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Synthesis of straight Y-shaped SiO_x nanorods by a simple thermal evaporation method

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ABSTRACT

The straight Y-shaped silicon oxide [SiO_x ($1 < x < 2$)] nanorods have been synthesized on Si wafers by thermal evaporation of mixed powders of silica and carbon nanofibers at 1300 °C and condensation on an Si substrate without assistance of any catalyst. The synthesized products were characterized by means of scanning electron microscopy, transmission electron microscopy, high resolution transmission electron microscopy, energy dispersive X-ray spectroscopy, and Raman spectrum. The results suggested that the straight Y-shaped nanorods are amorphous and consist only of silicon oxide, and these rods with diameters about 50–200 nm have a neat smooth surface. The growth of such silicon oxide nanorods may be a result of the second nucleation on the surface of rods causing a change in the growth direction of silicon oxide nanorods developed.

1. Introduction

In the recent years, there has been an increasing interest in the synthesis of various quasi one-dimensional nanosized materials such as nanotubes, nanowires, nanorods etc. These one-dimensional nanomaterials show some novel physical and chemical properties due to their peculiar structure and size effect, and they are one of the most promising elements for the fabrication of nanoelectronic devices [1,2] and integrated optical devices [3]. Among them, as an important member in the one-dimensional nanomaterials family, silica nanomaterials have been actively studied for a long time. Silica nanomaterials with various microstructures have been synthesized by utilizing a variety of methods, such as laser ablation [4], vapor–liquid–solid (VLS) [5,6], vapor–solid (VS) [7,8], sol–gel methods [9,10], and the bio-mimetic strategies [11].

In this paper, we report the synthesis and structure of very straight Y-shaped silicon oxide nanorods with fixed angles between the branches by thermal evaporation of mixed powders of silica and carbon nanofibers. These novel Y-shaped silicon oxide nanorods can be of interest, first, because, as far as the authors know, straight Y-shaped silicon oxide nanorods without metal catalyzer formed this way have not been recorded earlier in the literature. Second, these straight truly Y-shaped silicon oxide nanorods may provide useful applications not only in nanodevices design and fabrication but also in fiber-reinforced composites.

2. Experimental procedures

The straight Y-shaped silicon oxide nanorods were prepared in a horizontal electric resistance tube furnace with a gas supply and a control system. Fig. 1 shows a schematic diagram of the experimental setup employed during the course of the present work. A p-type Si (111) plate ($9 \times 2.5 \times 0.05$ cm^3) was used as substrate for the growth of the straight Y-shaped silicon oxide nanorods. The plate was ultrasonically washed in acetone for several minutes to clean the surface of the plate, and then rinsed with deionized water. The raw material was a mixture of silica and carbon nanofiber powders at a weight ratio of 2:1. Here, silica powder and carbon nanofibers in the raw material are synthesized by combustion and CVD method in our laboratory, respectively. It was placed in a ceramic boat that was covered with the cleaned Si plate, and then the boat was transferred into the centre of a ceramic tube mounted (in zone I) in the horizontal tube furnace with diameter 4.5 cm. Prior to heating the tube furnace was purged with N_2 gas for 10 min to

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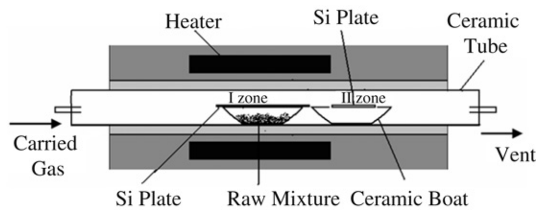

Fig. 1. A schematic diagram of the experimental setup.

eliminate air in the furnace. Under the ambient pressure and a constant flow of the mixture gas 3% H_2–Ar (50 sccm) and N_2 (50 sccm) were introduced into the tube, the furnace temperature was heated to 1300 °C and held for 2 h. After the furnace was cooled down to about 700 °C at 10 °C/min, and then cooled naturally to room temperature with the carrier gas the white products were observed on the surface of substrates in zone I.

The morphology of the as-synthesized products was examined by scanning electron microscopy (SEM, JEOL 6500F), and structural analysis was carried out using transmission electron microscopy (TEM, JEM-200CX) and selected area electron diffraction (SAD). Compositional analysis was performed by an energy dispersive x-ray spectrometer (EDS) attached to the TEM. The specimens for TEM analysis were prepared by dispersing the samples in ethanol followed by sonication for 10 min. A few drops of the suspension were dropped onto a microgrid covered with a holey graphite thin film. The Raman spectrum was measured with a Rainshaw optical confocal Raman spectrometer at room temperature. The 514 nm line of an Ar^+ laser was used as the excitation source.

3. Results and discussion

The SEM images of the as-synthesized products are shown in Fig. 2. It can be clearly seen that the as-synthesized products consist of many Y-shaped nanorods with straight branches (Fig. 2(a)). The majority of the Y-shaped silica nanorods have three long branches of up to several micrometers, while the others have two long branches and a short one of several tens of nanometers. Some silicon oxide nanorods branched several times to form multiple Y-shaped structures, which still keep their branches straight. Fig. 2(b) is the close-up view image of the white pane area marked in Fig. 2(a), it shows a straight Y-shaped silicon oxide nanorod with neat smooth surface and uniform branches of about 180 nm in diameter. The angles between the three branches in the sample have been measured on 10 different Y-shaped silicon oxide nanorods from SEM images. As a result, the angles are close to 120°. All the Y-shaped structures have very similar shape regardless of their different diameters. In order to clarify the composition of deposition, the sample was examined by EDS attached to the TEM. Fig. 3 shows a typical EDS spectrum of an individual nanorod. It is clearly shown that the nanorods consist of elements Si and O with an atomic ratio about 1:2. The Cu peaks come from the TEM grid.

A typical Raman spectrum taken from Y-shaped silicon oxide nanorods is shown in Fig. 4. It is well known that Raman scattering provides a particular insight into the microstructure and conformation of materials. Fig. 4 shows an asymmetrical sharp peak at 504 cm^{-1} with broadened linewidth. The result is consistent with that of Liang et a1 [5], who point out the shift and the broadened linewidth can be attributed to the effect of the oxygen deficiency such as forming neutral oxygen vacancies (≡ Si–Si ≡) [12], which may play a similar role as the non-crystalline silicon.

The structure of Y-shaped silicon oxide nanorods synthesized by thermal evaporation has been examined by using TEM and HRTEM. Fig. 5 are typical TEM images of Y-shaped silicon oxide nanorods. An individual Y-shaped silicon oxide nanorod (Fig. 5(a))

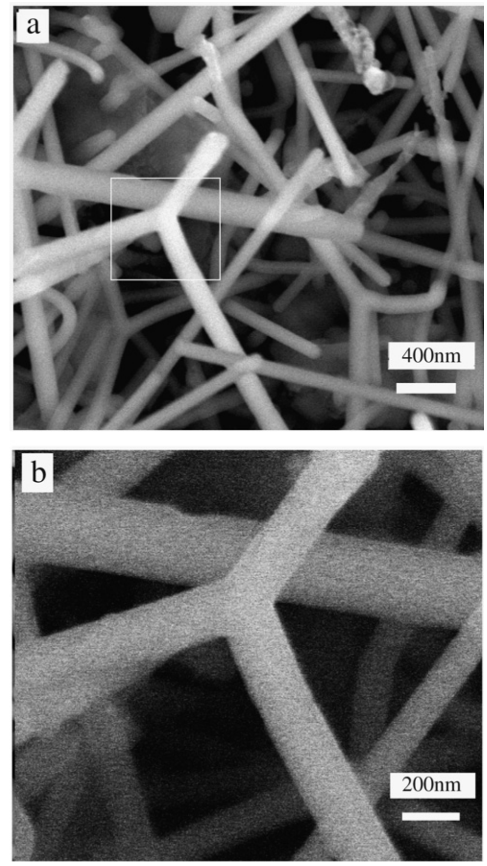

Fig. 2. (a) SEM image of as-synthesized Y-shaped silicon oxide nanorods; (b) close-up view showing Y-shaped structure in Fig. 2(a).

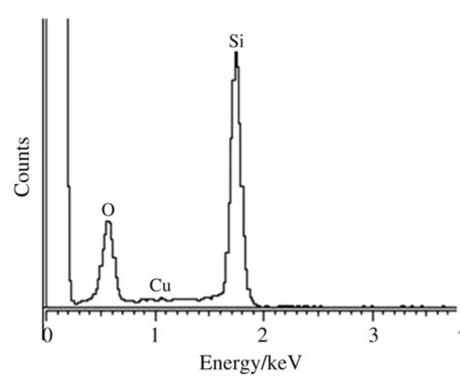

Fig. 3. A typical EDX spectrum of individual silicon oxide nanorods.

has neat smooth surface with diameter of about 50 nm. Fig. 5(b) shows a double straight Y-shaped structure with short and long branches. All branches have the same diameters in the double Y-shaped structure, in agreement with SEM observations. Fig. 5(c) is the enlarged image of the Y-shaped structures and the selected-area electron diffraction (SAED) pattern from the white round area marked in one branch (inset) with only diffusive rings (without diffraction spots), revealing the amorphous nature of the silicon oxide nanorods. Furthermore, Fig. 5(d) is the HRTEM image of the white rectangular area marked in Fig. 5(c), revealing that no fringes exist in the silicon oxide nanorods.

To understand the growth formation of Y-shaped structures, many questions about its formation must be clarified. For example, (1) How do we supply silica? (2) How do we supply carbon nanofibers? (3) How about the reactions of the mixed powers