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Growth of SiO_x nanowire bunches cocatalyzed with Ga and Ni

X. M. Cai,[a)] A. B. Djurišić, and M. H. Xie
Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China

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SiO_x nanowire bunches were fabricated on $Ni(NO_3)_2^*6H_2O$ solution-coated Si(111) substrates in a chemical vapor deposition system in the presence of Ga and under the flow of Ar and NH_3 gases. The roles of nickel nitrate hydrate, gallium, and ammonia in the formation of SiO_x nanowire bunches were investigated. It was found that Ni and Ga act as catalysts for the growth, while nickel nitrate hydrate also serves as a source of oxygen. The growth mechanisms of different nanowire structures obtained by varying the fabrication conditions are discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2081114]

I. INTRODUCTION

SiO_x nanowires may act as waveguides and be used as sensors with a higher sensitivity than the conventional optical fibers.[1] Amorphous SiO_x nanowires also show stable blue light emission,[2] which might have potential applications in, for example, integrated optical devices and high-resolution optical heads for scanning near-field optical microscopes.[3] Over the past few years, some researches have already been carried out on SiO_x nanowire growth. Sun *et al.*[4] used Sn as the catalyst and obtained jellyfishlike and cherrylike SiO_x nanowire structures. Pan and co-workers[5–7] used molten Ga decomposed from GaN powder as the catalyst and obtained five different SiO_x nanowire structures including fishbone-like, gourdlike, and octopuslike structures. Zhu *et al.*[8] heated SiC/Co powder and obtained SiO_x nanoflowers and observed nanowire loops. Wang *et al.*[3] obtained SiO_x nanowire arrays as the by-product during growth of GaN nanostructures with In (decomposed from In_2O_3) as the catalyst. SiO_x nanowires have also been fabricated with Fe (Refs. 2, 9, and 10) and Au (Ref. 11) as the catalysts, while some other morphological features such as nanosprings,[10] treelike, or tadpolelike nanowires[12] were all reported.

These interesting structures demonstrate the complexity of SiO_x growth. For example, from a single droplet of the catalyst, a bunch of SiO_x nanowires may be grown. SiO_x nanowires are amorphous. One wire may split up while many nanowires may branch together forming several nanowire bundles. Many of such features are unique to SiO_x, which are seldom observed in the growth of other nanomaterials. Therefore, it is of great fundamental interest as well as of application relevance to examine the structural and chemical contents of the SiO_x nanowires grown under various conditions. In this paper, we report the fabrication of SiO_x nanowires by using two metallic elements Ga and Ni as the catalysts. A few interesting morphologies are observed, whose formation mechanism will be discussed.

II. EXPERIMENT

One-side-polished Si(111) substrates were ultrasonicated sequentially in toluene, acetone, ethanol, and deionized water. $Ni(NO_3)_2^*6H_2O$ solution with a concentration of $5.5 \times 10^{-3} M$ was then deposited onto the unpolished side of the Si substrate and then dried at 110 °C. Gallium was placed in the middle of a quartz boat. The dried Si substrates were placed 2 mm downstream from the Ga droplet. The quartz boat containing the Si substrates and Ga droplet was then inserted in a quartz tube to be heated in a tube furnace after being pumped to a pressure of 3×10^{-1} torr. The temperature of the furnace was then raised to 950 °C from room temperature at a ramping rate of 35 °C/min and then maintained at 950 °C for 30 min under the flow of Ar (99.999%) and NH_3 (99.999%) gases of different flow rates. Afterwards, the gas flow was cut off and the furnace was cooled naturally back to room temperature under vacuum.

Three different sets of conditions were used in this experiment as summarized in Table I. The grown samples were characterized by field-emission scanning electron microscopy (SEM, Leo1530) and transmission electron microscopy (TEM, JEOL 2010F). Both SEM and TEM were equipped with energy dispersive x-ray (EDX) facilities.

III. RESULTS AND DISCUSSION

The typical morphologies of the products formed on substrates under condition I are shown in Fig. 1. There are jellyfishlike nanowire bunches, nanowire spheres, and some isolated but randomly aligned nanowires on the substrates. The EDX spectra show that the randomly aligned nanowires are SiO_x with $x \sim 1.6$ and the nanowire spheres are SiO_x with $x \sim 2.6$. The isolated randomly aligned SiO_x nanowires are over 20 μm long with a diameter of around 30 nm. The diameters of the SiO_x nanowires forming the spheres are about

TABLE I. Three growth conditions used in our experiments.

	Ga (mg)	Ar (sccm) (standard cubic centimeter per minute)	NH_3 (sccm)	Growth pressure (torr)
Condition I	1045.5	100	50	3.1–3.2
Condition II	1041.0	100	100	5.3–5.6
Condition III	1059.1	50	100	4.2–4.4

a)Electronic mail: caixm@hkusua.hku.hk

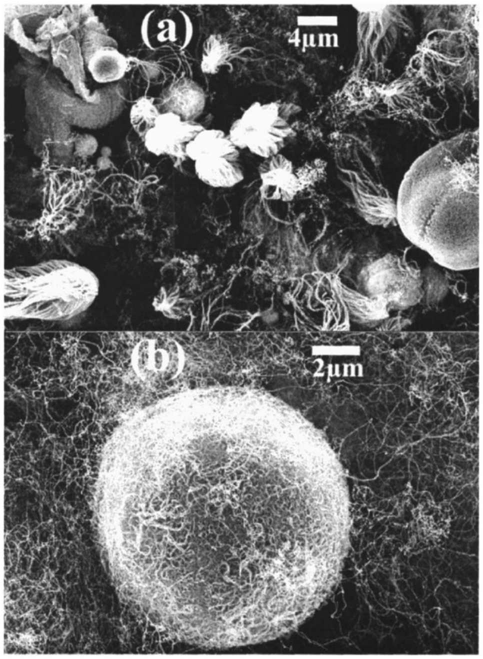

FIG. 1. SEM images of the samples grown with condition I with (a) showing the jellyfishlike nanowire bunches, and (b) showing one typical spherelike nanowire bunch.

30 nm. Similar SiO_x nanowire spheres with the SiO_x nanowire array forming the shells of the spheres were also observed by Wang *et al.*[3]

Several jellyfishlike nanowire bunches are shown in Fig. 2. From the images of Figs. 2(d) and 2(e), there appears a core inside the "head" of the jellyfish bunch, from which the nanowires started their growth. EDX measurements show that the heads of the jellyfishlike nanowire bunches contain Ni, Ga, Si, and O with the atomic percentages of 3, 6, 26, and 65, respectively, while the tails contain SiO_x with $x \sim 2$ only. The lengths of the jellyfishlike nanowire bunches are around 20 μm while the diameters are in the range of 12–64 nm. This morphology is different from those SiO_x nanowire bunches reported previously.[4–7] Here the nanowires grow not just from the lower hemisphere of the core but from the entire surface of the sphere. Another interesting phenomenon is the coalescence of the nanowires as shown in Fig. 2(f). SiO_x nanowire loops formed by coalescence of two nanowires initiated from the same catalyst particles have also been reported.[8] Another observation is the nonuniform diameter of the nanowires in a bunch as revealed in Figs. 2(c) and 2(e). Generally the roots of the nanowires are thicker than the tops, agreeing with that of Meng *et al.*,[13] but being different from that obtained by Pan and co-workers.[5–7]

Under condition II, several morphologies emerged as presented in Fig. 3. The first type shown in Figs. 3(a) and 3(b) can be characterized by growth of several nanowires from one single particle similar to that of Refs. 5–8. The particle shape is irregular, possibly due to the presence of the two catalysts (Ni and Ga). EDX data show that the particle is composed of Ni, Ga, Si, and O with the atomic percentages of 4, 9, 37, and 50, respectively, while the nanowires are SiO_x, with $x \sim 1.2$.

The second morphology as shown in Figs. 3(c) and 3(d) is Chinese lanternlike, where a nanowire bundle splits into a few smaller bundles but then rejoins, into one or fewer bundles. A similar structure has also been observed in a previous report.[14] Here from Fig. 3(d), it can also be observed that on one side of the Chinese-lanternlike nanowire bundles, the nanowires tangle and form a ropelike structure.

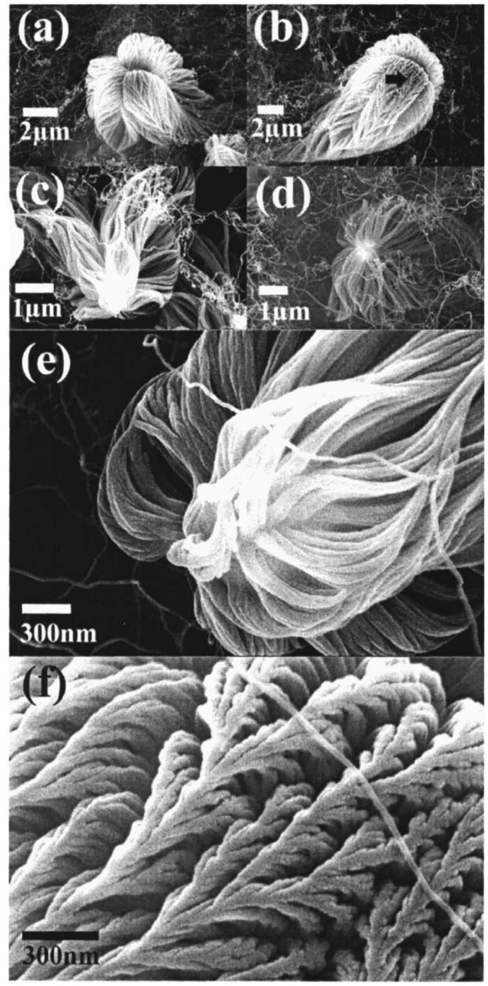

FIG. 2. SEM images of the typical jellyfishlike nanowire bunches grown with condition I, [(a)–(d)] Showing different jellyfishlike nanowire bunches. (e) Higher-resolution image of the head of a jellyfishlike nanowire bunch. A core and nanowires with nonuniform diameters can be observed. (f) Higher-resolution image of the arrowed area shown in (b). Nanowire coalescence can be observed.

The typical morphology obtained under condition III is shown in Fig. 4. Two typical octopuslike nanowire bunches are observed, one without spots on the "octopus legs" [Fig. 4(a) and 4(b)], while the other with spots [Fig. 4(c)]. The heads of the octopuslike bunches are of irregular shape. The diameters of the nanowires forming the legs of the octopuslike bunches are not quite the same, unlike that in Refs. 6 and 7. EDX measurements show that the octopus "heads" contain Ni, Ga, Si, and O with the atomic percentage of 1, 4, 64, and 16, respectively, while the legs contain SiO_x, $x \sim 0.1$. Both the head and the tail are highly Si rich.

TEM results of the samples grown under condition I are presented in Fig. 5. From Figs. 5(a) and 5(b), it can be seen that some nanowires have a core/shell structure and in most cases the core is not as long as the wire. High-resolution

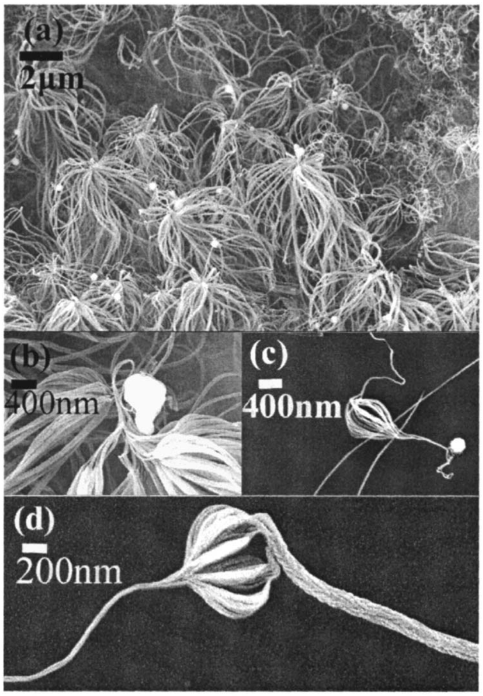

FIG. 3. Typical SEM images of the SiO_x nanowire bunches obtained with condition II. (a) Showing many nanowire bunches growing under nanoparticles. (b) Higher-resolution image of one nanowire bunch and one nanoparticle shown in (a). Branching growth can be observed. (c) One Chinese-lanternlike nanowire bunch grown under one nanoparticle. Both branching growth and coalescence are obvious. (d) Another Chinese-lanternlike nanowire structure. From its right side, a queue or ropelike nanowire bunch can be observed.

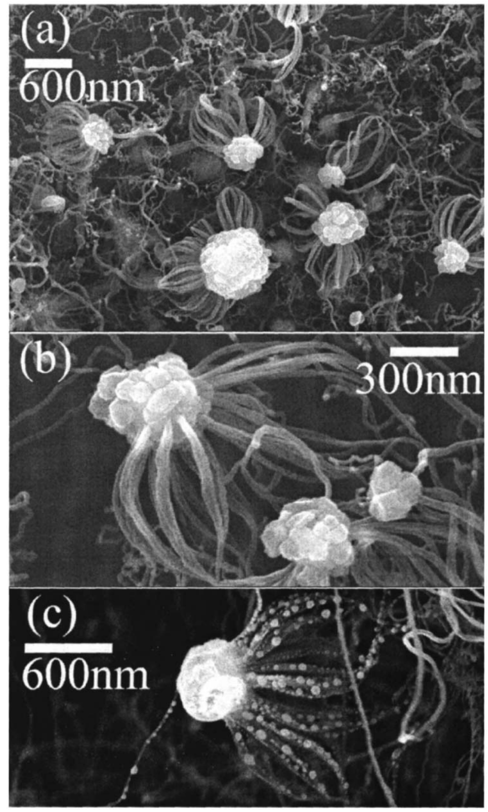

FIG. 4. Typical octopuslike nanowire bunches obtained with condition III. (a) Showing many octopuslike nanowire bunches. (b) Higher-resolution image of one bunch. It can be observed that the nanowires are not uniform in diameter. (c) Higher-resolution image of one octopus nanowire bunch with spotted nanowires.

TEM results show that the black core is crystalline while the shell is amorphous as shown in Fig. 5(c). EDX measurements within the TEM apparatus show that the core contains Ni, Ga, Si, and O, and that their atomic percentages are 24, 44, 17, and 15, respectively, while the shell contains SiO_x with $x \sim 0.3$. Comparing these values with those obtained with EDX-equipped SEM, one can find that the atomic ratio of Ga to Ni is in rough agreement, but Si to O is not. This is likely because EDX performed in the SEM provides an average of composition over a larger number of nanostructures due to their higher density and larger area measured. Similar nanostructures showing amorphous SiO_x shells and crystalline SiC (Refs. 8 and 15) or Si (Refs. 14 and 16) cores have also been reported. Nanowires without the core/shell structure but of amorphous SiO_x are shown in Fig. 5(d). TEM examinations of the samples grown under other conditions also show that the SiO_x nanowires are amorphous, in agreement with the literature.

In order to clarify the role played by $Ni(NO_3)_2$, Ga, and NH_3 in the formation of the SiO_x nanowire bunches, another set of experiments were conducted using the conditions similar to condition I detailed in Table I, but leaving out one of the sources each time for comparison. The resulting morphologies of the samples are shown in Fig. 6. Figure 6(a) presents the result without depositing $Ni(NO_3)_2^*6H_2O$ to the substrate. From the figure, it is observed that single nanowires growing out of isolated particles are produced instead of the nanowire bunches. EDX measurements suggest that the nanoparticles contain O, Si, and Ga with the atomic percentages of 7, 91, and 2, respectively, while the nanowires contain Si only. Obviously, Ga has catalyzed the growth of Si nanowire in this case.[16]

The result for growth without Ga is shown in Fig. 6(b). Particles 600 nm in size containing O, Si, and Ni with the atomic percentages of 11, 83, and 6, respectively, and separated Si nanowires are seen. It has been reported that Si nanowires can be grown by heating Ni-coated Si at 950 °C under Ar/H_2 flow.[17] Our results seem to agree with this assignment. Without NH_3, octopuslike nanowire bunches together with randomly aligned nanowires are obtained, as shown in Fig. 6(c). The head of the octopuslike bunch contains Ni, Ga, Si, and O while the tail contains only Si and O, suggesting the catalyzing effect of Ni and Ga. The morphology is similar to those reported.[5–7]

Based on these results, it can be concluded that Ga and $Ni(NO_3)_2$ are essential in the formation of the jellyfishlike SiO_x nanowire bunches, while the NH_3 affects the bunch morphology. It has been reported that at 900 °C, $Ni(NO_3)_2$ will decompose and NiO nanoparticles form.[18] Above 930 °C, Ni reacts with Si forming Si_2Ni eutectic alloy droplets.[17] At 950 °C, on the other hand, $GaSi_x$ with $x < 1\%$ and $NiSi_y$ with $y > 10\%$ will form. This may explain the results of Figs. 6(a) and 6(b), where the nanowires grown with $Ni(NO_3)_2$ only are much denser than that with Ga only, and the NiSiO particles are around 600 nm. It is Ni that plays the major role in etching Si to provide a Si source for SiO_x nanowire bunch growth.

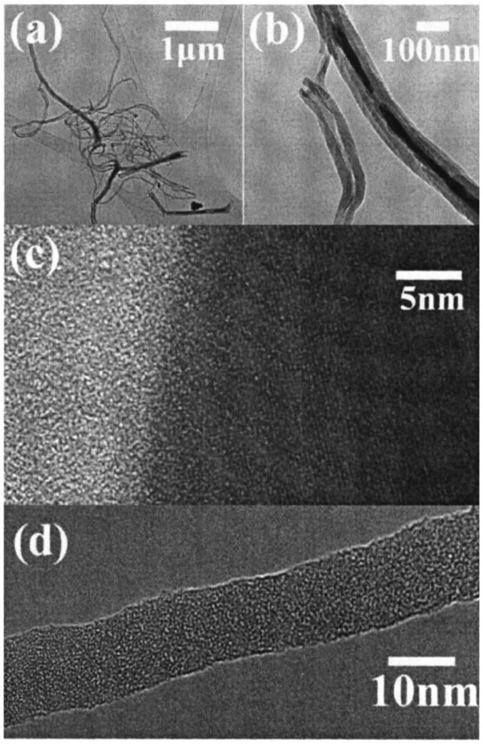

FIG. 5. TEM images of the materials grown with condition I. (a) Lower magnification images of the nanowires showing that some nanowires have a black core while others do not. (b) The core is not continous inside the nanowires. (c) Higher-resolution images of the crystalline core and the amorphous shell in (b). (d) Higher-resolution image of one amorphous nanowire without a core.

SiO_x nanowires can grow perpendicular to the surfaces of Ga balls.[5,16,19] Therefore, when the NiSiO particle surfaces are coated with Ga and when the liquid droplets get supersaturated with Si and O, SiO_x nanowires will grow from the whole surface and SiO_x nanowire bunches will form. Because the bonding of Si–O is stronger than that of Ga–O, only SiO_x will precipitate.[5] Since the samples grown with only Ga or $Ni(NO_3)_2$ contain only Si nanowires, the possibility of atmosphere leakage of the tube, the abundance of residual oxygen in the tube, and the presence of an oxide layer on Si wafer or oxygen contained in Ar or NH_3 sources can all be ruled out as the source of oxygen for SiO_x nanowire growth. Therefore, the relevant oxygen source in our system is the $Ni(NO_3)_2$ used in the experiment. At the presence of liquid Ga droplets, which strongly absorb O,[5] the oxygen source may be efficiently maintained in the chamber.

Finally, it seems also that NH_3 has some effects on the nanowire bunch formation, as varying the gas ratio of Ar to NH_3, the morphology will vary. However, further research is needed to elucidate the effects of NH_3 gas flow on the nanowire bunch morphology.

Though there are NH_3, Ga, and Ni in the system, and Ni can in principle catalyze[18] the growth of GaN nanowire, no GaN nanowire was actually obtained. The reason for this again needs further investigation. Notably, SiO_x nanowire formation was also observed during GaN nanowire fabrications by Wang *et al.*[3] and Zheng *et al.*[19]

Compared with other methods, this work suggests a convenient way of fabricating SiO_x nanowires at low temperature, short reaction time, and the easily available Si wafers as the Si sources. This is mainly attributed to the use of two elements as the catalysts. Indeed, combinations of two or more catalytic elements may improve nanowire growth and provide more flexibility for different morphologies of the nanowires.

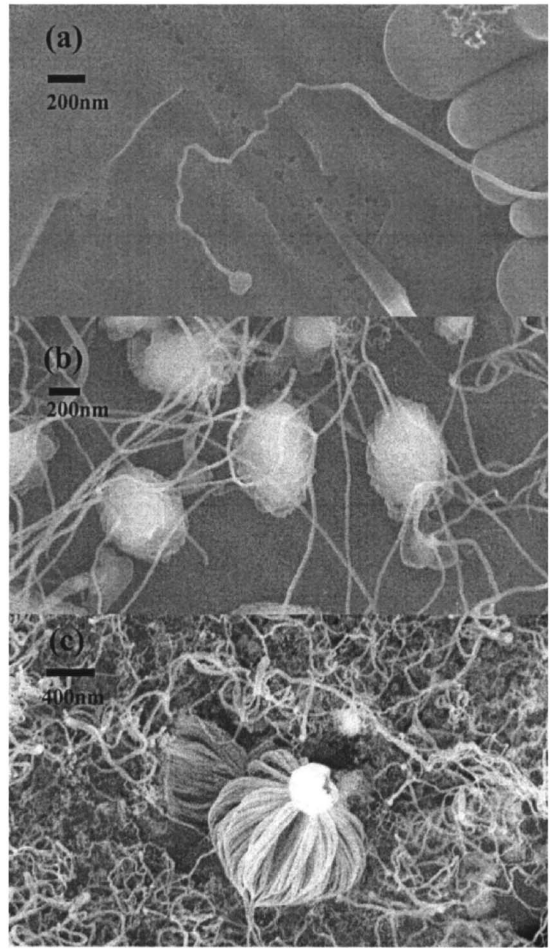

FIG. 6. SEM images of the samples grown with omitting one of the three—$Ni(NO_3)_2$, Ga, and NH_3—while keeping other parameters the same with condition I. (a) SEM images of the materials grown without $Ni(NO_3)_2$. Ga catalyzing Si nanowire growth was clearly observed. (b) The materials grown without Ga. Si nanowires and particles containing Ni, Si, and O were observed. (c) The materials grown without NH_3. Without NH_3, the morphology is different, suggesting that NH_3 plays a role in the jellyfishlike nanowire bunch formation.

IV. CONCLUSION

To conclude, amorphous SiO_x nanowire bunches have been grown in a tube furnace by employing Ga and Ni cocatalysts. The samples have been characterized by SEM, TEM, and EDX. Several different morphologies are observed depending on the growth conditions. It is found that Ga, $Ni(NO_3)_2$, and NH_3 all play important roles in the formation of jellyfishlike nanowire bunches. The role of $Ni(NO_3)_2$ is to etch Si from the substrate and to provide O for SiO_x nanowire growth. Besides trapping O from $Ni(NO_3)_2$, Ga will also catalyze the bunch growth of SiO_x nanowires.

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