Electron energy-loss and soft X-ray emission study of boron nanobelts

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Abstract. Electronic structure of individual boron nanobelts, which supposedly have α-tetragonal boron structure, was studied with electron energy-loss spectroscopy (EELS) and soft X-ray emission spectroscopy (SXES) in a transmission electron microscope. A boron K-shell excitation spectrum by EELS and boron K-emission spectra by SXES correspond to partial density of states of the conduction and the valence bands, respectively. Experimental results reveal that boron nanobelts are either a semimetal or narrow-gap semiconductor.

1. Introduction

Crystal structures of boron allotropes, for example, α- and β-rhombohedral boron (α-r-B and β-r-B) [1, 2] and α-tetragonal boron (α-t-B) [3], are composed of B₁₂ clusters. High symmetry of a B₁₂ cluster should increase the degeneracy and thus the value of the density of electronic states (DOS). A theoretical study of the α-r-B reported DOS peaks near the Fermi level [4]. The DOS peaks of the conduction band in single-crystalline α-r-B were confirmed by high-energy-resolution electron energy-loss spectroscopy (EELS) [5]. A theoretical study indicated that Li-doped α-r-B could be a superconductor when the Fermi level coincides with the DOS peaks [4]. Electronic structures of Li- and Mg-doped α-r-B were characterized by EELS [6]. Chemical shifts of the boron K-edge and a step-like onset, which indicates presence of the Fermi edge due to electron doping, were reported. Electrical transport measurements could not be conducted due to a small sample size. Transport measurements were reported, however, for the carrier doped β-r-B [7-9]. Although the electrical conductivity of β-r-B increased upon doping, metallization was not attained. Metallization of β-r-B was achieved by applying high pressure of 175 GPa [10]. Compressed β-r-B also showed superconductivity, and the transition temperature could be as high as 11.2 K at 250 GPa. Theory predicts pure α-t-B to be metal [11, 12]. Crystalline boron materials B₆₀C₂ or B₆₀N₂ have been produced [13], but not pure single-crystalline α-t-B.
Boron nanowires composed of B\(_{12}\) clusters have been synthesized. Their structures could be amorphous [14], \(\beta\)-r-B [15], \(\alpha\)-t-B [16, 17] or a yet unknown form [18]. In order to utilize those nanowires in nano-sized devices [19], it is necessary to characterize their physical properties.

Wang et al produced pure single-crystalline \(\alpha\)-t-B nanowires with rectangular cross-section and boron nanobelts (BNB) by laser ablation without any catalysts [16]. Kirihara et al measured electrical transport of single BNBs [19, 20]. They reported that the BNB is a semiconductor whose electrical conductivity exceeds 1000 times that of bulk \(\beta\)-r-B. They also reported field effect transistor measurements of the BNBs and electrical conductivity of Mg-doped BNBs [20]. BNB was classed as \(p\)-type semiconductor and the activation energies for carrier concentration and mobility were 0.07 eV and 0.19 eV, respectively. The electrical conductance of Mg-doped BNBs was 100 times higher than that of the undoped BNB at room temperature. We are not aware of spectroscopic studies of this material.

Electron energy-loss spectroscopy (EELS) and soft-X-ray emission spectroscopy (SXES) are powerful techniques coupled to a transmission electron microscope (TEM). Sato et al reported high energy-resolution EELS on individual double-walled carbon nanotubes (DWNTs) [21]. They confirmed that the observed peak structure originated from interband transitions intrinsic for a chiral structure of each DWCNT. Terauchi et al attached a wavelength-dispersive SXES device to a TEM [22]. They applied SXES to partial DOS of valence band and analyzed in detail the electronic structure of cubic BN, hexagonal BN, Al and an Al-Ni-Co alloy by combining EELS and SXES [23, 24].

In this paper, valence-electron and boron K-shell excitation spectra and a boron K-emission were measured by EELS and SXES, respectively, from single BNBs. The results were compared with those of \(\beta\)-r-B, and the band gap of BNB was estimated.

### 2. Experiment
BNBs were synthesized by laser ablation [16]. A single crystal of \(\beta\)-r-B (99.999 % purity) was studied for comparison. TEM images and electron diffraction patterns of BNBs were obtained using a JEM-2000FX TEM operated at 100 kV. Electron diffraction confirmed that the specimens were high quality single crystals of \(\beta\)-r-B and BNB. Individual BNBs were also characterized with a high energy resolution EELS microscope operated at 70 kV [25-27]. A collection semiangle was 5 mrad. The energy resolution was 0.17-0.25 eV at the full widths at half maximum of the zero-loss peak. SXES was carried out with a wavelength-dispersive soft X-ray spectrometer [22-24] attached to a JEM-2000FX TEM operated at 100 kV. The energy dispersion on a CCD detector was 0.2 eV/channel at the boron K-emission energy of 180 eV.

### 3. Result and discussion
Figure 1 shows a TEM image (a) and electron diffraction pattern (b) from a 40 nm wide BNB. The diffraction pattern was assigned to the [0 1 0] zone axis of \(\alpha\)-t-B.

Figure 2 shows a valence electron excitation spectrum of a single BNB in the range 1 - 40 eV. A spectrum of \(\beta\)-r-B is also shown for comparison. The steep intensity decrease around 1 eV is the tail of the zero-loss peak. Apparent onset energy of the BNB spectrum is observed at 1.7 eV marked by an arrow. This onset energy and small humps at 4.5, 7.0 and 9.5 eV should be due to interband transitions. Prominent peaks at 24 eV are due to the collective excitation of valence electrons (volume plasmon). The same energy for the two materials means that the density of valence electrons is the same in BNB and \(\beta\)-r-B.

Figure 3 shows boron K-shell excitation spectra (1s \(\rightarrow\) conduction band) of the BNB and \(\beta\)-r-B. The spectral shape corresponds to the DOSs of the conduction band with \(p\)-symmetry because the spectra were obtained under the dipole transition condition. The onset energy at 186.4 eV of the BNB is 1.4 eV lower than that of \(\beta\)-r-B. This lower onset energy indicates that the band gap is narrower in BNB than in \(\beta\)-r-B. In the BNB spectrum, peaks at 187.5, 189 and 191.8 eV should be attributed to...
Figure 1. (a) TEM image and (b) diffraction pattern of BNB.

Figure 2. Valence electron excitation spectra of BNB and β-r-B.

Figure 3. Inner-shell excitation spectra of BNB and β-r-B. CB refers to conduction band.

Figure 4. K emission (valence band→1s) spectra of BNB and β-r-B.

electronic states of B12 clusters of BNB. The difference of the number of the peaks between the two materials could reflect unequal distortions of the boron clusters [28].

Figure 4 shows boron K-emission spectra (valence band→1s) of single BNBS having the widths of 130 and 40 nm. The spectrum of β-r-B is also shown for comparison. The spectral shape corresponds to the DOS of the valence band with p-symmetry. The BNBS peak at 185.5 eV has slightly lower energy than the β-r-B peak at 186 eV. The onsets indicated by the vertical dashed lines, whose positions correspond to the top of the valence band, are almost the same in BNB and β-r-B. Additional shoulders marked by arrows are observed at 182 eV in BNB. They may indicate different inter-icosahedral cluster bonding states in BNB and β-r-B.

The DOS of the valence and conduction bands of BNB were recorded for the first time in this study. K-shell excitation spectra reveal that the onset energy is 1.4 eV lower in BNB than in β-r-B. Considering that the band gap of the β-r-B is 1.6 eV [5] and the energy of the top of the valence band is almost the same in BNB and β-r-B, the band gap of the BNB can be estimated as 0.2 eV ± 0.2 eV. We therefore conclude that BNB is a semimetal or a narrow-gap semiconductor. This result is inconsistent with the metallic behavior predicted by theory [12], which might be explained by
deviation of the real structure of BNB from the ideal $\alpha$-t-B. A further detailed study of the atomic structure of BNB is required.

4. Conclusion
Density of states of the valence and conduction bands in BNB was studied for the first time by EELS and SXES. The structure of BNB was believed to be same as that of pure $\alpha$-t-B, but the present results indicate it is not.

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