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Tailoring crystallinity and configuration of silica nanotubes by electron irradiation

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ABSTRACT

SiO_2 nanotubes show potential in applications such as nanoscale electronic and optical devices, bioseparation, biocatalysis, and nanomedicine. As-grown SiO_2 nanotubes in the previous studies always have an amorphous wall, and here we demonstrate the successful synthesis of single-crystal nanotubes for the first time by the heat treatment of SiC nanotubes at 1300 °C for 10 h under low-vacuum conditions. According to TEM observations, the single-crystal SiO_2 was α-cristobalite. We also demonstrate that single-crystal SiO_2 nanotubes can be transformed into amorphous SiO_2 nanotubes by electron beam irradiation. Moreover, we synthesized a crystalline/amorphous SiO_2 composite nanotube, in which crystalline and amorphous SiO_2 coexisted in different localized regions. In addition, for biomedical applications such as drug delivery systems, controlling the configuration of the open end, the diameter, and capsulation of SiO_2 nanotubes is crucial. We can also obturate, capsulate, and cut a SiO_2 nanotube, as well as modify the inner diameter of the nanotube at a specific, nanometer-sized region using the focused electron beam irradiation technique.

1. Introduction

Since carbon nanotubes (CNTs) were discovered in 1991 [1], the fabrication of one-dimensional nanostructures such as nanotubes, nanorods and nanobelts has generated a great deal of interest in nanotechnology. In particular, nanotubes represent an interesting and important class of nanomaterials with diverse applications including electronic devices and drug delivery because of their unique geometries and physical properties [2,3]. Not only is SiO_2 expected to be an excellent insulator for electronic device, but it is also a promising candidate material for optical devices; highly visible or/and ultra-violet photoluminescent SiO_2 nanomaterials have been reported [4–6]. It has been reported that SiO_2 nanotubes are useful in nanoscale electronic and optical devices [7]. Additionally, SiO_2 nanotubes have shown potential for use in applications in bioseparation and biocatalysis because of their hydrophilic character, facile colloidal suspension capabilities, and suitability for surface functionalization of both the inner and outer walls [8].

Many processes have been employed to synthesize SiO_2 nanotubes [9–12]. However, the as-prepared SiO_2 nanotubes always have an amorphous wall. The emission wavelength of crystalline SiO_2 may be different from that of amorphous SiO_2 because crystalline forms of SiO_2 such as α-quartz (5.59 eV) and α-cristobalite (5.68 eV), have different band gaps than amorphous SiO_2 (~9 eV) [13]. The mechanical and thermal properties such as elastic modulus [14] and thermal conductivity [15] of crystalline SiO_2 also differ from those of amorphous SiO_2. Moreover, it has been reported that ultrathin crystalline SiO_2 nanotubes have a different band gap and elastic modulus compared to bulk crystalline SiO_2, and the band gap decreases linearly with increasing stress [16]. The synthesis of crystalline SiO_2 nanotubes is, therefore, required for the development and expansion of SiO_2 nanotube applications. So far, it has been reported the synthesis of two dimensional crystalline SiO_2 sheet on substrates [17,18]. However, one dimensional crystalline SiO_2 nanotubes have yet to be synthesized. Here we report, for the first time, the synthesis of single-crystal SiO_2 nanotubes by the oxidation of SiC nanotubes. We also report the amorphization of single-crystal SiO_2 nanotubes by electron beam irradiation, which is important for the evaluation of the structural stability of the nanotubes.

For biomedical applications such as drug delivery systems, controlling the structure of the open end and the overall diameter of the SiO_2 nanotubes is crucial for controlling drug/DNA uptake and release rate, and to encapsulate the desired functional molecules or nanoparticles inside of SiO_2 nanotubes [19]. Capping of SiO_2 nanotubes has been achieved using chemical reactions, such

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as imine bond formation [20], or mechanical method, such as alumina microbead hammering treatment [21]. The diameter of SiO_2 nanotubes has been controlled by changing the feature size of the template materials [22]. However, these processes cannot be employed at the desired nanometer-size area of a SiO_2 nanotube. We also report on method for producing nanotube structural changes, such as capping, capsulation, diameter change, and precise cutting at the desired nanometer-size site using an electron beam irradiation technique.

2. Materials and methods

Both single-phase SiC nanotubes and C-SiC coaxial nanotubes were synthesized by the reaction of Si powder at 1200 °C in a vacuum for 100 h using CNTs as the template material. The details of the fabrication process and the characterization of single-phase SiC nanotubes and C-SiC coaxial nanotubes are described elsewhere [23,24]. These CNTs with Si powder reaction products were then heated at 1300 °C in a low vacuum of around 200 Pa for 20 h to synthesize single-crystal SiO_2 nanotubes.

The microstructures of these materials were observed using transmission electron microscopy (TEM, Model 2100F, JEOL Ltd., Akishima, Japan) operated at 200 keV. Prior to microscopy, the SiO_2 nanotubes were ultrasonically dispersed in ethanol for 20 min. Then, the dispersed SiO_2 nanotubes in ethanol were deposited on a holey-carbon copper grid sample holder and dried at room temperature. The grid sample holder, which deposited the SiO_2 nanotubes, was used for TEM observations. Electron energy loss spectroscopy (EELS, Enfina spectrometer, Nippon Gatan, Nishi-Tokyo, Japan) analysis was also carried out in order to evaluate the chemical composition of the crystalline SiO_2 nanotubes. Focused electrons beam of energy 200 keV was applied directly by the TEM on single-crystal SiO_2 nanotubes to evaluate their structural stability and alter their configuration. Images of the SiO_2 nanotubes before and after electrons beam irradiation were recorded by a CCD-camera connected to the TEM.

3. Results and discussion

3.1. Synthesis and microstructural observation of single-crystalline SiO_2 nanotubes

Fig. 1 shows TEM images and the corresponding selected area electron diffraction (SAED) patterns collected from C-SiC and SiC nanotubes heated at 1300 °C for 20 h in a low vacuum (~200 Pa) condition. According to the SAED patterns and high resolution TEM observations, the nanotubes synthesized in this study were single-crystalline, and the inter-planar spacings *d* were 0.40 nm and 0.31 nm, which correspond well with those of the {1 0 1} and {1 1 1} lattice planes, respectively, of α-cristobalite. This result indicates that the single-crystal nanotubes synthesized in this study were α-cristobalite nanotubes.

The core EELS spectrum taken from the single-crystal nanotubes shown in Fig. 1(a) is given in Fig. 2. The spectrum reveals the presence of Si-*L* and O-*K* edges whereas the C-*K* edge, which is located at 285 eV, is not observed. Fig. 2(b) also shows the Si-*L* energy loss near edge structure (ELNES) of the single-crystal nanotube. The Si-*L* ELNES has an edge onset at about 104 eV and is indicated by two distinct, separated peaks, positioned at about 109 and 116 eV. Schneider et al. reported that the Si-*L* ELNES of SiO_2 has two separate peaks, positioned at about 108 and 115 eV, whereas that of SiC exhibits only one dominant peak at 102 eV [25]. Furthermore, the threshold energy of the SiO_2 fine structure is about 105 eV, and that of SiC is about 101 eV [25]. An elemental quantification was also obtained from the EELS spectrum using the

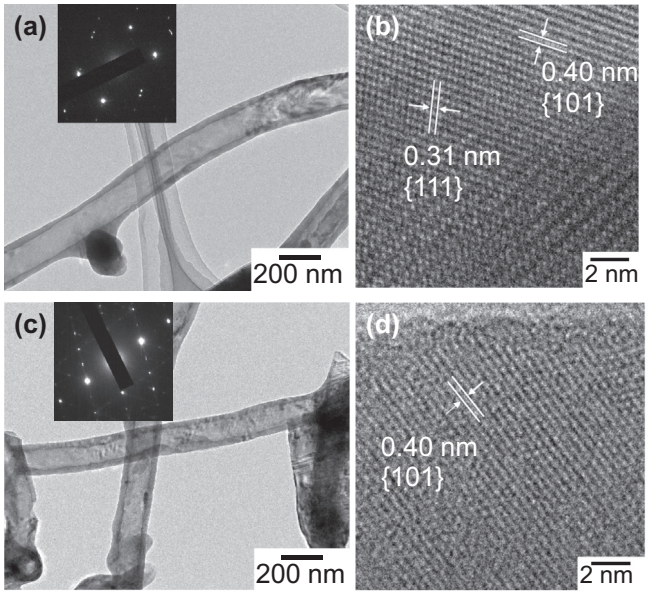

Fig. 1. Typical TEM images of single-crystal SiO_2 nanotubes. (a) and (c), low magnification. (b) and (d), high magnification.

method described by Eregton [26]. The atomic ratio of O to Si in the single-crystal nanotube evaluated from the EELS spectrum was approximately 2. From these results, we can confirm that single-crystal SiO_2 (α-cristobalite) nanotubes were successfully synthesized for the first time by the heat treatment of SiC nanotubes at 1300 °C for 20 h in a low vacuum.

The SiO_2 nanotubes are produced by the oxidation of SiC nanotubes at 1300 °C in a low vacuum following the equation:

$$SiC\ (solid) + 2O_2\ (vapor) \rightarrow SiO_2\ (solid) + CO_2\ (vapor) \quad (1)$$

Because residual O_2 gas is present in a low vacuum atmosphere (~10 Pa), oxidation of the SiC occurred. It is well known that crystalline phases of SiO_2 such as quartz, tridymite, and cristobalite on SiC substrate is produced by the oxidation of SiC substrate at temperatures higher than 700 °C [27]. At temperatures above 1200 °C, the initially amorphous SiO_2 crystallizes, beginning at the oxide-atmosphere interface, and then β-cristobalite crystals appear [28]. During cooling below 300 °C, β-cristobalite undergoes a phase transformation into α-cristobalite. Therefore, SiC nanotubes are transformed to single crystal α-cristobalite nanotubes by the oxidation of SiC nanotubes. Although the phase transformation of β- to α-cristobalite accompanies a decrease in volume by 4.9 vol% [29], no cracks were observed in the SiO_2 nanotubes.

In general, single-crystal ceramic nanowires, nanosheets, and nanotubes grow along directions parallel to crystal directions [29–32]. Although the SiO_2 nanotubes synthesized in this study are single crystalline, the SiO_2 nanotubes do not grow along crystal directions. The reason is considered that single-crystal ceramic nanomaterials in previous studies were formed by growing along directions parallel to crystal directions, while the single-crystal SiO_2 nanotubes in this study were produced by transforming from SiC nanotubes with complex configurations as template materials.

3.2. Amorphization of SiO_2 nanotubes by electron beam irradiation

The TEM images and the corresponding SAED patterns of the SiO_2 nanotubes before and after irradiation by focused electron beam are shown in Fig. 3(a) and (b), respectively. Although the SiO_2 nanotubes were single-crystalline before irradiation, they transformed completely into amorphous SiO_2 when exposed to a