Identification of ternary boron–carbon–nitrogen hexagonal phases by x-ray absorption spectroscopy

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Boron carbon nitride (BCN) films have been grown by B_4C evaporation with concurrent N_2^+ ion assistance, and have been characterized by x-ray absorption near edge (XANES) spectroscopy. Upon the nitrogen insertion, the film structure evolves from B_xC -like to h -BN-like. The hexagonal structure corresponds to a true ternary BCN compound that can be understood as h -BN with carbon incorporated in substitutional sites. The $C(1s)$ XANES presents π^* states characteristic of the BCN arrangement. The basal planes of the h -BCN phase are oriented perpendicular to the substrate, as derived from the angle dependence of the XANES signal. © 2001 American Institute of Physics. [DOI: 10.1063/1.1376428]

Boron carbonitride (BCN) compounds have attracted considerable interest as materials for hard coating applications¹ and as a semiconductor of varying gap.² Cubic BCN compounds (c -BCN) are expected to combine the properties of diamond and cubic boron nitride (c -BN) whereas hexagonal structures (h -BCN) are expected to behave as semiconductors with various band gap energies depending on the composition and structure. The synthesis of BCN seems possible based on the similar structure between graphite and hexagonal boron nitride (h -BN) and between diamond and cubic boron nitride (c -BN).

BCN films have been prepared by a large variety of deposition methods.³ Cubic structures have been only produced by high pressure and high temperature synthesis⁴ and magnetron sputtering^{3,5} but, in these cases, segregation of C and BN phases occur. Hexagonal ternary phases have been produced by chemical vapor deposition methods.^{6,7}

The characterization of the bonding structure of the BCN films has been commonly performed by x-ray photoemission^{6,8} and infrared spectroscopies.^{5,9} However, a definitive identification of the ternary phases has not been provided since the presence of BC, BN, and CN bonding is not enough to discern between a true ternary phase and a mixture of segregated binary phases. More information can be extracted from the $K-1s$ shell near-edge fine structure since it is very sensitive to local order arrangements and can be used to identify phases in complex systems.¹⁰ Therefore, electron-energy loss spectroscopy¹⁰ (EELS) in a transmission electron microscope or x-ray absorption near edge spectroscopy¹¹ (XANES) are more suitable techniques to obtain structural information. The structure of BCN films has been studied with EELS^{12–16} although a definitive proof of the synthesis of a ternary compound is still lacking. Moreover, in certain cases, phase segregation has been observed in both hexagonal¹² and cubic structures.¹³ The advantage of XANES is a resolution of ~ 0.1 eV, better than the resolution

of ~ 1 eV achieved with EELS. This is important to resolve sharp features in systems with a large number of different bonding possibilities like the BCN compounds. Despite this fact, no report of XANES analysis in BCN films has been published that we are aware of so far. In this letter, we report on the successful identification of hexagonal ternary BCN phases by XANES.

The BCN films were grown in a high vacuum chamber with a base pressure of 2×10^{-7} mbar on p -type (100) oriented Si substrates. The carbon and boron atoms were obtained by e -beam evaporation of boron carbide (B_4C). The vapor deposition rate was kept constant at ~ 4 Å/s during deposition by keeping the e -beam power at 525 W. The assistance was performed with a nitrogen ion beam with ion energies up to 1200 eV and ion fluxes up to 2.1 mA/cm². The ions impinged the sample with an incident angle of 45° with respect to the substrate normal. The deposition time was 10 min and the substrates were kept at 150°C . The typical thickness of the coatings is ~ 200 nm.

XANES measurements were performed at the beamline 8.2 of the Stanford Synchrotron Radiation Laboratory. The data were acquired in the total yield mode by measuring the sample photocurrent. The signal was normalized to the photocurrent from a gold-covered grid recorded simultaneously. The sample was oriented with respect to the incident beam near the 55° magic angle in order to avoid orientational effects, except when performing angle dependent studies.

The composition of the films was derived from the XANES spectra. The presence of different absorption edges for each element allows a quantification of the composition by considering the relative height of the absorption edge corrected with a proportionality factor, which is determined from comparison with reference h -BN and B_4C samples. Figure 1 shows a ternary diagram with the composition of all the samples grown. The composition is confined to a low-carbon region since the carbon content is intrinsically limited to 20 at. %, which is the carbon content of the B_4C starting material. Increasing either the N_2^+ ion energy or ion flux

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FIG. 1. Ternary diagram showing the composition of our BCN films (solid dots). The open dots represent reference composition values.

increases the nitrogen content. The stoichiometry saturates in the value $B_{45}C_{10}N_{45}$.

An evidence of the formation of a ternary compound can be extracted from XANES since it provides information on the local bonding environment of each element separately. Therefore, we can discern if mixing at the atomic level is produced. Figure 2 displays the $B(1s)$, $C(1s)$, and $N(1s)$ XANES edges for a set of BCN films with increasing nitrogen content. The films were measured as received and after annealing in vacuum at 500 °C. The annealing process removes the surface contamination without affecting the film structure. The spectra were normalized to the same height for comparison purposes. The spectra of highly oriented pyrolytic graphite (HOPG), diamond, B_4C , h -BN, and c -BN are shown as reference spectra.

The $B(1s)$ edge shows sharp peaks in the π^* region, between 188 and 196 eV, and a broad structure in the σ^* region, between 196–205 eV. The sample grown without nitrogen assistance (sample No. A) shows the typical spectral shape of an amorphous boron carbide film.¹⁷ The π^* resonance of h -BN at 192 eV^{18,19} is evident for nitrogen contents

around 20 at. % and becomes the dominant feature for higher nitrogen contents.

The shape of the $N(1s)$ confirms the formation of a h -BN-like compound. As the nitrogen content increases, the $N(1s)$ spectra resembles that of h -BN and the π^* resonance peak at 401 eV¹⁹ becomes more evident. The $N(1s)$ features are broad and impede extracting further information although subtle line shape changes are observed.

From the $C(1s)$ features, we can discern if carbon is incorporated in the h -BN-like network, therefore, if a true ternary compound is formed. The $C(1s)$ spectrum of boron carbide (sample No. A) shows four edges at 283, 287, 288, and 291 eV, which are sharper in crystalline B_4C than in amorphous B_xC .^{17,20} This structure is further smoothed as nitrogen is incorporated to the film in sample Nos. B and C. This result suggests the distortion of the B_{12} icosahedral units present in B_xC to accommodate the h -BN-like structure. With further nitrogen intake, a series of sharp carbon peaks resembling π^* resonances appear in the 285–290 eV region, superimposed to the boron carbide signal. The main peaks at 287.3 and 288.5 eV are labeled as C_1 and C_2 in the Fig. 2. The presence of the peak at 285.4 eV (labeled as G) corresponding to graphite indicates that there is some segregation of carbon in graphitic regions. The C_1 and C_2 peaks become the dominant features when the $B(1s)$ and $N(1s)$ edges indicate the formation of a h -BN-like material. These peaks cannot be assigned to any reference carbon-based material and, therefore, they are clearly related to the formation of the h -BN-like structure. We also checked carefully that none of these peaks correspond to carbon surface contamination by monitoring the oxygen signal.

The relation of the h -BN-like features and the carbon peaks is clearly verified from the spectra shown in Fig. 3. Figure 3 shows the angle dependent study of the XANES intensity. The XANES intensity from π^* states follows a

FIG. 2. XANES spectra for a set of BCN films with increasing nitrogen content, and spectra of reference samples (HOPG, diamond, B_4C , h -BN, and c -BN). Downloaded 25 Feb 2010 to 161.111.180.191. Redistribution subject to AIP license or copyright; see <http://apl.aip.org/apl/copyright.jsp>

FIG. 3. Normalized XANES spectra for various incidence angles of the synchrotron light. The B(1s), C(1s), and N(1s) features follow the same behavior indicating the formation of a ternary hexagonal compound. The signal anisotropy indicates a preferential orientation with the hexagonal planes perpendicular to the substrate surface.

cosine-squared dependence with the angle between the light and the π bonds.²¹ Therefore, we can detect if there is any preferential orientation of the basal planes from hexagonal structures. We can see that the intensity of the π^* peaks from B(1s) at 192 eV (labeled as B), N(1s) at 401 eV (labeled as N), C₁ and C₂ follow the same behavior whereas the graphite signal (peak G) shows no anisotropy. This result confirms the incorporation of carbon into the hexagonal structure and the formation of a ternary compound. The decrease of the signal with the incidence angle corresponds to a preferential orientation of the hexagonal planes perpendicular to the film surface. A similar orientation of basal planes in other hexagonal structures of binary compounds of B, C, and N has been previously reported.^{19,22,23} Since the hexagonal structures are mechanically anisotropic, the compressive stress induced in the films by the ion bombardment during deposition is easily relaxed when the basal planes orient perpendicular to the substrate.

The presence of different C(1s) peaks seems related to the different possible nearest neighbor environments of carbon in the hexagonal network. These states appear in the XANES spectrum as π^* resonances shifted in energy compared to graphite. These carbon states have different stability since some are more intense than others.

In summary, we have proven the formation of a ternary *h*-BCN compound. This compound results from the transition from a B_xC-like to a *h*-BN-like structure as the nitrogen content is increased. This hexagonal structure is dominant for nitrogen contents over 20 at. % and is oriented perpendicular to the substrate surface.

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