Local structure analysis of boron-doped graphite by soft x-ray emission and absorption spectroscopy using synchrotron radiation

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(Received 9 November 2010; accepted 1 August 2011; published online 7 September 2011)

The local structure of boron-doped highly oriented graphite films was determined via soft x-ray emission and absorption spectroscopy using synchrotron radiation. Analysis of the BK and CK x-ray emission spectra using the discrete variational-Xz molecular orbital method clarified that boron atoms are chemisorbed onto graphite by substituting for carbon atoms in the carbon hexagonal rings. Compared to graphite, boron-doped graphite exhibits spectral differences in the higher edge of the CK x-ray emission spectrum and the CK x-ray absorption edge. Such a spectral profile of boron-doped graphite, which reflects the band structure, is well explained by the chemisorbed boron structure. © 2011 American Institute of Physics. [doi:10.1063/1.3631108]

I. INTRODUCTION

Because boron (B) doping in graphite can effectively control the chemical/physical properties and electronic structure of graphite, various B-dopings in graphite have been reported since the 1960s.1–3 Recently, the local structure of B-doped graphite has been investigated using advanced spectroscopic methods1–9 such as x-ray diffraction (XRD), Raman spectroscopy, x-ray photoelectron spectroscopy,11 B nuclear magnetic resonance, scanning tunneling microscopy, atomic force microscopy, scanning-electron microscopy (SEM), transmission electron microscopy, etc. Many papers have suggested that a carbon (C) atom is substituted for by a B atom in the carbon hexagonal layer, rather than B intercalating in the graphite layers. Additionally, Hishiyama et al. have successfully doped B atoms into a highly oriented graphite film (HOGF) using a diffusion method.10 Although conventional XRD, SEM, Raman spectroscopy, electrical resistivity measurements, and magnetoresistance measurements estimate that the B atoms in B-doped HOGF (B-HOGF) dissolve into the carbon hexagonal layers by substituting for carbon atoms, the local structure around the B atoms is unclear on the atomic scale.

A powerful tool for analyzing the local structure on the atomic scale, as well as for evaluating the electronic structure, is soft x-ray spectroscopy using highly brilliant synchrotron radiation. In particular, high-resolution x-ray emission spectroscopy and x-ray absorption spectroscopy in the soft x-ray region are well suited for analyzing the local and electronic structures of light element materials because these spectroscopies can provide high-resolution elemental/orbital information due to the selection rule of the dipole transition. Additionally, the combination of soft x-ray emission and absorption spectroscopies11 can elucidate bandgap information because they can directly reflect the valence and conduction bands, respectively. For example, the local and band structures of carbon-related materials, including B4C,12 nano-carbons,13 polymers,14 organic semiconductors,15 and DNA duplexes,16 have been successfully evaluated. Furthermore, we have analyzed the local and/or electronic structures of B-doped diamond17 and B/C/N alloys18 using soft x-ray emission and absorption spectroscopies and theoretical analysis via the discrete variational (DV)-Xz method.19 However, few studies have examined B-doped graphite using soft x-ray emission and absorption spectroscopies.

Herein we analyze the local and electronic structures of B-HOGF. These structures are investigated using high-resolution soft x-ray emission and absorption spectra in the BK and CK region of B-HOGF, as well as by a theoretical analysis using the DV-Xz method.

II. EXPERIMENTS

B-HOGF samples were prepared by a previously reported diffusion method.10 HOGFs were derived from carbon films prepared from Kapton films 25 μm in thickness. Graphite films heated to 2500°C and 3000°C are denoted as HOGF2500 and HOGF3000, respectively. B atoms can diffuse into the HOGF2500 and HOGF3000 films upon heating to 2250°C and are denoted as B-HOGF2500 and B-HOGF3000, respectively. The estimated concentration of B in B-HOGFs is 0.4 to 2.2 at. %. Commercially available compounds, including highly oriented pyrolytic graphite (HOPG), hexagonal boron nitride (h-BN), boron oxide (B2O3), boron carbide (B4C), and amorphous boron (B), were also prepared as references.

Soft x-ray emission and absorption measurements using synchrotron radiation (SR) were performed at the Advanced Light Source. The x-ray emission spectra (XES) were measured using a grating x-ray spectrometer installed in beamline BL-8.0.1.20 The photon energies of the monochromatized incident SR beam were tuned to 230 eV for the BK region.
and 320 eV for the CK region in order to effectively excite the 1s-electrons and to prevent multiple ionizations. The estimated resolving powers ($E/\Delta E$) of the spectrometer were approximately 930 for the BK region and 630 for the NK region using a 40 μm entrance slit and a 600 mm$^{-1}$ spherical grating with a 10 m radius. Both the incident angle and the take-off angle to the sample plane were tuned to 45°. X-ray absorption spectra (XAS) were measured in BL-6.3.2 (Ref. 21) using the total-electron-yield (TEY) method. The estimated $E/\Delta E$ values were 3000 for the BK region and 2000 for the CK region using a 600 mm$^{-1}$ varied-line-spacing grating with a 40 μm slit. In order to investigate the orientation of the samples via angle dependent XAS, the incident angles to the sample plane were either 0° (normal incidence) or 45°.

III. RESULTS AND DISCUSSION

A. X-ray emission and absorption spectra

Figure 1 shows the XES in the BK and CK regions of B-HOGF2500, B-HOGF3000, and the reference samples. In the BK-XES, both B-HOGF2500 and B-HOGF3000 exhibit identical profiles, which are composed of a sharp main peak (denoted by a) at 182.6 eV with low-energy tailing (b) and a high-energy satellite peak (c). The difference in the characteristic peak profile of B-HOGFs as compared to the profiles of the reference boron compounds (h-BN, B$_2$O$_3$, B, B$_4$C) suggests that the chemical states of the B atoms in B-HOGFs differ from those in the reference boron compounds. In the CK-XES, the spectral profiles of basal HOGF2500 and HOGF3000 are similar to that of HOPG and consist of a main peak at 276.6 eV with low-energy tailing and a high-energy shoulder. Thus, the HOGFs are graphitized. Both B-HOGF2500 and B-HOGF3000 exhibit profiles similar to HOPG, indicating that the C atoms in B-HOGFs form a graphitic structure. However, the dip (d) at 280.7 eV for B-HOGFs is shallower than that of HOPG, implying that B-doping affects the electronic structure of graphitic carbon structures.

Figure 2 shows the XAS in the 180–320 eV region of B-HOGFs, HOGFs, and reference compounds. In the BK region, B-HOGFs exhibit small absorption peaks, whereas HOGFs do not exhibit peaks. This result confirms that the diffusion method can successfully dope B atoms into HOGFs. The atomic ratios of B/C can be estimated by comparing the absorption peak heights between the BK and CK regions. In the TEY-XAS measurements, the TEY efficiency of B is typically higher than that of C, as clearly shown in the spectrum of B$_4$C. Although the atomic ratio of B/C is 4 in B$_4$C, the absorption peak height ratio of B/σ* to C/σ* is 11.2 (≈ 0.73/0.065). Therefore, the TEY efficiency ratio of B/C is 2.8 (≈ 11.2/4). Applying this TEY efficiency ratio to B-HOGF3000 where the peak height ratio of B/σ* to C/σ* is 0.0202, the estimated atomic ratio of B/C is 0.72% (= 0.0202/2.8 × 100%), which agrees with a B concentration of 0.4 to 2.2 at. % in B-HOGFs. Figure 3 shows the XAS in the BK and CK regions of B-HOGFs and the reference samples. In the BK-XAS, B-HOGFs exhibit a sharp peak at 192 eV, which depends on the incident angle, and broad peaks around 200 eV. Compared to the XAS of the reference samples, the peak profile, including the incident-angle dependence of B-HOGFs, is similar to that of h-BN.
This suggests that the B atoms in B-HOGFs assume trigonal bonding and form an oriented structure similar to h-BN. In the CK-XAS, the spectral profiles of B-HOGFs and HOGFs are similar to HOPG and are composed of a $\pi^*$ peak at 285.5 eV and a $\sigma^*$ peak around 292 eV. Moreover, the incident-angle dependences of B-HOGFs and HOGFs are the same as that of HOPG. These observations confirm that the C atoms in B-HOGFs and HOGFs form oriented graphitic structures.

Figure 4 shows the higher-energy region of the CK-XES and the lower-energy region of the CK-XAS of B-HOGFs and HOGFs. The higher-energy edge in the CK-XES of B-HOGFs shifts to a lower-energy region around 284 eV relative to that for HOGFs. In the CK-XAS, B-HOGFs exhibit a lower-energy threshold near the 283.5–284.5 eV region. Such spectral differences clearly demonstrate a B-doping effect on the band structure because the XES and XAS reflect the valence bands and conduction bands, respectively. Therefore, XES and XAS demonstrate that the top of the valence bands shifts deeper, and new states are created at the bottom of the conduction bands in B-HOGFs.

**B. Spectral analysis using the DV-Xα molecular orbital method**

In order to determine the local structure of B-HOGFs from the measured soft x-ray spectra, theoretical spectral analysis was performed using the DV-Xα molecular orbital (MO) method. In the DV-Xα calculations, we focused on the BK-XES because the characteristic profile of B-HOGFs differs from those of the reference boron compounds. Additionally, the DV-Xα calculations more accurately reproduce the XES profiles by the density of states (DOS) than XAS.

The spectral analysis using the DV-Xα method considers two probable B-adsorption models: the chemisorption model, in which B atoms substitute for C atoms in the carbon hexagonal rings, and the physisorption model, in which B atoms are located on graphitic structures. Figure 5 shows the chemisorption and physisorption models for B-doped graphite. The cluster model of C$_{96}$H$_{24}$ (denoted by Graphite in the upper panel) and B-doped graphite (lower panel). Chemisorption models (Chem1-Chem4) and physisorption models (Phys0-Phys2) are adopted for B-doped graphite. In the chemisorption models, a B atom substitutes for a C atom in the center hexagonal ring of the Graphite. In the physisorption models, a B atom is located at the center of the hexagonal ring or on a C atom at various distances. Numbers 1-7 denote the seven atoms around the center hexagonal ring in all of the cluster models, as shown in the circle of Graphite.

Chosen as the basal graphitic cluster model, in which one hexagonal ring is located in the cluster center and the edge C atoms are terminated by hydrogen (H) atoms. Optimizing the structure of the Graphite using the commercially available molecular mechanics (MM2) method sets the C–C bond length at 1.43 Å, and the cluster is flat, as shown in the side view. In the chemisorption models of B$_x$C$_{96-x}$H$_{24}$ (x = 1-4, Chem1-Chem4), B atoms substitute for C atoms in the center hexagonal ring. The number of substituent B atoms varies from 1 to 4 in the cluster models of Chem1, Chem2 (-o, -m, -p), Chem3, and Chem4, respectively. In the Chem2-o, -m, and -p models, two B atoms substitute for two C atoms at the ortho, meta, and para positions, respectively. In the physisorption models of BC$_{96}$H$_{24}$, one B atom is placed at the center of the centered hexagonal ring (Phys0) or on the C atom with a distance of 1 (Phys1), 1.7 (Phys1.7), or 2 (Phys2) Å. The DV-Xα calculations were performed on the ground states with a basis set of 1s, 2s, and 2p orbitals for B and C atoms. In order to compare to the measured x-ray spectral profiles, the calculated DOSs of the focused atoms were
broadened with 0.5 eV wide Lorentzian functions, and the MO energy of the highest occupied molecular orbital (HOMO) was adjusted to 0 eV.

Figure 6 shows the occupied B-DOSs of the chemisorption models (left panel) and physisorption models (right panel) to the BK-XES of B-HOGF3000. According to the selection rule for the dipole transition in BK-XES, B2p-DOS reflects the XES. The chemisorption models confirm that the B2p-DOS profiles mutually differ among the models. However, the B2p-DOS of Chem1 well reproduces the characteristic of the BK-XES profile, which is composed of a main peak a with low-energy tailing b and a high-energy satellite peak c. Considering the B2s-DOS distribution, the main peak and high-energy satellite peak are attributed to π orbitals, and the low-energy tailing is attributed to σ orbitals hybridized by the B2p and B2s orbitals. In the physisorption models, each B2p-DOS does not reproduce the measured BK-XES. Therefore, the most plausible local structure of B-HOGFs is Chem1. It should also be mentioned for Chem1 that the substituent B atom does not have neighboring B atoms in the same hexagonal ring, which is consistent with a low B concentration of 0.72 at. % in B-HOGF3000.

Figure 7 shows the B-DOS of the substituent 1B atom (position number 1 in the basal Graphite model in Fig. 5) and C-DOSs of C atoms (numbered 2 C-4 C) in the center hexagonal ring of Chem1. The peak structures in the B2p-DOS of 1B correspond to some of the peak structures in the C2p-DOSs of 2 C-4 C atoms, suggesting that the B2p orbitals hybridize with the C2p orbitals in the hexagonal rings. In particular, the main peak with low-energy tailing and a high-energy satellite in B2p-DOS nearly correspond to the C2p-DOS profile of the 2 C atom, implying that the B atom forms hybridized covalent bonds with neighboring C atoms. Figure 8 shows the total C-DOSs of the 2 C-6 C atoms in Chem1 and Graphite and compares them to the CK-XES of the B-HOGF3000 and HOPG. The C2p-DOS of Graphite well reproduces the CK-XES of the HOPG. However, the C2p-DOS of Chem1 slightly differs from that of Graphite, as shown in the subtracted DOS spectrum of (Chem1) − (Graphite); the DOSs at −2 eV and around −4 eV in Chem1 are higher than those of Graphite. This difference in the C2p-DOS between
Chem1 and Graphite agree well with the spectral difference between B-HOGF3000 and HOPG, i.e., (B-HOGF3000) − (HOPG). This further supports the idea that Chem1 is a plausible local structure for B-HOGFs.

Figure 9 shows the net charge distribution and bond overlap population (BOP) around the substituent B atoms in Chem1. The net charge shows a positive charge of +0.2 for the 1B atom, which is valid because the number of electrons in a B atom is intrinsically less than that of a C atom. However, the BOP between the 1B atom and neighboring C atoms (2 C, 6 C, 7 C) has a fairly high value of 0.86, indicating covalent B–C bonds in the hexagonal rings. Figure 10 shows the DOSs of the B2p and B2p*-orbitals of the 1B atom and those of the C1s, C2p, and C2p*-orbitals of 2 C-6 C atoms in Chem1, and it compares them to the DOSs of the C1s, C2p, and C2p*-orbitals of 2 C-6 C atoms in Graphite. The unoccupied B2p*-DOS of the 1B atom and C2p*-DOSs of 2 C-6 C atoms are gray in the figure. The higher-energy edges of the occupied B2p- and C2p-DOSs in Chem1 and C2p-DOS in Graphite are aligned at 0 eV because the HOMO energy is adjusted to 0 eV. In the unoccupied DOS, the 1B atom exhibits a B2p*-DOS around 0 eV, which can be understood by the creation of a positively charged hole by B doping in the C matrix. Corresponding to the B2p*-DOS of 1B, the 2 C-6 C atoms also exhibit C2p*-DOSs around the 0 eV region, due to the hybridization of the B atom with the surrounding C atoms. However, C2p*-DOS is not present around 0 eV in Graphite. These differences in the unoccupied C2p*-DOSs between Chem1 and Graphite agree with the spectral difference in the absorption threshold of CK-XAS between B-HOGFs and HOGFs. In the inner DOS, C1s-DOSs of the 2 C and 6 C atoms, which bond to a B atom, shift 1.2 eV higher in Chem1 than in Graphite, which can qualitatively explain the spectral difference in the higher-energy edge of CK-XES between B-HOGFs and HOGFs.

From the spectral analysis of the BK- and CK-XES using the DV-Xz method, the most probable local structure of B-HOGFs is the chemisorption of a B atom that substitutes for a C atom in the hexagonal ring, as well as sp² bond hybridization of the B atom with neighboring C atoms. As shown in Fig. 3, such a local structure composed of an sp²-hybridized B atom in the sp²-hybridized C atoms can explain the XAS profiles of the B-HOGFs; B-HOGFs exhibit similar XAS profiles in the BK region of h-BN and in the CK region of HOPG.

IV. CONCLUSION

In order to reveal the local structure of B-doped graphite (B-HOGF), we measured the XES and XAS using synchrotron radiation. The BK-XES of the B-HOGFs exhibit a characteristic spectral profile and have the same CK-XES as graphite. The BK- and CK-XAS of the B-HOGFs have profiles similar to those of h-BN and graphite, respectively. From the spectral analysis of BK- and CK-XES using the DV-Xz method, and considering chemisorption and physisorption models, the DOS of the chemisorption model in which a C atom in the hexagonal ring is substituted for by a B atom can well reproduce the measured XES profiles. In the local structure, the B atom forms covalent bonds hybridized by sp² orbitals with neighboring C atoms. The chemisorption model can also explain the XAS profiles of the B-HOGFs. Additionally, the measured spectral differences in the higher-energy edges of CK-XES and the absorption threshold of CK-XAS between B-HOGFs and HOGFs can be well explained by the band structure differences between the chemisorbed structure and graphite. Therefore, the most probable local structure of B-doped graphite is the chemisorption of B atoms, which substitute for the C atoms in the carbon hexagonal rings of graphite. Additionally, this paper demonstrates that soft x-ray emission and absorption spectroscopies are powerful methods for analyzing the local structure of B/C compounds.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan under Contract No. 20560628.