X-RAY ABSORPTION STUDY OF PULSED LASER DEPOSITED BORON NITRIDE FILMS

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ABSTRACT

B and N K-edge x-ray absorption spectroscopy measurements have been performed on three BN thin films grown on Si substrates using ion-assisted pulsed laser deposition. Comparison of the films’ spectra to those of several single-phase BN powder standards shows that the films consist primarily of \( sp^2 \) bonds. Other features in the films’ spectra suggest the presence of secondary phases, possibly cubic or rhombohedral BN. Films grown at higher deposition rates and higher ion-beam voltages are found to be more disordered, in agreement with previous work.

INTRODUCTION

Near-edge x-ray absorption spectroscopy is well-known as a method for characterizing the bonding and orientation of organic molecules adsorbed on thin-film surfaces. Subsequent work has shown that core-level x-ray absorption is also a useful technique for characterizing the unoccupied electronic states of low-atomic-number solids. A number of x-ray absorption studies have focussed on graphite and diamond, the two common crystalline phases of carbon. Other researchers have compared the spectra of amorphous carbon and hydrogenated diamond-like carbon thin films to those of the bulk crystalline phases.

Boron nitride is isoelectronic to carbon and has both hexagonal and cubic phases analogous to graphite and diamond. In hexagonal BN (hBN), B and N atoms in alternate layer planes lie directly on top of one another in an AA’A stacking arrangement, as opposed to the staggered ABA stacking in graphite, which causes C atoms in neighboring layers to be offset. Rhombohedral BN (rBN) differs from hBN only in its staggered ABCA stacking. Previous NEXAFS studies have compared the B and N K-edge spectra of well-ordered hexagonal, cubic, wurtzite and rhombohedral BN powders. The insight obtained through analysis of the powder spectra can be used to interpret similar data taken on thin BN films, which are likely to find use as both tribological coatings and as wide-gap semiconducting materials.

EXPERIMENTAL DETAILS

The three BN films used in this study were produced by ion-assisted pulsed laser deposition onto heated silicon substrates, as detailed previously. Deposition conditions are summarized in Table 1. Infrared transmission measurements (not shown) on these films revealed absorption at wavelengths characteristic of both the cubic and hexagonal phases, allowing an estimate of their volume fraction. The purity of the three types of BN powder was determined using x-ray diffraction (not shown) to be greater than 90%.

B and N K-edge x-ray absorption spectra were obtained at both the 8-1 and 8-2 beamlines
Table 1: Parameters obtained from fits to the B K-edge spectra of two types of BN powder and three BN/Si films prepared by ion-assisted pulsed laser deposition under slightly different conditions. The $sp^3$ fraction in the films was estimated using infrared transmission measurements. NA = not applicable.

| Peak Energy (eV) | Peak Separation (eV) | Rel. Integ. Intens. | Lorentzian Width |
|------------------|---------------------|---------------------|------------------|
| $V_{ion} = 0.48$ kV; Ar and N ions; deposition rate 0.4 Å/s; approx. 30% $sp^3$ and 70% $sp^2$ |
| 192.05           | NA                  | 1.0                 | 0.10             |
| 192.69           | 0.64                | 0.37                | 0.18             |
| 193.27           | 0.58                | 0.25                | 0.16             |
| 193.89           | 0.62                | 0.26                | 0.23             |
| $V_{ion} = 0.48$ kV; N ions only; deposition rate 0.4 Å/s; approx. 15% $sp^3$ and 85% $sp^2$ |
| 191.74           | NA                  | 1.0                 | 0.10             |
| 192.39           | 0.65                | 0.31                | 0.18             |
| 192.98           | 0.59                | 0.16                | 0.16             |
| 193.6            | 0.63                | 0.21                | 0.16             |
| $V_{ion} = 1$ kV; N ions only; deposition rate 1.7 Å/s; approx. 100% $sp^2$ |
| 191.93           | NA                  | 1.0                 | 0.52             |
| 192.69           | 0.76                | 0.19                | 0.17             |
| 193.19           | 0.5                 | 0.18                | 0.27             |
| 194.0            | 0.81                | 0.22                | 0.37             |
| hBN powder       |
| 192.0            | NA                  | 1.0                 | 0.04             |
| rBN powder       |
| 192.26           | NA                  | 1.0                 | 0.10             |
| 192.92           | 0.659               | 0.30                | 0.02             |
| 193.52           | 0.60                | 0.27                | 0.02             |
| 194.3            | 0.78                | 0.34                | 0.1              |

at SSRL, as well as at the IBM/U8 beamline at NSLS. Details of the data acquisition have been reported previously.[5, 7] A simple polynomial was adequate to fit the background of the powder spectra but it was necessary to use a gaussian-broadened step function[1] to fit the background intensity for all the films’ B K-edge spectra. The position of the step was fixed at 2.125 eV above the B 1s $\pi^*$ peak, the energy where $\sigma^*$ absorption begins in cBN. The absolute energies of spectral features are reproducible to within 0.3 eV from run to run, but the relative energies of the features are reproducible to within 0.05 eV.

RESULTS

Figure 1a shows the B K-edge spectra of the three BN/Si films, while Figure 1b shows the spectra of hBN, rBN and cBN powders, which have been described in detail previously.[5] The most notable feature of the hBN and rBN powder data is the presence of the $\pi^*$ feature at 192.0 eV, which is characteristic of $sp^2$ bonding.[3, 4] This $\pi^*$ feature is absent in cBN powder due to the $sp^3$ nature of the bonding. In the $sp^2$-bonded layered materials, the $\pi^*$ feature has been described as a core exciton whose position below the conduction-band edge
is a result of a 1.3 eV excitonic binding energy. \[10\] Comparison of the data Figures 1a and 1b shows that the bonding in the BN/Si films is predominantly \(sp^2\), similar to the hBN powder. However, there are three sharp peaks that appear in the B spectra of all three BN films just above the \(\pi^*\) peak but which don’t appear in the hBN data. Parameters obtained from fits to these smaller peaks are collected in Table 1 along with fit parameters from the hBN and rBN powders. The BN/Si films’ spectra also have a peak at 199 eV in the middle of the empty \(\sigma^*\) band which is not present in any of the powder spectra.

N K-edge spectra for the BN/Si films and the three BN powders are shown in Figure 2. The first peak at 402 eV in the \(sp^2\)-bonded materials is again a \(\pi^*\) feature, although it is not as intense or as far below the conduction-band edge as in the B K-edge spectra. In the Wannier model of excitonic behavior, the intensity and binding energy of an exciton are reduced when the core hole is created on the anionic site. \[10\] Overall the film data is similar to that for hBN and rBN, although the intensity of the \(\pi^*\) peak at 402 eV is reduced with respect to that of the the \(\sigma^*\) peak at 408.5 eV in the films compared to the hBN or rBN standards.

**DISCUSSION**

Because infrared spectroscopy on these BN films has indicated the presence of cBN, it is logical to ask whether the unexplained features in the films’ spectra may result from a combination of hBN and cBN states. In fact, the occurrence of a step near 194 ev in the background intensity of the films’ B K-edge spectra is probably an indication of the cBN phase. The peak at 199 eV in the BN/Si B K-edge data may also be due to a contribution from cBN. Also attributable to cBN is the increased intensity of the \(\sigma^*\) peak with respect to the \(\pi^*\) peak in the films N K-edge spectra. The size of the above-mentioned deviations from the hBN spectra appears to be correlated with the amount of cBN indicated in each film by the IR measurements.

The three fairly narrow peaks near 192.6, 193.2, and 194.0 eV in the films’ B K-edge data (see Table 1) do not have analogs in the cBN or hBN data, nor are there similar features in the K-edge spectra of disordered C films. With much lower energy resolution, Fomichev and Rumsh previously reported a single broad peak near 194.0 eV in their study of hBN powder. The nearly constant energy spacing shows that these peaks are not a Rydberg series and the approximately 0.6 eV magnitude of the spacing rules out an origin involving lattice vibrations. The proximity of these sharp peaks to the \(\pi^*\) excitonic peak suggests a related origin. One possibility is that stacking in the films is disordered and that the individual peaks represent different stacking configurations. Given that BN films are often non-stoichiometric, another possibility is that these peaks represent a quasi-bound final state formed by a photoelectron and a N vacancy. The most obvious possibility is that these peaks are due to the presence of rBN, whose B K-edge spectrum shows similar small peaks, as documented in Table 1. The unidentified peaks would then be due to modification of the \(\pi^*\) bonding by the ABCA stacking that is characteristic of rBN. Positive identification rBN as a minor constituent of these films would require further study.

A closer look at Table 1 and Figures 1a and 2a shows that the peaks for the film synthesized with the higher ion beam voltage and higher deposition rate are considerably broader than those for the other two films. Energetic ions have likely caused damage to this film, corroborating the findings of a previous IR and photoemission spectroscopy study by Wada and Yamashita on ion-assisted evaporation of BN films. Wada and Yamashita also observed metallic B and a smaller amount of cBN in material grown at deposition rates above
Figure 1: a) B K-edge x-ray absorption spectra for three BN/Si films. The x-ray flux was directed onto the films at normal incidence. Notice the 3 small peaks between the $\pi^*$ peak at 192.0 eV and the onset of the $\sigma^*$ band at 197 eV. b) B K-edge spectra for hBN, cBN, and rBN powders.
Figure 2: a) N K-edge x-ray absorption spectra for three BN/Si films. All data were taken with x-rays at normal incidence. b) N K-edge spectra for hBN, cBN, and rBN powders.
1 Å/s. These results are consistent with the observation (see Table 1) that the film synthesized at the higher deposition rate has a lower fraction of \( sp^2 \)-bonded material. Given the evident degree of disorder in this film, the recent observation of a preferred crystallographic orientation came as a surprise. NEXAFS and transmission electron microscopy experiments showed the hexagonal layer planes were oriented close to orthogonal to the substrate. This orientation is contrary to that usually observed in thin graphite films, where the c-axis is typically normal to the film-substrate interface.

CONCLUSIONS

B and N K-edge spectra have been acquired on both single-phase BN powders and on BN/Si films fabricated using ion-assisted pulsed-laser deposition. Comparison with the powder data shows the films to be primarily \( sp^2 \)-bonded. Systematic differences between the films’ spectra and that of pure hBN suggest that another phase is present, probably the cBN that has been observed with infrared transmission measurements. Three sharp peaks appear in the films’ B K-edge spectra between the usual \( \pi^* \) and \( \sigma^* \) bands. These peaks may be related to disorder or may indicate the presence of the rBN phase in the films. Angle-dependent x-ray absorption studies have shown that the BN/Si films are preferentially oriented with the hexagonal axis nearly in the film plane. Transmission electron microscopy and photoemission studies are underway to help clarify issues of film morphology and stoichiometry. The near-edge x-ray absorption spectra of thin BN films are proving to be more complex to interpret than those of vapor-deposited C films.

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