Electronic and bonding structures of B-C-N thin films investigated by x-ray absorption and photoemission spectroscopy

S. C. Ray, H. M. Tsai, C. W. Bao, J. W. Chiou, J. C. Jan, K. P. Krishna Kumar, and W. F. Pong[a]
Department of Physics, Tamkang University, Tamsui, Taiwan 251, Republic of China

M.-H. Tsai
Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China

S. Chattopadhyay and L. C. Chen
Centre for Condensed Mater Sciences, National Taiwan University, Taipei, Taiwan 106, Republic of China

S. C. Chien, M. T. Lee, and S. T. Lin
Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106, Republic of China

K. H. Chen
Institute of Atomic and Molecular Science, Academica Sinica, Taipei, Taiwan 106, Republic of China

X-ray absorption near-edge structure (XANES) and valence-band photoelectron spectroscopy (PES) were used to investigate the electronic and bonding structures of B-C-N thin films. The intensities of the sp^2-bonded features in the C K-edge XANES spectra are found to generally decrease as the C concentration increases, whereas the intensities of the sp^2-bonded features in the spectra of N K-edge XANES increase with the N concentration. The decrease of the intensities of the sp^2-bonded features in the C and N K-edges XANES spectra correlates with the increase of the C/B and N/B concentration ratios and the increase of Young's modulus. Valence-band PES spectra are found to be insensitive to the variations of the B and C concentrations in B-C-N compounds © *2004 American Institute of Physics.* [DOI: 10.1063/1.1759392]

I. INTRODUCTION

The search for super hard materials, which are almost as hard as or even harder than diamond, is of both fundamental and technological interest. The boron-carbon-nitrogen (B-C-N) system is one of the most promising material for hard coating applications, since it exhibits high hardness, low coefficient of friction, high thermal stability, and electrical resistivity.[1,2] In our previous study the atomic and electronic structures of B-C-N films were examined using x-ray diffraction and x-ray absorption near-edge structure (XANES) spectra, which revealed that B-C-N thin films have a ternary phase not a mixture of segregated binary phases.[3] Based on surface acoustic wave spectroscopy measurements, Young's modulus was found to increase with the C concentration in B-C-N films.[2] Jiménez *et al.* have studied several binary compounds of B, C, and N.[4–6] In this study, we have focused on the characteristics of local electronic and bonding structures of ternary B-C-N films using C and N K-edges XANES and valence-band photoelectron spectroscopy (PES) measurements. Mechanical properties of B-C-N films, such as the Young's modulus or hardness, have also been systematically investigated.

II. EXPERIMENTAL DETAILS

XANES and valence-band PES measurements were carried out using a high-energy spherical grating monochromator and low-energy spherical grating monochromator (LSGM) beamlines, respectively, with electron-beam energy of 1.5 GeV and maximum stored current of 200 mA, at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The C and N K-edges XANES spectra were obtained using the sample drain current and fluorescence modes, respectively. All XANES spectra were normalized using the incident beam intensity I_0 after preedge background subtraction and by keeping the area under the spectra in the energy range between 315 and 330 eV for C K-edge and 440–455 eV for N K-edge fixed. The LSGM beamline for the valence-band PES measurement was under a base pressure of $\sim 5 \times 10^{-10}$ Torr during measurements, which has an EAC-125 hemispherical electron energy analyzer. The samples were cleaned by repeated cycles of 0.5–2.0 KeV Ar$^+$ bombardment. The hexagonal (h)-B-C-N films with various compositions listed in Table I were deposited by dual-gun magnetron sputtering and were characterized by x-ray diffraction.[3] Young's modulus was observed to increase from 94.0 ± 4.8 GPa to 122.8 ± 17.3 GPa as the C concentration of the films was increased from 20.1% to 47.8%. Details of the preparation of samples are given elsewhere.[2]

[a]Author to whom correspondence should be addressed: Electronic mail: wfpong@mail.tku.edu.tw

TABLE I. Atomic compositions, atomic ratios, and Young's modulus of the ternary B-C-N alloy films.

Sample No.	Concentration				C/B atomic ratio	N/B atomic ratio	Young's modulus (GPa)
	B	C	N	O			
BCN34	55.2	20.1	16.3	9.4	0.36	0.29	94.0± 4.8
BCN35	44.4	33.5	15.8	6.3	0.75	0.36	110.3±15.6
BCN36	31.2	47.8	15.4	5.5	1.53	0.49	122.8±17.3
BCN37	37.9	41.5	15.1	5.4	1.09	0.40	114.4± 9.1
BCN38	35.7	43.5	15.3	5.9	1.22	0.43	102.6± 4.6

III. RESULTS AND DISCUSSION

Figure 1 displays the C K-edge XANES spectra of the B-C-N samples and reference diamond, graphite, CN_x, and BC_x films. The peak at ~285.5 eV (labeled as G) in the graphite π^* region lines up with the π^* feature in the graphite spectrum, which indicates the presence of graphitelike sp^2-bonded carbon atoms. Features C_1 and C_2 located at ~286.9 and 288.8 eV in the CN_x and BC_x spectra are primarily a ssociated with the C—B bond[7] and C≡N bond,[8] respectively. The presence of features C_1 and C_2 show the incorporation of carbon into the formation of a ternary B-C-N compound. The feature at ~293 eV (C_3) in the σ^* region (290–303 eV) corresponds to transitions from the C $1s$ to the σ^* states.[5] The features in the π^* region of the spectra of samples 34 and 35 (lower C) are well resolved. However, the features in the spectra of samples 36–38 (higher C) are less resolved and resemble closer to those of the CN_x and BC_x samples. The inset of Fig. 1 presents a magnified π^* region of the C K-edge XANES spectra of the B-C-N films after subtraction of the background represented by a best-fit Gaussian curve shown by the dashed line. Using the B, C, and N compositions listed in Table I, the inset of Fig. 1 shows that the intensities of the G, C_1, and C_2 features decrease as the C concentration increases. This trend can be explained by the substitution of B and N atoms by the C atoms, which forms h-B-C-N ternary alloy and reduces the C sp^2 bonding states in the B-C-N films.

Figure 2 presents the N K-edge XANES spectra of the B-C-N films and the reference CN_x and h-BN samples. The figure shows that the general features in the spectra of B-C-N films resemble more closely those of h-BN than CN_x. The similarity between the N K-edge spectra of B-C-N films and that of h-BN indicates the formation of an h-BN-like local
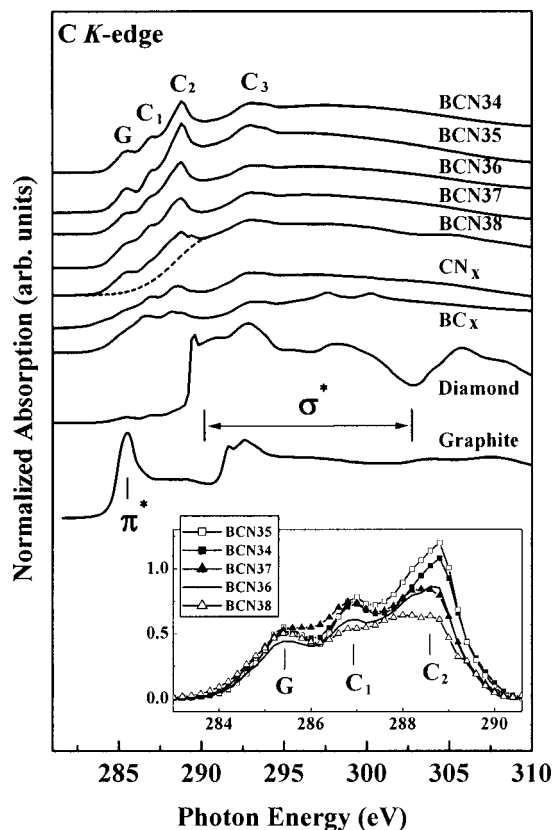

FIG. 1. Normalized C K-edge XANES spectra of a series of B-C-N films and reference CN_x, BC_x, graphite, and diamond samples. The inset presents the magnified π^* region of the C K-edge XANES spectra of the B-C-N films after the background was subtracted.
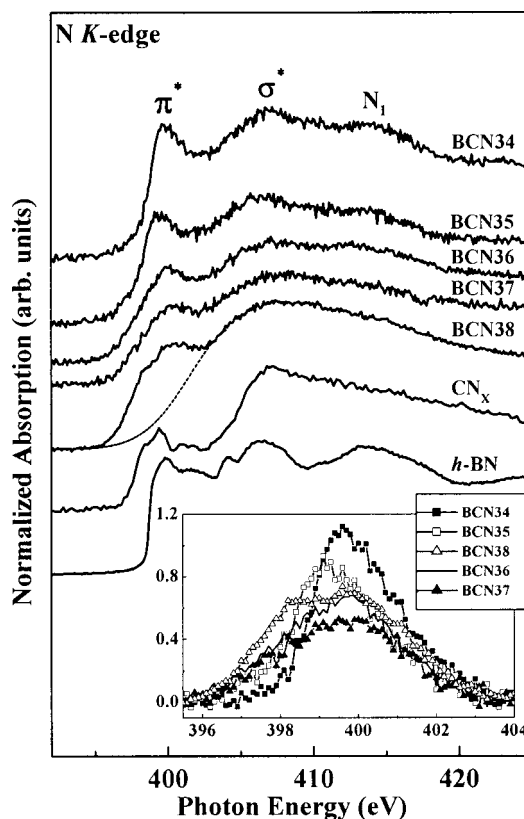

FIG. 2. Normalized N K-edge XANES spectra of a series of B-C-N films and reference CN_x and h-BN samples. The inset presents the magnified π^* region of the N K-edge XANES spectra of the B-C-N films after the background was subtracted.
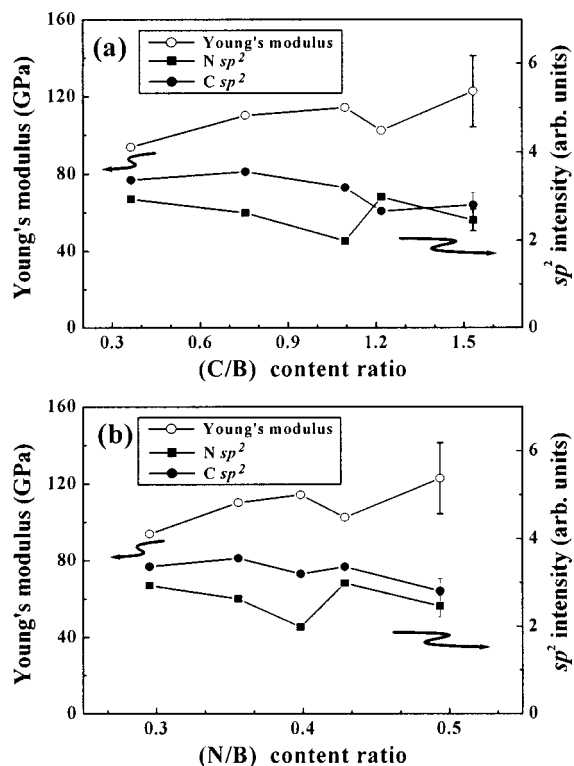
FIG. 3. Young's modulus and integrated intensity of the sp^2-bond features at the C and N K-edges as functions of the (a) C/B and (b) N/B atomic ratios, respectively, for the B-C-N films.

FIG. 4. Valence-band PES spectra of the B-C-N films obtained with a photon energy of 40 eV. The inset shows normalized PES spectra.

structure in the B-C-N films. The feature centered at ~399.8 eV and the relatively broad feature centered at ~407 eV are attributable to π^* and σ^* resonances,[8] respectively. The broadness of the π^* and σ^* features suggests the presence of various bonding environments around the N atoms in B-C-N. Ripalda *et al.* attributed the broad feature centered at ~413 eV (marked as N_1) to the σ^* resonance related to the N=C double bond.[9] After subtraction with a Gaussian background indicated by the dashed line, the magnified π^* region of the N K-edge XANES spectra of the B-C-N films is shown in the inset of Fig. 2. The figures in the inset clearly show that the π^* resonance feature is enhanced as the N concentration increases, which implies that the N atoms in the B-C-N films prefer to form N sp^2 bonds.

Figures 3(a) and 3(b) plot the Young's moduli given in Table I and the integrated intensities of the sp^2-bond features lying between 283.0 and 290.2 eV for carbon and between 396 and 403 eV for nitrogen as functions of the C/B and N/B concentration ratios, respectively. Both Figs. 3(a) and 3(b) reveal a trend that the integrated intensity of C and N sp^2 bonds generally decreases and Young's modulus increases with the C/B and N/B concentration ratios except a dip at C/B=1.22 and N/B=0.43. The abnormal dip of Young's modulus at C/B=1.22 and N/B=0.43, which corresponds to sample 38, can be seen to correlate with the abnormal increase of the C/B and N/B concentration ratios that do not follow the trend. Thus, this particular sample might have a fluctuation of the local bonding configuration that occurred during the deposition process. C sp^3 and sp^2 bonds are known to contribute generally to the hardness and softness of
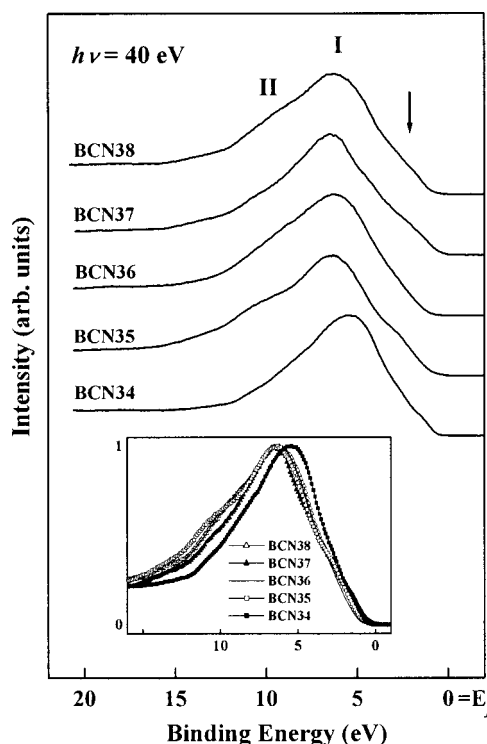
carbon-related materials, respectively.[10] The results obtained in this study are compatible with this picture. The intensities of the C and N sp^2-bonded features decrease as the C/B and N/B concentration ratios increase, implying that the C and N sp^3-bonded features increase with Young's modulus. In the studies of carbon nitride and boron carbide, C atoms have been observed to form sp^2 bonds with N and B atoms, respectively.[7,9] However, in the B-C-N ternary alloys, N-B bonds are also formed together with the formation of the C—N and C—B sp^2 bonds. This result suggests that the decrease in the intensities of the C and N sp^2-bond features as the C/B and N/B concentration ratios increase is primarily due to the decrease in the number of the C—N, C—B, and N—B bonds.

Figure 4 shows valence-band PES spectra obtained using incident photon energy of 40 eV. The maximum intensity was normalized to unity for comparison as shown in the inset of Fig. 4. The valence-band PES spectra of the B-C-N films contain two main features (**I** and **II**) arising predominantly from combinations of the C—N, C—B, and N—B π- and σ-bond states, respectively, in the 3.5–11 and 11–15 eV regions. The feature between 0 and 3.5 eV (marked by the arrow) is primarily associated with the C—C π bonds.[11–13] Features **I** and **II** in the PES spectra of sample 34 have significantly lower binding energies than those of samples 35–38 as shown in the inset of Fig. 4. Since sample 34 has a significantly larger O concentration than those of samples 35–38 (Table I), this chemical shift may be caused by the negatively charged O impurities. For samples 35–38, the O impurity contents are much smaller and do not deviate much and their PES spectra are relatively similar. The similarity of the valence-band PES spectra of samples 35–38 with signifi-

cant variations in the B and C contents suggests that C—B, C—N and N—B bonds contribute similarly to the valence band.

In a previous report for amorphous (*a*) Si-C-N films,[10] Young's modulus and the population of the sp^2 bonds were found to decrease (increase) with the increase of the C (N) concentration. This observation indicated the formation of graphitelike carbon nitride alloys and suggested that the hardness of the *a*-Si-C-N films predominantly depend on the nitrogen not carbon composition. In the present study of the B-C-N films, the population of C and N sp^2 bonds decreases and the Young's modulus increases with the C/B and N/B concentration ratios. The present observation indicates the formation of diamondlike B-C-N alloys and suggests that the hardness depend on the C/B and N/B concentration ratios not on the individual C, N, and B concentrations.

IV. CONCLUSIONS

In conclusion, we have found that the *h*-B-C-N ternary alloy films were formed by substitution of B and N atoms by C atoms with the formation of the C—N, C—B, and N—B bonding structures. The decrease of the intensities of the sp^2-bonded features in the C and N K-edges XANES spectra correlates with the increase of the C/B and N/B concentrations ratios and Young's modulus.

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