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# Synthesis of coaxial nanowires of silicon nitride sheathed with silicon and silicon oxide

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## Abstract

Coaxial nanowires, with about 45 nm in diameter and about 15  $\mu$ m in length, have been synthesized by reaction of silicon dioxide nanoparticles with active carbon at 1450°C in flowing nitrogen atmosphere. Their structures consist of an  $\alpha$ -phase silicon nitride core, an amorphous silicon and a silicon dioxide outer shell, similar to those of coaxial nanocables. The formation mechanism of the coaxial nanowires is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Nanostructures; C. Transmission electron microscopy; D. Electronic transport

# 1. Introduction

The discovery of carbon nanotubes [1] has attracted intense experimental and theoretical interest in such structures. Theoretical investigations on carbon nanotubes suggest that their electronic properties can be tuned from metal to semiconductor with a small gap, depending on the tube diameter and chirality [2,3]. The idea of making nanodevices such as nanometer-scale electronic switches by connecting pure carbon nanotubes has been first proposed [4]. This idea has also promoted syntheses of heteroatomic nanotubes and multilayered nanotubes such as BN nanotubes [5] and nanotubes in the B-C-N ternary system [6,7]. Recently, coaxial nanocables comprising silicon carbide and silicon oxide sheathed with boron nitride and carbon have been successfully synthesized and a great potential application in electronic transportation or nanodevices has been suggested on the basis of their electronic and structural properties [8]. Therefore, it is very important to synthesize coaxial nanocable comprising different kinds of nanotube in axial or radial direction for making nanometerscale electronic devices with a variety of functions. However, the synthesis of one-dimensional nanoscale structure materials still remains to be a challenge. As for the synthesis of nanorods, Dai et al. [9] first succeeded in preparing carbide nanorods by the nanotube template

method and thought that carbon nanotubes were converted into carbide nanorods through reaction with a volatile metal oxide. Then Han et al. exploited the method to obtain GaN [10] and  $Si_3N_4$  [11] nanorods by the reaction of carbon nanotubes with a volatile metal oxide in ammonia and nitrogen atmosphere, respectively.

In this paper, we report the synthesis of a kind of new coaxial nanostructure material, i.e. silicon nitride nanowires sheathed with silicon and silicon oxide layers, by the reaction of silicon oxide nanoparticles and active carbons. The formation mechanism is also discussed.

## 2. Experimental

The preparation processes were as follows: first,  $SiO_2$  nanoparticles with average dimension about 20 nm were prepared according to Ref. [12]; polyethylene glycol 6000 (50 g) put in alumina crucible was thermally decomposed into active carbons in nitrogen atmosphere at 700°C for 3 h. Then the mixture of SiO<sub>2</sub> nanoparticles (5 g) with active carbon powders (5 g) was ball-milled for 20 h, and pressed to several circular pellets under pressure of 10 MPa. The pellets were calcined at 1450°C in flowing nitrogen atmosphere for 2 h. Wool-like products depositing on the surface of the pellets were collected for characterizing.

X-ray powder diffraction patterns of the products were obtained with Philips PW 1700 X-ray diffractometer with

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Fig. 1. X-ray diffraction pattern of the coaxial nanowires; T shows high-temperature phase of SiO<sub>2</sub>.



Fig. 2. (a) TEM image of the coaxial nanowire. (b) A magnified image of the coaxial nanowire. (c) SAED pattern of the coaxial nanowire along [ $\tilde{1}11$ ] direction shows  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>.



Fig. 3. HREM image of the coaxial nanowire; the sheath is amorphous layers. The distance between the parallel fringes is 0.433 nm along the [101] direction, which shows that the center core of the coaxial nanowire is  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>.

Cu-Kα radiation. Transmission electron microscopy (TEM) images of the products were taken with a JEM-200CX transmission electron microscope. High-resolution electron microscopy (HREM) images of the products were taken on a JEOL-2010 transmission electron microscope. Energy dispersive X-ray (EDX) spectra of the products were recorded by OXFORD-6498 energy dispersive X-ray spectrometer attached HREM.

## 3. Results and discussion

Fig. 1 shows the X-ray powder diffraction pattern of the products. It is identified as a mixture of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub>. As shown in Fig. 1, the peaks assigned to  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> are stronger than those of SiO<sub>2</sub> labeled as T, which indicates the products are dominantly α-Si<sub>3</sub>N<sub>4</sub>. A general overview of the low-magnification TEM image of the product shown in Fig. 2(a) indicates that the products are rod-like structure with about 15 µm in length and 45 nm in diameter. A magnified TEM image as shown in Fig. 2(b) indicates that each individual nanowires observed in low-magnification TEM images is actually a composite nanowire consisting of a crystalline core with about 15 nm in diameter and a surrounding amorphous sheath with about 15 nm in thickness. Selected area electronic diffraction (SAED) pattern as shown in Fig. 2(c) indicates the crystalline core of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> with [111] axis parallel to the electron beams. A HREM image as shown in Fig. 3 indicates that lattice interlayer



Fig. 4. A schematic illustration of the coaxial nanowire; a and b (solid arrows) indicate the positions of the electronic probe.

distance of parallel fringes from the core is 0.433 nm, being the (101) spacing of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and the sheath is amorphous layer. EDX quantitative microanalysis across a nanocable has been carried out. Fig. 5(a) indicates the percentage of oxygen (65.82 at.%) and silicon (34.18 at.%) when the electron probes are concentrated on the outer layer, and Fig. 5(b) shows that of silicon (65.40 at.%), nitrogen (18.00 at.%) and oxygen (16.60 at.%) on the center region, and Fig. 5(c) indicates that of silicon (52.94 at.%), nitrogen (0.00 at.%), oxygen (65.82 at.%) for the region between a and b as marked in Fig. 4. Because atomic ratio of the oxygen and silicon on the outer layer approaches 2:1 from Fig. 5(a), the outer layer is SiO<sub>2</sub>. After the contribution of Si in the center core (Si<sub>3</sub>N<sub>4</sub>) and the outer layer (SiO<sub>2</sub>) is subtracted on basis of Fig. 5(b), silicon about 43.6 at.% is still left in the intermediate region. Similarly, as the contribution of Si in the outer layer  $(SiO_2)$  from Fig. 5(c) is deducted, silicon about 20.03 at.% still remains. The difference of the silicon content results from the different thickness of the redundant silicon region where the electron probes go through. Therefore, it demonstrates that the sheath has a redundant silicon region from the outsider to the inside. That is to say, the structure of the products consists of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> nanowires sheathed with amorphous Si and SiO<sub>2</sub> layers as shown in Fig. 4. Because both Si and SiO<sub>2</sub> are amorphous, resulting in their small contrast on TEM photograph, it is difficult to identify their clear interface. The lattice of the amorphous Si and SiO<sub>2</sub> lacks in periodicity, so it is also impossible to observe their lattice fringe on HREM image. Solid arrows labeled a and b in Fig. 4 indicate the positions of the electron probes, which are concentrated on the outer layer and the center region in EDX analysis, respectively. Because amorphous silicon is semiconducting, while  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> are insulators, the prepared nanowire is of the structure of an insulator-semiconductor-insulator in the radial direction, similar to coaxial nanocables. This structure characteristic



Fig. 5. EDX spectra of the coaxial nanowire. (a). The electronic probe is concentrated on the periphery (a in Fig. 4). (b). The electronic probe is concentrated on the center region (b in Fig. 4). (c). The electronic probe is concentrated on the region between a and b in Fig. 4.

of the product may have a potential application in electronic transportation and nanodevices.

Considering that no droplets are observed on their ends of the nanowires, the growth mechanism of the nanowire can be explained in terms of the vapor–solid (VS) mechanisms [13,14]. The chemical reaction is expressed as follows [15–17]:

 $C (solid) + SiO_2 (solid) = SiO (vapor) + CO (vapor)$  (1)

SiO(vapor) + C(solid) = Si(vapor) + CO(vapor) (2)

 $2\text{SiO}(\text{vapor}) = \text{Si}(\text{vapor or solid}) + \text{SiO}_2(\text{solid})$  (3)

 $3Si (vapor) + 2N_2(gas) = \alpha - Si_3N_4(solid)$ (4)

The above growth process can be divided into three steps. The first step is the formation of nuclei of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and the one-dimensional growth of the nuclei through reactions (1)-(4). Both active carbon and nanoscale  $SiO_2$  are sufficiently ball-milled to form a great many of interfaces between the reactants, which is beneficial to the reactions. Si vapor is produced through reactions (2) and (3). In gas phase, the nuclei of silicon nitride is synthesized through reaction (4), and deposits on the surfaces of the reactant nanoparticles to form the center of the one-dimensional growth of silicon nitride. The HREM image shown in Fig. 3 suggests that the nanowires of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> grow in the [101] crystallographic direction. The reaction forming  $\alpha$  and  $\beta$  phase silicon nitride is kinetically competitive. Since the experimental reaction takes place in gas phase and silicon (gas) move easily to combine with nitrogen molecules, the obtained product is almost pure  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> [14]. The second step is the formation of the coating of Si and SiO sheath on the surface of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> nanowires. Due to the greater molar mass of SiO (gas) compared with Si (vapor), the diffusive rate of Si vapor is faster than that of SiO vapor in the process of the reaction. Si (gas) molecules arrive on the surface of silicon nitride core prior to SiO (gas) molecules. However, the reaction rate of reaction (4) is slower so that a small amount of Si remains, both Si and SiO deposit on the surface of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> nanowires, respectively, to form sheath structure. The third step is that SiO (vapor) reacting with O<sub>2</sub> forms SiO<sub>2</sub> (solid) on the outer shell during cooling.

### 4. Conclusions

A new type of coaxial nanowire made of an  $\alpha$ -phase silicon nitride core, an amorphous silicon and silicon dioxide have been successfully synthesized by a reaction of silicon dioxide nanoparticles with active carbon at 1450°C in flowing nitrogen atmosphere. They may have potential applications in nanometer-scale electronic transportation and nanodevices due to the semiconducting characteristic of the amorphous silicon.

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