Synthesis of nanotubes and nanowires of silicon oxide

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Now one-dimensional structures with nanometer diameters are of great potential for testing and understanding fundamental concepts about the roles of dimensionality and size in optical, electrical, and mechanical properties and for applications in the semiconductor industry as well as mechanical and chemical areas. Since the discovery of carbon nanotubes in 1991 [1], the preparation of one-dimensional structures of nanotubes and nanowires have attracted a wide attention. In recent years, there has been intense interest surrounding the fabrication of nanotubes and wires of oxides have also been synthesized with the sol-gel template method. There are two main templates applied for producing oxide nanotubes. One involves carbon nanotubes as the template, which is coated with tetraethylorthosilicate or some other such precursor which is then oxidized. The inorganic hollow nanotubes of SiO_2, Al_2O_3, V_2O_5 and MoO_3 are prepared in this way [2]. The other involves a membrane as the template, by which the inorganic nanofibers, such as TiO_2, MnO_2, Co_3O_4, WO_3 and ZnO have been formed, the desired materials being synthesized within the pores of nanoporous membranes [3, 4]. Recently, multi-element nanocables comprising multiple phases were successfully synthesized by means of laser ablation [5, 6], and many mesoporous metal oxides and hybrid hollow spheres were fabricated by the template method [7, 8].

There is currently an intensive effort to develop large-scale semiconductor nanowire or nanotube materials, such as Si and silicon oxide SiO_x ($1 < x < 2$), with the uniform wide range of sizes up to 30 nm, which would open up new opportunities in the semiconductor and catalysis industries, but these structures are difficult to achieve at present. Although silica tubes with large diameter (about 1 μm) or imperfect SiO_2 nanotubes have been prepared [9, 2], from the view of applications in the future, a detailed study on the macroscopic synthesis of aligned nanotubes and nanowires of silicon oxide with about 30 nm diameter will be significant. Here we report the macroscopic preparation of aligned silicon oxide nanotubes, bamboo-like nanofibers and nanowires with a uniform diameter of ∼30 nm using an ordered nanochannel-arrays of anodic alumina as templates.

The ordered nanochannel-arrays of anodic alumina were prepared via the anodization of an aluminum textured pattern on the surface [10] in a 3% oxalic acidic solution under the constant-voltage condition (40 V). It is about 6 μm and contains ordered cylindrical pores with the uniform diameter of 20–30 nm almost perpendicular to the film surface. The aligned silicon oxide nanostructures were prepared on this anodic alumina using a sol-gel method. At first, 52 ml of tetraethyl orthosilicate (TEOS) was added slowly into 115 ml ethanol to form TEOS solution. Secondly, 115 ml portion of ethanol were mixed with 18 ml of H_2O and 0.27 ml of HCl. Then the second solution was added slowly into TEOS solution whilst stirred in a bath to yield a silica sol at room temperature. After aging the sol for some days at room temperature or 50 °C, the highly ordered nanochannel-array of anodic alumina began to be dipped into the sol for 1 min, and then was removed and dried for more than 1 day. Finally, the sol-containing anodic alumina were heated in air at 200 °C for 1 day. We employed scanning electron microscopy (SEM, Jeol S500) and transmission electron microscopy (TEM, Jeol 3000F) to observe the morphology of the nanostructures obtained. For the SEM and TEM experiments, we used a chemical solution (H_3PO_4, CrO_3 and H_2O) to dissolve partly or entirely

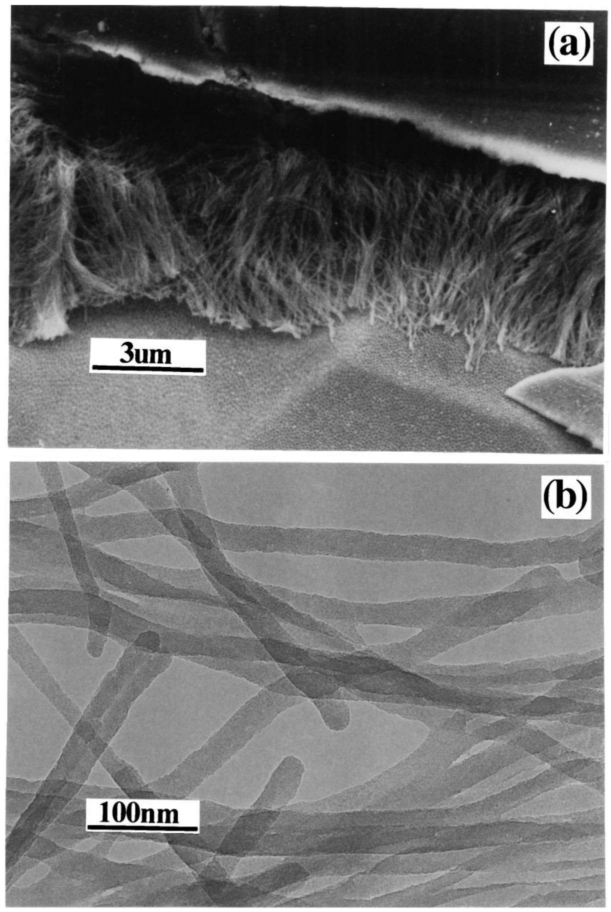

Figure 1 SEM (a) and TEM (b) images of silicon oxide nanowires obtained by immersing the ordered anodic alumina for 1 min in the sol which is aged at room temperature for 2 days.

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the anodic alumina templates by controlling the reaction time and temperature.

As illustrated in the SEM patterns of silicon oxide nanowires produced by the sol-gel template method, optimization of the experimental parameters allow the macroscopic preparation of aligned silicon oxide nanowires with about 30 nm diameter. Fig. 1 shows SEM and TEM images of silicon oxide nanowires obtained by immersing the ordered anodic alumina for 1 min in the sol which is aged at room temperature for 2 days. The low magnification SEM image (Fig. 1a) indicates that a lot of aligned silicon oxide nanowires with the length of about 6 μm can be observed between a silicon oxide thin film and the aluminum. In this case, the anodic alumina is removed effectively by chemical dissolution. Here the silicon oxide thin films can be removed by polishing the surface of the template with sand paper before chemical dissolution. From the TEM picture of the nanowires produced (Fig. 1b), the amorphous nanowires with the diameter of 22–30 nm are shown and none of the hollow cores in these nanowires has been observed. The diameters ($\sim$30 nm) and lengths ($\sim$6 μm) of the nanowires are almost consistent with those of the pores in the original anodic alumina.

Tubules are obtained if the aging time is more than 23 days. Fig. 2 shows the surface SEM (a) and TEM (b) images of the silicon oxide nanotubes produced at 23 and 30 days of aging time. The surface SEM photograph is taken from the specimen with silicon oxide thin films entirely removed with sand paper and the anodic alumina partly dissolved. It demonstrates that the nanotubes originate from the pores in the anodic alumina which are widened by chemical dissolution and possess an open structure. The TEM photograph gives a clear view of the structure of these silicon oxide nanotubes whose diameters are almost equal to those of the channels in the original anodic alumina template, and the wall sizes are about 3–7 nm. However, some nanowires can be observed amongst the nanotubes, probably caused by the existence of solid core in one fiber; in other words, one nanofiber we observed is composed partly of hollow core and partly of solid core. The solid core part may be formed at the bottom of the anodic alumina template.

The morphology of the silicon oxide nanostructures is also determined by the temperature of sol. To explore that further, before dipping we have heated the silica sol at 50 °C for 15 days. The TEM observations show that the bamboo-like nanofibers are formed macroscopically. It is of interest to note that the morphologies are almost the same if the ordered anodic alumina templates are immersed in the heating sol for a short time (5 s), which indicates that the sol temperature takes an important role in the formation of the bamboo-like nanofibers. Meanwhile, with aging time increasing (from 2 to 15 days), the morphology of the inside of the nanofibers becomes more rough and the amount of hollow core increases.

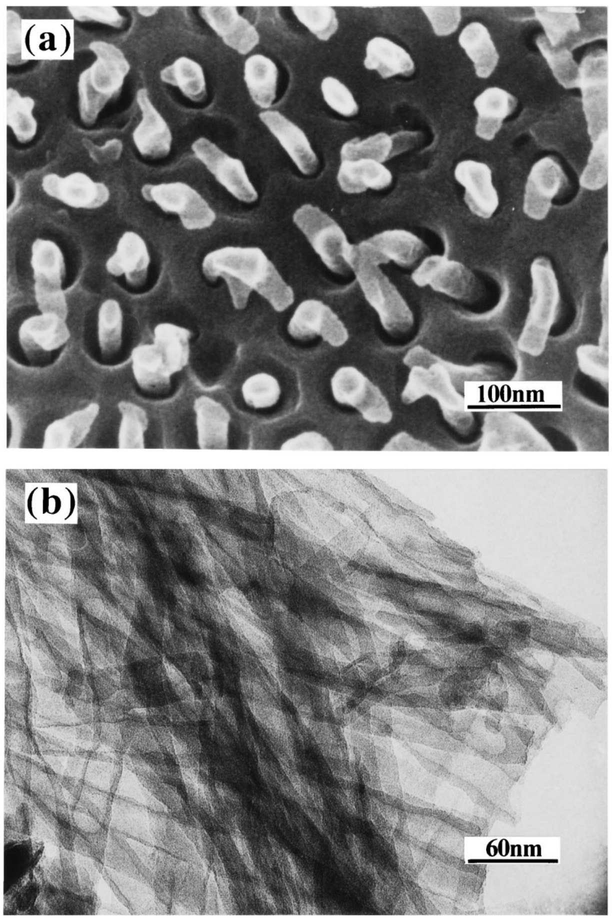

Figure 2 Surface SEM (a) and TEM (b) images of the silicon oxide nanotubes. The diameters of the nanotubes are approximately 30 nm, having wall sizes of about 3–7 nm.

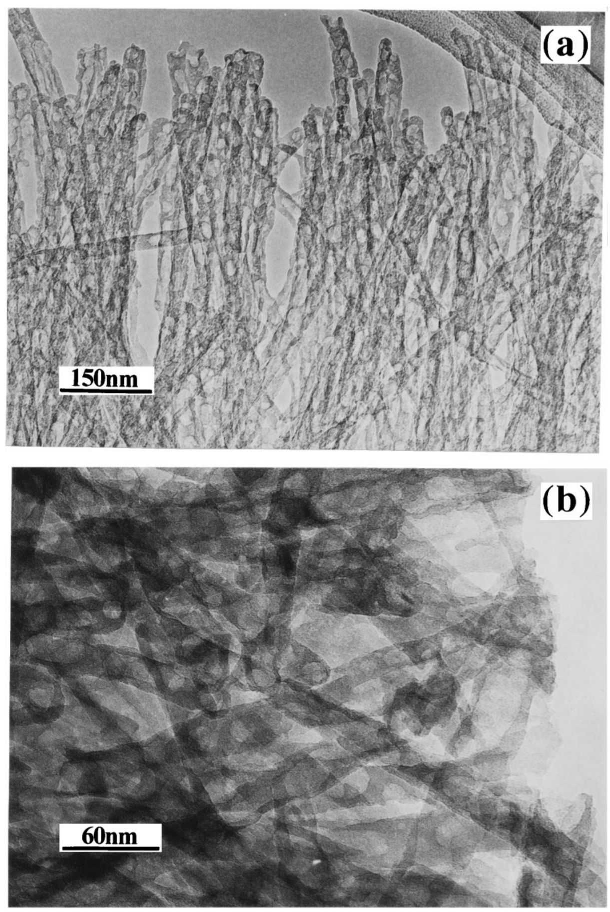

Figure 3 TEM morphologies of bamboo-like nanofibers. (a) Low magnification and (b) enlarged image. The sol was aged at 50 °C for 15 days.

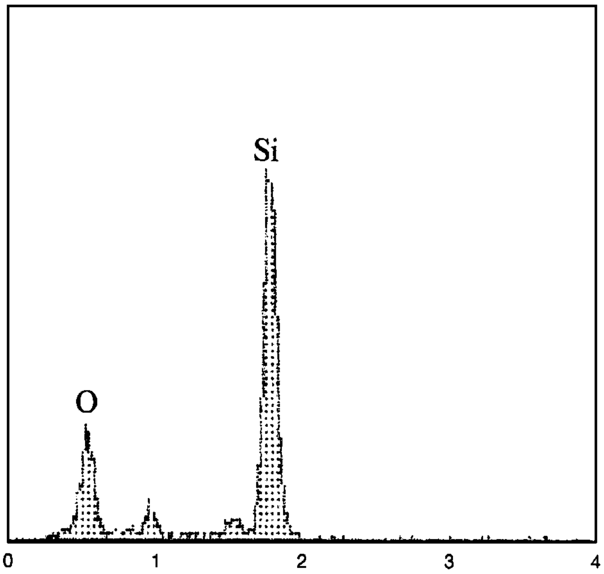

Figure 4 EDX spectrum from nanotubes in Fig. 2b.

The EDX spectrum (Fig. 4) from the nanotubes in Fig. 2b reveals that these nanostructures are composed mainly of silicon and oxygen, and are silicon oxide. These silicon oxide nanostructures may be converted to SiO_2 glass nanostructures by heating them to above 1000 °C in air.

It is confirmed that, with this method, long and aligned nanowires or nanotubes as well as multielement nanocable or nanotubes comprising different composition layers can be synthesized. Although the detailed mechanism for the formation of silicon oxide nanostructures in these anodic alumina templates is still a point that needs further exploration, these aligned nanostructures obtained by us are of great potential for use as intensive blue light emitters [11] for semiconductor full-color displays in integrated optical devices and also as catalyst materials.

The sol-gel template method has been used to macroscopically prepare aligned silicon oxide nanostructures. The nanotubes, bamboo-like nanofibers and nanowires with uniform diameter of ∼30 nm were synthesized using an ordered nanochannel-array of anodic alumina as templates, which were observed to grow out of each pore of the anodic alumina templates. These nanostructures may have prospective applications in the semiconductor and catalysis industries, though the details of the formation mechanism need further study.

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