Smooth silicon oxide nanowires under supercritically hydrothermal conditions


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Abstract

Large-scale amorphous silicon oxide nanowires (SiONWs) have been synthesized from silicon monoxide powder under supercritically hydrothermal conditions. The SiONWs with smooth surface can reach tens of microns long. Selected area electron diffraction (SAED) shows that the samples are completely amorphous. Energy-dispersive X-ray spectrometry (EDX) analysis reveals that the SiONWs consist of Si and O elements in atomic ratio approximately to 1:1.5. Photoluminescence (PL) shows luminescence in both blue and visible. During the growth process, the H⁺ and OH⁻ blocks the defects located on the surface of the SiONWs and lead to the constant growth of the SiONWs.

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1. Introduction

The discovery of Si whiskers [1], which are totally compatible with Si-based microelectronics, has attracted much attention for its potential applications in electronic nanodevices and fundamental studies of the effects of dimensionality and size on physical properties of the materials. On the other hand, silicon oxide, as an important candidate for photoluminescence materials, has been actively studied for a long time. Recently, considerable effort has been devoted to synthesizing silica one-dimensional (1D) nanomaterials by employing different techniques and explaining by different growth mechanism, such as vapor–liquid–solid (VLS) [1–3], solution–liquid–solid (SLS) [4], oxide-assisted growth [5] and catalytic chemical vapor deposition mechanism [6]. It is very interesting that silica may form some novel morphologies such as silica nanoflowers [7], silica nanocords [8], silica nanowires ‘bundles’ and ‘nanobrush’ arrays and silica nanotubes [9], and treelike and tadpolelike SiOₓ nanostructures [10]. Their various promising properties were also investigated, especially their optical properties. Intrinsic structural defects and extrinsic environment influences are generally used to explain some luminescence properties of silica [11–13]. Silica nanowires have potential application in high-resolution optical heads of scanning near-field optical microscope or nanointerconnection in future integrated optical device because of theirs intensive light emission [12]. Silica waveguides with diameters larger than the wavelength of transmitted light are also used in optical communications, sensors and other applications. Minimizing the width of the waveguides is desirable for photonic device applications, but the fabrication of low-loss optical waveguides with subwavelength diameters remains challenging because of strict requirements on surface roughness and diameter uniformity. Subwavelength-diameter silica wires for low-loss optical wave guiding have been fabricated by Tong...
et al. [14] using a two-step drawing process, which showed surface smoothness at the atomic level together with uniform diameter. Although silica nanowires with diameters ranging from ten to several hundreds of nanometers have been obtained with other methods [9], however, the diameter fluctuation and sidewall roughness of those wires make them unsuitable for low-loss optical wave guiding. Moreover, for most of the methods, a metallic catalyst must be used at least, which will impact on the properties of silica 1D nanomaterials, and the yield is little with a high cost and complex technologies. Therefore, it is important to synthesize nanoscale wires which show surface smoothness together with uniform diameter in large quantities without any metal remain that can meet the demands of further applications. In this letter, we report the synthesis of amorphous silicon oxide nanowires (SiONWs) with smooth surface and uniform diameter in large quantities by the supercritically hydrothermal process without any metallic catalyst. The formation of initial SiONWs and the growth process are discussed in detail to explain the possible growth mechanism of SiONWs.

2. Experimental

The system was the same as that used for synthesis of silicon nanotubes, which was described in detail elsewhere [15,16]. A mixture of 0.5 g silicon monoxide powder (purity: 99.99%, Particle size: ~73 μm, density: 2.1 g/cm³) and 50 ml deionized water used as the starting materials were put into a reaction kettle with a volume of 1000 ml. Subsequently, the reaction kettle was sealed and heated to 400–470 °C, 6–10 MPa, and then the temperature and pressures were maintained for 20 h. During the reaction, the rotating speed for the stirrer equipped in the reaction kettle was set up to 200 r/min. And the reaction kettle was cooled naturally. After the experiment, colorless and transparent products were found to deposit onto the interior wall of the reaction kettle and collected for various characterizations. The as-synthesized SiONWs were stable in air.

A JEOL JEM-3010 high-resolution transmission electron microscope (HRTEM) operating with a 300 KV accelerating voltage, equipped with energy-dispersive X-ray spectroscopy (EDX INCA, OXFORD) with sensitivity limit of 0–1 at.% (depends on element), and a JEOL JSM-6700 field emission scanning electron microscopy (FESEM) were used for morphological and chemical composition analysis. Photoluminescence (PL) spectrum was measured in a F4500 fluorescence spectrophotometer with a Xe lamp at room temperature. The excitation wavelength was 418 nm.

3. Results

Fig. 1(a) shows a typical SEM image of the as-synthesized SiONWs under supercritically hydrothermal conditions. In Fig. 1(a), the as-synthesized products displays straight and symmetrical distribution morphology with the diameter ranging from tens to hundreds of nanometers and the length up to tens of microns. In contrast to the morphology of silica nanowires produced by Lee et al. [17], there are no particles can be seen in our products, which indicates that the as-synthesized products are quite pure. The structures of the SiONWs were further studied by TEM. Fig. 1(b) shows a typical TEM image revealing the general morphology of the SiONWs. Most of the SiONWs have a smooth morphology. No core-shell structure can be seen in the SiONWs, which often appear in silicon nanowires synthesized by the oxide-assisted growth process. The selected area electron diffraction (SAED) pattern shown in the inset in Fig. 1(b) reveals that SiONWs are completely amorphous states. SEM image of the single SiONW with higher-magnification (Fig. 2(a)) shows no visible irregularity in the surface of the SiONW. The HRTEM image of the single SiONW (Fig. 2(b)) shows that the sidewalls of the SiONWs have very smooth surface. The maximum diameter variation ΔD is less than 5 nm over the length L of the nanowires. The smooth surface and small sidewall roughness of these nanowires may be suitable for low-loss optical wave guiding [14]. Fig. 2(d) is the high-magnification transmission electron microscope image of the tip of the SiONW, showing that no metallic catalyst exist at the tip. The EDX spectrum shown in Fig. 2(c)
reveals that the SiONWs are composed of silicon and oxygen, but no other elements exist. Further quantitative analysis shows that the atomic ratio of Si:O is about 1:1.5.

Blue light emission at 445.6 nm, 468.6 nm and a weak visible luminescence peak at 624.6 nm are observed from the Fig. 3. The peak at about 468.6 nm was from neutral oxygen vacancy (≡Si–Si≡). Compared with Ref. [18], the shoulder peak at 445 nm changes into an intensive peak. The shoulder peak at 468.6 nm in Fig. 3 approaches the peak at 470 nm in Ref. [12]. Yu et al. [12] and Kar and Chaudhuri [18] have attributed the peak at 445.6 nm (~2.8 eV) emission in silica nanowires to the same origins of the 2.7 eV emission in bulk silica according to the discussion of Nishikawa et al. [19]. The PL spectroscopy shows a intense peak at 445 nm which often be observed in the previous PL results of SiO₂ nanowires [12,18]. It is worthy to note that the PL spectroscopy also show a peak at 624.6 nm which was observed in silicon nanowires [20]. The peak at 624.6 nm is not the secondary harmonic oscillation of the laser source because the PL was measured at room temperature using a Xe lamp with 418 nm excitation wavelength. According to the discussion of Sham et al. [20], the 624.6 nm luminescence may be attributed to interface defects between Si and silicon oxide, and suboxide and quantum-confined silicon crystallites with a slightly larger size (2 < d < 5 nm) [20]. This result indicates that as-grown SiONWs may contain small unoxidized Si nanocrystallites contributing to the luminescence, a quantum confinement behavior [21].

4. Discussion

To elucidate the growth mechanism of the SiONWs, both the tip and middle part of the SiONWs were examined in detail by HRTEM and EDX. As shown in Fig. 2(d), no metallic catalysts can be clearly observed at the tip of the as-grown SiONWs. The HRTEM image of middle part of the SiONWs is shown in Fig. 2(b). Except for the
smooth surface, no amorphous SiO$_2$ shell is observed from the surface of the SiONWs, while it often can be seen in silicon nanowires. The chemical composition at the tip and the middle part of SiONWs was analyzed by EDX revealing that the tip and the middle part of SiONWs are only composed of Si and O with an atomic ratio of 1:1.08 and 1:1.6 respectively. The results indicate that the SiONWs are nonstoichiometric. The results also indicate that there is more oxygen at the middle part than at the tip, which may be attributed to the adsorbed OH$^-$ from the ionization of water under high temperature and high pressure conditions [22]. Moreover, we have analyzed the SiONWs with different diameter by EDX and also found that there is more oxygen at the middle part than at the tip.

We now discuss the reason that amorphous material is formed in a form of nanowire, which is similar to the one-dimensional crystalline semiconductor wires of Si and Ge [23,24]. It is well known that three models can explain the growth mechanism of one-dimensional materials. One is the conventional spiral growth mechanism, which concerns the existence of a screw dislocation whose line is parallel to the axis of the nanowire. In this model, the spiral plane perpendicular to the dislocation line provides a growth step, which serves as a low-energy site, so that the growth rate along the axis direction is much faster than that of the radius direction, and there exists a conical tip at one end of the nanowires or whisker [25,26]. The dislocation model loses its meaning for our case because the nanowires are amorphous. The second is the vapor–liquid–solid (VLS) mechanism, in which an intermediate nanoparticle is located at one end of nanowires and serves as catalyst. We can rule out the VLS mechanism because there is not any catalyst at the tip of the SiONWs, as shown by EDX and HRTEM, and the source material is high pure silicon monoxide. The most likely mechanism to explain the growth of the SiONWs seems to be analogous to the oxide-assisted growth process proposed by Lee et al. [5,27,28]. In contrast to the conventional VLS mechanism, the oxide-assisted growth process relies on an oxide or a redox reaction instead of a catalytic metal or metal compound to assist the formation of nanowires. For the oxide-assisted growth, the important characterization is the oxide outer shell which prevents the growth along the cross direction. However, in our products there is no oxide outer shell on the surface of the SiONWs and our products are amorphous.

Here, a water-assisted growth model of amorphous SiONWs is suggested according to the analysis on the HRTEM and EDX results and the model proposed by the others under different synthesis conditions. The growth model is shown in Fig. 4. Under high temperature and high pressure conditions, the SiO is evaporated from the silicon monoxide powder and decomposed into gaseous Si and SiO$_2$. And at the same time, H$_2$O vapor is ionized into H$^+$ and OH$^-$ [22]. Therefore, five species are contained in the vapor, i.e., H$^+$, OH$^-$, SiO, SiO$_2$ and Si. There is a temperature gradient in the reaction kettle at the perpendicular direction. The SiO vapor phase has a priority to liquefy into SiO droplet because of a higher freezing point of SiO than that of Si and SiO$_2$. Therefore, the SiO droplets directly deposit onto the upper surface of the reaction kettle where the temperature is lower than that of bottom. And the SiO droplets serve as the sites for adsorption of Si and SiO$_2$ from the vapor. Meanwhile the Si and SiO$_2$ vapor are adsorbed into the SiO droplet continuously where Si reacts with SiO$_2$ as the following process under supercritically hydrothermal conditions: Si + SiO$_2$ $\rightarrow$ SiO$_x$ ($x > 1$). SiO$_x$ nanowires are less stable than Si and SiO$_2$ because SiO$_x$ is nonstoichiometry and the SiO$_x$ nanowires contain a great deal of surface structural defects ($\equiv$Si–O–Si$^-$ and $\equiv$Si–O$^-$) on the surface due to the large surface/volume ratio. These defects result from the splitting of the $\equiv$Si–O–Si$^-$ regular bonds at the moment of the SiONWs formation. With respect to the adsorption–desorption process, the SiONWs are in a nonequilibrium condition. It is worth noting that H$_2$O vapor is ionized into H$^+$ and OH$^-$ under high temperature and high pressure conditions. When the H$^+$ and OH$^-$ are adsorbed into the surface of the droplet, the defects of $\equiv$Si–$^-$ and $\equiv$Si–O$^-$ on the surface of the SiO$_x$ nanowires were blocked by OH$^-$ and H$^+$ respectively, forming $\equiv$Si–OH on the surface [29]. The H$^+$ and OH$^-$ may play an important controlling factor during the growth of SiO$_x$ nanowires [30,31]. Because the H$^+$ and OH$^-$ can reduce the adsorption activity of the SiONWs surface which is similar to the results reported in Ref. [29] that water molecules completely reduce the adsorption activity of the silica nanoparticle surface. As a consequence, the SiONWs come to an equilibrium condition and grow along a direction. Based on the above analysis of chemical composition at the tip and the middle part of SiONWs by the EDX, it is more believed that the more oxygen at the middle part of the SiONWs is from OH$^-$ which is adsorbed on the surface of the SiONWs to form $\equiv$Si–OH and to stabilize the structure.
5. Conclusions

In summary, we have synthesized amorphous SiONWs which exhibit smooth and straight morphology in high yield without catalysts from silicon monoxide under hydrothermal conditions. The SiONWs have a uniform diameter and long length. EDX and SAED analysis show that the SiONWs are amorphous silicon oxide nanowires. The growth mechanism of SiONWs is different from the oxide-assisted growth mechanism of Si nanowires. The water plays an important role during the growth process which provides H⁺ and OH⁻/CO³ under supercritically hydrothermal conditions. The H⁺ and OH⁻ block the defects on the surface of the SiONWs and stabilize the structure as well as assist the growth of SiONWs along the axial direction. The amorphous SiONWs show a blue light emission at 445.6 nm, 468.6 nm and a visible light emission at 624.6 nm.

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