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Formation of Silicon-Doped Boron Nitride Bamboo Structures Via Pyrolysis of a Polymeric Precursor

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In this paper, we report the growth of bamboo-like silicon-doped boron nitride nanotubes via catalyst-assisted pyrolysis of a boron-containing polymeric precursor. The morphologies and structures of the nanotubes were characterized using electron microscopy and Raman spectroscopy. Two types of nanotubes are observed, one from a base-growth mode and the other from a tip-growth mode. The type II nanotubes contain encapsulated catalytic nanoparticles at the tip of every compartment. This unique structure is a promising candidate for applications in many nanodevices.

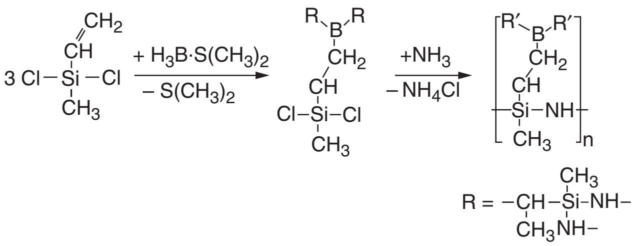
I. Introduction

Boron nitride (BN) is an important engineering material, which has widespread uses in thermal and structural applications.[1] Because of the structural similarity between BN and graphite (both have a layered structure), the synthesis of BN nanotubes attracted considerable interest shortly after the discovery of carbon nanotubes.[2] In contrast to carbon nanotubes, the electronic properties of BN nanotubes with ∼5.5 eV band gap are remarkably stable and independent of diameter, helicity, and the number of layers, highly promising for semiconductor devices.[2–4] In addition, BN nanotubes are chemically inert, making them suitable as a "protecting shield" for the materials encapsulated inside.[5–7] Up to date, various technologies, such as arc-discharge, laser ablation, chemical vapor deposition, carbon nanotube template, and specially designed chemical reaction, have been developed for the synthesis of BN nanotubes.[2,8–12]

In this paper, we report the synthesis of silicon-doped BN nanotubes with a bamboo structure via catalyst-assisted pyrolysis of a boron-containing polymeric precursor. A similar technique has been used to grow one-dimensional nanostructures of silicon carbides and nitrides by using polysilazanes as precursors.[13–19] The bamboo-like structures have been characterized using electron microscopy and a Raman spectrometer. The results reveal that there are two types of nanotubes: one has a hollow structure, grown via a base-growth mode, and the other contains Fe nanoparticles within the tip of each compartment, grown via a tip-growth mechanism.

II. Experimental Procedure

The synthesis, characterization and pyrolysis of the boron-containing polymeric precursor used in the current study have been previously reported by Weinmann *et al.*[20] We prepared the precursor according to the same procedure:



The as-synthesized precursor was then cross-linked by heat treatment at 250°C for 1 h. At this temperature the precursor was transformed into yellow powders. The cross-linked powders were mixed with 5 wt% $FeCl_2$ powders (Beihua Fine Chemicals Company Ltd., Beijing, China) using high-energy ball milling for 70 h in a N_2 atmosphere. The mixture was then placed in a boat of high-purity Al_2O_3 and heat treated at 1350°C for 3 h followed by furnace cooling. The heat treatment was performed under flowing ultra-high purity N_2 at a rate of 10 mL/min.

The morphologies, structures, and compositions of the pyrolyzed products were examined using scanning electron microscopy (SEM, JEOL JSM-6301F, Akishima, Japan), transmission electron microscopy (TEM, FEI Tecnai F30, Eindhoven, the Netherlands) operating at 300 kV with detectors for energy-dispersive X-ray spectroscopy (EDS) and for electron energy filtered TEM (EFTEM) with a Gatan Imaging Filter (Gatan, Pleasanton, California), and Raman spectroscopy.

III. Results and Discussion

The SEM observation of the as-pyrolyzed sample reveals that a small amount of nanotubes with a bamboo structure was formed on the surface of un-reacted powders. These bamboo-like nanotubes are 80–200 nm in diameter and up to several micrometers in length.

Closer examination using TEM reveals two types of BN nanotubes. Figure 1(a) shows a typical TEM image of the type I nanotube, which consists of a hollow compartment, resembling the structure of bamboo. The micrograph reveals closed tips with no encapsulated catalytic particles (see arrows ①) and open roots separated from the catalytic particles (see arrow ②). The wall thickness increases because of the connection with the compartment layer, but the outer diameter of the tube remains almost the same. Figure 1(b) shows a typical EDS spectrum obtained from this nanotube. The nanotube consists mainly of B, N, and Si (the Cu peaks originate from the Cu mesh of the TEM grid). The B/N/Si ratios calculated from the spectrum are about 1:1:0.06, suggesting the presence of doped silicon

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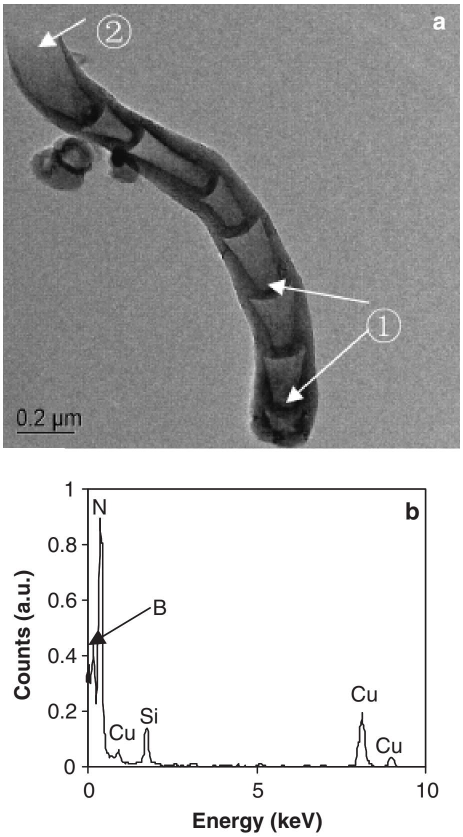

Fig. 1. (a) A transmission electron microscopy bright-field image of the type I silicon-doped boron nitride nanotube with bamboo structure; and (b) energy dispersive X-ray spectroscopy spectrum of the nanotube showing that the tube consists of boron, nitrogen and silicon.

atoms in BN nanotubes. The lack of encapsulated catalytic particles within tips indicates that the type I nanotube develops from a base-growth mode, similar to that previously observed in the growth of carbon nanotubes with a bamboo-like structure.[21,22]

Further analysis of the type I nanotube is presented in Fig. 2. Figure 2(a) shows a TEM image of a part of the type I nanotube. The high-resolution TEM (HRTEM) image of Fig. 2(b) was recorded from area A marked in Fig. 2(a). The interlayer spacing measured from the image is (0.37 ± 0.02) nm. This value is larger than the interplanar distance of 0.333 nm measured in bulk hexagonal/rhombohedral BN[1] and stoichiometric BN nanotubes.[23] The larger interlayer spacing can be attributed to the silicon doping. Figure 2(c) shows an HRTEM image from area B marked in Fig. 2(a). The area where the flat tip meets the side wall contains a number of defects: stacking faults or half-atomic plane terminating at edge dislocations. An enlarged view of such defects is shown in Fig. 2(d). The formation of these defects is likely because of a kinetic reason, i.e., the growth process of the BN is controlled by kinetics rather than thermodynamics.[24]

The type II BN nanotube is presented in Fig. 3. The TEM image (Fig. 3(a)) reveals that the morphology of the type II nanotube is different from that of the type I nanotube (Fig. 1(a)). More interestingly, nanoparticles of 20–50 nm are found at the tip of every compartment of the bamboo. Elemental EFTEM distribution maps (Figs. 3(b)–(g)) acquired with the three-window method[25] suggest that the nanotubes mainly consist of boron and nitrogen, while the encapsulated pure Fe particle apparently develops from the decomposition of the FeCl$_2$ catalyst. The structure in which the tip of every compartment contains an encapsulated catalytic particle is rather unique. Usually, encapsulated catalytic particles were observed in the nanotube/nanobamboo structures formed in a tip-growth mode, but typically only one particle is found in the tip of the tube or in the first compartment.[12,26] The mechanism of the formation of such an unusual structure is not clear at present. A possible explanation may be some kind of an interconnection between different nanotubes during growth. Another interesting issue is that the catalytic particle is pure Fe rather than a metallic alloy as observed in other catalyst growths of BN and/or carbon nanotubes.[12,26] This suggests that the growth of the BN nanotube in the current study could occur by surface interaction and diffusion of B-N species on the surfaces of Fe particles. Nevertheless, this unique structure could be useful in nanodevices because the encapsulated nanoparticles are protected by inert BN nanotubes and thus can survive harsh environments.

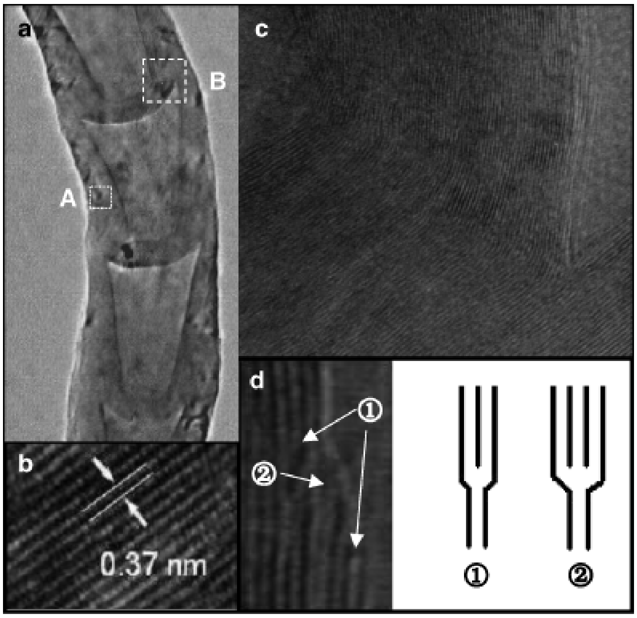

Fig. 2. (a) A transmission electron microscopy bright-field image of the type I boron nitride nanotube; (b) high-resolution micrograph recorded from area marked A in (a); (c) high-resolution transmission electron microscopy (HRTEM) image recorded from area marked B in (a) and (d) enlarged HRTEM image of the joining area between side wall and tip, showing edge dislocations containing one and two half atomic planes, as indicated by ① and ②, respectively.

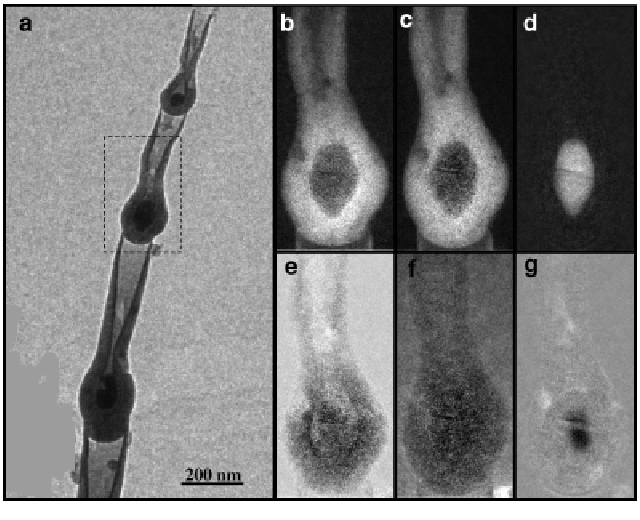

Fig. 3. (a) A transmission electron microscopy bright-field image of the type II boron nitride nanotube; and (b–g) elemental distribution maps of N, B, Fe, Si, C and O, respectively. The maps were acquired with the three-window method at the K edges of N, B, C and O, and at the L edges of Si and Fe.

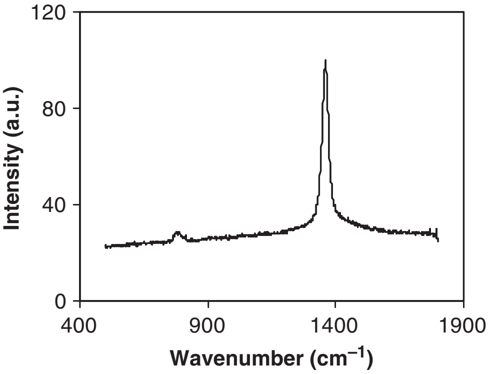

Fig. 4. Raman spectrum of the boron nitride nanotubes.

Further characterization of the structure of the Si-doped BN nanotubes was carried out using Raman spectroscopy. The Raman spectrum of the nanotubes in Fig. 4 shows two peaks at 781 (weak) cm^{-1} and 1360 (strong) cm^{-1}, respectively. A previous study[27] revealed that hexagonal BN (h-BN) has the major Raman signal at 1366 cm^{-1}, attributed to a counter-phase in-plane vibration mode. Wu *et al.*[28] observed a blue shift of $\sim$2.1 cm^{-1} in BN and BCN nanotubes. The present result suggests that for the Si-doped BN nanotubes, the peak is shifted $\sim$ 6 cm^{-1} to a lower wave number (red shift). The red shift is likely because of the silicon dopant, which destroys the otherwise perfect structure of BN nanotubes and causes a decrease in bonding strength.

Based on the above observation, the mechanism for the growth of the bamboo structures is a solid–liquid–gas–solid (SLGS) process as described inYang et al.[14,16,29] At the beginning of the process, the amorphous SiBCN reacted with Fe to form a liquid Si–Fe–C–B alloy at a temperature higher than the eutectic temperature of the system, and meanwhile released N_2 gas. Further reaction of the SiCN and the liquid alloy formed a liquid phase supersaturated with Si, C, and B. This supersaturated liquid phase then reacted with N_2 gas (at least part of the N_2 was provided by the protection gas) on the liquid/gas interface to precipitate the BN bamboos. The reason for the precipitation of BN rather than silicon nitride or silicon carbide is not clear at present, because all three phases (BN, SiC, and Si_3N_4) are stable according to the phase diagrams for the annealing conditions used in the current experiment.[20]

IV. Summary

Silicon-doped BN nanotubes with a bamboo structure are synthesized by pyrolysis of a B-containing polymeric precursor in the presence of a catalyst. Two types of nanotubes are synthesized: one type forms via a base-growth mode and the other via a tip-based mode. A unique structure develops in which the tip of every compartment of the nanotube has an encapsulated nanoparticle. This unique structure could inspire some new applications in nanodevices.

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