed, we note that, at the region of SiO_2 nanowire formation, the silicon wafer was etched away to depths of ~50−100 μm after 5 h of reaction and that most of the etched region was still covered with many large molten Ga droplets. These large Ga droplets are thought to be formed in the early stage of the reaction, since in the later stages this region is covered by

(20) Zhu, Y. Q.; Hsu, W. K.; Terrones, M.; Grobert, N.; Terrones, H.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Mater. Chem.* **1998**, *8*, 1859−1864.

a thick layer of high density CSRs, as shown in Figure 2. Throughout the entirety of the synthesis, the Ga droplets on the surface of the silicon wafer continuously etch the silicon wafer, allowing the Si species to be continuously fed into the vapor phase and sustain the SiO_2 nanowire growth. The differences in morphology and inner structure between the products grown on the different substrates can be correlated to concentration differences of the Si species above the two kinds of substrates. The Si concentration above the silicon wafer is much higher than that above the alumina plate, resulting in the products grown on silicon wafer having a larger size and higher density than those grown on alumina plate.

Second, it is apparent that considerable amounts of oxygen are involved in the growth of SiO_2 nanowires. The oxygen may come from (i) the oxide layer on the silicon wafer surface, (ii) the residue oxygen in the reaction chamber, (iii) the Ar gas, or (iv) the leakage of our vacuum system. Although the oxygen from the former three sources may contribute to the formation of the SiO_2 nanowires, we do not think the amount of oxygen is high enough to be responsible for the whole product of SiO_2 nanowires. Therefore, we believe that the dominant source of oxygen originates from the system leakage. For our vacuum system, we calculated a flow rate of air into the system to be about 0.5 sccm and estimated a partial pressure of oxygen in the reaction chamber to be about 1 Torr of the total reaction pressure of 400 Torr. To further understand the effect of oxygen, we intentionally introduced 1 sccm of pure oxygen along with 50 sccm of Ar into the reaction chamber (the partial pressure of oxygen in the total reaction pressure was about 7.8 Torr). As a result, neither Ga ball nor SiO_2 nanowire was found on the silicon wafer or alumina plate because whole GaN powders were oxidized into stable Ga_2O_3 powders. This indicates that the partial pressure of oxygen in the reactor is a critical factor in the growth of SiO_2 nanowires.

Third, due to the presence of oxygen in the reaction chamber, the following reactant species may be involved in the vapor gas: Si, O, Ga, SiO, SiO_2, Ga_2O, GaO, and Ga_2O_3 (in the growth model depicted in Figure 7, we simply consider a vapor composed of Ga, Si, and O). These reactant species deposit and dissolve into the Ga balls, and the following main reactions may occur:

$$\mathrm{Si} + 2\mathrm{O} = \mathrm{SiO_2} \tag{1}$$

$$2\mathrm{Ga} + 3\mathrm{O} = \mathrm{Ga_2O_3} \tag{2}$$

$$2\mathrm{SiO} = \mathrm{SiO_2} + \mathrm{Si} \tag{3}$$

$$2\mathrm{Ga_2O} + \mathrm{Si} = \mathrm{SiO_2} + 4\mathrm{Ga} \tag{4}$$

$$2\mathrm{GaO} + \mathrm{Si} = \mathrm{SiO_2} + 2\mathrm{Ga} \tag{5}$$

For element Si and Ga, since the bond energy of Si−O bond (185 kJ/mol) is about three times higher than the Ga−O bond (59 kJ/mol),[21] the Si will preferentially combine with O to form stable SiO_2. For reactions 4 and 5, the standard free energy changes are −198 and −1468 kJ/mol, respectively; therefore, both reaction should proceed. These thermodynamic data suggest that SiO_2 should be the main products in our reaction. Our experimental results are in good agreement with this prediction.

Fourth, the strong ability of liquid Ga for absorbing O from vapor is responsible for the formation of the SiO_2 nanowires. To illustrate this point, two experiments were conducted with varying catalysts and SiH_4 as a Si source in the reaction system shown in Figure 1. When Ga from the thermal decomposition of GaN was used as a catalyst, a large quantity of cometlike structures and a small amount of carrot-shaped rods, as those shown in Figures 4 and 2, respectively, were obtained. However, when Au nanoparticles were used as a catalyst, randomly distributed Si nanowires were observed.

Finally, our extended experiments demonstrate that by directly dispersing the liquid Ga onto the silicon wafer, SiO_2 nanowires can grow perpendicularly from the Ga ball's entire surface, forming a nanowire layer around the Ga ball; however, the yield was very low and neither CSRs nor cometlike structure was formed.

Conclusions

Highly aligned and closely packed SiO_2 nanowire bunches were synthesized in a high yield by using molten Ga as catalyst and silicon wafer as Si source via a VLS process. Unlike any previously achieved results using Au and transition metals as catalysts, the Ga-catalyzed VLS growth exhibits many interesting new growth phenomena. The use of Ga provides opportunities for the development of low-temperature VLS routes for nanowire synthesis. Indeed, our extended experiments show that by using Ga as catalyst, carbon nanotubes and GeO_2 nanowires can be synthesize at temperature below 800 °C.[22] In addition, we anticipate to grow Si nanowires by using Ga as catalyst in a high-vacuum reaction system without leakage.

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(21) *Lange's Handbook of Chemistry*, 14th ed.; Dean, I. A., Ed.; McGraw-Hill: New York, 1992.

(22) In both carbon nanotubes and GeO_2 nanowires synthesis, Ga catalyst particles prepared by the thermal decomposition of GaN were used as catalyst. For carbon nanotube synthesis, C_2H_2 was used as C source and the products were deposited on the alumina plate. For GeO_2 nanowire synthesis, Ge wafer was used as the Ge source and growth substrate.