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Short communication

Si–O–C nanotubes from pyrolyzing polycarbosilane in a mesoporous template

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Abstract

Si–O–C nanotubes were produced by pyrolyzing polycarbosilane (PCS) inside cylindrical pores of anodized aluminum oxide (AAO) templates between 900 and 1100 °C. The diameters of these nanotubes were between 250 and 350 nm. The Si–O–C nanotubes were analyzed by SEM, TEM, EDS, FTIR and Raman spectroscopy. The nanotubes were composed of a mixture of oxycarbide glass and carbon clusters. The ratio of Si:O:C in the nanotubes was about 1:0.97:3.3. Electron emission of the Si–O–C nanotubes was investigated by the current–voltage characterization at an anode-to-specimen distance of 67 μm. The electric field for obtaining electron emission to a current density of 10^{-4} A/cm^2 from the Si–O–C nanotubes was about 7 V/μm.

Keywords: Anodized aluminum oxide; Electron emission; Nanotube; Polycarbosialne

1. Introduction

Mesoporous materials have been used as templates for the synthesis of a variety of nanotubes and nanowires [1,2]. The template-modulated method has an advantage in obtaining ordered arrays of nanotubes with uniform tube dimensions. Diameter and length of the nanotubes made from the template-modulated method can be controlled by dimensions of the cylindrical pore in the mesoporous template. Ordered arrays or membranes of nanotubes can be produced by using a template with ordered pores. Carbon nanotubes (CNTs) have been produced by using mesoporous templates made of anodized aluminum oxide (AAO) [3–14] and mesoporous silica [15,16]. The CNTs have been produced by cracking hydrocarbon gases via chemical vapor deposition (CVD) directly on the pore surface of the AAO template [8–12] or with aid of metallic catalysts inside the pores [3–8]. The CNTs have also been generated by pyrolyzing a thin layer of polymeric material, which was previously coated on the surface of the pores in the templates by the polymerization of acrylonitrile [13] or furfuryl alcohol [12,14]. CNTs 30–300 nm in diameter have been obtained from these template-modulated method, depending on the original pore size in the template [9,12–14]. The diameter of these CNTs from the template-modulated synthesis can be larger than those from the catalytic CVD, which are limited to about 100 nm [17–19]. The tube wall of these CNTs from the template-modulated synthesis can be composed of a graphitic multi-walled structure [8], stacked flake of carbon layers [12] or an amorphous structure [10].

Nanotubes and nanorods with constituents other than pure carbon are also of interest in a wide range of applications including field emitters [20], sensors [21] and catalyst supports [22,23]. Nanotubes of SiC_x and SiO_x have attracted attention [22–27]. Synthesis of hollow SiC nanotubes is still a challenge although it has been achieved by disproportionation reaction of SiO with CNT [22,24]. Instead, nanorods and whiskers of SiC have been generated from various processes [23,28–32]. Our previous work on the attempt to generate SiC nanotubes by catalytic pyrolysis of a Si-containing polymer only yielded CNTs [33]. On the other hand, SiO_x nanotubes can be generated by various methods including direct synthe-

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sis from chemical reactions [25] and the template-modulated synthesis using a sol–gel process [26] or a plasma-enhanced CVD [27]. Silicon oxycarbide has been developed as modification of silicate glasses [34]. Silicon oxycarbide, a carbon containing silicate, has been synthesized as tetrahedral network of Si–O and Si–C [34,35], carbon-dispersed black glass [34] and porous glass [36]. The Si–O–C has a wide range of applications such as structural materials [37], reinforcement materials [38] and catalyst support [39]. Si–O–C has been prepared as bulk [40], foams [37] and fibers [38,41,42]. However, nanotubes comprising Si–O–C has not been reported.

The template-modulated method may provide a route toward the production of a variety of nanotubes. In this paper, polycarbosilane (PCS), a Si-containing polymer which has been used for the production of SiC fibers [29,30], SiC whiskers [31,32] and Si–O–C fibers [41,42] was selected as the precursor to make nanotubes inside the cylindrical pores of AAO templates. Morphology, composition and structure of the nanotubes are inspected and electron emission of the nanotubes is characterized.

2. Experimental details

Anodic aluminum oxide (Anodisc 13, Whatman Inc.) with an average pore size of 0.2 μm and a membrane thickness of 60 μm was used as template for the nanotube preparation. The AAO template was placed on top of a stainless steel mesh and sealed in a syringe filter holder (Gelman Laboratory). Precursor solution was prepared by dissolving 0.5 g of polycarbonsilane (PCS, Nippon Carbon Co., M_w 1400 g/mol) in 10 ml of methyl-isobutyl-ketone (MIBK, Tedia Co., 99%). About 0.2 ml of the precursor solution was filled in the top housing of the syringe holder then pumped out through an outlet at the bottom of the syringe holder. Thus, the precursor solution was filled inside the pores in the AAO template. The precursor-infiltrated template was then taken out and heat-treated in a vacuum furnace at a pressure of about 8×10^{-5} mbar. The heat treatment was carried on by three sequential heating steps including: (1) driving out the solvent at 100 °C for 1 h, (2) decomposing the PCS at 450 °C for 1 h and (3) pyrolyzing the sample between 900 and 1100 °C for 1 h. In order to obtain the nanotubes for subsequent analysis, the AAO template was removed away by dissolving it in 1 M NaOH solution. Then the nanotubes were collected on top of a PTFE membrane (Whatman Inc.) with a pore size of 0.2 μm and washed with de-ionized water.

Morphology of the samples was investigated by a scanning electron microscope (SEM, JEOL JSM-6500F) and a transmission electron microscope (TEM, JEOL JEM-2010). An electron diffraction pattern for a selective area (SAD) on the nanotube was also taken in the TEM. Composition of the nanotube was analyzed by an energy dispersive X-ray spectroscopy (EDS, Link ISIS 300 Energy) in the TEM using a 14 nm electron beam. The nanotube sample was collected on copper grids with lacey network for the TEM observation and EDS analysis. Chemical identification of the nanotubes was characterized by a Fourier transformed infrared spectrometer (FTIR, FTS-40, Digilab) and a Raman spectrometer (Rainshaw 2000). Electron emission property of the nanotube was investigated in a field emission measurement system, which was evacuated to a pressure of 10^{-7} mbar by using one set of turbomolecular and mechanical pumps. The nanotube-containing AAO specimen was adhered to a grounded aluminum stage via silver paste, then baked at 110 °C for 20 min. A gold anode of 1 mm in diameter was placed on top of the specimen and connected to the positive lead of a Keithley 237 source-measurement system. Distance between the anode and the surface of the grounded specimen was adjusted by a micromanipulator.

3. Results and discussion

PCS was able to fill inside the pores of the AAO template by pumping the precursor solution through the template in this study. Fig. 1 shows surface morphology of the AAO template before and after the infiltration process. The pores of the blank AAO is empty before the infiltration of the precursor

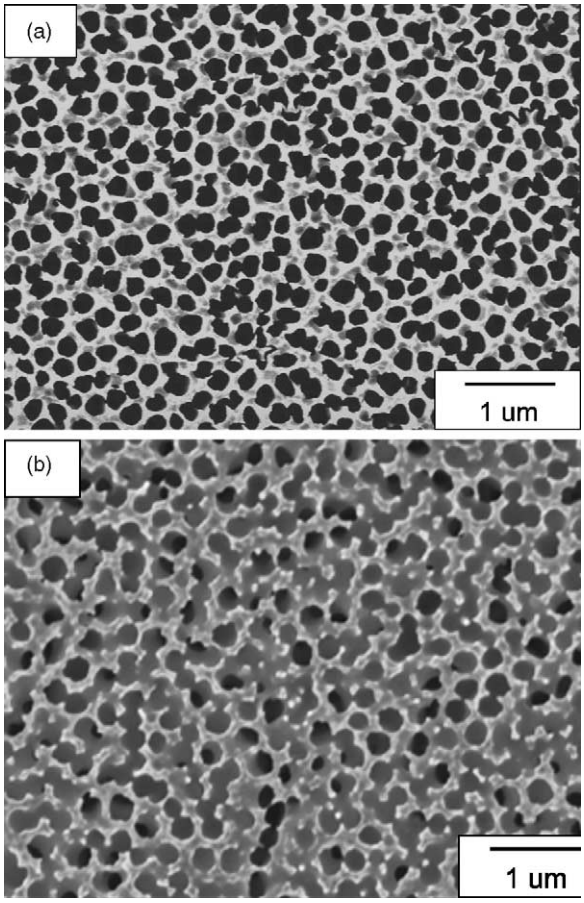

Fig. 1. SEM image of the surface morphology of (a) a blank AAO template and (b) an AAO template after being filled with PCS and heated at 450 °C for 1 h.