Application of resonant X-ray emissions for molecular/electronic structure analysis of boron nitrides

Y. Muramatsu1,2,a, H. Kouzuki2, T. Kaneyoshi2, M. Motoyama2, A. Agui3, S. Shin3, H. Kato4, J. Kawai5

1 NTT Integrated Information & Energy Systems Laboratories, 3-9-11 Midori-cho, Musashino-shi, Tokyo 180, Japan
2 Hyogo Prefectural Institute of Industrial Research, 3-1-12 Yukihira-cho, Suma-ku, Kobe 654, Japan
3 The Institute for Solid State Physics, The University of Tokyo, 3-2-1 Midori-cho, Tanashi-shi, Tokyo 188, Japan
4 Photon Factory, National Laboratory for High Energy Physics, 1-1 Oho, Tsukuba-shi, Ibaraki 305, Japan
5 Department of Materials Science and Engineering, Kyoto University, Yoshidahoncho, Sakyo-ku, Kyoto 606-01 Japan

Accepted: 6 March 1997

Abstract. We describe the application of resonant X-ray emissions for molecular/electronic structure analysis of boron nitrides using quasimonochromatic undulator radiation at the Photon Factory. Prominent resonant X-ray emissions due to B1s→B2p4→B1s−1 transitions were observed in w-BN composed of four-fold boron atoms and in h-BN composed of three-fold boron atoms, when the photon energy of the incident undulator beams coincided with the B1s→B2p4 absorption energy. However, no resonance was observed in c-BN composed of four-fold boron atoms. The resonant X-ray emission reflects the electronic structure of unoccupied molecular orbitals which strongly depend on the conformations of the boron atoms. These findings confirm that resonant X-ray emissions can be useful indices for molecular and electronic structure analysis of boron nitrides.

PACS: 78.70.En

Resonant X-ray emissions which are highly dependent on the excitation energy near the X-ray absorption threshold have recently been observed in several compounds using synchrotron radiation [1–3]. From the study of the resonant X-ray emissions, we can investigate the excitation dynamics in the interaction process of photons and electrons. The electron transition process in the resonant X-ray emissions has been revealed by taking advantage of the energy tunability and high brilliance of the synchrotron radiation, and can be categorized mainly into two processes: one is the direct recombination of excited electrons, which are called participator electrons, into specific unoccupied orbitals, with the inner core holes; the other is modulated X-ray emission due to the electron correlation between valence electrons and excited electrons, called spectator electrons, in the unoccupied orbitals. From the viewpoint of analysis methods, the resonant X-ray emission of the direct recombination might be used as an index for molecular structure analysis and electronic structure analysis, because the resonant X-ray emissions sensitively reflect the electronic structure of unoccupied orbitals which are strongly dependent on the valence orbital structure based on chemical bonding conformations.

Resonant X-ray emissions have often been observed as high-energy satellites in ordinary fluorescent X-ray emission spectra. The origin of the high-energy satellites in the BK X-ray emission spectra of boron oxide (B2O3) in which boron atoms take a three-fold coordination was shown to be resonant X-ray emissions by using energy-tunable quasimonochromatic undulator radiation [4]. Luck et al. [5] also demonstrated that high-energy satellites observed in the BK X-ray emission spectra of boron oxide derivatives in minerals such as Al2BO3, Be2(B2O5)2, OH, and B(OH)3 depend on the chemical states and coordination of boron atoms. To further clarify the correlation between the resonant X-ray emissions and the coordination of boron atoms or the chemical states, we have focused on boron nitride (BN), because of its various crystal structures and coordination systems such as cubic (c-), wurtzite (w-), and hexagonal (h-), where the first two structures take tetrahedral four-fold coordination of boron atoms and the third takes a triangular three-fold coordination. In this paper, the BK X-ray emission spectra of the c-, w-, and h-BNs excited quasimonochromatic undulator radiation are described, focusing on the resonant X-ray emissions, and the feasibility of using the resonant X-ray emissions as an analysis method is demonstrated.

1 Experimental

Figure 1 shows the crystal structures of c-, w-, and h-BNs. The coordination of the boron atoms is tetrahedral in c- and w- due to sp3 orbitals, which results in a three-dimensional diamond-like structure, while the triangular coordination in h-BN due to sp2 orbitals results in a two-dimensional layered structure. The crystal structure of c-BN belongs to a face-centered cubic structure, while that of w-BN belongs to a close-packed hexagonal structure [6]. The layered crystal structure of h-BN consists of hexagonal B3N3 units, and its
interlayer B–N bonds are attributed to the van der Waals force resulting in a bond that is weaker than the intralayer B–N bonds. Samples of c- and h-BNs were commercially obtained and w-BN was synthesized using shock-compression methods [7]. Each crystal structure of the powdered BN samples was identified as single crystals by X-ray diffraction. The purity of the samples was guaranteed to be more than 99.9%.

Spectral measurements of the X-ray emission and absorption were carried out at undulator beamline BL-16 of the Photon Factory (PF). In the X-ray emission spectrum measurements, quasimonochromatic undulator first harmonics were incident normal to the samples, and the photon energies of the first harmonics near the boron K-shell threshold were varied by controlling the undulator magnetic gap. The peak energy of the undulator first harmonics $\varepsilon_1$ can be described as $5.9355 \times 10^3/(\mu( \text{cm})(1 + K^2/2))$ in the 2.5-GeV PF synchrotron ring, where $\lambda u$ is the periodic length of the undulator magnets and $K$ is a specific parameter that characterizes the emission features of the undulator radiation. The parameter $K$ can be described as $11.2 B$ (Tesla), where $B$ is the strength of the magnetic field in the undulator magnetic gap. Therefore, $\varepsilon_1$ is approximately proportional to the magnetic gap length, because the strength of the magnetic field is inversely proportional to the magnetic gap length. The bandwidth of the undulator first harmonics $\Delta \varepsilon_1$ can be described as $\varepsilon_1/N$ by assuming an ideal emittance from the undulator radiation source, where $N$ is the periodic number of the undulator magnets. In the BL-16 undulator magnets, the periodic length of $\lambda u$ is 12 cm and the periodic number of $N$ is 24. Figure 2 shows the spectral profile of the incident quasimonochromatic undulator first harmonics obtained by varying the magnetic gap from 92 mm to 100 mm. The peak energy of the undulator first harmonics can be varied from 180 eV to 230 eV covering from below the boron K-absorption edge to the continuum by controlling the undulator magnetic gap. The bandwidth of the first harmonics was observed to be about 12 eV, which agrees with the theoretical value considering the real source size and radiation angle.

We obtained X-ray emission spectra using an entrance-slitless-type grating spectrometer [8] that consisted of a variable-spacing concave grating with an average groove density of 2400 lines mm$^{-1}$ and a gas-flow proportional counter. The resolving power of the X-ray spectrometer was tuned to be 1.8 at 200 eV using a 100-μm exit slit. In absorption spectral measurements, the fluorescence yield method was used to prevent the spectra being affected by an electric charge build-up in the insulator BN samples. Undulator first harmonic beams monochromatized with a 2-m grazing incidence monochromator [9] that had an energy resolution of 0.8 eV were incident on the samples, and the fluorescent B K X-rays emitted from the samples were monitored with a gas-flow proportional counter in the X-ray spectrometer.

The BN samples were held in a 10$^{-6}$ Torr vacuum and sample decomposition due to irradiation by undulator radiation was barely observed in either the X-ray emission or absorption measurements for several hours with a stored beam current of more than 250 mA in the 2.5-GeV PF synchrotron ring. Details of these spectral measurements are described elsewhere [10].

2 Results and discussion

Figure 3 shows the fluorescence yield absorption spectra of c-, w-, and h-BNs at the boron K-shell threshold. The absorption thresholds of c- and w-BNs are observed at a similar energy near 194 eV, and there is a sharp structure at 195 eV in w-BN. Another sharp absorption peak is observed at 191.5 eV in w-BN. The spectral shape of h-BN shows a sharp absorption peak at 191.8 eV and at 197.5 eV in the continuum. Comparing these results with the density of states (DOS) for unoccupied B2p* of c-, w-, and h-BNs calculated by Kaneyoshi et al. [11] using discrete variational (DV) Xα methods, we found that the sharp absorption peaks at 191.5 eV and 195 eV in w-BN, and 191.8 eV and 197.5 eV in h-BN correspond to the electron transitions of 1s-B2p*.

Figure 4 shows the X-ray emission spectra of c-, w-, and h-BNs, respectively, obtained by varying the undulator magnetic gap from 92 mm to 100 mm. In the spectrum of c-BN, a main emission peak at 184 eV, a low-energy satellite at
171 eV, and no distinct high-energy satellites were observed at each magnetic gap. A small broad peak near 194 eV observed at a magnetic gap of 94 mm may be due to elastic scattering of incident undulator first harmonics because the peak shape is similar to the spectral shape of the incident undulator first harmonics. In w-BN, the main emission peak at 184 eV and a low-energy satellite at 171 eV were observed at each magnetic gap, which are similar to those of c-BN. However, double-peaked high-energy satellites appeared in the energy region from 190 eV to 196 eV when the magnetic gap was tuned to 95 mm and 94 mm, where the photon energy of the incident undulator first harmonics coincided with that of the satellites. In h-BN, the main emission peak at 182 eV and a low-energy satellite at 170 eV were observed at each magnetic gap. Two high-energy satellites at 192 eV and 197 eV appeared at both the 94-mm and the 95-mm magnetic gap, and one at 192 eV appeared at the 93-mm gap. These two high-energy satellites appeared only when the photon energy of the undulator first harmonics coincided with that of the individual satellites.

Figure 5 shows the X-ray emission spectra of c-, w-, and h-BNs excited with a 94-mm magnetic gap, at which

![Fig. 3. Fluorescence-yield X-ray absorption spectra of c-, w-, and h-BNs at the boron K-shell threshold](image1)

![Fig. 5. X-ray emission spectra of c-, w-, and h-BNs obtained at an undulator magnetic gap of 94 mm, superimposed on the absorption spectra](image2)

![Fig. 4a-c. X-ray emission spectra of c-, w-, and h-BNs obtained by varying the undulator magnetic gap from 92 mm to 100 mm a c-, b w-, and c h-BN](image3)
the most intense high-energy satellites were obtained in \( w \)- and \( h \)-BNs, on which absorption spectra are also superimposed. The main emission peaks and low-energy satellites in each spectrum are clearly due to \( B_2p-B_1s^{-1} \) and \( B_2p \) hybridized with \( N_2s \)-\( B_1s^{-1} \) transitions, respectively [12]. These peaks are ordinary fluorescent X-ray emissions, which can also be obtained by high-energy excitation of X-rays from ordinary X-ray tubes or electron beams. The major component of the \( B_2p \) DOS in four-fold boron atoms in \( c \)- and \( w \)-BNs is \( \sigma \)-bonding, and that in three-fold boron atoms in \( h \)-BN is \( \pi \)- and \( \sigma \)-bonding. Therefore, the energy shift of the main emission peaks between the four-fold boron in \( c \)- and \( w \)-BNs and the three-fold boron in \( h \)-BN may reflect the difference in the major components between the \( \sigma \)- and \( \pi \)-bondings. Comparing the high-energy satellites with the absorption spectra, the double-peaked satellites in \( w \)-BN coincide with the sharp absorption peak at 191.5 eV and 195 eV. The two satellites in \( h \)-BN also coincide with the sharp absorption peak at 191.8 eV and 197.5 eV. Considering the absorption peak assignment of the \( B_1s-B_2p\pi^* \) transitions from the above-mentioned DV-Xa calculations, we can conclude that the double-peaked high-energy satellites of \( w \)-BN are resonant X-ray emission due to the \( B_1s-B_2p\pi^*-B_1s^{-1} \) transitions as in \( h \)-BN [13]. The resonant X-ray emission of \( w \)-BN and no resonance of \( c \)-BN shows that the \( \pi \)-portion of tetrahedral bonding in \( w \)-BN is larger than that in \( c \)-BN.

Using the peak shift of the main emission peaks in the ordinary fluorescent B K X-ray emission spectra, triangular \( h \)-BN can be distinguished from tetrahedral \( c \)- and \( w \)-BNs. However, it is hard to distinguish \( c \)-BN from \( w \)-BN by using ordinary fluorescent B K X-ray emission spectra. On the other hand, we can clearly distinguish between \( c \)-, \( w \)-, and \( h \)-BNs by using the resonant X-ray emissions observed as high-energy satellites. From the standpoint of analysis methods, this confirms that the resonant X-ray emissions can be useful indices for characterizing the molecular structure or electronic structure of boron nitrides. These high-energy satellites can also be weakly observed in ordinary fluorescent X-ray spectra excited by high-energy X-rays from conventional X-ray tubes or by electron beams, because of excitation by the low-energy portion of the Bremsstrahlung of the incident beams. However, the intensity of these satellites is too weak to use them for analysis indices. Therefore, resonant X-ray emission spectroscopy for molecular/electronic structure analysis can be practically achieved by using synchrotron/undulator radiation, utilizing the energy tunability to match the incident energy to the resonant X-ray emission peaks and the high brilliance to enhance the resonant X-ray emission intensity.

3 Conclusion

Selectively excited X-ray emission spectra of \( c \)-, \( w \)-, and \( h \)-BNs at the boron K-shell threshold were measured by using quasimonochromatic undulator radiation. Resonant X-ray emissions due to \( B_1s-B_2p\pi^*-B_1s^{-1} \) transitions appeared as high-energy satellites in \( w \)- and \( h \)-BNs, and we can clearly distinguish between \( c \)-, \( w \)-, and \( h \)-BNs from the spectral feature of the resonant X-ray emissions. In tetrahedral coordination boron atoms, resonant X-ray emission was observed in \( w \)-BN, but there was no resonance in \( c \)-BN. This shows that \( \pi \)-bonding portion in \( w \)-BN is larger than that in \( c \)-BN. It can therefore be confirmed that resonant X-ray emissions are useful indices for molecular structure and electronic structure analysis.

References