X-ray Absorption Near Edge Structure Study of BN Nanotubes and Nanothorns

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Two boron nitride (BN) nanostructures, the bamboo-like nanotubes and nanothorns where the nanosize *h*-BN layers are randomly stacked looking like thorns, were synthesized selectively via thermal chemical vapor deposition of B/B₂O₃ under the NH₃ flow at 1200 °C. Electron energy-loss spectroscopy reveals the N-rich *h*-BN layers with a ratio of B/N = 0.75–0.85. Angle-resolved X-ray absorption near edge structure of these two N-rich nanostructures has been compared with that of *h*-BN microcrystals. The π^* transition in the N K-edge shifts to the lower energy by 0.8–1.0 eV from that of *h*-BN microcrystals, and the second-order signals of N 1s electrons become significant. We suggest that the N enrichment would decrease the band gap of nanostructures from that of *h*-BN microcrystals. The Raman spectrum shows the peak broadening due to the defects of N-rich *h*-BN layers.

I. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991,¹ immense efforts have been devoted to investigate the synthesis, properties, and potential applications of the nanotubular structure which is analogous to graphite. Boron nitride (BN) nanotubes are very attractive materials because their physical and chemical properties could complement those of CNT.^{2–5} Unlike CNTs, however, the calculated band structure of single-walled BN nanotubes shows semiconducting properties with a nearly constant band gap (5.5 eV) which is weakly dependent on the tube diameter and chirality.^{2,3} The multiwalled BN nanotubes have a mechanical strength similar to that of CNTs (elastic modulus ≈ 1.2 Tpa).⁵ Therefore, they are particularly useful for the applications where high-strength fiber or uniform band structure is desired.

Due to the similarities of lattice parameters between graphite and hexagonal BN (h-BN), the structures of multiwalled BN nanotubes are usually explained in terms of CNT models. It is believed that the BN nanotubes are constructed by rolling up h-BN sheets that the B atoms are bonded to three nearest N atoms by strong covalent bonding of the sp² hybridized orbitals. The B atoms interact with the N atoms of the nearest layers by a van der Waals force. The spacing between layers is about 3.3 Å, which is close to that of CNTs.⁴ Okada et al. reported a reduced band gap of double-walled BN nanotubes with respect to h-BN, by the local-density approximation calculations.⁶ Recently, Fuentes et al. suggested the band gap reduction of multiwalled BN nanotubes by 0.6 eV from that of polycrystalline *h*-BN, caused by the curvature of the sheets and the appearance of some sp³ hybridization, using electron energy-loss spectroscopy.⁷ These recent findings suggest that the electronic structure of BN nanostructures can be quite different from that of bulk h-BN.

Until now, the diverse multilayered BN nanostructures, such as nanotubes,^{4,8-17} nanowires,^{18,19} nanospheres,²⁰⁻²² and nanoparticles,^{23,24} have been synthesized by a number of research groups. Despite tremendous synthesis works, however, the detailed electronic structure of BN nanostructures has been rarely investigated. The objective of the present study is to elucidate experimentally the basic question of how much difference exists in the electronic structure between the bulk and the nanostructures and how the electronic structure of nanostructures depends on the morphology or structure. We prepared two different nanostructures by thermal chemical vapor deposition method. One is the BN nanotube having a typical bamboo-like structure where the compartment layers separate the tube inside. Another nanostructure is composed of the thorn-like BN layers stacked with random orientations, which we call "nanothorns". The morphology and structure of these two nanostructures were analyzed by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS), and Raman spectroscopy. The electronic structure of BN layers has been thoroughly examined by angleresolved X-ray absorption near edge structure (XANES) spectroscopy. We have focused on the comparison of their B and N K-edges XANES spectra with that of commercial *h*-BN powders (microcrystals).

II. Experimental Section

B pieces (99%, MaTeck) and B₂O₃ powders (98%, Aldrich) were ball-milled separately for 20 h, using a mechanical ball mill system (Spex 8000M). About 0.1 g of ball-milled powders were placed in a quartz boat inside a quartz tube reactor. Alumina substrates were coated with FeCl₂·4H₂O (99%, Aldrich) ethanol solution, producing the iron nanoparticles deposited on the substrate. The substrate covered the quartz boat containing the B source. The temperature was set at 1200 °C, and the growth time was 2 h. For the synthesis of BN nanothorns, NH₃ was introduced into the quartz tube when the temperature

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Figure 1. (a) SEM micrograph showing high-density wool-like microballs grown on the substrate. (b) TEM image showing the fibrous morphology. (c) Magnified TEM image for the edge part of nanothorns with its corresponding SAED pattern (inset). (d) Atomic-resolved view showing that high-crystalline curved BN layers randomly fold.

approached 500 °C. The BN nanotubes were exclusively synthesized using the NH₃ flow only at 1200 °C. After the reaction, a white colored product deposited homogeneously on a large area of the substrates. The size, structure, and composition of the product were examined by SEM (Hitachi S-4300), TEM (JEOL JEM-2010), EELS (GATAN GIF-2000) attached to TEM (TECNAI G²), and Raman spectroscopy (Renishaw 1000) using the 514.5 nm line of an argon ion laser.

The B and N K-edges XANES measurements were performed at the U7 beam line of the Pohang Light Source (PLS). Details of the design of the monochromator and of the spectral resolution of the beam line are given elsewhere.²⁵ The spectral resolving power $(E/\Delta E)$ of the incident photon is about 5000 at 400 eV. The angle of incident X-ray beam to the sample plane is tuned from 15° to 90°. All spectra were taken in a total electron yield mode recording the sample current at room temperature. The measurement was performed in an ultrahigh vacuum chamber with a base pressure $\leq 7 \times 10^{-10}$ mbar. All spectra were taken in a total electron yield mode recording the sample current at room temperature. The photon energy was calibrated by the second peak in the π^* transition of N₂ gas to be 401.1 eV as a reference. To eliminate the effect of incident beam intensity fluctuations and monochromator absorption features, all spectra were normalized by a reference signal from an Au mesh with 90% transmission.

III. Results

Detailed morphologies and structures of thorn-like nanostructures are shown in Figure 1. The SEM image shows highdensity wool-like microsized balls having an average diameter of 1.2 μ m, deposited on the substrates with a thickness of 10 μ m [Figure 1a]. TEM image reveals that these microsize balls are composed of the entangled fibrous layers looking like thorns





Figure 2. (a) SEM micrograph of high-density nanotubes grown on the substrate. (b) TEM image showing that all nanotubes exhibit the bamboo-like structures. (c) A typical nanotube and the corresponding SAED pattern (inset). (d) Atomic-resolved TEM image showing the highly crystalline (002) basal planes.

[Figure 1b]. A magnified image reveals the randomly folded layers at the edge part of the nanothorns [Figure 1c]. The inset is its corresponding selected-area ED (SAED) pattern that the circles originate from the random direction of h-BN sheets. The atomic-resolved image clearly depicts that they are composed of highly crystalline BN sheets and less than 20 sheets are curved toward random direction [Figure 1d]. The distance between the h-BN sheets is about 0.33 nm.

Figure 2a shows the SEM image for high-density BN nanotubes grown on a large area of the substrate. The length is in the range of $20-30 \ \mu$ m. They uniformly have a bamboo-like structure in which the inside is separated by a series of compartment layers [Figure 2b]. The average diameter is about 120 nm. The surface is periodically bumpy due to the roundly curved compartment layers. TEM image of a selected nanotube is shown in Figure 2c. The spots in the SAED pattern can be indexed as the (002) basal planes of *h*-BN layers [inset of Figure 2c]. Atomic-resolved image shows the (002) basal planes aligned along the tube axis, with a high degree of crystalline perfection [Figure 2d].

Figure 3 displays the EELS (or energy-filtered TEM) imaging of BN nanotubes. The corresponding TEM image is shown in Figure 3a. The elemental mapping of B and N atoms was obtained using the energy loss of K-shell edges, $\Delta E = 188$ and 400 eV, respectively, as shown Figure 3, parts b and c. The brighter points represent a higher concentration of element. Figure 3d shows the background-subtracted EELS spectrum for the center and edge parts of the nanotube and for the edge parts of the nanothorns. The spot size of the electron probe is about 2 nm. The spectrum shows two distinct absorption features corresponding to the known K-shell ionization edges of B and N atoms, revealing that the nanostructures are composed of only B and N atoms. A detailed inspection of the near-edge fine structure of B atoms confirms the sp² hybridization state,



Figure 3. (a) TEM image of BN nanotubes and its elemental maps of (b) B and (c) N obtained by EELS imaging using inelastic electrons corresponding to the energy loss of each element. (d)EELS data for the center and edge parts of nanotubes as marked in (a), and the edge part of nanothorns. It shows two distinct absorption features starting at 188 eV and another at 400 eV, corresponding to the known K-shell ionization edges for B and N, respectively.

distinguished by the sharply defined $1s \rightarrow \pi^*$ transition at 192 eV and $1s \rightarrow \sigma^*$ transition at above 195 eV. In the N K-edge region, a defining π^* transition at 401 eV matches to trivalent N atoms in the hexagonal lattice. The intensity ratio of the π^* transition to the σ^* transition (π^*/σ^*) is larger for the edge part than for the center part of the nanotubes, which is due to the BN planes parallel to the surface of the nanotubes.²⁶ The

nanothorns show a higher intensity ratio of π^*/σ^* than the nanotubes. Using Software (DigitalMicrograph for GMS1.2, Gatan Inc.), the average B/N ratio is obtained to be 0.75 \pm 0.05 and 0.8 \pm 0.07 for the center and edge parts of nanotubes, respectively, showing the average B/N ratio of 0.78. The nanothorns show the same B/N = 0.85 \pm 0.1 irrespective of the position, which is larger than the nanotubes.

Figure 4 shows B and N K-edges XANES measured from h-BN microcrystals, nanothorns, and nanotubes. For h-BN microcrystals, the spectrum was measured at the incident angles of 15, 45, and 90°. In the B K-edge spectrum, a sharp peak at 191.8 eV is due to the B 1s $\rightarrow \pi^*$ (2p_z) transition, showing a clear fingerprint of sp² hybridization [Figure 4a].^{27,28} The broad absorption features above 197 eV can be assigned to the B 1s $\rightarrow \sigma^*$ (2p_{x,y}) transition. There are satellite peaks (labeled A–C) around the B 1s $\rightarrow \pi^*$ transition that are separated with an equidistance interval of ~ 0.6 eV. The similar assignment can be made for the N K-edge spectrum shown in Figure 4b. The spectrum of *h*-BN microcrystals is composed of the N 1s $\rightarrow \pi^*$ transition $(2p_z)$ at 401.4 eV and the two peaks corresponding to the N 1s $\rightarrow \sigma^*$ transitions (2p_{x,v}) at 408.2 and 415.2 eV, respectively. The intensity ratio of π^*/σ^* increases as the incident angle increases, indicating that the π orbital of the *h*-BN layers is aligned perpendicularly to the incident X-ray beam. Our spectrum is consistent with that reported by Muramatsu et al.29

For two BN nanostructures, the spectrum was measured at the incident angles of 45 and 90°. The signal at the incident angle of 15° is not displayed due to a low signal-to-noise ratio. The intensity ratio of π^*/σ^* is not varied as much as that of *h*-BN microcrystals, indicating the more random orientation of π orbitals toward the incident X-ray beam. The intensity ratio of π^*/σ^* of the nanothorns is larger than that of the nanotubes over the angles. The spectral features are significantly distinguished from those of *h*-BN microcrystals. The major differences arise as follows. (1) The peak position of the π^* transition in the B K-edge is almost the same. In contrast, the peak positions of the π^* transition in the N K-edge are 400.6 and 400.4 eV, corresponding to the lower energy shifts of 0.8 and 1.0 eV from that of *h*-BN microcrystals for the nanothorns and



Figure 4. XANES spectra of (a) B K-edge and (b) N K-edge of h-BN microcrystals, nanothorns, and nanotubes.



1250 1300 1350 1400 1450 1500 Raman shift (cm⁻¹)

Figure 5. Raman spectra of *h*-BN microcrystals, nanothorns, and nanotubes. The excitation source is a 514.5 nm argon ion laser.

nanotubes, respectively. (2) The intensity ratio of π^*/σ^* at any incident angle is larger than that of the *h*-BN microcrystals measured at the incident angle of 90°. (3) Intense spectral features appear between 200 and 205 eV in the B K-edge region, corresponding to the second-order signals of the N 1s electrons, as marked by the arrows.

Figure 5 displays Raman spectra of *h*-BN microcrystals and two BN nanostructures at room temperature. The *h*-BN microcrystals show a strong band at 1367 cm⁻¹, which is assigned to a Raman active mode E_{2g} due to in-plane atomic displacement of B and N atoms against each other.³⁰ The peak position of nanothorns and nanotubes shows a higher-frequency shift from that of microcrystals, by 3 cm⁻¹. The full-width at halfmaximum (fwhm) is 13, 28, and 38 cm⁻¹, respectively, for *h*-BN microcrystals, nanothorns, and nanotubes.

IV. Discussion

Intensity (arb. units)

Two nanostructures have been categorized on the basis of distinct morphology and structure. The nanotubes have the seriously curved BN compartment layers to form uniformly the bamboo-like tubular shape. The compartment layers exhibit a nearly cage-like morphology. The nanothorns consist of the randomly folded h-BN layers whose curvature appears to be an intermediate between the bulk crystals and the nanotubes. Based on the density functional tight binding calculations, Fowler et al. suggested a stable N-rich cage structure, in which the cage is constructed with odd-numbered rings containing the N-N bonding.³¹ Golberg et al. observed extremely high N content inside the BN fullerene-like multilayered nanocages by EELS.²⁰ Therefore, the curved BN layers of nanothorns and nanotubes would favor the higher N content, resulting in the ratio of B/N < 1, as determined by EELS. The nantotubes would contain more N atoms than the nanothorns, due to the cagelike compartment layers.

The A–C satellite peaks around the B 1s $\rightarrow \pi^*$ transition of XANES could be explained by the N-void defects of BN layers. Recently, Jiménez et al. studied the bonding modification of Ar⁺ and N₂⁺ sputtered *h*-BN films.³² They observed new satellite π^* peaks with an equidistance interval of 0.63 ± 0.03 eV, and explained the origin as related to the local structural defects in hexagonal bonding formed by the ion bombardment. Based on the short-range sensitivity of the XANES technique, the peaks A, B, and C were assigned to $B-(BN_2)$, $B-(B_2N)$, and elemental B configurations, respectively. The nanostructures exhibit the less obvious satellite peaks originating from the N-void defects. The second-order peaks of the N K-edge in the B K-edge region between 200 and 205 eV were observed by a number of research groups.^{33–35} Even the monochromatic X-ray beam has inevitably some weak second-order harmonic content. In the case of the nanostructures, the intensity of second-order signals is greatly enhanced, which probably implies a higher N content than that of the microcrystals. The more intense secondorder signals of nanotubes than that of the nanothorns would be due to the more N-rich BN layers.

Therefore, the XANES data of two nanostructures are correlated well with the EELS data as follows. (1) The significant intensity of the second-order peaks of N 1s is consistent with the B/N < 1 ratio of EELS. The lower B/N ratio of nanotubes has the larger intensity of second-order peaks of N 1s. (2) The ratio of π^*/σ^* is smaller for the nanotubes than for the nanothorns. The rolling of BN basal planes required in the formation of nanotubes would perturb the energy level of π^* orbitals more significantly. In addition the higher amount of defective N-rich bonding may disturb the π^* orbitals.

The nanothorns and nanotubes show 0.8 and 1.0 eV shift of π^* transition in the N K-edge region, to the lower energy region from that of *h*-BN microcrystals, respectively, following the N content. In the case of CNTs, the N-doping reduces the band gap and leads to the metallic behaviors regardless of a tube chirality.³⁶ Therefore, we suggest that the peak shift would correspond to the reduction of the band gap by the N-rich BN layers. We observed that the intensity ratio of π^*/σ^* of nanostructures at all angles is larger than that of h-BN microcrystals measured at the incident angle of 90°. The N-N bonding of N-rich layers would increase the density states of π^* orbitals, leading to the higher intensity of the π^* transitions. We conjecture the presence of N2 in the N-rich BN nanostructures, as suggested by Goldberg et al.²⁰ Although the π^* feature of free N₂ gas is identified at 401.1 eV, that of intercalated N₂ between the BN layers may shift to the lower energy region. Another possibility is the formation of rhombohedral BN (r-BN) phase, which was suggested by other groups.^{37,38} However, the XANES of *h*-BN and *r*-BN films was reported to be nearly the same.²⁷ We need more data to make conclusions about the origin of the enhanced π^* transition at this moment. The EELS and XANES of other BN nanostructures having different B/N ratio are presently being study.

Nemanich et al. reported that the E_{2g} mode shifts to higher frequency and broadens as the average crystal grain size of BN nanoparticles decreases.³⁹ The peak broadening and the peak shift to the higher frequency have been recently observed for the BN nanotubes by Wu et al.⁴⁰ From the relationship formula between the peak shift and the average grain size,³⁹ we estimated the effective grain size to be about 12 nm for the BN nanostructures. The relationship formula between the peak broadening and the average grain size predicts the grain size to be 27 and 14 nm, respectively, for the nanothorns and nanotubes. More broadening of the nanotubes would be due to the increased defects in the more N-rich BN layers compared to those of the nanothorns, which is consistent with the result of EELS and XANES.

V. Conclusions

The bamboo-like BN nanotubes and the BN nanothorns were synthesized selectively via thermal chemical vapor deposition of B/B_2O_3 under the flow of NH₃ at 1200 °C. We investigated

the detailed electronic structure of the BN nanotubes and nanothorns using EELS and angle-resolved XANES. The EELS data reveal the N enrichment with a ratio of B/N = 0.75 - 0.8and 0.85 for the nanotubes and the nanothorns, respectively. The B and N K-edge XANES show the distinct features from that of h-BN microcrystals. The nanothorns and nanotubes show the lower energy shift of π^* transition in the N K-edge by about 0.8 and 1.0 eV, respectively, and the enhanced second-order signals of N 1s electrons in the B-K edge region. We suggest that the N-rich BN layers would reduce the band gap of nanostructures relative to that of h-BN microcrystals and enhance the second-order signals of N 1s. In both EELS and XANES, the smaller intensity ratio of π^*/σ^* for the nanotubes than for nanothorns was explained by the higher amount of defective N-rich bonding. Raman spectrum of BN nanostructures show a peak shift to the higher frequency region (3 cm^{-1}) and the significant peak broadening compared to that of the h-BN microcrystals. The greater broadening of the nanotubes than those of the nanothorns could be due to the increased defects in the more N-rich layers. The present understanding will lead to an understanding of the electronic structure of the BN nanostructures, which is a prerequisite to particular applications such as nanoelectronic devices.

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