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Atomic structure of boron nitride nanotubes with an armchair-type structure studied by HREM

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Abstract

Hexagonal networks of boron nitride (BN) nanotubes were investigated by high-resolution electron microscopy (HREM) and image simulation. From HREM images, lattice planes of {002} and hexagonal rings of a BN nanotube were confirmed. Asymmetrical layer arrangements were found, and a structure model for double-walled BN nanotube with an armchair-type structure has been proposed.

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Many studies have been made on the atomic arrangements and electronic structures of carbon fullerenes, nanotubes and nanocapsules [1–6], because they provide band gap energies dependent on the helical structures and diameters [2,3]. Boron nitride (BN) has hollow cage structures similar to fullerenes [4,7,8], nanotubes [3,4,9–14] and nanocapsules [4,9,15,16], which is expected to show various properties such as chemical stability, semiconductivity and heat resistance. These materials are expected to be useful as nanoscale devises such as single-electron devices, magnetic refrigerators, nanodiodes, nanotransistors and gas storage materials [17]. However, few experimental and theoretical studies have been reported on the detailed structure of the BN nanotubes and BN fullerenes [18,19].

Although BN nanotubes have a hexagonal ring structure, which is similar to carbon nanotubes, high-resolution electron microscopy (HREM) [20] images of BN nanotubes have been found to depict only straight lines [21]. Since there are many atoms along the electron beam on the side of the tube, these atoms easily satisfy the Bragg's diffraction condition. On the other hand, it is difficult to take an image of hexagonal networks that should appear at the center of nanotubes because of limit of resolution and diffraction conditions [22]. Although the network structure of carbon nanotubes has already been observed by scanning tunneling microscopy (STM) [23], the hexagonal network of BN nanotube has never been observed by STM because it is an insulator. The purpose of the present work is to observe directly hexagonal networks of BN nanotubes by HREM image analysis using multi-slice simulations.

BN nanotubes produced by arc-melting of YB_6 powder were used for HREM observation [14,24]. YB_6 powder (4.0 g, 99.6%, Kojundo Chemical Lab. Co., Ltd) was set on a copper mold in an electric-arc furnace, which was evacuated down to 1.0×10^{-3} Pa. After introducing a mixed gas of Ar (0.025 MPa) and N_2 (0.025 MPa), arc-melting was applied to the samples at an accelerating voltage of 200 V for 10 s. Arc-melting was performed with a vacuum arc-melting furnace (NEV-AD03, Nissin Engineering Co., Ltd). Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM observation was performed with a 300 kV electron microscope (JEM-3000F) equipped with side-entry goniometers having a point-to-point resolution of 0.17 nm. To avoid sample damage by electron irradiation, the

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electron beam for HREM observations was minimized by using smaller spot size. The HREM images recorded on negative films were digitized by a film scanner, and the gray scale of digitized images is 256.

For image processing of the observed HREM images, Digital Micrograph software (Gatan, Inc., California) was used. The digital image was masked and fast Fourier transformed. To compare the observed image with proposed BN nanotube models, HREM images were produced by the multi-slice method using the Mac Tempas software (Total Resolution, CA, USA). The parameters used in the calculations are as follows: radius of the objective aperture $= 6.3\ \text{nm}^{-1}$, spherical aberration $C_s = 0.6$ mm, spread of focus $\Delta = 8$ nm and semiangle of divergence $\alpha = 0.55$ mrad. Atomic structure models were built by Chem3D software (Fujitsu Corp., Chiba, Japan).

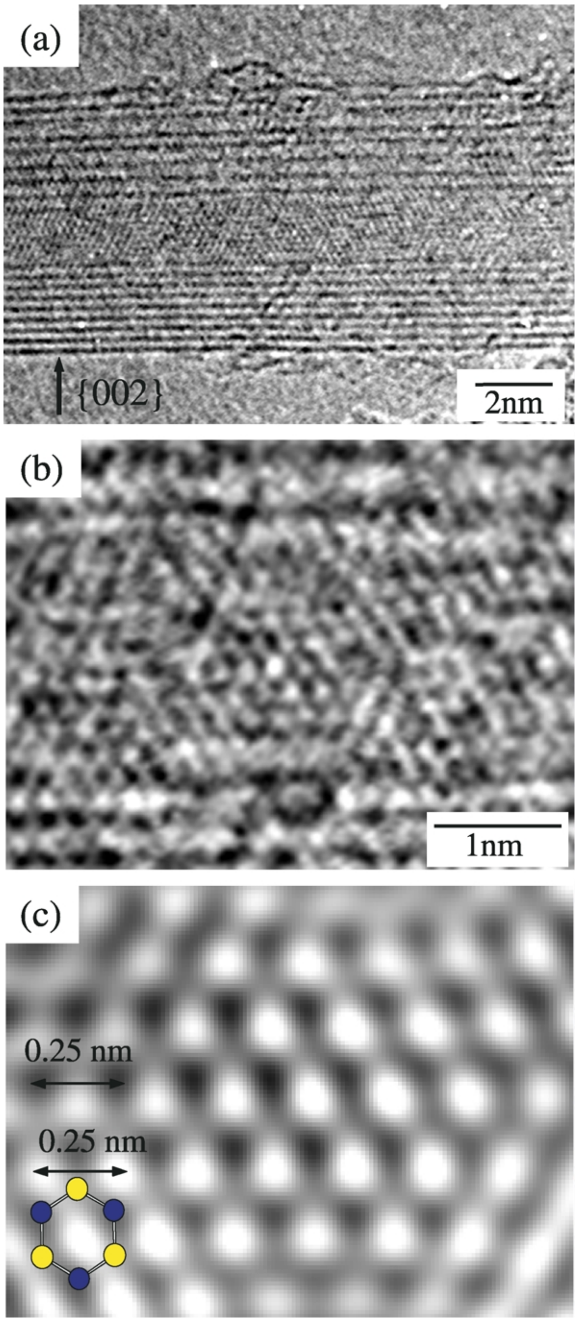

Fig. 1. (a) HREM image, (b) enlarged image and (c) processed image of BN nanotube produced from YB_6 powder.

A HREM image of a BN nanotube produced from YB_6 powder by arc melting is shown in Fig. 1(a). The image is recorded close to the Scherzer defocus. The width of the multi-walled BN nanotube is 8.5 nm. The BN nanotube consists of nine layers and has asymmetric layer-arrangement. A layer distance of one side of the tube is 0.34 nm. Layer distance of another side is in the range of 0.34–0.51 nm, which is larger than that of {002} of ordinary hexagonal BN (0.33 nm). Diameters of the first and second internal nanotubes are 1.7 and 2.6 nm, respectively. Lattice

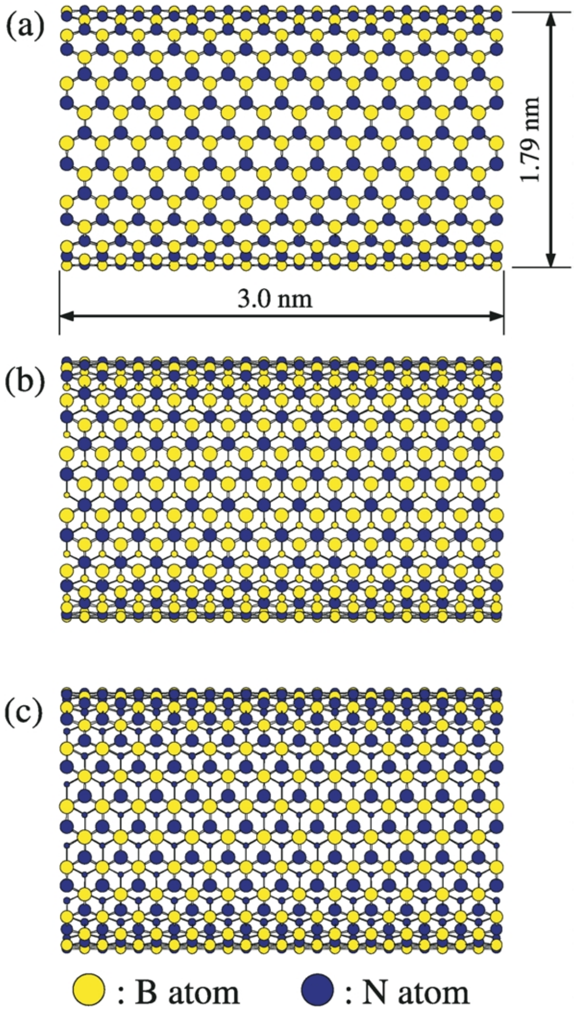

Fig. 2. Proposed structure models of single-walled BN nanotubes.

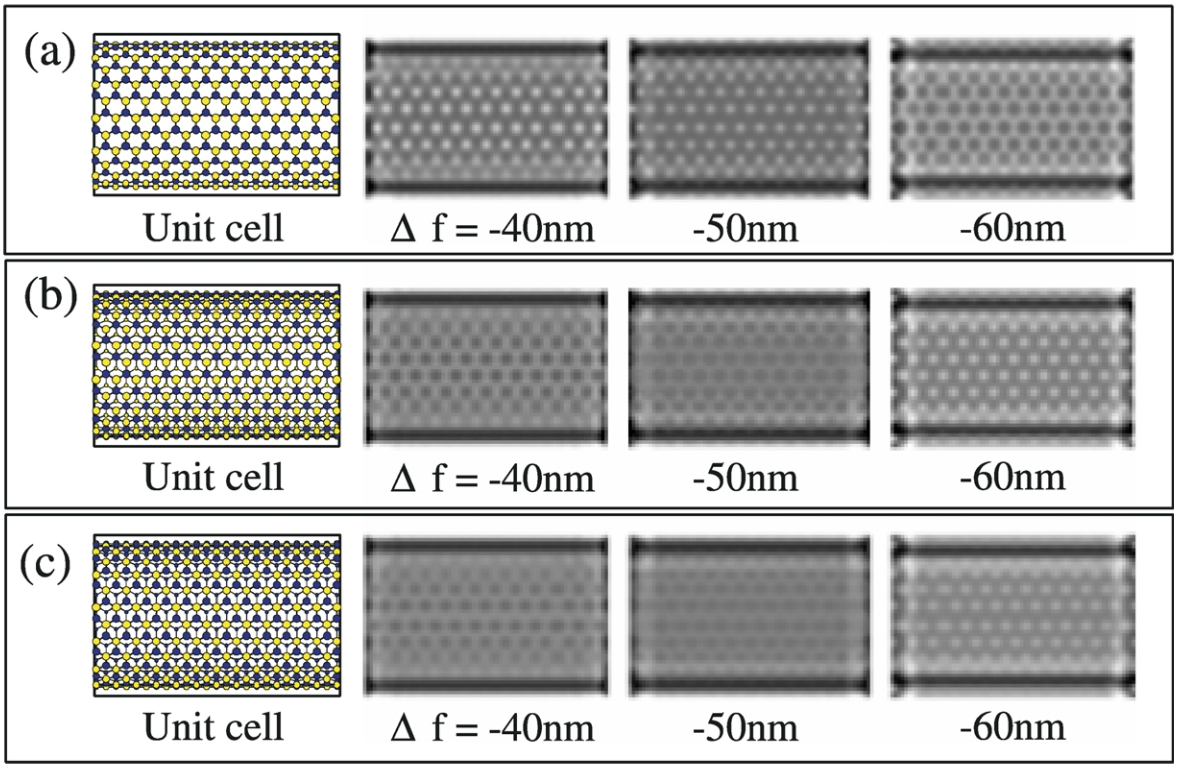

Fig. 3. (a)–(c) Calculated HREM images of Fig. 2(a)–(c), respectively.

fringes of hexagonal BN rings are observed in the center of nanotube.

Fig. 1(b) is an enlarged image of the center of the BN nanotube, and Fig. 1(c) is the processed image to observe the atomic arrangements clearly by using Fourier filtering. In Fig. 1(c), lattice fringes of the {100} planes clearly appear. Each distance of the black and white dots is 0.25 nm, as shown in Fig. 1(c), and black contrasts would correspond to hexagonal BN rings. From the HREM image and the diameters of the tube, it is considered that the first and second internal BN nanotubes have chiral vectors of (13, 13) and (19, 19) with an armchair-type structure, respectively.

Three proposed models with a single layer structure are shown in Fig. 2. Length and width of the models are 3.0 and 1.79 nm, respectively, which correspond to those of the observed first internal BN nanotube. Each model has the same armchair-type structure, and mismatch of atomic arrangements between front and back of the BN nanotube is observed in Fig. 2(b) and (c).

Based on the projected structure models, image calculations were carried out for various defocus values to investigate imaging conditions of the HREM images, as shown in Fig. 3. For a single walled BN nanotube, the experimental image of Fig. 1(c) agrees with HREM images of Fig. 3(a) calculated at the defocus value in the range of -40 to -50 nm. In fact, the observed HREM image was taken close to the Scherzer defocus of -41.2 nm. HREM images of Fig. 3(b) and (c) showed opposite contrast at Scherzer defocus, compared to the observed HREM image.

From the single-walled structure of Fig. 2(a), a structure model of double-walled BN nanotube was proposed as shown in Fig. 4(a). Some atoms outside of the BN nanotube overlap with atoms of internal BN nanotube. Length and width of the internal tube are 3.0 and 1.79 nm, respectively. Length and width of the outside tube are 2.0 and 2.61 nm, respectively. Layer intervals of lattice fringes of {002} planes are adjusted with observed ones (Fig. 1(a)). In Fig. 4(a), layer intervals of bottom and top are 0.34 and 0.48 nm, respectively. Fig. 4(b) is simulated HREM images based on the structure model of Fig. 4(a), and an image calculated at -40 nm agrees well with the observed image.

As shown Fig. 1(a), multi-walled BN nanotubes with asymmetry layer-arrangements were often observed. The asymmetry layer-arrangements would be due to arrangements of B and N atoms on different layers. For hexagonal BN, B atoms usually exist just above the N atoms with the layer interval of 0.34 nm. However, the layer distances would be larger if the nearest atomic bonding between layers are B–B or N–N. From this consideration and experimental results, a proposed model of Fig. 4(a) would be one of the adequate models in this paper.

In conclusion, a BN nanotube, which consists of hexagonal-rings with an armchair-type structure, was directly observed, and an atomic structure model was

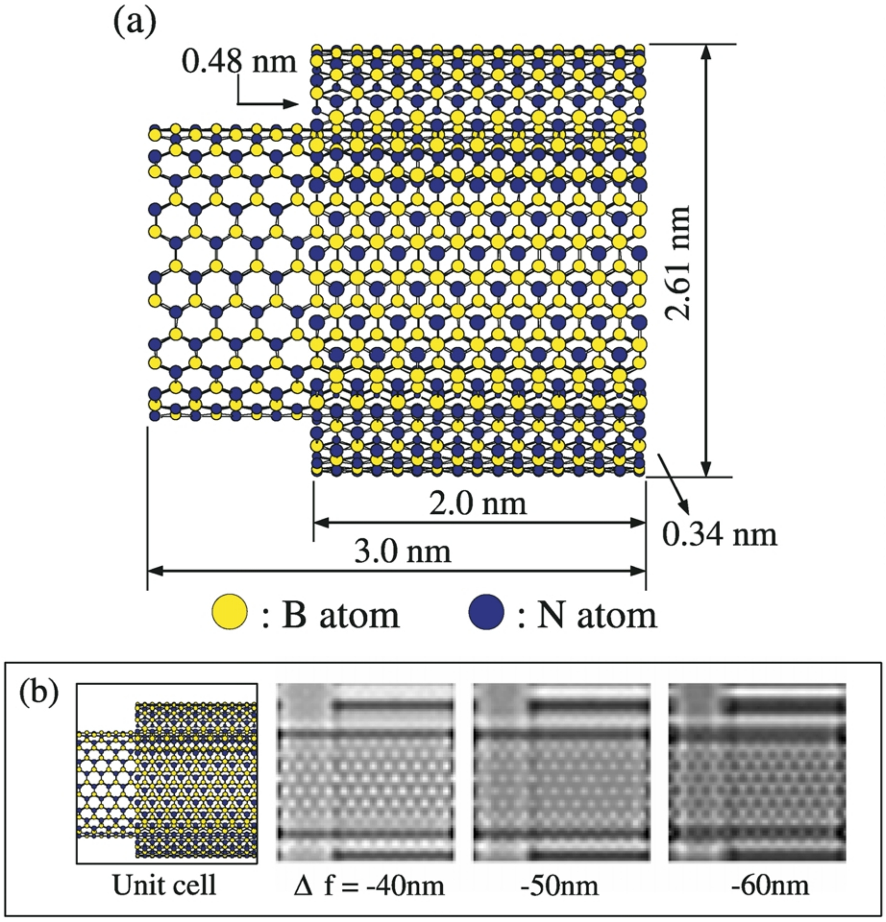

Fig. 4. (a) Proposed structure model of double-walled BN nanotubes. (b) Calculated HREM images of (a) as a function of defocus values.

proposed from HREM analysis using image simulation and image processing.

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