CARBON 71 (2014) 1–10

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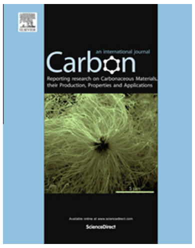

A polarization rule on atomic arrangements of graphite-like boron carbonitride

Iwao Shimoyama *, *Yuji Baba, Tetsuhiro Sekiguchi*

Surface Reaction Dynamics Research Group, Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai-mura 2-4, Naka-gun, Ibaraki 319-1195, Japan

ARTICLE INFO

Article history:
Received 2 July 2013
Accepted 27 November 2013
Available online 3 December 2013

ABSTRACT

B and N *K*-edge near-edge X-ray absorption fine structure (NEXAFS) spectra of boron carbonitride (B–C–N) films prepared by ion beam deposition are interpreted by molecular orbital calculations with the core–hole effect. Model clusters with different atomic arrangements are compared in terms of photoabsorption cross section (PACS) and net charge, and they are classified into two groups, *i.e.*, polarization and non-polarization types. PACS of π^* peaks near the lowest unoccupied molecular orbital (LUMO) state increase at B *K*-edge and decrease at N *K*-edge for polarization type and *vice versa* for non-polarization type. Based on a comparison between experimental and theoretical results, we propose a rule for atomic arrangements of boron, carbon, and nitrogen atoms in graphite-like B–C–N. Finally, the relationship between the rule and structural stability is discussed.

1. Introduction

Graphite-like boron carbonitride (B–C–N) is a series of compounds, which have a honeycomb structure like graphite and medium compositions of $B_xC_yN_z$ between graphite and hexagonal boron nitride (*h*-BN). Since graphite-like B–C–N can have a variety of electronic structures from a metal to an insulator, a variety of applications, *e.g.*, luminescent materials, photo-energy conversion, transistors, and sensors, has been proposed [1].

Recently, these materials have also attracted much attention as catalysts. Some groups have reported that catalytic activity in the oxygen reduction reaction is drastically enhanced by substitutional doping of B and/or N atoms in π-conjugated carbon materials like carbon nanotubes and glassy carbons [2–5]. Preceding works have reported that these materials can have a comparable catalytic activity to Pt and have excellent chemical stability.

Another interesting application is in electronic devices with graphene. Band-gap control is a key issue for the development of graphene devices. It has been reported that a layered structure of graphene and *h*-BN forms a band-gap of about 50 meV in graphene by closing the interlayer distance [6]. If graphite-like B–C–N with a variety of electronic structures are used instead of *h*-BN, it would be possible to control the band-gap of graphene precisely.

Over the last few decades, many methods have been attempted to synthesize these materials [7–21]; however, there remain two large unsolved problems. One is the phase separation between graphite and *h*-BN, which are major by-products. These are not only included in almost all B–C–N materials but the often dominant species [22,23]. Thus far, no large-scale and high-yield synthesis method has been established for graphite-like B–C–N that is not merely a mixture of graphite and *h*-BN.

Another problem is the synthesis of single-phase materials. Most B–C–N products have complicated structures in which various compositions and crystal structures are included. While some polymorphs have been theoretically proposed for graphite-like BC_2N [24], nobody has succeeded in

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* *Corresponding author.*
E-mail address: shimoyama.iwao@jaea.go.jp (I. Shimoyama).
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http://dx.doi.org/10.1016/j.carbon.2013.11.066

identifying any of them. It is indicated that these polymorphs have a variety of electronic structures from metals to insulators depending on atomic arrangement [24]. It is also indicated that catalytic activity is influenced by arrangement of doped atoms in a π-conjugated carbon matrix [4]. Thus, atomic arrangement is an indispensable factor for material design of graphite-like B–C–N.

X-ray diffraction has been widely used for structural analysis of B–C–N materials. Some groups have observed intense diffraction lines of graphite and *h*-BN, giving evidence of the phase separation between graphite and *h*-BN [10,22,25–27]. Some reported unknown lines that are not observed in graphite and *h*-BN, and suggested the existence of crystalline B–C–N [15,19,25,26,28]. To the best of our knowledge, however, the atomic arrangement has not been clarified yet.

X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) are also frequently used for the characterization of B–C–N materials, and many groups have indicated the existence of B–C–N moiety, along with graphite and *h*-BN [9–11,14–22,27–33]. However, interpretation of chemical bonds is not easy, because there are many combinations between B–N, B–C, C–N, and C–C bonds in the honeycomb matrix. B, C, and N photoelectrons often form broad and featureless peaks in XPS spectra, which obscure assignment based on chemical shift. FT-IR is a powerful tool for identifying chemical bonds. However, most B–C–N compounds show complicated spectra in which many vibrational modes overlap each other, and the interpretation of the spectra includes some obscurity. Hence, atomic arrangements around B, C, and N atoms are still unclear from XPS and FT-IR. In this context, multifaceted characterizations using various methods are necessary.

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy is a powerful tool for the analysis of B–C–N materials because of the following characteristics. One is specificity due to core excitation as well as XPS, and the other is polarization-dependence analysis using a property of synchrotron radiation. NEXAFS has been used for B–C–N films formed by ion beam assist deposition, chemical vapor deposition, RF magnetron sputtering, ball milling, and ion beam deposition (IBD) [12–14,19,27–29,34–37]. Existence of B–C–N moiety was also confirmed by NEXAFS, which showed some components that were not observed for graphite and *h*-BN. Some groups have reported that B–C–N consisted of a π-conjugated system with a layered structure and that a variety of bonds between B, C, and N atoms was formed [12,27,37].

Our group has also used NEXAFS for the characterization of B–C–N films prepared by IBD [37]. Since B *K*-edge NEXAFS showed spectral features that were different from those of *h*-BN, we concluded that some B–C–N compounds were formed. However, the details of B *K*-edge NEXAFS were not discussed, and we did not report any results of N *K*-edge NEXAFS in our previous work. Until now, only a limited number of works have been reported on the theoretical interpretation of NEXAFS of graphite-like B–C–N. Wibbelt et al. [38] predicted electron-energy-loss near edge structure (ELNES) spectra of graphite-like BC_2N calculated by a multi-scattering approach. Their calculation can be used for NEXAFS interpretation because ELNES and NEXAFS give similar information on electronic structures of unoccupied states; however, their calculation is not sufficient, because only an atomic arrangement was supposed for graphite-like BC_2N. Muramatsu [39] calculated the unoccupied density of states of graphite-like BC_2N with three different atomic arrangements using the discrete variational (DV)-Xα method. This work can be helpful to interpret NEXAFS spectra; however, the core–hole effect was not taken into account in this work, which is necessary for the interpretation of core–hole spectroscopies like NEXAFS [40]. Because of this, discussion was lacking on the relationship of peak energies observed in NEXAFS.

In the present work, we present unpublished experimental data and perform theoretical calculations of NEXAFS using the DV-Xα method with core–hole effect. Comprehensive interpretation is provided for both B and N *K*-edges NEXAFS from the comparison of graphite-like BC_2N model structures with variety of atomic arrangements. Based on the relationship between experimental and theoretical results, we propose a rule for atomic arrangement in graphite-like B–C–N.

2. Experimental

B–C–N films were prepared by IBD as described elsewhere [20,21]. Fragment ions produced by ionization of borazine ($B_3N_3H_6$) were irradiated onto the surface of highly oriented pyrolytic graphite (HOPG) with an acceleration energy of 3 keV. B–C–N films with different composition ratios were formed by changing the ion fluence in the range of 10^{15}–10^{17} ions/cm^2. Sample preparation and characterization were performed in the same ultra-high vacuum chamber to avoid contamination with air.

All experiments were performed at the BL-11A beamline of the Photon Factory in the High Energy Accelerator Research Organization. Using the linear polarization property of the beamline, we measured the polarization dependence of the NEXAFS by changing incidence angle θ of X-rays in the range of 20°–90°, where θ was defined as the angle between the surface normal and the polarization vector of the X-rays. NEXAFS spectra were obtained by measuring total electron yield. For a comparison of samples prepared at different fluences, we also measured NEXAFS spectra of all samples at the magic angle (= 54.7°) at which polarization dependence is canceled out.

Compositions of the samples were estimated from XPS with a monochromatic soft X-ray of 700 eV. B, C, and N 1s photoelectrons were measured by a concentric sector-type analyzer (VG Microtech, Ltd., Model CLAM2). We confirmed by XPS measurements that the influence of oxygen contamination was negligible for all samples.

3. Experimental results

Fig. 1 shows B and N *K*-edges NEXAFS spectra of samples prepared at 800 °C. Four curves in each panel correspond to the results of four samples in respective order of deposition. All spectra were measured at the magic angle. The peak at 192 eV in the B *K*-edge and the peak at 401.7 eV in the N *K*-edge increased with fluence. Since these peaks correspond to the π* peaks of *h*-BN, which are indicated as vertical broken lines, these results mean *h*-BN became dominant with fluence. The composition ratio estimated by XPS (Fig. S1) also shows that B and N content increased with fluence, and they