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Organic Nanowire-Templated Fabrication of Alumina Nanotubes by Atomic Layer Deposition

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ABSTRACT

Alumina nanotubes were fabricated by a template method. Tris-(8-hydroxyquinoline) gallium (GaQ_3) organic nanowires were used as a soft template for coating with alumina using an atomic layer deposition technique. The deposition was conducted at 25 °C by using trimethylaluminum and distilled water as the precursors of Al_2O_3. Amorphous alumina nanotubes were obtained after removing the GaQ_3 by dissolving in toluene or by heat treatment at 350 °C. The amorphous nanotubes could be crystallized by heating at 900 °C for 1 h in vacuum.

Nanotubes are interesting and have useful characteristics owing to the shape and quantum-size effects. Special attention has been paid to the preparation of metal oxide nanotubes because of their possible applications in electrochemical processes and catalysis.[1−3] Various methods have been reported to fabricate oxide nanotubes of silicon,[4] vanadium,[5] titanium,[6−9] aluminum,[10−12] and others.[13] Alumina nanotubes, due to the large surface area, could be a good material for catalysis, absorbent, and catalyst support of transition element clusters in the automotive and petroleum industries.[14,15] Furthermore, the photoluminescence of alumina nanotubes can be expected for applications in optoelectronics and biotechnology.[16] The most common synthetic strategy for alumina nanotubes is based on the template synthesis due to its simple and easier processing at low temperatures. For example, porous anodic alumina (PAA) membrane,[16−19] surfactants,[15,20,21] and 1-D nanostructures[22] are often used as the template. Among them, 1-D nanostructures are more useful as a template to fabricate nanotubes of various materials.[23,24] The advantages of this method are the high aspect ratio and high productivity of nanotubes that can be formed. In addition, there are no inevitable impurities left in the final product. However, there have been only a few investigations of this method to prepare alumina nanotubes. One of the major problems associated with the nanowire-templated process is that it is difficult to control the uniformity and dimension of the final product. The reason for this is that the process often involves a physical vapor deposition (PVD),[25] chemical vapor deposition (CVD),[25] or sol−gel[26] technique. Each of these deposition methods has significant process limitation. For example, PVD process does not permit conformal coating because it is a direct line-of-sight deposition. Nonuniform deposition usually occurs in the CVD process because of rapid consumption of the precursor. The substrate for the sol−gel coating needs uniform wetting that is usually difficult to achieve.

Because of the limitation of the above traditional processes, atomic layer deposition (ALD) was applied in the present fabrication process. It is a unique process that produces highly conformal films and allows atomic-scale thickness control.[27] The technique is based on a sequence of two self-limiting reactions between the gas-phase precursor molecules and a solid surface. During the reaction sequence, only one reactant is present in the reaction zone at a time. This procedure prevents unwanted gas phases in the reactor in contrast to chemical vapor deposition. Because only a finite number of reactive sites exist on the surface, reaction with these surface species is inherently self-limiting. Dense and pinhole-free films are produced when the two reactions are finished. Conformal coating can be applied to high-aspect-ratio geometries and porous structures. However, the substrate surface needs to be activated when applying ALD.[28,29] In this study, a simple method using GaQ_3 as the template to fabricate alumina nanotubes by ALD is presented. The

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advantage of using GaQ_3 organic nanowires as the template is that the molecules have functional groups that can react directly with the ALD precursors without any surface modification. Furthermore, the organic nanowires can then be removed by a simple process such as dissolution by an organic solvent or heat treatment to obtain the nanotubes. To date, there has been no report on the preparation of alumina nanotubes by using organic nanowires as the template.

A thermal evaporation technique was employed to fabricate the GaQ_3 organic nanowires. The method has been described elsewhere.[30] Briefly, a graphite boat was used as a resistive heater, and the temperature was controlled by a power supply along with a K-type thermocouple. Commercial GaQ_3 powder was placed in the graphite boat, and the silicon substrate was placed under a stainless steel cold trap filled with liquid nitrogen, which was 10 cm above the boat. The chamber was first evacuated to 2.7×10^{-4} Pa, and He at a selected pressure, typically at 9.3 kPa, was then introduced into the chamber. The GaQ_3 powder was sublimed to form nanowires on the cold substrate after the temperature of the graphite boat had reached 330 °C. The He pressure played a key role in controlling the diameter of the nanowires. When the pressure increased, GaQ_3 nanowires with a larger diameter would be obtained (see the Supporting Information). Alumina thin film was then coated on the GaQ_3 nanowires by ALD using trimethylaluminum (TMA) and H_2O as the precursors with the substrate temperature at 25 °C. Each cycle consisted of a precursor pulse for 1 s and a purge with N_2 for 10 s. The thickness of alumina shell could be controlled by the number of precursor/purge cycles. The average growth rate for Al_2O_3 was 1.1 Å/cycle. The GaQ_3 template could be further removed either by dissolution in toluene for 1 h or by heat treatment at 350 °C for 10 min.

Figure 1a shows the TEM image of the GaQ_3 nanowires. They are approximately 1 μm in length and 30−70 nm in diameter. Unlike single-wall carbon nanotubes,[28,29] the GaQ_3 nanowires, with many quinoline ligands, undergo exchange reaction with water to form hydroxyl groups[31] on the surface that can react directly with the ALD precursors without any modification. An amorphous Al_2O_3 film was then uniformly deposited on the GaQ_3 nanowires by applying 100 or 200 cycles of ALD. The Al_2O_3-coated GaQ_3 core−shell nanowires were formed, as shown in Figure 1b−d. Under transmission electron microscopy (TEM), the contrast of the image can be seen from the atoms because of different atomic numbers. The atoms with a larger atomic number diffract more incident electrons and form a darker image than those with a smaller one. The core with a darker contrast is GaQ_3, and the shell with a lighter contrast is alumina. In Figure 2, because of the strong atomic number contrast of high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), the core containing Ga also appears darker in the image. In addition, the signals of Ga and Al could be observed from the line-scan spectra of the core−shell nanowire. The signal of Ga only appears at the center of the nanowire. The signal of Al spreads across the whole nanowire and especially stronger on both edges. Because the

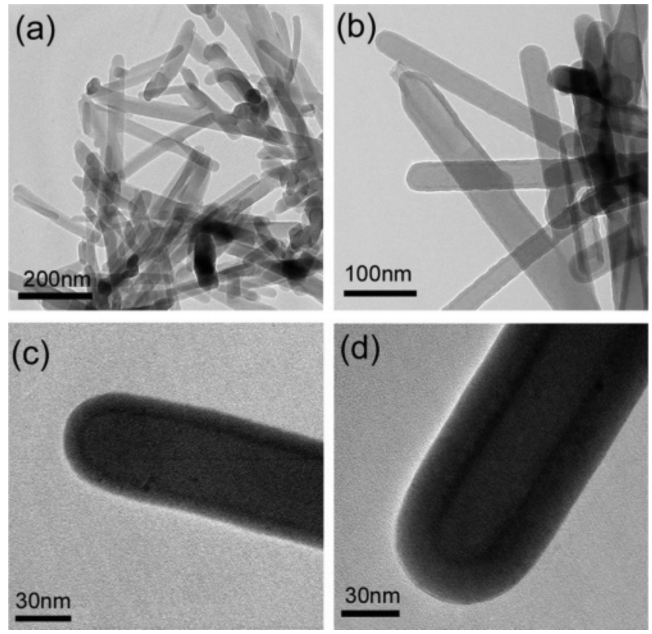

Figure 1. TEM images of the nanowires. (a) GaQ_3 nanowires prepared by thermal evaporation, (b) and (c) GaQ_3−Al_2O_3 core−shell nanowires fabricated by 100 cycles of ALD, and (d) same as (c), 200 cycles of ALD.

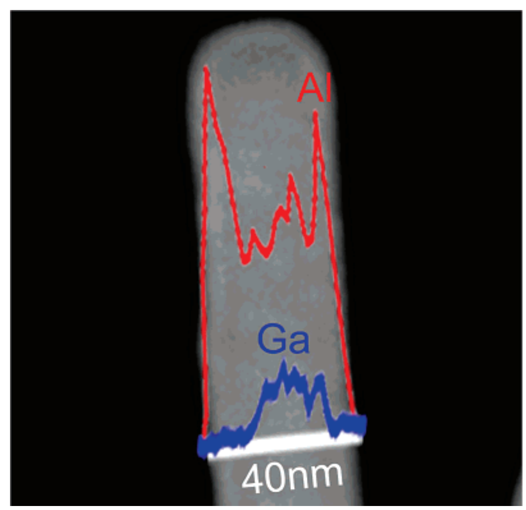

Figure 2. HAADF-STEM image and line spectra of Ga and Al of a GaQ_3−Al_2O_3 core−shell nanowire.

growth rate of ALD is 1.1 Å/cycle, the thickness of the alumina shell can be well controlled by the number of deposition cycle, in contrast to the other soft template method such as surfactant, which is difficult to control the dimension of alumina nanotubes.[15,20,21] As shown in parts c and d of Figure 1, approximately 11 and 22 nm thick shells were fabricated by applying 100 and 200 cycles of ALD, respectively.

PAA has been often used as a template to prepare alumina nanotubes. The process usually involves anodization in an acidic solution[16,18] or etching the template in a basic solution.[19] These processes may cause some problems such as inevitable impurities due to electrochemistry and damage of the final product. The GaQ_3 molecule has very low polarity because it has a 3-fold symmetry with three

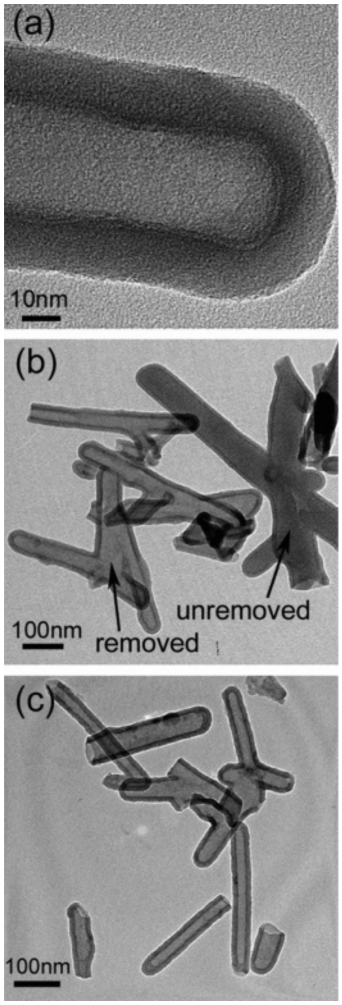

Figure 3. TEM images of the nanostructures. (a) An Al_2O_3 nanotube after the GaQ_3 nanowire was removed by toluene, (b) image contrast of $GaQ_3-Al_2O_3$ core−shell nanowires before and after removal of GaQ_3, and (c) Al_2O_3 nanotubes to show the open end after removal of GaQ_3.

quinolines surrounding around the gallium atom. Therefore, toluene is a suitable solvent to dissolve the GaQ_3 nanowires. After the Al_2O_3-coated GaQ_3 nanowires were immersed in toluene for 1 h, the inner GaQ_3 nanowires were dissolved. Figure 3a shows the TEM image of an Al_2O_3 nanotube after removing the GaQ_3 nanowire in toluene. The removing process did not change the morphology and size of the tubes. The only difference was a lighter contrast of the inner part due to removal of the GaQ_3 nanowires, as shown in Figure 3b. The GaQ_3 nanowires could also be removed by heat treatment at 350 °C for 10 min. The energy-dispersive X-ray (EDX) spectrum of the inner part of the nanotubes showed that the gallium signal was absent, and the ratios of aluminum and oxygen signals at inner and outer parts of the nanotubes were both nearly 2 to 3. For these two removing methods, there was no difference in the morphology and size of the nanotubes. It also demonstrated that there was no inevitable impurity left. During the removal process, the GaQ_3 nanowires have to leave from some outlet. Therefore, most alumina nanotubes have an open end, as shown in Figure 3c. The open end of the tubes offers the outlet for the GaQ_3 nanowires, whether by dissolution or by heat treatment.

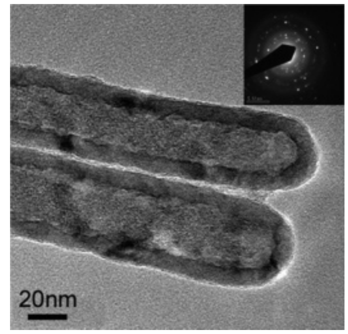

Figure 4. TEM image of the alumina nanotubes after heat treatment at 900 °C for 1 h. The inset shows the electron diffraction pattern of alumina.

Because the alumina nanotubes were amorphous, crystallization treatment was performed. Crystallization of alumina begins at 900 °C.[32] When the temperature increased from 350 to 900 °C, the crystallinity of the nanotubes increased, but the morphology remained unchanged. When the specimen was heated at 900 °C for 1 h, the alumina nanotubes became polycrystalline, as shown in Figure 4. Although the anneal temperature was as high as 900 °C, the nanotubes did not aggregate due to the high calicination temperature of alumina.

In conclusion, we have developed an ALD process to fabricate alumina nanotubes by using GaQ_3 organic nanowires as the template. The alumina nanotubes had a high aspect ratio and good uniformity. The thickness of the nanotubes could be precisely controlled by the cycle number. The GaQ_3 nanowires did not need any surface modification during the ALD process and were easy to remove by toluene or heat treatment. It provides a new approach for preparing other kinds of oxide nanotubes as long as the oxide can be coated on an organic template.

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Supporting Information Available: SEM images of GaQ_3 nanowires prepared under different helium pressures. This material is available free of charge via the Internet at http://pubs.acs.org.

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