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Structural Studies of Thin Film Boron Nitride by X-ray Photoelectron Spectroscopy 1)

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ABSTRACT

Structural properties of rf sputtered boron nitride films were studied as a function of deposition parameters such as nitrogen pressure, substrate temperature and substrate bias using X-ray photoelectron spectroscopy and Auger electron spectroscopy. Composition and information on chemical bonding of resultant films was determined by XPS. XPS core level spectra showed that ratio of boron to nitrogen varied from 3.11 to 1.45 with respect to partial nitrogen pressure. Curve fitting of XPS spectra revealed three kinds of bonding mechanism of boron in the films. XPS peak positions of both B 1s and N 1s shifted to higher energy with higher nitrogen pressure as well as increase in substrate bias voltage. AES was used to see possible contamination of films by carbon or oxygen as well.

INTRODUCTION

Boron Nitride has been known as a wide bandgap semiconductors with a number of important applications in the modern technology. Potential use for BN thin films are diverse and include photoconductors, high temperature dielectrics and heat dissipation coating for various sensor materials, and wear-resistant coatings as well[1-4]. Therefore the use of BN in the electronics industry has been studied extensively. Especially it has been known that structure of BN have considerable effects on the properties of thin film BN. Several characterization techniques have been used to investigate the structure of thin film BN[1, 3-5]. Among these, XPS has been one of the most widely used techniques[3,5] and known to provide three types of information[1], core level spectra, valence level spectra and Auger series related spectra. In the study of BN, mostly the core level and the valence band spectra have been widely used[2-4]. Core level spectra of both B 1s and N 1s are primarily used to identify formation of boron nitride as well as to determine composition of films[2]. Another important use of the core level spectra is to obtain information on the chemical environment of boron atoms in the BN film[5-6]. It has been well known that there is almost always nitrogen deficiency in BN films, thus it is very important to determine bonding mechanism of boron in the films.

Although the core level XPS spectra of B 1s and N 1s have been extensively used to verify formation of BN, however, hardly any systematic study have been done on shifting of these peaks with respect to composition of films or deposition parameters. Therefore, in this study, XPS core level spectra of B 1s and N 1s was used to determine the composition of rf sputtered BN films. Positions of these peaks were monitored

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with respect to partial nitrogen pressure as well as substrate bias.

EXPERIMENTAL DETAILS

BN films were rf sputtered from MRS 8667 multitarget sputtering machine from a 4 inch diameter boron nitride target (99.99%). Partial pressure of nitrogen was varied from 0.2 mTorr to 4.0 mTorr. Total pressure of Ar/N_2 mixture was kept fixed at 8 mTorr for all films. Information on the preparation of BN films was published in detail elsewhere.

XPS and AES spectra were taken by Physical Electronics PHI 5500 multitechniques surface analyzer, which was equipped with AES, XPS and secondary ion mass spectrometer(SIMS). The test chamber was evacuated by a sputter ion pump with auxiliary titanium sublimation pump. A base vacuum was about 7×10^{-10} torr. All the measurements were done in the vacuum better than 2×10^{-9} torr. For XPS measurements, Mg Kα radiation with a energy of 1253.6 eV was used as the excitation source and an analyzer energy was kept at 71.55 eV for XPS multiplex measurements. To avoid possible shift of peaks by static charging due to insulating nature of samples, all XPS peaks were referenced to 1s peak of adventitious carbon at 284.6 eV, measured with an accuracy of 0.1 eV. Ratio of boron-to-nitrogen was determined from the ratio of the area of B 1s and N 1s peaks.

RESULTS AND DISCUSSION

AES and XPS spectra provide invaluable information on local environment of chemical bonding in solids. In figure 1, AES and XPS survey spectra of boron nitride films sputtered at 4 mTorr of partial nitrogen pressure. It was seen that BN films mostly consists of boron and nitrogen with little amount of carbon and oxygen. However, in the case of AES technique, no detailed analysis was possible due to static charging.

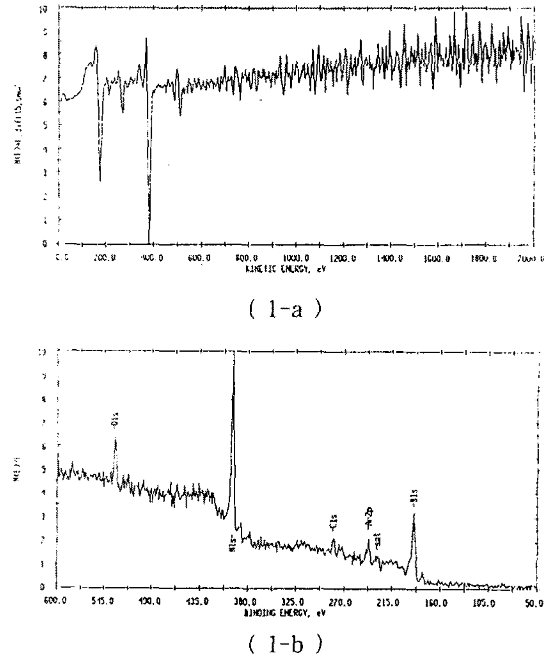


Figure 1. AES(a) and XPS(b) survey spectra of a BN film sputtered at 4mTorr N_2.

XPS core level peaks of B 1s and N 1s for the same film were given in figure 2. Peak positions of both peaks well agree with values reported by other investigators[6-7]. In boron nitride, ratio of boron-to-nitrogen plays an important role to determine properties of films and it is dependent on deposition parameters[5]. In this study, ratio of boron to nitrogen was obtained from the ratio of the area of B 1s and N 1s peaks from XPS multiplex spectra. These results were summarized in Table 1. From the table, it was shown that resultants films were not stoichiometric but boron rich BN. However, Ikeda et al[1] reported that cubic phase could be achieved with a B/N ratio of 1.2-1.6 while near stoichiometric films or with B/N ratio less than 1.0 was found to have amorphous structures.

Table 1. Ratio of B/N as a function of partial nitrogen pressure

Nitrogen pressure(mTorr)	boron/nitrogen
0.5	3.11
1.0	2.34
3.0	2.05
4.0	1.45
5.0	1.45

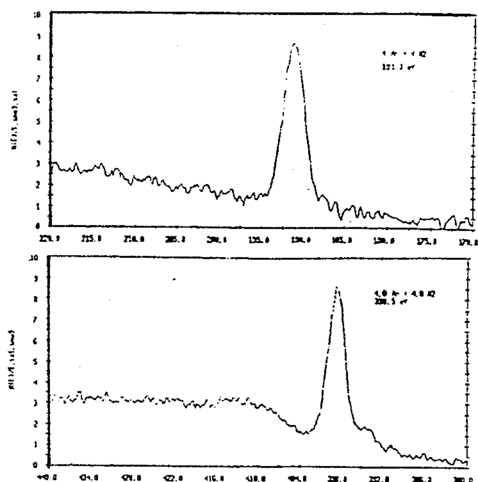
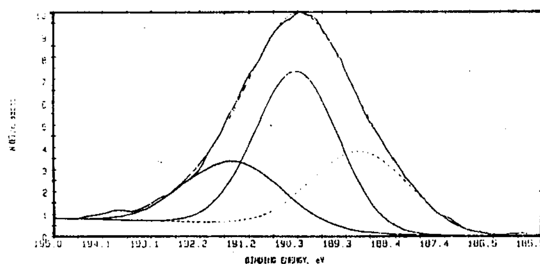
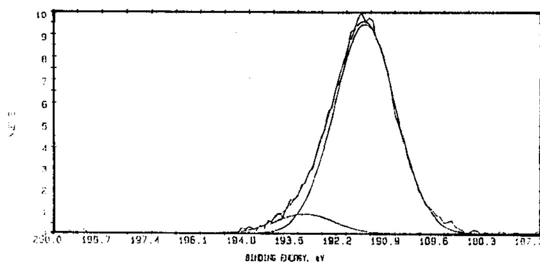


Figure 2. XPS core level peaks of B 1s(top) and N 1s of the BN film sputtered at 4 mTorr N_2.

Cubic phase BN consists of sp_3 bonding[8] while hexagonal phase BN has sp_2 bonding in which each boron atom is bonded with three nitrogen. In order to find out how boron atoms bond to other atoms, experimental XPS data of BN sputtered at a partial nitrogen pressure of 4 mTorr was fit to three peaks with FWHM of 2.0 eV which was obtained from a standard bulk type hexagonal sample. This result was shown in figure 3. To validate the curve fitting, a commercial hexagonal BN sample was analyzed by the same method and the resultant XPS peaks were given as well. Peak positions and the relative areas of peaks determined from sputtered samples and the commercial sample were summarized in table 2.



(3-a)



(3-b)

Figure 3. XPS B 1s core peak of the sputtered BN film(a) and the commercial hexagonal sample(b) by curve fitting.

Table 2. XPS peak positions of B 1s

Sample identification	Peak position (eV)	Relative area (%)	Possible source
Standard	193.32	8.7	B_2O_3
hexagonal BN	191.71	91.3	BN(sp_2)
BN	191.90	15.9	BN(sp_2)
(4 mTorr, N2)	190.29	60.2	BN*
	188.84	23.9	segregated boron

* : Some of boron atoms were thought to be partially substituted by nitrogen.

In table 2, the main peak with the highest energy was thought to be due to boron nitride[4], the lowest peak due to boron atoms which substituted for nitrogen and bonded to three boron atoms(segregated borons), the peak with an intermediate energy was thought to be boron atoms which were bonded to two nitrogen atoms and one boron atom instead of three nitrogen atoms. According to this, it was seen that the resultant BN films were boron rich with some segregated boron atoms. The standard hexagonal sample showed the relative area of 92% for the peak of 190.4 eV and 8% for the peak of 193.32 eV. This was in the reasonable margin of the known composition (~95% BN, ~5% B_2O_3) of the commercial bulk sample.

Effects of substrate bias on BN films was also investigated. IR transmission of BN film sputtered at 4 mTorr, N_2 was given in figure 5. As substrate bias voltage increased, the peak around 1100 cm^{-1} became stronger while the peak around 1378 cm-1 decreased. By many researchers, the peak around 1100 cm^{-1} has been regarded as a evidence of formation of cubic phase BN especially with decrease of the peak at 1378 cm^{-1}. Accordingly, in our case, this was assumed to indicate formation of cubic phase BN in our film as well. Therefore, it is possible to say that the substrate bias causes weakening of hexagonal structure and supports formation of cubic phase BN. These results well agree with the result by Raman spectroscopy from our previous study on the optical properties of BN. XPS spectra of this film was shown in figure 5 with respect to original peaks with no substrate bias. It was seen that substrate bias caused B 1s and N 1s peaks to higher binding energy by about 0.9 eV and 0.2 eV, respectively. Increase in partial nitrogen pressure showed the same effect of shifting both B 1s and N 1s peaks to higher energy side. These results were summarized in table 3.

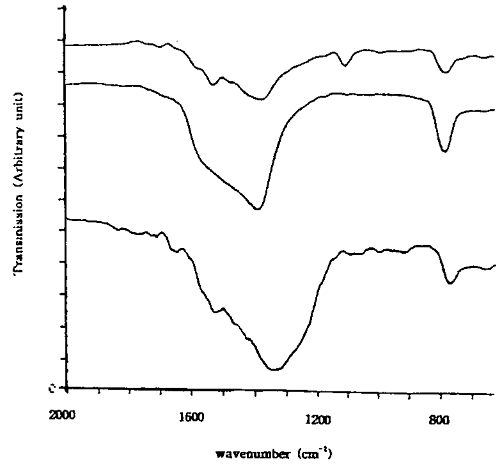


Figure 4. Effects of the substrate bias on IR transmissions peaks.

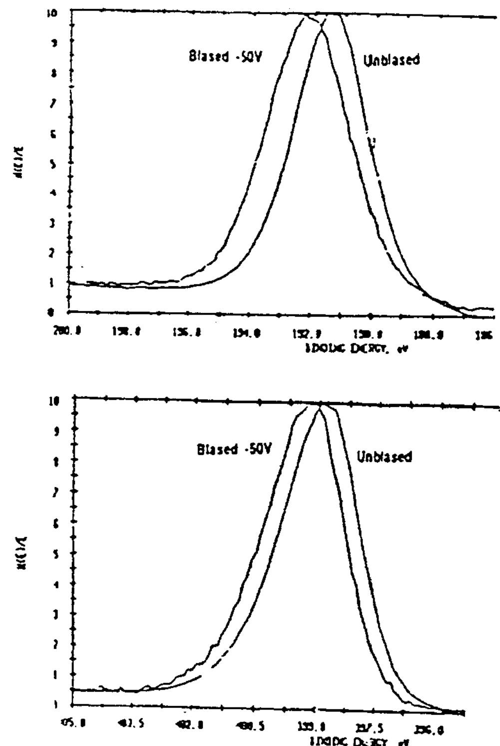


Figure 5. Effects of the substrate bias on the XPS B 1s peak(top) and N 1s peak

Table 3. Peak positions of B 1s and N 1s core level with respect to deposition parameters.

Deposition parameters		Peak positions (eV)	
P_{N_2}(mTorr)	Bias(V)	B 1s	N 1s
0.2	Not applied	190.0	397.9
1.0	Not applied	190.2	397.7
2.0	Not applied	191.4	398.8
4.0	Not applied	191.4	399.0
4.0	-20	192.0	399.3
4.0	-60	192.3	399.3

According to the earlier study[2], the shift of both B 1s and N 1s peaks with increase in the nitrogen partial pressures seems to have its origin in the fact that increase in the nitrogen partial pressure enhances ordering along with the increase of interplanar B-N bonds for the hexagonal phase BN in the film. The shift of two peaks due to substrate bias seems to be due to weakening of hexagonal structure. In table 4, the effects of deposition parameters on the properties of rf sputtered boron nitride films were summarized.

Table 4. Summary of deposition parameters on the properties of rf sputtered boron nitride films.

Properties	Deposition Increase N2 pressure	Parameters Increase bias
XPS peak position		
B 1s peak	To higher energy	To higher energy
N 1s peak	To higher energy	To higher energy
Refractive index	Decreasing	Decreasing
Optical gap	Increasing	Increasing
IR band	sharpening	Broadening

CONCLUSIONS

XPS spectra showed that B/N ratio of rf sputtered BN film was in the range of 3.11 - 1.45. According to XPS study, resultant BN films were boron rich with some segregated boron atoms. It was seen that substrate bias caused B 1s and N 1s peaks to higher binding energy by about 0.9 eV and 0.2 eV, respectively. Increase in partial nitrogen pressure showed the same effect of shifting both B 1s and N 1s peaks to higher energy side. The shift of B 1s and N 1s peaks due to substrate bias seems to be due to weakening of hexagonal structure.

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