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Characterization of Silicon Oxide Nanowires Prepared by Hydrothermal Treatment Using Slow Dissolution of Bulk Glass Source Materials

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Silicon oxide nanowires were successfully synthesized using a low-temperature hydrothermal treatment (200°C) without the use of metallic catalysts. Scanning electron microscopy and transmission electron microscopy (TEM) revealed nanowires having uniform distribution and straight morphology with diameters ranging from 50 to 100 nm and lengths up to ca. 60 μm. TEM results suggest that the nanowires consist of a crystalline core and an amorphous sheath. The nanowires were produced by hydrothermal treatment based on our original concept of slow structure formation by the dissolution of bulk glass source materials (borosilicate glasses), which can be used to supply a continuous source solution.

I. Introduction

Nanoscale one-dimensional materials[1,2] have attracted considerable attention due to their electromechanical, optoelectronic, and electrochemical properties. In particular, one-dimensional silicon oxide nanowires are of significant importance for photoluminescence, localization of light, near-field optical microscopy, low-dimensional waveguides, and nano-interconnection integrated optical devices.[3–9] However, complex and severe conditions are necessary to prepare silicon oxide nanowires by conventional methods such as chemical vapor deposition and physical vapor deposition, which require the use of metallic catalysts, precise control of the carrier gas (composition, flow rate, and pressure) and high temperatures (>900°C).[10–14] On the other hand, Chen *et al.*[15] have reported the fabrication of silicon oxide nanowires under mild conditions, and further development of silicon oxide nanowire fabrication routes will make the large-scale manufacture and application of such a material possible.

Recently, we developed the preparation of *b*-axis-oriented high-silica zeolite ZSM-5 thin films by a novel *in situ* hydrothermal method (200°C) based on an original concept of slow film formation by the dissolution of bulk glass source materials (silicate glasses).[16,17] This method is excellent for the control of the nanoscale morphologies and structures of the products, because the bulk glass source materials can be continuously supplied to a dilute source solution. Therefore, we expected that the fabrication of silicon oxide nanowires could be achieved under such mild hydrothermal conditions using appropriate bulk source materials. Here we report a simple method for the preparation of silicon oxide nanowires using borosilicate glass as a bulk glass source material without any metallic catalyst.

II. Experimental Procedure

Silicon oxide nanowires were prepared on dense stainless-steel (SUS304, Nilaco Co., Tokyo, Japan) substrates by hydrothermal treatment with bulk glass source materials and reaction solutions. Borosilicate glass (particle size ca. 250 μm) with a molar composition of $SiO_2:Al_2O_3:B_2O_3:Na_2O:MgO:CaO = 43:1.0:42:20:11:9.5$ was used as a bulk glass source material. The reaction solution, which contained tetrapropylammonium hydroxide (TPAOH) as an alkali source, was prepared with a molar composition of TPAOH: $H_2O = 18:10\,000$. Both the glass particles (0.5 g) and the substrate were immersed in the reaction solution in a 25 mL Teflon™-lined stainless-steel autoclave. The substrates were always positioned at the top of the reaction solution with the surface facing downward to avoid excess deposition of the synthesized particles. The autoclave was placed in an oven at 200°C for 24 h. After hydrothermal treatment, the substrates were washed with deionized water and dried at 50°C.

The morphologies of the samples were observed using scanning electron microscopy (SEM; JSM-6380A, Jeol Co., Tokyo, Japan) and transmission electron microscopy (TEM; EM-002B, Topcon Co., Tokyo, Japan). The compositions of the samples were analyzed using energy-dispersive X-ray spectroscopy (EDS; EX-23000BU, Jeol Co.). Chemical bonding characterization of the samples was performed using Fourier transform infrared spectroscopy (FT-IR; FT/IR-350, Jasco Co., Tokyo, Japan).

III. Results and Discussion

SEM observation (Fig. 1(a)) revealed uniformly sized and highly elongated nanowires with diameters ranging from 50 to 100 nm and lengths up to ca. 60 μm. In contrast to typical silicon oxide nanowires prepared by conventional methods with a metallic catalyst,[6,10] the growth points (indicated by a white arrow in Fig. 1(b)) of the samples were smooth, because no metallic catalysts were used in the preparation. Figure 2 shows the EDS spectrum of the sample after washing with HCl to remove adsorbed impurity species such as Na from the bulk source material. No morphological change was observed due to the HCl washing. The EDS analysis revealed that the sample contained Si, Al, and O, with an estimated Si:Al atomic ratio of 15:1.

Figure 3 shows the FT-IR spectrum of the prepared sample. For comparison, FT-IR spectra of borosilicate glass (the bulk glass source material) and quartz glass, which consist entirely of Si and O atoms, are also shown in Fig. 3. The sample spectrum was similar to that of quartz glass, which indicated that the nanowires consisted mainly of silicon oxide. The enlarged peak around 1100 cm^{-1}, which was attributed to stretching vibration modes of the SiO_4 tetrahedron,[18] was shown in the inset of Fig. 3. The sample peak shifted toward the low wavenumber side (ca. 1078 cm^{-1}) compared with that of quartz glass (ca. 1099 cm^{-1}). It is known that an increase of Al content in the

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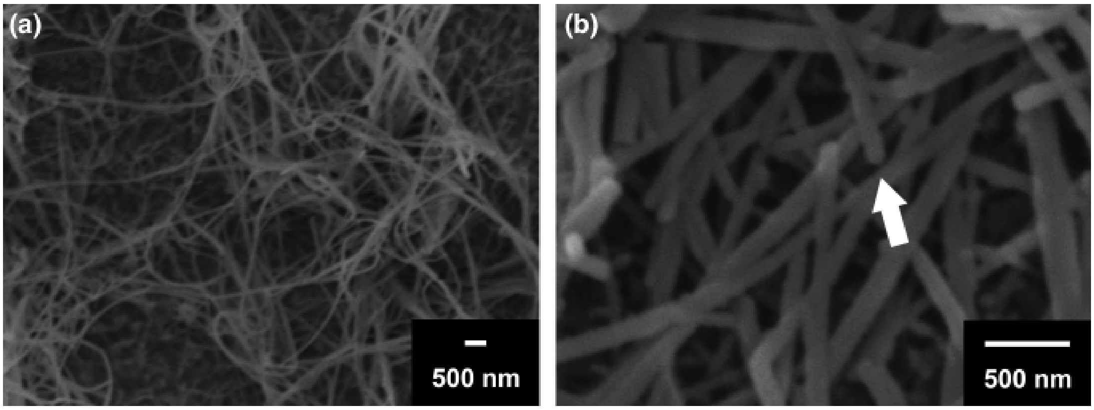

Fig. 1. Scanning electron microscopy images of (a) the sample resulting from 0.5 g of bulk glass source material solution and (b) the growth point (white arrow).

SiO_4 tetrahedron network results in peak shift toward a lower wavenumber,[18] which corresponds to the EDS results.

Figure 4 shows a typical TEM image indicating the general morphology of the nanowire sample. Most of the nanowires had a smooth morphology with a diameter of ca. 70 nm. A typical electron diffraction pattern of the sample is shown in the inset of Fig. 4. Although the observed complex spots could not be indexed, the result suggests that the nanowires were crystalline. In addition, it was revealed that the nanowires consisted of a high-electron-density core with a diameter of ca. 50 nm and a low-electron-density sheath with a thickness of ca. 10 nm. The difference in electron density between the core and the sheath suggests that the nanowires consisted of a crystalline core and an amorphous sheath.

In order to understand the effect of the source solution concentration on the nanowire growth process, the same preparation was performed with an increased amount of the bulk glass source material (2.0 g). The increase in the amount of the bulk glass source material implied an increase in the total surface area of the bulk source material, which resulted in an increase of the dissolution rate of the source material. The resulting samples did not show a uniform nanowire morphology, but were rod-like particles with relatively thick diameters and very short lengths, as shown in Fig. 5. This indicates that the concentration of the source solution played a significant role in the formation and growth of the nanowires. Growth mechanisms, such as vapor–liquid–solid[19] and oxide-assisted growth (OAG)[20–23] mechanisms, have been proposed for the formation of silicon oxide nanowires and silicon nanowires. The formation mechanism of the core/sheath structure nanowires prepared in the present study may be similar to that of silicon nanowires formed according to the OAG mechanism, where the outer sheath prevents growth along the transverse direction. Therefore, it is considered that the formation of the nanowires may be explained by the OAG mechanism, although the exact mechanism in this case is not yet clear. Further investigation into the formation mechanism is in progress.

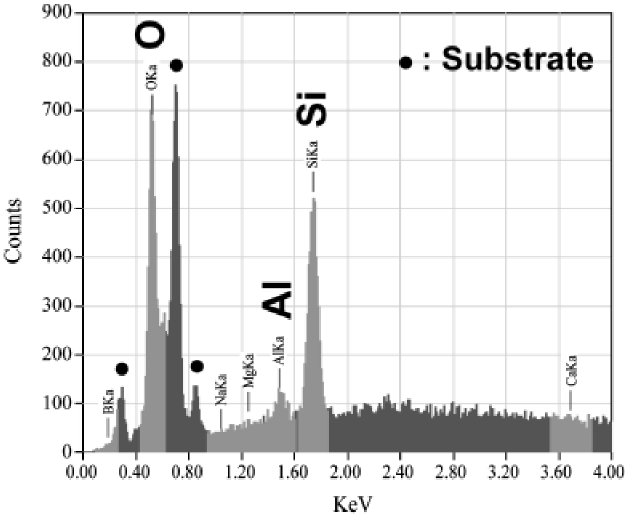

Fig. 2. Energy-dispersive X-ray spectroscopy spectrum of the sample after HCl treatment.

IV. Conclusions

Silicon oxide nanowires with diameters ranging from 50 to 100 nm and lengths up to ca. 60 μm were synthesized successfully without using metallic catalysts by low-temperature hydrothermal treatment. The TEM observation suggested that the nanowires consisted of a crystalline core with a diameter of ca. 50 nm and an amorphous sheath with a thickness of ca. 10 nm. The

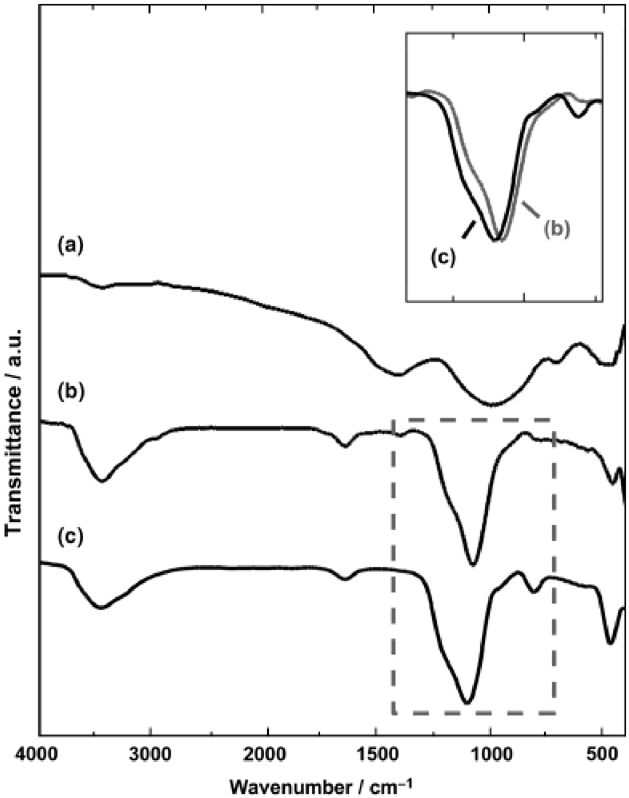

Fig. 3. Fourier transform infrared spectra of (a) borosilicate glass as a source material, (b) the prepared sample, and (c) quartz glass for comparison.

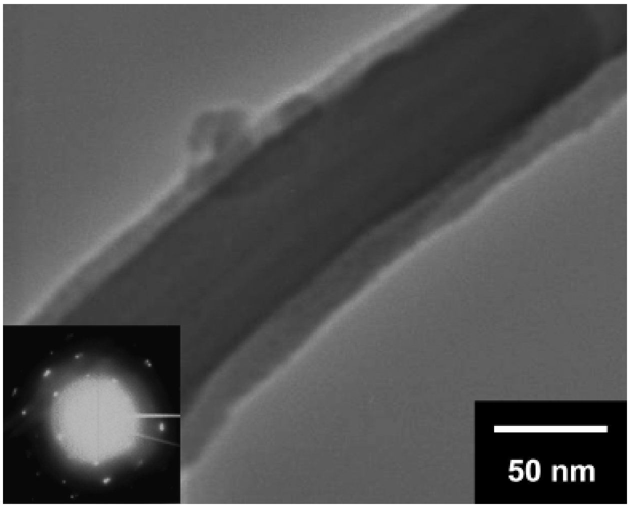

Fig. 4. Transmission electron microscopy image of the prepared sample. The inset shows an electron diffraction pattern of the sample.

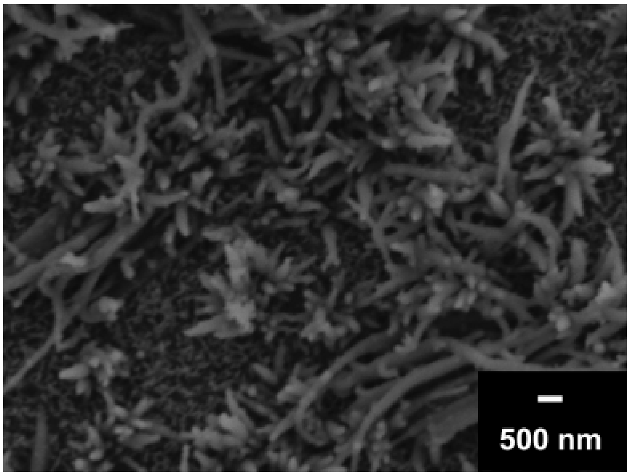

Fig. 5. Scanning electron microscopy image of the sample prepared using 2.0 g of the bulk glass source material.

preparation method is based on our original concept of slow structure formation by the dissolution of bulk glass source materials (borosilicate glasses), which can continuously supply a source solution. The present study revealed that the concentration of the source solution played a significant role in the formation and growth of the nanowires. This simple preparation method under mild conditions may have a potential for industrial-scale application.

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