Preparation of Aligned Amorphous Silica Nanowires

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Highly aligned amorphous silica nanowires were prepared on silicon substrate. The products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), and selected-area electron diffraction (SAED). The photoluminescence (PL) spectrum of silica nanowires showed strong blue emission peaked at 401 and 440 nm under 274 nm excitation wavelength. The growth mechanism of the nanowires was proposed.

Nanomaterials are increasingly receiving great interests and have been developing extensively in recent years. Various nanotubes, nanobelts, nanowires, and whiskers of different chemical compositions have been made of SiC,[1] GaN,[2] mullite,[3] CdS,[4] et al. Among these materials, silica-based nanostructures and silicon oxide nanowires have attracted considerable attention because of their potential applications in opto-electronics or reinforcement materials. Some investigations on the photoluminescence properties of amorphous silicon oxide have been developed.[5–8] Commonly, silicon oxide nanowires have been synthesized by the laser ablation technique,[9] metallic catalyst-assisted routes,[10–14] and electrochemical method.[15] In this paper, we reported a simple and efficient method for the large-scale synthesis of highly aligned silica nanowires directly on the silicon substrates starting from amorphous silica powders as raw material. The optical properties and the growth mechanism of the nanowires were also studied.

The sol–gel-derived amorphous SiO_2 powders doped with Ni and active carbon were used as source materials, the weight ratio was SiO_2:C:Ni = 1:1:0.005. The clean silicon (100) wafer was used as substrate. The source powders were placed in an alumina boat and the substrate was loaded 10 mm away from the powders at the downstream end of the boat. Then the boat was placed in a tubular furnace. The furnace was heated to 1300 °C (heating rate of 8 °C/min) under NH_3 atmosphere (99.9%, flow rate of 100 mL/min) and kept at this temperature for 8 h. The furnace was cooled on standing and the white cotton-like layer was formed on the whole silicon substrate.

The as-synthesized products were characterized and analyzed by scanning electron microscopy (SEM, Hitachi S-3500) equipped with EDS, TEM, (Hitachi H-800) and SAED. For SEM investigations, after pre-sputtering with a conducting layer of Au, the products together with the growth substrate were directly transferred into the SEM chamber. Some products scratched from the substrate were used for EDS analysis. For TEM studies, some samples scratched from the substrate were ultrasonically dispersed in ethanol and dropped on Cu grids coated with amorphous carbon. Photoluminescence spectrum (PL, Hitachi 850 fluorescence spectrophotometer) was measured at room temperature using a Xe lamp with 274 nm excitation wavelength in the spectral range of 340–460 nm.

The low magnification SEM image (Figure 1a) shows that the products formed on the silicon wafers are grown homogeneously fibrous structure with lengths of several hundreds micrometers, which is highly aligned and closely packed on the substrate. The higher magnification image (Figure 1b) indicates that the products are made of nanowires and the diameters are in the range from 80–100 nm. EDS results show that the nanowires are composed of Si and O with the atomic ratio close to 1:2. No other element such as Ni is detected at the 2 atom % sensitivity level of the instrument.

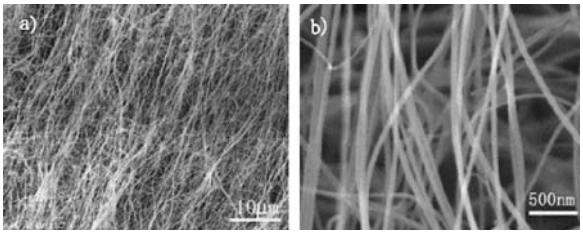

Figure 1. SEM images of the products. (a) Low-magnification of the sample on the substrate. (b) High-magnification image.

TEM image of silica nanowires indicates that the nanowires have a uniform diameter along their whole length. The average diameter of the nanowires is about 80 nm. The surface of the nanowires is smooth and no catalytic particles are found on the tips of the nanowires. The electron diffraction pattern (inset in Figure 2) shows that the nanowires are completely amorphous.

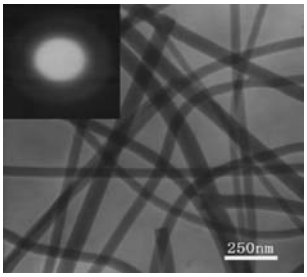

Figure 2. TEM image of the products (the inset shows the SAED).

In Figure 3, the PL spectrum shows two distinguishable peaks at 401 nm (3.1 eV) and 440 nm (2.8 eV), which are similar to the PL spectrum bands usually observed in amorphous silica nanowires. It is reported that the 2.7 eV band is the characteristic of silica, which is ascribed to the neutral oxygen vacancy (≡Si–Si≡) on the basis of ab initio molecular-orbital calculations. The 3.1-eV band corresponds some intrinsic diamagnetic defect center, such as the twofold coordinated silicon lone-pair centers (O–Si–O).[16] These defects are clearly due to high oxygen deficiency in sample preparation and they are also radiative recombination

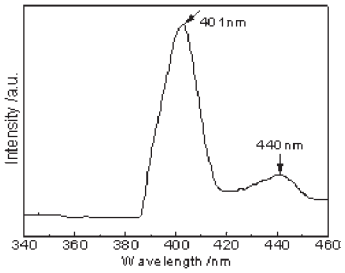

Figure 3. PL spectrum of the silica nanowires.

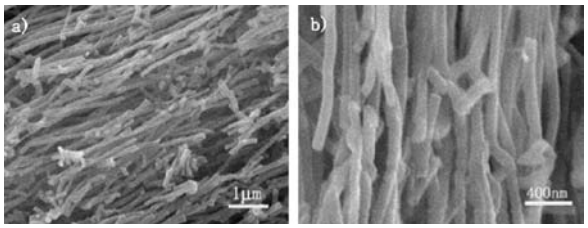

Figure 4. SEM images of the silica nanorods. (a) Low-magnification of the nanorods. (b) High-magnification image.

centers for blue luminescence. Because the blue light emission materials have long been of great interests for semiconductor full-color display, the silica nanowires may play an important role in fundamental research and technological applications.

In the experiment, it is interesting to find that some aligned nanorods (Figure 4) were formed on the edge of the back of the silicon substrate. The nanorods are uniform with diameter of about 100 nm and length up to several micrometers. EDS analysis shows that the nanorods are consisted of Si and O and the atomic ratio is 33.8:66.2, which is in good agreement with SiO_2.

Some comparative experiments were performed to determine which parameters controlled the growth of the aligned nanowires. Silicon wafers with different orientations ((111) or (100)) were used as substrates, the result suggests that the yield of silica nanowires is independent of the orientations of the silicon substrate. Furthermore, the silicon substrates dipped and undipped by the catalyst have no effect on the yield of the nanowires. However, the source powders in the boat with catalyst and without catalyst lead to different results of the produce of nanowires. That is to say, the catalyst in the source powders is an important factor. We think that Ni catalyst particles act as nucleation center and lead the nanowire growth. Aligned silica nanowires could also be formed when Ar (99.9%, O_2 20 ppm) instead of NH_3 was used, but the experiments conducted in the air or in the high vacuum condition demonstrate that no aligned nanowires formed. So, a certain amount of oxygen in the gas plays an important role for the growth of silica nanowires. To further understand the effect of O_2, we intentionally introduced a small amount of O_2 along with Ar or NH_3 after the furnace was pumped. Silica nanowires could also be formed. However, the amount of O_2 could not exceed a limit (about 5 mol %) in the mixture gas. Otherwise silica nanoparticles would be formed. So the quantity of O_2 in the reactor is a critical factor for the growth of silica nanowires. Finally, the experiment without silica powders and active carbon was carried out and no nanowires were formed on the silicon substrate, which suggests that the SiO gas generated by reduction of SiO_2 powders with activated carbon is a key factor too.

On the basis of the experiments aforementioned, the catalyst in the source powders is a key factor. But no catalytic droplets are found in the end of nanowires. So the traditional VLS growth mechanism is unsuitable here. By considering all the results, a growth mechanism can be proposed as follows.

$$SiO_2\ (s) + C\ (s) \rightarrow SiO\ (g) + CO\ (g)$$

$$SiO\ (g) + 1/2O_2\ (g) \rightarrow SiO_2\ (s)$$

In this process, the catalyst was evaporated towards the substrate to promote nucleation. The SiO (g) also arrived at the substrate with the carrier gas, which diffused to the top regions of the nucleation sites. Because of the presence of little amount of O_2, which mainly came from the residue in the reaction chamber or from the silica powders and the carrier gas, SiO was oxidized directly to form SiO_2 nanowires. The nanowires aggregated to form aligned structures by the weak van der Waals' attraction between them.

In summary, we succeed in the preparation of the amorphous silica nanowires by a simple method. The nanowires have uniform diameter and are highly aligned with smooth surface. A growth mechanism was proposed on the basis of some comparative experiments. The results show that the catalyst, SiO (g) and little amount of O_2 are main factors for the growth of the aligned nanowires. The intensive blue light emission was observed which could be attributed to defect centers of oxygen deficiency in the nanowires. These properties suggest that highly aligned silica nanowires will have great promising applications in integrated optical devices.

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