Experimental and numerical analysis of flow path change in rock fracture under hydrothermal condition

Watanabe N., Iijima H., Hirano N., Tsuchiya N.

Journal or publication title: AIP Conference Proceedings
Volume: 987
Number: 1
Page range: 133-136
Year: 2008
URL: http://hdl.handle.net/10097/53125
doi: 10.1063/1.2896959
High energy-resolution EELS study of the electronic structure of boron nitride cones

M.Terauchi*, M.Kawana*, M.Tanaka*, K.Suzuki†, A.Ogino†,
and K.Kimura†

*Research Institute for Scientific Measurements, Tohoku Univ., 2-1-1 katahira, Aoba-ku, Sendai 980-8577, Japan
†Department of Advanced Materials Science, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Abstract. Electron energy-loss spectra were obtained from a single boron-nitride cone (BN cone) with an apex angle of 20 degrees, which is made of curved BN layers. The spectra obtained from the tip region showed the $\pi$ plasmon peak at 7.4 eV, which is smaller than that of bulk hexagonal boron-nitride ($h$-BN) composed of flat BN layers. The smaller $\pi$ plasmon energy indicates that the bandgap energy of the BN cone is smaller than that of $h$-BN. The intensity distribution of the $\pi-\sigma$ plasmon peak is explained by the surface loss-function. The B K-shell electron excitation spectra were obtained from the bottom edge region. The spectra showed additional peak intensity compared with that of bulk $h$-BN.

INTRODUCTION

Graphitic cones were discovered by Ge and Sattler [1] and those with different apex angles were found by Krishnan et al. [2]. The graphitic cones were revealed to consist of a pile of mono-layer graphitic cones. BN cones were found by Bourgeois et al. [3], whose apex angles ranged from 84 to 130 degrees. They proposed a structural model, in which a conical BN layer is helically wound about the cone axis. BN cones with an apex angle of 20 degrees were produced by Kimura et al. and were reported to have a structure consisting of a pile of monolayer BN cones [4]. There is no experimental report yet about the electronic structure of those cone structure materials.

Terauchi et al. [5] measured electron energy-loss spectra of single BN nanotubes and found that BN nanotubes with smaller diameters have smaller bandgap energies than bulk hexagonal boron nitride ($h$-BN). BN layers of smaller diameter BN nanotubes have stronger curvatures. BN cones have different curvatures of BN layers between the tip and the bottom regions. Thus, the bandgap energy of a BN cone may be different between those regions. The BN cone has edges of BN layers. The electronic state of the edge is expected to be different from that of the $h$-BN layer itself.

We have investigated bandgap energies of the tip and the bottom regions of a...
single BN cone and compared with that of \( h \)-BN. The density of states of unoccupied states at the bottom region was investigated by taking B 1s electron excitation spectra.

**EXPERIMENTAL**

BN cones were produced by thermal annealing of a mixed powder of \( \beta \)-rhombohedral boron and \( h \)-BN at 1200 °C under lithium vapor. Almost all BN cones observed have an apex angle of about 20 degrees. Only one BN cone with an apex angle of about 85 degrees has been found. BN cones with other apex angles have not been observed. Electron energy-loss spectra were taken by a high energy-resolution EELS electron microscope (HREA80) [6]. The valence excitation spectra and B 1s excitation spectra were taken from 30nm and 90nm specimen areas, respectively. Energy resolutions of those spectra were about 0.2eV.

**RESULTS AND DISCUSSION**

Figure 1 shows (a) an electron microscope image of a BN cone and (b) EELS spectra obtained from the tip region (A) of about 10nm diameter and the bottom region (B) of about 40nm diameter of the BN cone. An EELS spectrum of \( h \)-BN is also shown for comparison.

The spectra (A) and (B) show the \( \pi \)-plasmon peaks at 7.4eV and 7.6eV, respectively. Those energies are smaller than that of \( h \)-BN (8.2eV). The smaller
energies were attributed to smaller $\pi \rightarrow \pi^*$ transition energies (bandgap), which may be due to the curving of BN layers as in the case of BN nanotubes [6]. The decrease of bandgap energy for the curved of BN layers can be explained as follows. The bandgap of a BN layer exists at point $P$ of the Brillouin zone boundary [7]. At this point, the $\pi$ and $\pi^*$ bands are only constructed by $N\,p_z$ and $B\,p_z$ orbitals, respectively. Curving of a BN layer introduces $\sigma$-interaction between the $N\,p_z$ and $B\,p_z$ orbitals. This causes an increase of the widths of $\pi$ and $\pi^*$ bands, resulting a decrease of the minimum $\pi \rightarrow \pi^*$ transition energy (bandgap). A little smaller $\pi$-plasmon energy of (A) than that of (B) can be interpreted by the fact that the average curvature of the tip region A is larger than that of the bottom region B. The energy values and the intensity distributions of the $\pi+\sigma$ plasmon peaks of A and B are not explained by the volume loss-function $\text{Im}[-1/\varepsilon]$ but by the surface loss-function $\text{Im}[-1/(\varepsilon+1)]$ as in the case of BN nanotubes [6], where $\varepsilon$ is a dielectric function of bulk $h$-BN.

Figure 2 shows a boron K-edge spectrum obtained from the bottom region B in Fig.1(a), where edges of BN layers are exposed. The spectrum of bulk $h$-BN is also shown for comparison. The spectrum of the BN cone shows not only $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ peaks, which already appear in the spectrum of bulk $h$-BN, but also an additional peak indicated by an arrow A. The peak energy is 1.6 eV smaller than that of $1s \rightarrow \pi^*$ peak. The spectral intensity between $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ peaks indicated by an arrow B is higher than that of bulk $h$-BN. The extra intensities A and B may be due to the edge states of BN sheets. The onset energy of the upper spectrum indicated by a vertical line is about 1 eV smaller than that of the lower spectrum of $h$-BN. This smaller onset may be interpreted by a change of the binding energy of inner-shell electrons (chemical shift) because the charge distribution at the edge region should be different from that of $h$-BN sheets. We performed DV-X$\alpha$ calculations of flat BN sheets [8] to examine whether such a chemical shift appears for the edge region. The calculated result showed that the chemical shift of B atoms at the extreme edge was about +0.7 eV and that of the second

![Figure 2. B K-edge spectra of the bottom region B of the BN cone in Fig.1(a) and bulk h-BN.](image-url)
nearest B atoms from the edge was about -0.7eV. The chemical shift of the third nearest B atoms from the edge was very small. Thus, the smaller onset energy of the B K-edge spectrum of the bottom region in Fig.2 may be explained by the chemical shift of the second nearest B atoms from the edge.

CONCLUDING REMARKS

The electronic structure of a single BN cone was revealed for the first time by a high energy-resolution electron energy-loss spectroscopy (EELS) microscope [6]. EELS microscopy is powerful to obtain the density of states of the conduction band as well as the dielectric properties from a specified small specimen area. However, the method to obtain the density of states of the valence band from a small specimen area has not been available yet. So, the energy-resolution of X-ray emission spectroscopy based on transmission electron microscopy should be improved for the investigation of the valence band of the fullerene materials [9].

ACKNOWLEDGEMENTS

The authors thank Mr.F.Sato of Research Institute for Scientific Measurements, Tohoku University for his skillful technical assistance. The present work was supported partly by a Grant-in-Aid for Scientific Research on the Basic Research (No.10640295) and the Priority Area "Fullerenes and Nanotubes" (No.11165204, No.11165209) from the Ministry of Education, Science, Sports and Culture of Japan.

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