Valence Band Structure and Decay Process in the Inner-Shell Excitation of Boron Oxide

Yasuji Muramatsu,1,2* Hisataka Takenaka,2 Takashi Oyama,1 Takayoshi Hayashi,1 Melissa M. Grush1 and Rupert C. C. Perera4
1 NTT Lifestyle and Environmental Technology Laboratories, Musashino, Tokyo 180-8585, Japan
2 NTT Advanced Technology Corporation, Musashino, Tokyo 180-8585, Japan
3 University of Tennessee, Knoxville, Tennessee 37996, USA
4 Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

The electronic structure and radiative/non-radiative decay processes in the inner-shell excitation of \(B_2O_3\) were investigated using soft x-ray emission and photoelectron spectroscopy. Based on density of states calculations, the electronic structure of \(B_2O_3\) as probed by x-ray emission spectroscopy (XES) and photoelectron spectroscopy (PES) arises from hybridized sp2-planar B—O bonding in B—O3 triangular units. A fairly non-dispersive band structure was also suggested by excitation energy-dependent XES. XES and PES indicated both a resonant radiative decay process and a resonant non-radiative decay process with \(\pi^*\) excitation at the B K threshold. A small resonant radiative decay peak was observed with \(\pi^*\) excitation at the O K threshold, probably due to a more weakly bound \(\pi^*\) state at the O K threshold than at the B K threshold. Copyright © 1999 John Wiley & Sons, Ltd.

INTRODUCTION

Boron oxide (\(B_2O_3\)) is a useful material especially in the ceramic and glass industries. In addition, it is also interesting from a solid-state-physical point of view because it has a complex crystal structure that produces a range of optical characteristics. Spectroscopic studies of \(B_2O_3\) are therefore important both for characterizing these materials for industrial use and for understanding their electronic structure. The characterization of \(B_2O_3\) and related materials has typically been done using conventional optical spectroscopy1 and several theoretical studies2,3 have also been conducted. In contrast, only a few soft x-ray spectroscopic studies using highly brilliant synchrotron radiation have been conducted to investigate the electronic structure of \(B_2O_3\).4,5

Soft x-ray spectroscopy using synchrotron radiation has become a powerful tool for characterizing materials and analyzing electronic structure.6 Excitation energy-dependent x-ray emission spectroscopy (XES) and photoelectron spectroscopy (PES) using monochromatized synchrotron radiation as the excitation source provide information not only on the electronic structure but also on the decay processes in the inner-shell excitation. Photoelectron studies on hexagonal boron nitride (h-BN),7 cubic boron nitride (c-BN)8 and gaseous boron trifluoride (BF3)9,10 and x-ray emission studies on h-BN4 and c-BN11 have clarified the electronic structure and resonant phenomena of the radiative and non-radiative decay processes in these boron compounds. In \(B_2O_3\), XES studies at the B K threshold1,2 have shown that resonant radiative decay occurs in the excitonic \(\pi^*\)-orbital. However, XES experiments at the O K threshold and PES studies are still needed to clarify the electronic structure and resonant decay processes in the inner-shell excitation of \(B_2O_3\).

We therefore applied both XES and PES to \(B_2O_3\) using highly brilliant synchrotron radiation. We measured the excitation energy-dependent x-ray emission spectra at both the B K and O K thresholds and the excitation energy-dependent photoelectron spectra at the B K threshold of \(B_2O_3\). In this paper, we describe excitation energy-dependent XES at the B K and O K thresholds and excitation energy-dependent PES at the B K threshold of \(B_2O_3\), and discuss the electronic structure of the valance band and the resonant radiative/non-radiative decay processes.

EXPERIMENTAL

Sample preparation

Commercially obtained bulk \(B_2O_3\) samples were used for the XES measurements and \(B_2O_3\) thin films were used for PES measurements to prevent electrical charging during the synchrotron irradiation of the samples. The thin films were prepared by depositing 5.5 nm thick boron films on Si(100) substrates using electron magnetic sputtering; the samples were then heated at 550°C for 1 h in an oxygen atmosphere to oxidize the boron. These prepared boron oxide thin films were confirmed by x-ray diffraction and x-ray absorption measurements.

The x-ray diffraction pattern of the boron oxide thin films was in good agreement with the standard diffraction pattern of \(B_2O_3\). Figure 1 shows the x-ray absorption spectra of (a) the boron oxide thin films and (b) commercially obtained bulk \(B_2O_3\) at the B K threshold. The spectrum
Figure 1. (a) Total electron yield (TEY) x-ray absorption spectrum of B$_2$O$_3$ thin films measured at BL-1A at the PF. The excitation energy for the excitation energy-dependent PES measurements is denoted by Ea–Es. (b) Partial fluorescence yield (PFY) and TEY x-ray absorption spectra of bulk B$_2$O$_3$ measured on BL-8.0 and BL-6.3.2, respectively, at the ALS. The excitation energy for excitation energy-dependent XES measurements is denoted by Xa–Xc.

Spectral measurements

XES of the bulk B$_2$O$_3$ was performed using a grating x-ray spectrometer installed at BL-8.0 at the ALS. A 1500 lines mm$^{-1}$ grating with a 5 mm radius of curvature was used for the B K measurements and a 1500 lines mm$^{-1}$ grating with a 10 mm radius of curvature was used for the O K spectra. The resolving power of the x-ray spectrometer was estimated to be 500 for the B K region and 370 at the O K with a 100 μm wide spectrometer entrance slit. The excitation energy of the incident beam was varied from 191.6 eV (denoted X in Fig. 1) to 224.6 eV (Xa) in the B K region and from 531.4 eV (denoted 1 in Fig. 4) to 559.4 eV (a) in the O K region to investigate the band structure and radiative decay processes in the individual inner-shell excitations. PES of the B$_2$O$_3$ thin films was carried out on BL-1A at the PF. The energy of the monochromatized incident beam was calibrated by recording the kinetic energy of the Au 4f photoemission. The monochromatized beam was incident normal to the sample and the emitted photoelectrons were monitored using an electron energy analyzer. The incident photon energy was varied from 175.6 eV (denoted by Es in Fig. 1) to 220.6 eV (Ea) to investigate the non-radiative decay processes. No spectral shape changes or peak shifts in the PES measurements of the B$_2$O$_3$ thin films were observed during the 2 h of synchrotron irradiation at a fixed incident energy, confirming that there was no electrical charging on the thin films.

RESULTS AND DISCUSSION

Valence band structure

The XES traces of the bulk B$_2$O$_3$ in the B K and O K regions and the PES trace of the B$_2$O$_3$ thin films are shown in Fig. 2. Based on the selection rule for dipole transitions,
the B K and O K x-ray emission spectra result from the B2p–B1s and O2p–O1s transitions, respectively. The spectra were measured using ‘off-resonance’ excitation. The excitation energy in the XES measurements was tuned about 20 eV higher than the threshold (209.6 eV for B K and 549.4 eV for O K) and that in the PES measurements was tuned about 20 eV lower than the B K threshold (175.6 eV). The energy of these spectra were normalized and aligned with respect to the Fermi edge. The density of states (DOS) spectra of B2O3 calculated by Li and Ching [2] using first principles calculations with a local density approximation are superimposed on the x-ray emission spectra. The hexagonal structural model of B2O3, in which boron atoms form sp2-planar bonding in B—O3 triangular units was used in these calculations. The s and p portions of the DOS of boron atoms are superimposed on the B K and those of oxygen atoms are superimposed on the O K x-ray emission spectra.

In the B K x-ray emission spectrum, a main peak was observed at 181 eV with a high-energy shoulder and a low-energy satellite at 167 eV. As will be shown later in Fig. 3, the peak near 194 eV can be assigned to excitonic emission and a small peak at 175 eV can be assigned to the third-order diffraction of the O K x-ray emission peak. (The O K-edge can be excited due to higher order x-rays from the beamline monochromator and the undulator.) In the O K x-ray emission spectrum, a sharp main peak was observed at 525.5 eV with a small peak at 520 eV. From comparison of the measured spectral features of the B K and O K x-ray emission spectra with the calculated DOS spectra of boron and oxygen atoms, the main peak with a high-energy shoulder in the B K x-ray emission spectrum can be assigned to B2p and the low-energy satellite to hybridized B2p–O2s. The two-peak structure of the O K x-ray emission spectrum can be assigned to O2p. In the photoelectron spectrum, three peaks were observed at binding energies of 8 eV (denoted as E1 in the Fig. 2), 12 eV (E2), and 26 eV (E3). Comparing the photoelectron spectrum with the B K and O K x-ray emission spectra, the former spectral features can be assigned as follows: E1 is due to O2p, E2 is predominantly due to B2p with slight contributions from O2p and E3 is composed of B2p, B2s and O2s components. The shoulder near 15 eV is largely due to B2s.

Radiative decay process

The excitation energy dependence of the B K x-ray emission spectrum of bulk B2O3 is shown in Fig. 3. The excitation energy was varied from 191.6 eV (denoted by Xx), which is below the threshold, to 224.6 eV (Xa). The excitation energy positions on the absorption spectra are indicated in Fig. 1(b) as Xa–Xx. In the 224.6 eV excitation spectrum, the main peak at 181 eV can be assigned to B2p and the low-energy satellite at 167 eV to hybridized B2p–O2s, as discussed above. The 175 eV peak arises due to third-order diffraction of the B K x-ray emission peak, as evidenced by the peak energy corresponding to one-third of the peak energy of the O K x-ray emission and the peak shape and intensity showing little dependence on the excitation energy from the B K threshold to the continuum. Both the main peak and the low-energy satellite shift by about 2 eV toward lower energy with π+ excitation at 193.6 eV (Xh). This peak shift and spectral feature change of the main peak can be explained by the change in initial and final state screening effects produced by the absence of electrons excited to the bound excitonic π*-orbital, which we call ‘spectator’ resonant inelastic x-ray scattering (RIXS). The intense emission peak near 194 eV with 193.6 eV excitation is due to x-ray scattering caused by the direct recombination of the participator electrons in the π*-orbital with the B1s core holes, which we call here ‘participator’ resonant elastic x-ray scattering (REXS). The high-energy satellite, denoted by asterisk in Fig. 3, appears near 192 eV with 201.6 eV (Xe) and 202.6 eV (Xd) excitations, and it clearly appears near 194 eV with excitation above 205.6 eV (Xc). This satellite may be explained by a ‘shake-up’ satellite. The satellite observed near 194 eV with excitation above 205.6 eV may especially be due to the direct recombination effect of the core excitons; inelastic collisions of outgoing electrons can excite valence electrons to the excitonic π*-orbital, and excited electrons can decay to B1s core holes via x-ray emission. The high-energy satellite can therefore be assigned to two processes depending on the excitation energy. One is participator REXS with π+ excitation at 193.6 eV and the other is ‘shake-up’ emission with higher energy excitation. These spectral features of the excitation energy dependent x-ray emission spectra of B2O3 at the B K threshold correspond well with previous measurements.

Copyright © 1999 John Wiley & Sons, Ltd.

X Ray Spectrom. 28, 503–508 (1999)
From the excitation energy dependent XES measurements, we can obtain general information about the band dispersion. In the excitation energy dependent B K x-ray emission spectrum of the B$_2$O$_3$, the positions of the main peak and the low-energy satellite are almost independent of the excitation energy above 193.6 eV with $\pi^*$ excitation. This suggests that the band structure of B$_2$O$_3$ is fairly non-dispersive in the B2p valence and conduction bands, which is consistent with the theoretically calculated band structure.

Figure 4 shows the excitation energy-dependent O K x-ray emission spectrum and the PFY and TEY absorption spectra of B$_2$O$_3$. The excitation energy for the XES measurements was varied from 531.4 eV, which is below the threshold, to 5559.4 eV on the continuum, resulting in the emission spectra labeled a–l. In the absorption spectra, the sharp peak observed at 536.5 eV can be assigned to transitions to the $\pi^*$-orbital. In the x-ray emission spectrum, the main peak at 525.4 observed with excitation energies above 536.4 eV is shifted to 525.0 eV for excitation energies below 536.4 eV, and the low-energy satellite peak is also shifted depending on the excitation energy. This slight peak shift in the $\pi^*$ excitation is due to spectator RXS. However, no REXS in the $\pi^*$ excitation was observed in the O K region. This slight shift of the main peak and the low-energy satellite and the absence of REXS with $\pi^*$ excitation show that the bound electron state of the $\pi^*$-orbital at the O K threshold is weaker than that at the B K threshold. The lack of any shift of the main peak at energy excitations above the $\pi^*$ state shows that the band structure is fairly non-dispersive, which is consistent with theoretical band calculations.

Non-radiative decay process

The excitation energy dependent photoelectron spectrum of the B$_2$O$_3$ thin films at the B K threshold is shown in Fig. 5. The excitation energy was varied from 175.6 eV (denoted by Ea), which is below the threshold, to 220.6 eV (Ea) on the continuum. The excitation energy positions on the absorption spectrum are shown in Fig. 1(a) as Ea–Ea. In this excitation energy dependent photoelectron spectrum, three peaks, denoted by E$_1$, E$_2$, and E$_3$, were observed in the valence band at 8, 12 and 26 eV.

Figure 4. Top: O K-edge PFY and TEY absorption spectra of bulk B$_2$O$_3$. The excitation energy position for the excitation energy-dependent XES is denoted by a–l. Bottom: excitation energy-dependent XES of bulk B$_2$O$_3$ at the O K threshold.

Figure 5. Excitation energy-dependent photoelectron spectra of B$_2$O$_3$ thin films at the B K threshold. Excitation energy positions on the absorption spectra are denoted in Fig. 1(a) by Ea–Ea.
respectively. As described earlier, E₁ is due to O₂p, E₂ is predominantly due to B₂p with slight contributions from O₂p and E₃ is composed of B₂p, B₂s and O₂s components. The normal B KVV Auger features consisted of three peaks, denoted by A₁₋₃ in Fig. 5; they were observed at excitation energies of 197.2 eV (E₁) and higher. Hence the broad peak structure near 200 eV in the TEY absorption spectrum shown in Fig. 1 is mainly due to this normal B KVV Auger process.

The excitation energy dependence on the peak intensity of the three valence peaks was clearly observed at the B K threshold. Figure 6 shows the peak intensities of the three valence peaks as a function of the photon energy, which corresponds to constant initial state (CIS) spectra. These spectra for E₁, E₂ and E₃ were resonantly enhanced at 193.6 eV with excitonic π⁺ excitation. This resonant non-radiative decay with excitonic π⁺ excitation was caused by the direct recombination of core excitons, which can generally be called a participator Auger process. Core excitons in the π⁻-orbital recombine and emit valence electrons with an energy transfer, resulting in the enhancement of the valence band intensities because their final state is the same as in direct photoemission. However, the degree of enhancement differed among E₁, E₂ and E₃. The peak of E₂ was most strongly enhanced with π⁺ excitation, which can be explained by the overlapping of the resonant Auger peak on the E₂ peak, as described later. The E₂ peak was more strongly enhanced than the E₁ peak in the resonance, resulting in peak intensity inversion of E₁ and E₂ observed between on-resonance and off-resonance, as shown in Fig. 5. As described earlier, the major portion of the molecular orbitals in E₂ was B₂p and that in E₁ was O₂p. Therefore, the enhancement of the E₂ peak with π⁺ excitation suggests a strong correlation between the π and π⁺ orbitals of boron atoms in the participator Auger process. A similar peak intensity inversion of the valence peaks at the B K threshold has been observed in gaseous BF₃,⁹,¹⁰ but not in h- and c-BN.⁷,⁸ This suggests that the B₂p orbital is more hybridized with N₂p orbitals in the B—N bonds of BN than with O₂p orbitals in the B—O bonds of B₂O₃ or with F₂p orbitals in the B—F bonds of BF₃.

Auger features with three peaks (denoted by A₁', A₂', and A₃') were also observed with π⁺ excitation near 194 eV, probably due to the resonant 'spectator' Auger process leaving excited electrons in the excitonic π⁺-orbital as spectators. As shown in the spectra measured with 193.6 eV excitation, the broad A₁' peak overlaps the E₁ photoelectron peak. In the resonant spectator Auger process, the kinetic energy of Auger electrons generally shifts to a higher level owing to the electronic screening effect created by the spectator electrons. Although it is difficult to measure accurately the kinetic energy shift between the resonant and normal Auger electrons because of the broad Auger peak features and the overlapping of the A₁' and E₃ peaks, the energy shift in the resonant Auger features was measured as being of the order of 1 eV. This measured screening effect of B₂O₃ is of the same order as that of h- and c-BN.⁷,⁸

**CONCLUSION**

The electronic structure and radiative/non-radiative decay processes in the inner-shell excitation of B₂O₃ were investigated by XES and PES using synchrotron radiation. The XES and PES features off-resonance were explained by the theoretically calculated DOS spectra of the hexagonal B₂O₃ model,² which indicates that the electronic structure was formed by hybridized sp²-planar B—O bonding in B—O₃ triangular units. A fairly non-dispersive band structure was suggested by the excitation energy-dependent XES measurements, which is also consistent with band calculations. From the excitation energy-dependent XES and PES measurements, both a resonant radiative decay process and a resonant non-radiative decay process were observed with π⁺ excitation at the B K threshold. The resonant decay process of B₂O₃ with π⁺ excitation can be described as follows: (1) a direct recombination of participator electrons with B1s core holes resulting in both resonant elastic x-ray scattering (participator REXS) and enhanced valence electron emission (participator Auger); and (2) an electronic screening by the spectator electrons excited in the excitonic π⁻-orbital resulting in both resonant inelastic x-ray scattering (spectator RIXS) and resonant Auger electron emission (spectator Auger). However, little resonant radiative decay was observed with π⁺ excitation at the O K threshold, probably owing to the weakly bound π⁺ state at the O K threshold. This study demonstrated that the combination of XES and PES measurements is useful for analyzing the valence electronic structure of multi-elemental materials, and that the combination of excitation energy-dependent XES and PES measurements is also powerful for investigating the decay process of inner-shell excitation.

**Acknowledgments**

We express our thanks to Professor Thomas A. Callcott of the University of Tennessee and to Dr Eric M. Gullikson and Dr James H. Underwood of Lawrence Berkeley National Laboratory for their helpful support with the spectroscopic measurements at the Advanced Light Source. We are also grateful to Professor Masaharu Oshima of the University of Tokyo and Professor Satoshi Maejima of Kochi Women’s University for their support of the PES measurements at the Photon Factory.
REFERENCES