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Ion irradiation-induced novel microstructural change in silicon carbide nanotubes

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ABSTRACT

In-situ TEM was used to observe the microstructural changes of SiC nanotubes under ion irradiation, and the results are significantly different from those of bulk SiC. The nanotubes possess better resistance against amorphization by irradiation, having a higher critical irradiation dose at room temperature. At room temperature, both the outer and inner diameters of the SiC nanotubes increase during irradiation till complete amorphization, and decrease afterwards. The lattice plane spacing of SiC crystals increases with increasing ion fluence due to the increasing disorder. At 700 °C, both the inner and outer diameters change very little during ion irradiation; and the lattice plane spacing decreases slightly, which is not consistent with previous studies of bulk SiC. The reason is that, in the nanotubes, the number of inherent defects that buffer the residual stress in it can be reduced. A new structure with smaller crystal segments is produced in the SiC grains of nanotubes to relieve the residual stress, instead of inducing structural defects and nanotube contraction. From these results, ion irradiation clearly induces novel microstructural changes in SiC nanotubes, due to the nanosizing and tubal configuration of the material.

1. Introduction

Silicon carbide (SiC) is among the most important wide-band gap semiconducting materials for use under high temperature and high power [1]. It may also be used in structural materials at high temperatures due to its excellent mechanical properties [2]. Therefore, SiC offers exciting opportunities in electronic devices and structural materials at high temperature [1,2]. On the other hand, one-dimensional nanostructured materials such as nanotubes, nanorods, and nanowires are known to have novel properties different from their bulk counterpart, because of their fascinating geometries and nanometer size [3,4]. In particular, nanotubes represent an interesting and important class of nanostructured materials due to their excellent physical properties. Therefore, SiC nanotubes may possess different properties from bulk SiC. So far, we have succeeded in synthesizing SiC nanotubes by the reaction of multi-walled carbon nanotubes (MWCNTs) with Si powder in vacuum [5,6]. The prepared SiC nanotubes exhibited photoluminescence (PL) consisted of a dominant peak at around 2.5 eV, which is higher in energy compared with the band-gap of bulk 3C-SiC at 2.23 eV [7]. In addition, the SiC nanotubes have been demonstrated to be bioactive for the first time among SiC materials [8].

Compared to other materials, bulk SiC also shows excellent irradiation resistance [9,10]. Irradiation with energetic particles normally causes the formation of atomic defects that spoil the material properties. However, ion irradiation has been recently used to intentionally induce defects and modify the structure, in order to tailor the properties of nanomaterials such as CNTs [11–13] and ceramic nanowires [14–16]. Our group has reported the transformation of polycrystalline SiC nanotubes to amorphous nanotubes or polycrystalline/amorphous heterostructured ones by an ion irradiation technique [17]. Yet the associated microstructural changes have not been fully investigated. So far, it has been also reported that using nanosized metal particles increases the sputter yield [18] and decreases the melting temperature compared to bulk metals [19]. Therefore, irradiation of SiC nanotubes may cause interesting effects. Here, we systematically investigated the microstructural change of SiC nanotubes under ion irradiation by in-situ transmission electron microscopy (TEM) observation.

2. Experimental

Commercial MWCNTs (GSI Creos Corporation, Tokyo, Japan)

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were used as the template material. C-SiC coaxial nanotubes, which were MWCNTs sheathed in a SiC layer, were synthesized by heating MWCNTs with Si powder without direct contact at 1200 °C for 100 h in a vacuum of around 5×10^{-4} Pa. Then, single-phase SiC nanotubes were formed by the heat treatment of C-SiC coaxial nanotubes at 800 °C for 4 h in air to remove the carbon. The SiC nanotubes were treated with 5 M NaOH solution at 60 °C for 24 h to eliminate the SiO_2 layer formed on their surface during the heat treatment in air, rinsed with ultrapure water, and then dried at room temperature. To completely remove Na ions from their surface, the SiC nanotubes were then treated with 0.1 M HCl solution, rinsed with ultrapure water, and once again dried at room temperature [8]. Finally, they were dispersed in ethanol, deposited on a holey-carbon molybdenum grid sample holder, and dried at room temperature. The molybdenum grid holder with SiC nanotubes was irradiated with 200-keV Si ions from a 400-kV ion implanter at either room temperature or 700 °C in a TEM apparatus (Model JEM-4000FX, JEOL Ltd., Akishima, Japan) operating at 400 kV.

In-situ TEM observation under ion irradiation was carried out at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) facility of the National Institutes for Quantum and Radiological Science and Technology, Japan. The projected range of 200-keV Si ions into SiC target is calculated to be approximately 177 nm by SRIM 2008 program [20], indicating that almost all the irradiated Si ions completely penetrated the SiC nanotubes. The ion fluence was up to 9.2×10^{20} ions/m^2, and the corresponding irradiation damage was calculated by SRIM 2008 to be 24.1 displacement per atom (dpa). The circumstantial microstructural observations of the SiC nanotubes before and after ion irradiation were performed through TEM (Model 2100F, JEOL Ltd., Akishima, Japan) operating at 200 kV. Electron energy-loss spectroscopy (EELS, Enfinium spectrometer, Nippon Gatan, Nishi-Tokyo, Japan) was performed to evaluate the plasmon energies of SiC nanotubes before and after the ion irradiation.

3. Results

3.1. Microstructural change of SiC nanotube by ion irradiation at room temperature

The typical TEM images and selected area electron diffraction (SAED) pattern of a single SiC nanotube before ion irradiation are shown in Fig. 1. From the low-magnification TEM image, the average outer and inner diameters of the nanotube are 158 ± 16 and 104 ± 12 nm, respectively, and the average wall thickness is 27 ± 4 nm. From the high-resolution (HR) TEM image and SAED

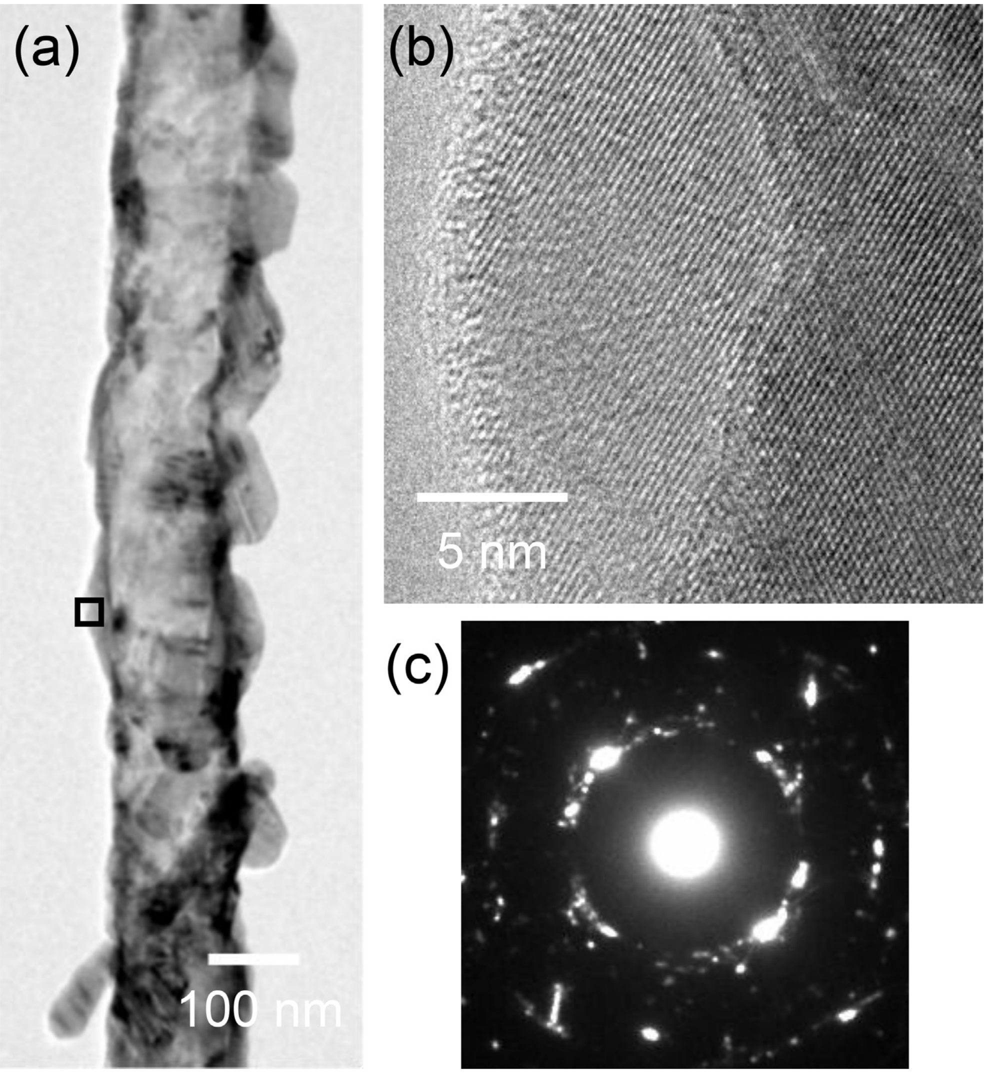

Fig. 1. Typical TEM images and SAED patterns of a SiC nanotube before ion irradiation. (a) Low-magnification TEM image, (b) high-resolution TEM image, and (c) SAED patterns.