

Optical band gap and refractive index of c-BN thin films synthesized by radio frequency bias sputtering

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Boron nitrogen (BN) films with the different cubic phase content were deposited on Si and fused silica substrates by radio frequency bias sputtering from a hexagonal BN target by using a two-stage deposition process. The BN films were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and UV-visible transmittance and reflection measurements. The optical absorption coefficient α and the refractive index n were calculated from the transmittance and reflection spectra. With increasing the c-BN content the absorption edge shifts to the higher energy, indicating that the optical band gap of the BN films increases with cubic BN content. The optical absorption behavior of BN films shows characteristics of amorphous materials. The dependence of α on the photon energy was fitted by the Urbach tail model and the band-to-band transition model at the two different energy regions, and the optical band gap of the BN films were obtained from the fits. In addition, the refractive index indicates obvious difference for the BN films with different cubic phase content. © 2001 Kluwer Academic Publishers

1. Introduction

It is well known that cubic boron nitride (c-BN) is a promising candidate for hard coatings because of its extreme hardness, chemical inertness and good thermal stability. Besides, c-BN is transparent in the infrared and visible parts of the spectrum, and thus is sought after as a protective coating for optical elements and optical windows. The optical properties of c-BN crystals prepared by high temperature high pressure (HTHP) have been reported previously [1–4]. The fundamental optical absorption edge determined from reflection and transmittance measurements by Miyata *et al.* [2] is 6.1 ± 0.2 eV. Recently Eremets [3] investigated optical properties of c-BN single crystals in the spectral range from 400 to 50000 cm^{-1} by Raman scattering, absorption and reflection spectra. Both the static and high frequency dielectric constants ϵ_0 and ϵ_∞ were obtained and found to be 6.80 and 4.46, respectively.

For c-BN prepared by HTHP, its industrial applications are seriously restricted because of its small crystal size. Since the synthesis of c-BN thin films under low

pressure was first reported by Sokolowski [5] in 1979, great efforts have been made to grow c-BN thin films from a gaseous phase. There are few reports about optical properties of c-BN thin films probably due to the difficulties in synthesizing high quality c-BN films, except that a few reports [6–8] are concerned with the optical behavior of hexagonal boron nitride (h-BN). Only recently, the investigation of the optical properties of c-BN films becomes possible because of the successful growth of c-BN films with a high cubic phase content by applying the ion bombardment during film growth. In this paper, the optical properties of the c-BN thin films prepared by RF bias sputtering were investigated using the UV-visible transmittance and reflection spectra.

2. Experimental

The c-BN thin films were deposited on Si(100) substrates by conventional radio frequency (RF) bias sputtering (13.56 MHz) from a h-BN target in pure Ar

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discharge by using a two-stage deposition process [9, 10]. The substrates were fused silica flats and IR-transparent silicon (100) wafers. The substrate temperature varied from 423 K to 573 K. The reactor was evacuated to the base pressure of 1×10^{-5} Torr and then back filled with Ar (99.99% purity) to a pressure of 1×10^{-2} Torr. To enhance ion bombardment of the growing films, a negative bias was applied to the substrate electrode by a direct current power supply. The substrate negative bias voltage ($-U_s$) during growth process varied from 0 to -150 V. The RF power was kept constant at 400 W throughout the series of experiments. Before sputter deposition the substrates were cleaned in an ultrasonic bath of special cleaning solution and then sputter etched for several minutes. The films were deposited for 2 h and the film thickness, as measured by a TENCOR alpha-step profilometer, was usually kept between 300 to 600 nm. Reference 9 gives details of the two-stage deposition process, as well as the results of film characterization and the effects of $-U_s$ on c-BN growth. The deposited films were examined primarily by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The FTIR transmission measurements were carried out at normal incidence and room temperature in a WQF-4000 spectrophotometer.

The transmittance $T_e(\lambda)$ and reflectance $R_e(\lambda)$ were measured as a function of incident photon wavelength at wavelengths between 200 and 1200 nm from films deposited on fused silica using Shimadzu UV-3101(PC) spectrophotometer at normal incidence. The light sources of the spectrophotometer were tungsten and deuterium lamps, the detectors were PM and PbS, respectively. The spectrophotometer was used in double-beam mode with a bare substrate in the reference beam to obtain transmittance data through the film alone. In reflection mode, the spectrometer was calibrated using an Al mirror as standard. The reflective index n and the absorption coefficient α can be determined from the measured $T_e(\lambda)$ and $R_e(\lambda)$ and the following equation group [11]

$$R_e = R + \frac{R(1 - R)^2 \exp(-2\alpha d)}{1 - R^2 \exp(-2\alpha d)};$$

$$T_e = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \quad (1)$$

where d is the film thickness, and in the case of normal incidence, R can be expressed simply as a function of the refractive index n , i.e., $R = (\frac{n-1}{n+1})^2$. Heil and Aita [12] calculated the absorption coefficient α only from the second equation of the above equation group, i.e. assuming $R_e = R$, it is oversimplified obviously.

3. Results and discussion

FTIR transmittance spectra of the BN films deposited on silicon substrates with the different $-U_s$ are shown in Fig. 1. The film A deposited with $-U_s = 0$ V reveals clearly the IR characteristics of h-BN,—i.e., a strong unsymmetrical band at 1380 cm^{-1} and a weaker band

TABLE I The substrate negative bias voltage, the c-BN content, the optical band gap and the Urbach energy data for the films A, B, C, D and E

Film	$-U_s$ (V)	c-BN content (%)	B/N ratio	E_g (eV)	E_0 (eV)	n (300 nm)
A	0	0	1.08	4.3	0.59	1.60
B	90	37	1.12	5.1	0.67	1.70
C	110	63	1.10	5.5	0.73	1.75
D	130	72	1.14	5.7	0.74	1.84
E	150	88	1.07	>6.0	1.15	1.88

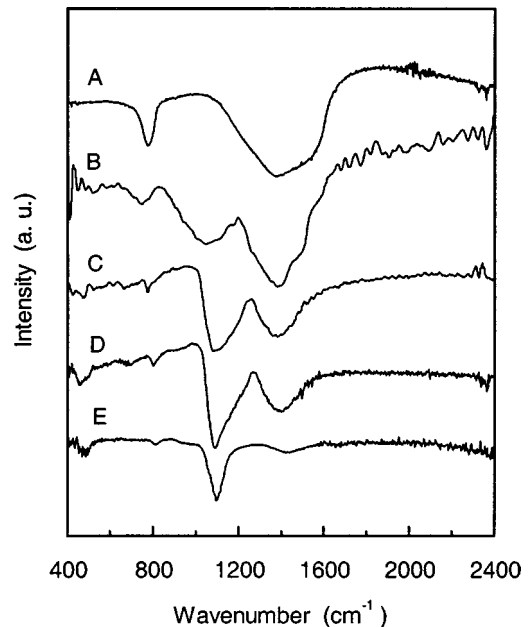


Figure 1 FTIR transmittance spectra of the BN films deposited on silicon substrates with the different $-U_s$. (a) 0 V, (b) 90 V, (c) 110 V, (d) 130 V and (e) 150 V.

at 780 cm^{-1} . This indicates that the film A is composed of the single h-BN phase. However, for the films B, C, D and E deposited with the different $-U_s$ from 90 to 150 V, an additional stronger absorption peak near 1080 cm^{-1} resulted from the TO mode of c-BN was observed. The deviation of the c-BN peak position from the IR peak of c-BN crystal at 1065 cm^{-1} is due to the large compressive stress in the films. It is obvious that the films B, C, D and E deposited with $-U_s$ consist of both cubic phase and hexagonal phase. The c-BN content, estimated by taking the ratio of the c-BN peak height to the sum of the h-BN peak height at 1380 cm^{-1} and the c-BN peak height at 1080 cm^{-1} , is 38%, 63%, 72% and 88% for the film B, C, D and E, respectively. The c-BN content and the film deposition parameter (i.e. $-U_s$) are listed in Table I. We can see that the c-BN content increases continuously with the increase of $-U_s$ above 90 V.

Fig. 2 shows typical XPS results of a c-BN thin film. It can be seen from Fig. 2 that there are two peaks centered at 398.8 eV and 191.5 eV, corresponding to the 1s binding energies of nitrogen and boron atoms [13], respectively. Moreover, the B/N ratio of the films, as determined from the integral areas of the XPS spectra and sensitivity factors, was listed also in Table I.

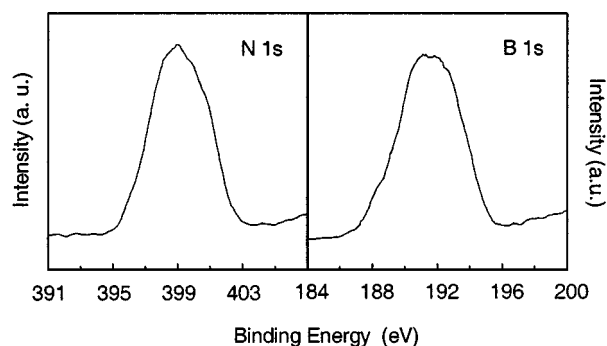


Figure 2 Typical B 1s and N 1s XPS spectra of a BN thin film.

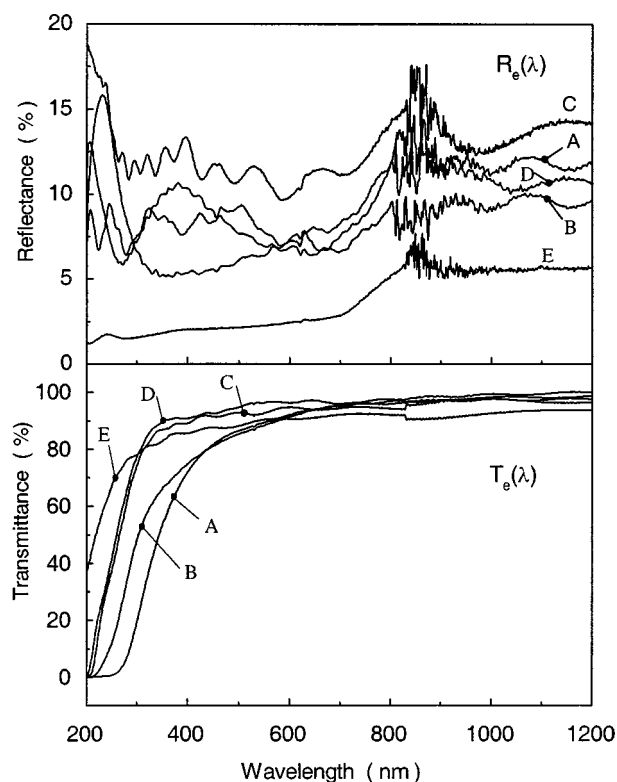


Figure 3 Optical reflectance spectra $R_e(\lambda)$ (upper diagram) and transmittance spectra $T_e(\lambda)$ (lower diagram) of the BN films A, B, C, D and E.

From Table I, it can be seen that these films have good stoichiometry.

The optical reflectance spectra $R_e(\lambda)$ and transmittance spectra $T_e(\lambda)$ of the five BN films were shown in Fig. 3, respectively. Interference phenomenon is evident in these spectra. The film thickness obtained from the interference is in good agreement with the results measured by profilometer. In the transmittance spectra of the five BN films, the transmittance keeps a near constant value of 90% within the visible region. With increasing c-BN content the optical absorption edge shifts to the higher energy, indicating that the optical band gap E_g of the BN films increases with increasing c-BN content.

The absorption coefficient α calculated from the measured transmittance spectra $T_e(\lambda)$ and reflectance spectra $R_e(\lambda)$ using equation group 1 is shown as the function of incident photon energy $h\nu$ in Fig. 4. Five curves shown in Fig. 4 have some similar characteristics, and four regions can be distinguished from the

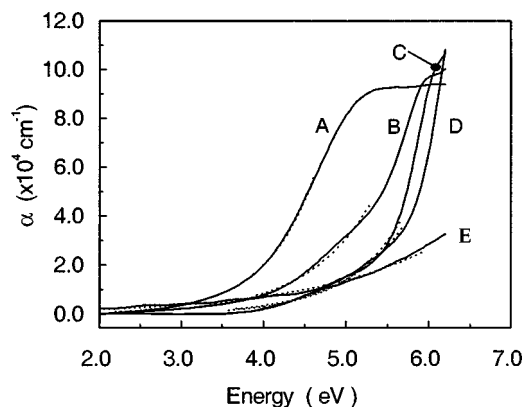


Figure 4 The absorption coefficient α calculated from the transmittance and reflectance measurements $T_e(\lambda)$ and $R_e(\lambda)$ using Equation 1 as a function of incident photon energy $h\nu$ for the five BN films. The dashed lines are the fits of the absorption tails of the five films to the Urbach equation.

curves. These curves have a very low absorption at the lower energy, followed by a region in which α varies exponentially as $h\nu$, and then α increases with $(h\nu)^p$, at last α reaches saturation at the higher energy region. Because the upper energy limit of the spectrophotometer at 6.2 eV is reached, the curve D does not show the saturation region and the curve E does not show the latest two regions.

Generally, the optical absorption edge of an amorphous semiconductor consists of two important regions, i.e., a low energy region I in which α varies as $\exp h\nu$, and a high energy region II in which α varies as $(h\nu)^p$, $p = 1/2$ for a direct band gap material and $p = 2$ for an indirect band gap material. In amorphous semiconductors, region I is due to a broadening of states because of the disordered structure of the films and to the presence of exponentially distributed states below the absorption edge extending into the gap of the films. The exponential tail can be characterized by the Urbach expression [14]

$$\alpha = \alpha_0 \exp(h\nu/E_0) \quad (2)$$

where α_0 is a constant, E_0 is the Urbach energy and yields an indication of depth-of-tail levels extending into the forbidden gap below the absorption edge. The larger the value of E_0 , the greater is the compositional, topological or structural disorder, and the greater is the coordination [15]. The dashed lines shown in Fig. 4 show the fits of the absorption tails of the five films to the Urbach equation. The Urbach energies obtained from these fits are also listed in Table I. From Table I it can be seen that the value of E_0 increases with the increase of the c-BN content. This can be explained by the following. Because c-BN is sp^3 -bonded and h-BN is sp^2 -bonded, an increase in the c-BN content, i.e., the increase of the ratio of $sp^3 : sp^2$, means that the film has a higher coordination. A possible interpretation is that the films having lower coordination (with more sp^2 h-BN) more easily form ideal amorphous networks with fewer defects and voids and perhaps less departure from optimum covalent bond angles and lengths than in those with higher coordination (with more sp^3 c-BN).

So the film with the higher c-BN content has the greater Urbach energy. It is also reported that this correlation between the Urbach energy and the coordination existed in many amorphous semiconductors [15].

Hexagonal BN is a direct band gap material, while c-BN is an indirect band gap semiconductor. The absorption coefficient α varies as $(h\nu)^p$ in region II, which be due to band-to-band transitions, where $p = 1/2$ for direct band gap h-BN and $p = 2$ for indirect band gap c-BN. Therefore, for the film A composed of the single h-BN phase and the film B composed predominately of h-BN phase, the absorption coefficient α has the form of $\alpha h\nu = K_1(h\nu - E_g)^{1/2}$ in region II, where K_1 is a material constant. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 5a for the films A and B. The optical band gap energies of 4.3 eV for the film A and 5.1 eV for the film B are calculated from the X-axis intercept of the linear part of the plot $(\alpha h\nu)^2$ versus $h\nu$, corresponding to a direct transition. On the other hand, the films C, D and E consist of both h-BN and c-BN phase, the α in region II can not be fitted according to the direct band gap h-BN ($p = 1/2$) nor the indirect band gap c-BN ($p = 2$). Therefore, we have to consider an effective medium approach for this case. For the simplest purpose, we suppose $p = 1$, then for the films C, D and E the α has the form of $\alpha h\nu = K_2(h\nu - E_g)$ in region II, where K_2 is also a material constant. A similar result was also reported in amorphous Se by Davis [16]. Fig. 5b shows the plot of $(\alpha h\nu)$ versus $h\nu$ for the films C, D and E. The E_g of 5.5 eV for the film C and 5.7 eV for the film D are also determined from the X-axis intercept of the linear part of the plot $(\alpha h\nu)$ versus $h\nu$ in Fig. 5b. Because the upper limit of the spectrophotometer is reached, region II is not displayed for the film E with 88% c-BN content, but it is obvious that there will yield a result of $E_g > 6.0$ eV if the incidence photon energy is high enough. To our knowledge, the c-BN film with so wide band gap was not reported previously.

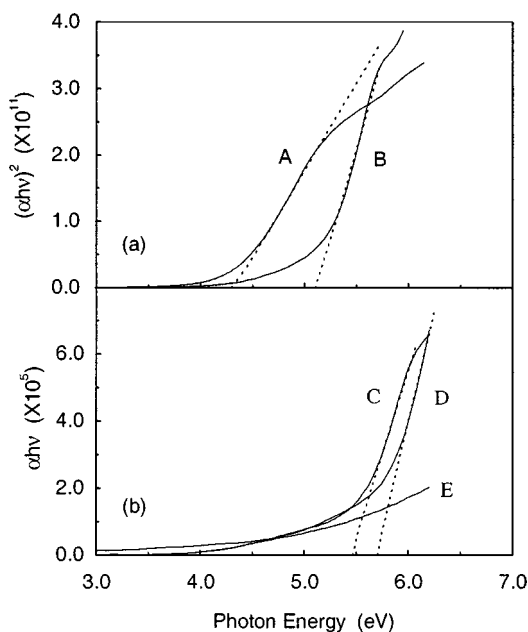


Figure 5 (a) Determination of the optical band gap of the films A and B from the plot of $(\alpha h\nu)^2$ versus $h\nu$. (b) Determination of the optical band gap of the films C, D and E from the plot $(\alpha h\nu)$ versus $h\nu$.

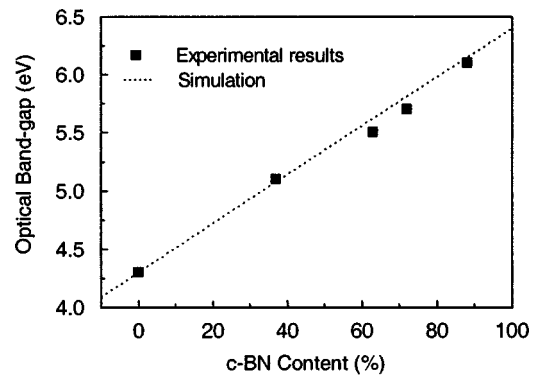


Figure 6 Dependence of the obtained optical band gap E_g on the c-BN content. The dashed line is the simulation of the empirical formula Equation 3.

The optical band gap determined from this method is also listed in Table I.

The dependence of the optical band gap E_g on the c-BN content is shown in Fig. 6. One can see that the E_g of BN films increases continuously with increasing c-BN content. The E_g of h-BN crystal was reported extensively in the range of 3.8–5.0 eV [17, 18], while the E_g of single crystal c-BN was about 6.4 eV [1]. According to an effective medium approach, the E_g of BN films with two phases should increase with the increase of c-BN content. Therefore, we propose that E_g of the mixed phase BN can be described by the following empirical formula

$$E_g(\text{eV}) = E_h \times \chi_h + E_c \times \chi_c = 4.3 \times \chi_h + 6.4 \times \chi_c \quad (3)$$

where χ_c is the c-BN content in the films, E_c (6.4 eV) and E_h (4.3 eV) are the optical band gap of phase-pure c-BN and h-BN, respectively. The corresponding results obtained from the empirical formula 3 are plotted as the dashed line in Fig. 6, which is in good agreement with the experimental results.

The refractive index n was also obtained from $T_e(\lambda)$ and $R_e(\lambda)$ and Equation 1. The variation of the refractive index n as a function of photon energy $h\nu$ for the film A, C and E is shown in Fig. 7. For the films C and E, a monotonic increase with the photon energy is observed from the near infrared to the ultraviolet

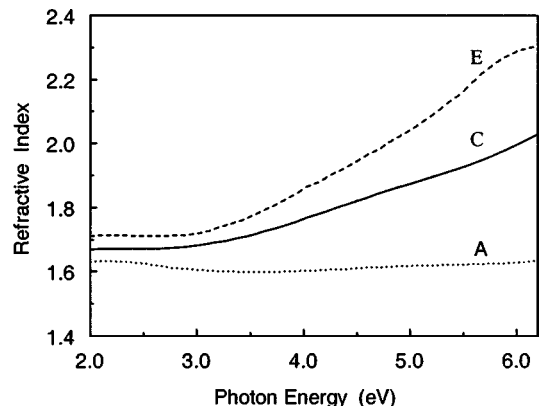


Figure 7 Variations of the refractive index n as a function of photon energy $h\nu$ for the film A, C and E.

region. The refractive index of the film E, varies from 1.71 to 2.23 with the photon energy varying from 2.0 to 6.0 eV. However, for the film A, composed of h-BN phase of lower density, the refractive index values vary between 1.60 and 1.63 in the energy range 2.0 to 6.2 eV, which is much lower than that of the mixed phase BN films (such as the films C and E). It is obvious that with increasing c-BN content the refractive index value of the film increases, which can be due to that the density of h-BN is lower than that of c-BN. Similar results have also been reported by other researchers [19–21]. The refractive index of bulk c-BN at visible frequencies is reported about 2.1 [3], and the refractive index of c-BN-containing films has been found to be approximately 1.9–2.1 [19–21]. On the other hand, the optical properties of h-BN are highly anisotropic; the refractive indexes parallel and perpendicular to the *c* axis are 2.05 and 1.65, respectively [22]. Moreover, the boron content has an effect [19] on the refractive index of h-BN thin films also.

4. Conclusion

The optical absorption coefficient α and the refractive index *n* of the BN thin films with the different cubic content have been determined from the UV-visible transmittance and reflection measurements. The optical absorption edge of BN films consists of a low energy region in which α increases exponentially as incident photon energy $h\nu$, and a high energy region, in which α varies as $(h\nu)^p$. These two regions were fitted by the Urbach tail model and the band-to-band transition model with an effect medium approach. The Urbach energy and the optical band gap obtained from these fits increase with increasing the c-BN content. The former can be due to that h-BN more easily forms ideal amorphous networks than c-BN. The dependence of the E_g of mixed phase BN on the c-BN content may be described by an empirical formula, which is in good agreement with the experimental results. The maximum optical band gap of BN films exceeds 6.0 eV, which is comparable to that of c-BN single crystal. Additionally, the refractive index of h-BN films is obviously lower than that of c-BN films.

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