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, 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 about 0.006 mol % Si. Ga has already been used as a solvent in the low-temperature synthesis of GaAs and GaP whiskers and GaAs1-xPx crystals. Recently, Chen et al. 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. 1,5,7 Thus, it is reasonable for us to anticipate the synthesis of one-dimensional Si-based nanomaterials, 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 SiO2 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 SiO2 nanowire growth. (ii) Each Ga droplet could simultaneously catalyze growth of hundreds of thousands of SiO2 nanowires, and the nucleation occurred continuously during whole growth process. (iii) The SiO2 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 and Fe 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.

(17) The formation of SiO2 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 conducted 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 ~2 × 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.

**Materials and Substrates.** GaN powders (99.99%) were used as received from Alfa Aesar. Ultrahigh-purity argon (99.999% of purity with O2 and H2O 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 SiO2 Nanowires.** The experimental setup for SiO2 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 cm2) is placed on the middle part of a wide alumina plate (10 × 3 cm2), 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 ~2 × 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 N2. 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, there may also exist gallium oxide clusters, such as GaO, 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 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 SiO2 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 SiO2 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 JEM 2000F at 200kV), and energy-dispersive X-ray spectroscopy (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.
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 Ìm 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. 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 Ìm). Quantitative EDS analyses of the nanowires show that the nanowires have a composition close to SiO2; 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 SiO2 nanowires that grow out perpendicularly from the surface of the ball’s lower hemisphere (Figure 3b–g); that means, each Ga ball can simultaneously catalyze growth of many SiO2 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 SiO2 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 SiO2 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
It 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 $30^\circ$ to $60^\circ$ to the axis of the tube, and the two ends of the wires respectively construct the tube’s inner and outer walls. The outer wall of the tube is relatively smooth, while the inner wall is rough, and it usually exhibits a stairlike structure with almost the same step height of $\sim 10 \mu$m (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 the 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 $10-50$ $\mu$m, 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 $5-30$ $\mu$m and lengths $<500$ $\mu$m; the diameters of the molten Ga balls are in the range of $5-20$ $\mu$m. 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 $30^\circ$.

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.
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. 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 SiO₂, which is contradictory to the conventional VLS-grown samples. First, electron diffraction patterns (insets in Figure 5a,b) reveal the following similarities for our two kinds of 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 nm) through the split growth. The arrows show the nanowires’ growth direction.

**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 SiO₂ 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 SiO₂ 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 SiO₂ 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

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To further understand the effect of oxygen, we intentionally introduced 1 sccm of pure oxygen along with a pressure of 400 Torr. To further understand the effect of oxygen, we intentionally introduced 1 sccm of pure oxygen along with (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$_2$O$_3$ powders. This indicates that the partial pressure of oxygen in the reactor is a critical factor in the growth of SiO$_2$ nanowires.

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$_2$O$_3$ 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, Si$_2$, Ga$_2$O, GaO, and Ga$_2$O$_3$ (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:

$$\text{Si} + 2\text{O} = \text{SiO}_2 \quad (1)$$

$$2\text{Ga} + 3\text{O} = \text{Ga}_2\text{O}_3 \quad (2)$$

$$2\text{SiO} = \text{SiO}_2 + \text{Si} \quad (3)$$

$$2\text{Ga}_2\text{O} + \text{Si} = \text{SiO}_2 + 4\text{Ga} \quad (4)$$

$$2\text{GaO} + \text{Si} = \text{SiO}_2 + 2\text{Ga} \quad (5)$$

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 comet-like 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 comet-like 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 synthesized 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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$^{(22)}$ In both carbon nanotube synthesis, C$_2$H$_2$ 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.