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Electronic and optical properties of boron nitride nanotubes

Takeo Oku[a,*], Naruhiro Koi[b], Katsuaki Suganuma[b]

[a]Department of Materials Science, The University of Shiga Prefecture, Hassaka 2500, Hikone, Shiga 522-8533, Japan
[b]Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

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Abstract

Boron nitride (BN) nanotubes were fabricated, and their electronic and optical properties were investigated by scanning tunneling microscopy (STM) and optical absorption at room temperature. STM images showed atomic arrangements of BN nanotubes, and its chirality was directly observed. The current–voltage characteristics of the BN nanotubes showed onset voltage at 5.0 V, and the optical absorption spectrum of BN nanotubes showed a peak at 4.8 eV.

Keywords: A. Nanostructures; B. Chemical synthesis; C. Scanning tunneling microscopy; D. Electronic structure

1. Introduction

Various kinds of carbon nanotubes have been produced and widely studied. Carbon nanotubes become both a semiconductor and a metal due to their diameters and chiralities, which are promising as single-electron transistors, gas storage materials, magnetic refrigerators and other nanoscale devices [1]. Several studies have also been reported on boron nitride (BN) nanomaterials such as BN nanotubes [2–4], BN nanocapsules [5], BN nanoparticles [6] and BN clusters [4,7]. BN nanotubes have a wide band gap (e.g.) of ~6 eV and non-magnetism, independent of the tube diameters [8]. The BN nanotubes would be expected to show various electronic, optical and magnetic properties such as Coulomb blockade, photoluminescence and superparamagnetism, which would be useful as nanocables, high heat-resistant semiconductors and insulator lubricants [9,10].

The BN nanotubes have a hexagonal ring structure with various chiralities, which is similar to carbon nanotubes. In order to investigate the chiralities of BN nanotubes, electron diffraction patterns have been used commonly [11]. High-resolution electron microscopy (HREM) is also used for structure analysis of BN nanotubes, and lattice images on the side of the tubes had been easily taken because of the Bragg's diffraction condition. On the other hand, it is difficult to take an image of the hexagonal network that should appear at the center of the BN nanotubes because of the resolution limit, overlapping of atoms, electron beam damage and so on. Although the network structure of carbon nanotubes has already been observed by scanning tunneling microscopy (STM) [12], only few works on the STM observation of the hexagonal plane of BN nanotubes have been reported because of the insulating behavior [13].

The purpose of the present work is to study atomic structures and properties of BN nanotubes by STM and optical measurements. In order to determine the nanotube structures, hexagonal networks of BN nanotubes were directly observed in the atomic level by STM. To understand the atomic and electronic structures of the BN nanotubes, molecular orbital calculation was carried out.

2. Experimental procedures

Fe_4N (99%, Kojundo chemical laboratory (KCL) Co. Ltd., Saitama, Japan) and boron (B) powders (99%, KCL) were used as raw materials [14,15]. Their particle sizes were about 50 and 45 μm, respectively. After Fe_4N and B (weight ratio WR = 1:1) were mixed by triturator, the samples were set on an alumina boat and annealed in the

*Corresponding author. Tel.: +81 749 28 8368; fax: +81 749 28 8590.
E-mail address: oku@mat.usp.ac.jp (T. Oku).

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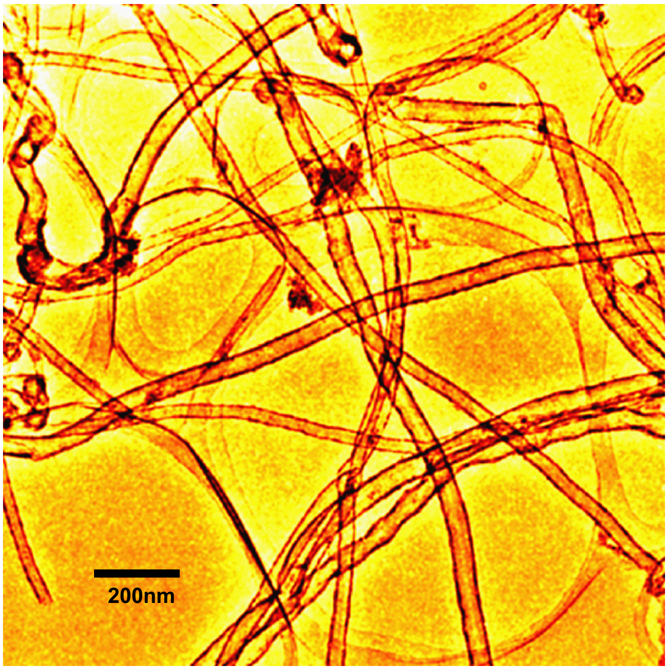

Fig. 1. Transmission electron microscopic image of BN nanotubes.

furnace. The furnace was programmed to heat at 6 °C/min from ambient temperature to 1000 °C and hold for 1 h and then cool at 3 °C/min to ambient temperature. Nitrogen pressure was 0.10 MPa, and its gas flow was 100 sccm (standard cubic centimeter per minute).

As-produced soot synthesized from Fe_4N/B via the above method was purified by the following steps. The as-produced soot was poured in 4 M HCl solution and stirred for 4 h at room temperature. The green color of the solution provides an indication of the dissolution of Fe ions. After HCl treatment, the samples were poured in 1 M HNO_3 solution and stirred for 30 h at 50 °C. The yellow color of the solution provides an indication of the dissolution of boron. After both acid treatments, the solution was filtered and rinsed with deionized water until the pH of the filtrate became neutral and dried. Then, the samples were poured in pyridine to eliminate bulk BN, and high-purity BN nanotubes with a cup-stacked structure were obtained by collecting the supernatant [16].

To observe the morphology of the samples, transmission electron microscopy (TEM) and HREM observations were performed with a 300 kV electron microscope (JEM-3000F), which has a point-to-point resolution of 0.17 nm. STM observations were performed with an STM system

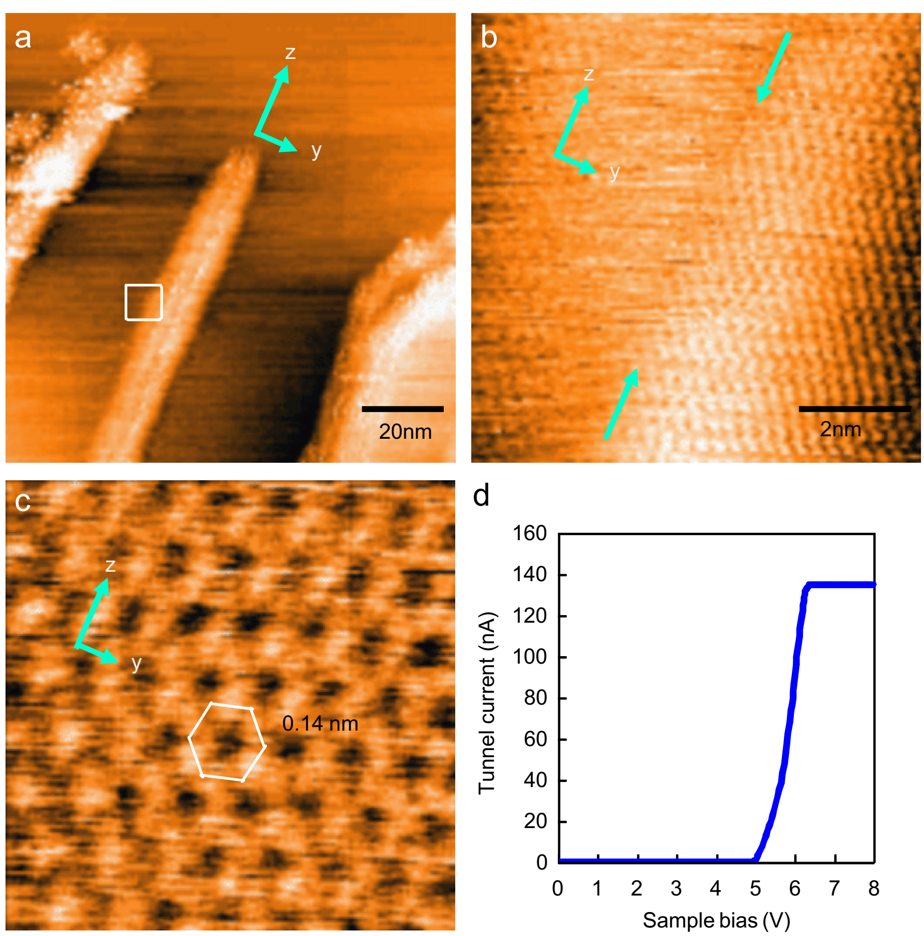

Fig. 2. (a) STM image of BN nanotubes on HOPG. (b) Enlarged image of the surface of the BN nanotube indicated by a square in (a). (c) Enlarged STM image of the BN nanotube. (d) I–V characteristic of the single BN nanotube.

(easyScan, Nanosurf AG) in air at room temperature. Pt/Ir wires with a diameter of 0.25 mm were used for STM tips. The STM tips were checked by imaging atoms on highly oriented, pyrolytic graphite (HOPG). UV–visible optical measurements were carried out at room temperature (spectrophotometer, Hitachi, U-4100). The molecular structures were optimized by CS Chem3D (CambridgeSoft), and molecular orbital calculations were carried out by MOPAC.

3. Results and discussion

Fig. 1 shows a TEM image of BN nanotubes after purification process. Fe nanoparticles and bulk BN were eliminated during the process. Diameters of BN nanotubes were in the range of 20–100 nm, and their length was ~10 μm. The STM image of BN nanotubes on HOPG is shown in Fig. 2(a). Three BN nanotubes are observed in the image, and the smallest one is selected for enlarged observation and electronic measurements. The nanotube axis is indicated as the *z*-axis. An enlarged image of the surface of the BN nanotube is shown in Fig. 2(b). The surface of the BN nanotubes is indicated by arrows. A lattice image of the BN nanotubes is observed, and an enlarged STM image of the BN nanotubes is shown in Fig. 2(c). Hexagonal arrangements of dark dots are observed, which correspond to the size of the six-membered rings of BN. Current–voltage (*I–V*) measurements were also carried out for the BN nanotubes, as shown in Fig. 2(d). The *I–V* curve indicates an onset voltage at 5.0 V, which is almost comparable to the energy gap of BN nanomaterials [4].

An optical absorption spectrum of BN nanotubes is shown in Fig. 3. In Fig. 3, a strong peak is observed at 4.8 eV, which corresponds to the energy gap of BN nanotubes, and this value is almost the same as the STM measurements. A broad, weak peak is also observed at around 3.4 eV, which is considered to be the impurity level (oxygen or hydrogen) of the BN layers, as reported previously [4,17]. Fig. 4 is a schematic illustration of the Van der Waals force distribution of a BN nanotube. There is a space inside the BN nanotube, which would be expected to be a container for atomic storage.

Carriers of BN nanotubes were found to be holes, which indicates that the BN nanotubes were p-type semiconductors [18]. The origin of p-doping seems to be the excess boron. The bandgap energy was measured to be ~4.0 eV, which is comparable to the present study, and the energy barrier of ~0.3 eV exists at the metal/BN interface [18]. This kind of BN nanotubes are expected as future nanoscale devices such as field effect transistors [18], field emission devices [19,20] and optoelectronic devices [21,22].

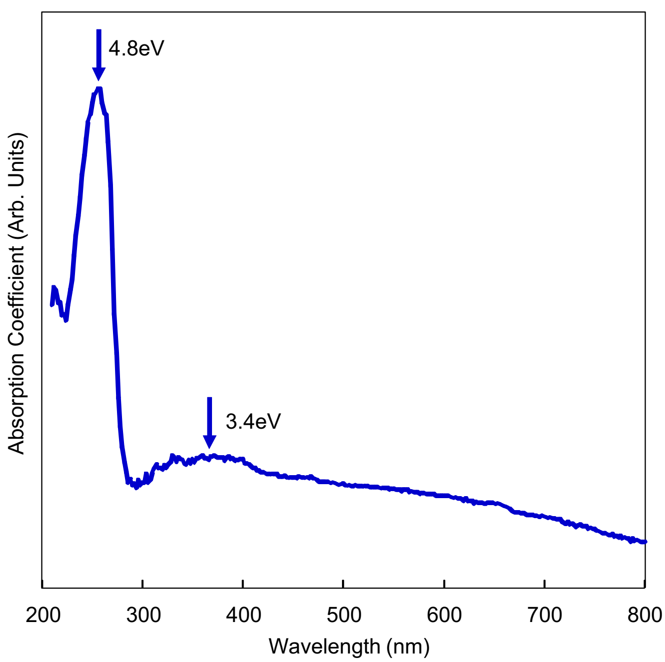

Fig. 3. Optical absorption spectrum of BN nanotubes.

4. Conclusions

Nanostructures and properties of BN nanotubes were investigated after synthesis and purification. STM observation showed the atomic arrangement of BN nanotubes directly, and the structure of the BN nanotube was found

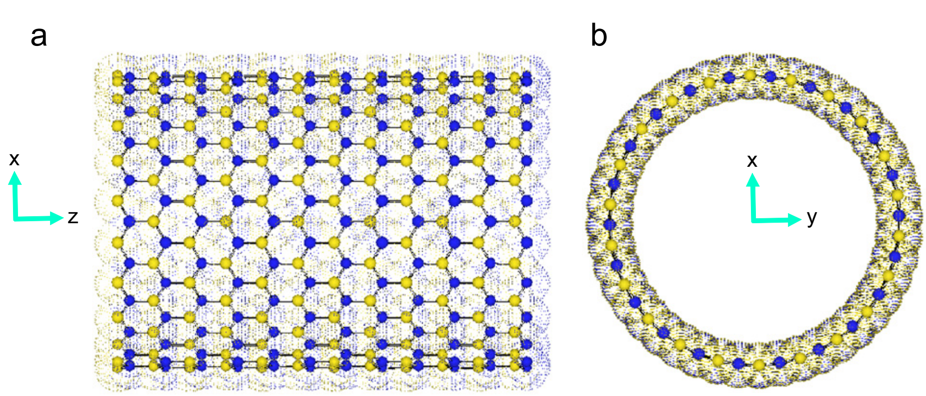

Fig. 4. Van der Waals force distribution in BN nanotube: (a) perpendicular to and (b) along the nanotube axis.

to have almost zigzag-type structure. I–V measurements of the BN nanotubes showed the onset voltage at 5.0 V, which almost agrees with the optical absorption peak at 4.8 eV.

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