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Hot-Filament-Assisted Electron Beam Deposition of Crystalline Cubic Boron Nitride Thin Films[1]

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Polycrystalline cubic boron nitride films have been deposited by hot-filament-assisted electron beam deposition. The films deposited with solid boron and N_2 gas are characterized by X-ray diffraction and transmission electron microscopy, which show that the films are composed of crystalline boron nitride along with h-BN. The FTIR absorption spectra of the films showed absorption bands at 1095 cm^{-1}, indicating the formation of a c-BN phase and also a sharp assymetric absorption band near 1380 and 940 cm^{-1}, corresponding to h-BN. X-Ray photoelectron spectroscopy revealed that the layers are essentially boron nitride but we cannot specifically attribute the different peaks to h-BN or c-BN. © 1995 Academic Press, Inc.

INTRODUCTION

Recently, new processes for the deposition of cubic boron nitride have been investigated, wherein BN films have been deposited from the vapor phase at low temperatures (1–4). Wada and Yamshita (5) deposited BN films containing c-BN phase by ion beam deposition. Saitoh and Fugimoto (6) deposited BN films containing c-BN grains by using an ion beam of nitrogen with high energy and simultaneously evaporating boron. Other processes for the preparation of c-BN have been reported, such as activated reactive evaporation with a gas activation nozzle (7), reactive rf sputtering (8), ionized evaporation (9), ion beam evaporation (10), plasma chemical transport (11), rf plasma chemical vapor deposition (12), single source for CVD of BN films (13–16), plasma-enhanced CVD of BN (17), production of BN films by an arc-like plasma enhanced ion plating method (18), and low energy ion beam enhanced chemical vapor deposition (19). However, the obtained films consisted of c-BN and h-BN or amorphous BN, though the content of the c-BN phase in the films was not high. We have deposited BN films by hot-filament-assisted electron beam deposition and found it to contain c-BN along with small amounts of h-BN (20).

In this report, BN films were deposited on Si substrates with a hot tungsten filament to activate the nitrogen gas, and an e-beam was employed for evaporating the boron metal. The composition of the deposited films was studied by X-ray photoelectron spectroscopy (XPS). The experimental system consists of a reaction chamber with circulating water as coolant. The substrates were at a distance of 20 cm above the boron source, which is heated by an e-beam. The tungsten filament was heated by a dc power supply to activate the N_2 gas, which is placed in the path of the boron vapor, between the boron source and substrate holder. The activated gas is directed toward the hot filament by a thin stainless steel tube. During the deposition, the filament was kept white hot. The substrates were heated using a resistive heater mounted on the sample holder itself.

The substrates used for the study were *n*-Si(111) and NaCl single crystals. Before being loaded into the reaction chamber, the Si samples were degreased ultrasonically in an organic solvent and etched with HF acid, rinsed with running deionized water, blown dry with nitrogen gas, and loaded directly into the vacuum chamber. The NaCl crystals were cleaned by being dipped in DI water and dried. The substrates were further cleaned *in situ* by an argon ion plasma for 1 min at 500°C. Then the substrates were cooled and maintained at 400°C, at which temperture the deposition was carried out. N_2 gas was introduced into the reaction chamber via a precision-controlled needle valve till the pressure increased to 7×10^{-5} Torr. This constant pressure was maintained throughout the deposition. Boron metal was evaporated by an e-beam of energy of 5 KeV and 100 mA current. The thickness of the films was controlled with a water-cooled quartz crystal thickness monitor. Films of BN about 2000 Å thick were deposited at the rate of 0.2 nm/sec. The typical experimental conditions under which the BN films were deposited are given in Table 1. The crystal structure was determined by X-ray diffraction (XRD) (Philips, CuKα target), transmission electron microscopy (TEM) (JOEL, 1200 EX, Japan), scanning electron microscopy (SEM) (Hitachi S 520, Japan) and the composition of the film was

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TABLE 1

Item	Conditions
N_2 pressure (99.9% pure)	10^{-5} Torr
Substrate temperature	400°C
Filament temperature	2000°C
Electron beam energy	5 KeV
Source-to-substrate distance	20 cm
Electron beam evaporant	Boron (99.999%)

TABLE 2

	d value (Å)			
2*θ*	Obs.	Lit.	*I*/*I*o (%)	(*hkl*)
42.9	2.1	2.088	100	(111)
50.2	1.81	1.808	2	(200)

established by FTIR absorption spectroscopy (Nicolet 740), X-ray photoelectron spectroscopy (VG MKII ESCA).

The X-ray diffraction pattern of the BN films deposited on Si(111) substrates shows a (200) reflection at $d = 181$ Å in addition to the (111) reflection at $d = 2.1$ Å, which is the characteristic reflection of c-BN. Measured *d* spacings of the diffraction peaks in c-BN thin films are compared with the *d* spacing of the bulk c-BN from JCPDS data. All the lines of the deposited BN films match the reported values very well. Table 2 shows the observed *d* values compared with the JCPDS data and the corresponding planes. This confirms the cubic nature of the BN films deposited.

Phase identification and microstructure observations of the films were also carried out by transmission electron diffraction (TED). The specimens were prepared for electron diffraction by depositing films on NaCl single crystals, dipping the crystal in water, and lifting the films onto a copper grid. Figure 1 shows the electron diffraction pattern from the deposited films. As can be seen, a polycrystalline structure was formed under the deposition conditions explored in this study. The films displaying evidence of c-BN consisted of aggregated and individual crystallites. From the diameters of the rings, the *d* values for the various plane reflections were calculated. Gold was used as the reference from which the camera constant of the microscope was calculated. This is used to obtain the *d* values for the BN films. The diffraction rings correspond to those of the cubic phase with the zinc blende

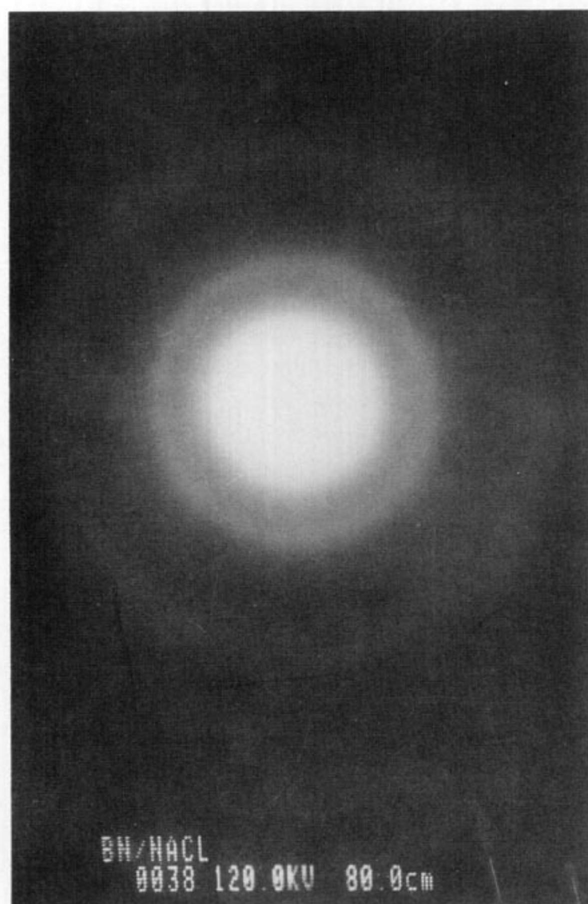

FIG. 1. Transmission electron diffraction pattern of BN films.

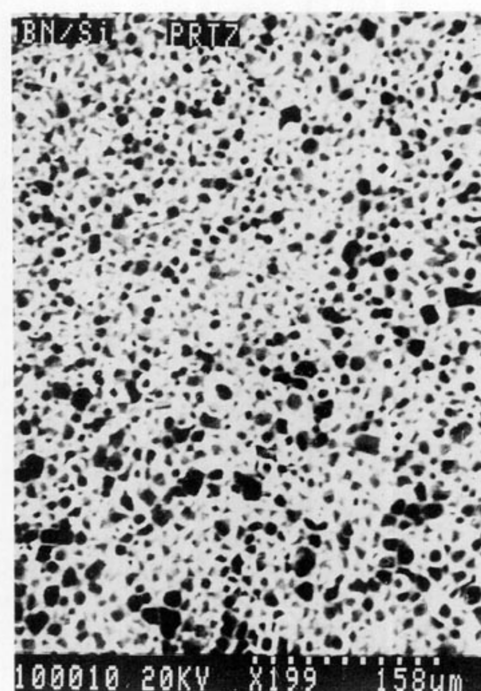

FIG. 2. SEM micrograph of BN film.

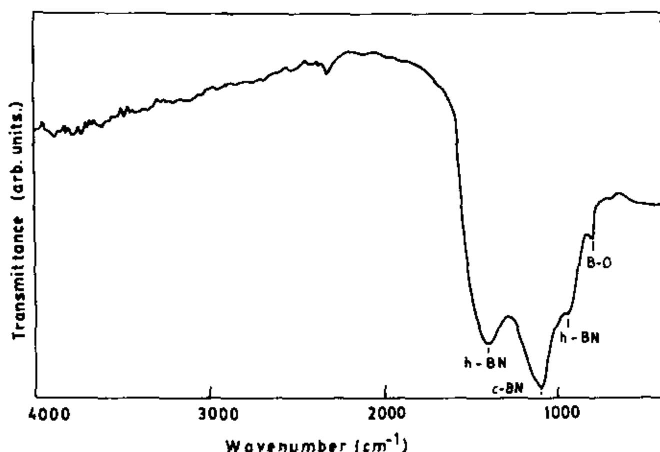

FIG. 3. FTIR spectrum of BN film.

structure. Experimental conditions under which films are deposited cause the presence of well-crystallized c-BN. The results of TED and XRD show a good consistency. The lattice constant of c-BN crystallites was calculated to be 3.65 Å comparable to a value of 3.61 Å for well-crystallized high-pressure-synthesized c-BN (21).

Scanning elecron microscopy of BN/Si shows good crystalline quality of the deposited films. The films show granularity with reasonable compactness and uniform grain size, as shown in Fig. 2.

The FTIR spectrum of the BN films show (Fig. 3) sharp bands at 750, 940, 1095, and 1380 cm^{-1}. The band at 750 cm^{-1} is attributed to a B–O stretching vibration, similar to that reported at 738 cm^{-1} by Paul *et al.* (22). The absorption at 1095 cm^{-1} is due to *c*-BN and the bands at 1380 and 940 cm^{-1} are due to h-BN (29). These characteristic bands always distinguish h-BN from c-BN. Since the spectrum exhibits absorption bands corresponding to both h-BN and c-BN, it suggests that the deposited films are composed of both phases.

X-Ray photoelectron spectroscopy studies were performed to determine the different elements present in the deposited samples and also to determine their chemical bonding. The XPS measurements were carried out on a VG Scientific ESCA MK II electron spectrometer with an Al$K\alpha$ anode ($h\nu$ = 1253.6 eV). The general spectrum shows the presence of C, N, O, and B. In every spectrum the correction due to charging effects has been considered, taking C1*s* at 285 eV. This carbon correction is calculated to be 4 eV. Figure 4 shows the X-ray photoelectron spectrum of B1*s* in the deposited films. This envelope clearly shows the presence of four different species at about 189, 190.37, 191.62, and 193.87 eV. The peak at about 189 eV is attributed to free boron. This peaks agrees with the B1*s* spectra in metallic boron (23). The peaks at 190.37 and 191.62 eV (26) are assigned to boron bonded to nitrogen species and the one at the highest binding energy value, 193.87 eV, is attributed to boron oxide (24–28). The value of boron compound with nitrogen is reported to be around 190.4 eV (23). The presence of the boron oxide species is also confirmed by observing the O1*s* spectrum of this sample. Figure 6 shows the O1*s*

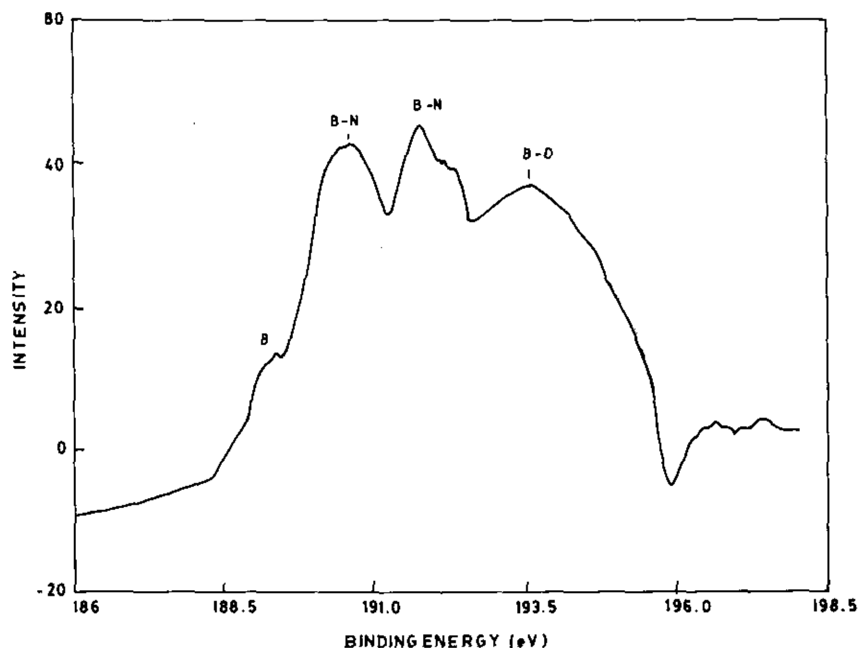

FIG. 4. X-ray photoelectron spectrum from the B1*s* core levels in the BN film.

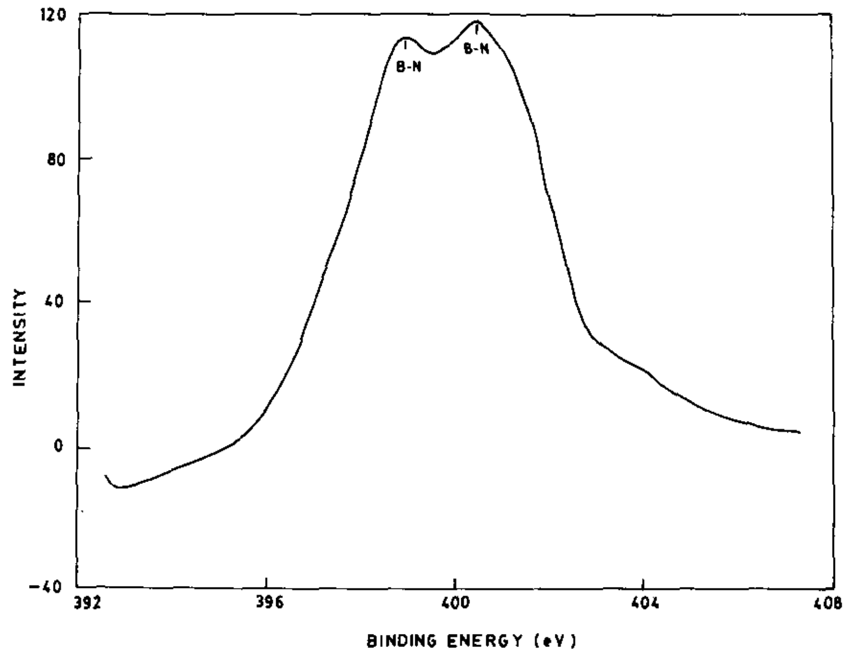

FIG. 5. X-ray photoelectron spectrum from the N1*s* core levels in the BN film.

spectrum, which is clearly composed of two subpeaks, one due to adsorbed oxygen at about 532 eV and other due to boron oxide at about 530.5 eV. The B–O vibration is also seen in the FTIR spectrum (Fig. 3) as well. Figure 5 shows the XPS N1*s* spectrum of the deposited sample. This figure clearly shows two humps. These are attributed to the two B–N species, as observed in the B1*s* spectrum (Fig. 4). However, from the present XPS studies we are not able to distinguish and assign the corresponding peaks to c-BN and h-BN.

In conclusion, the BN films have been deposited by hot-filament-assisted electron beam deposition from solid

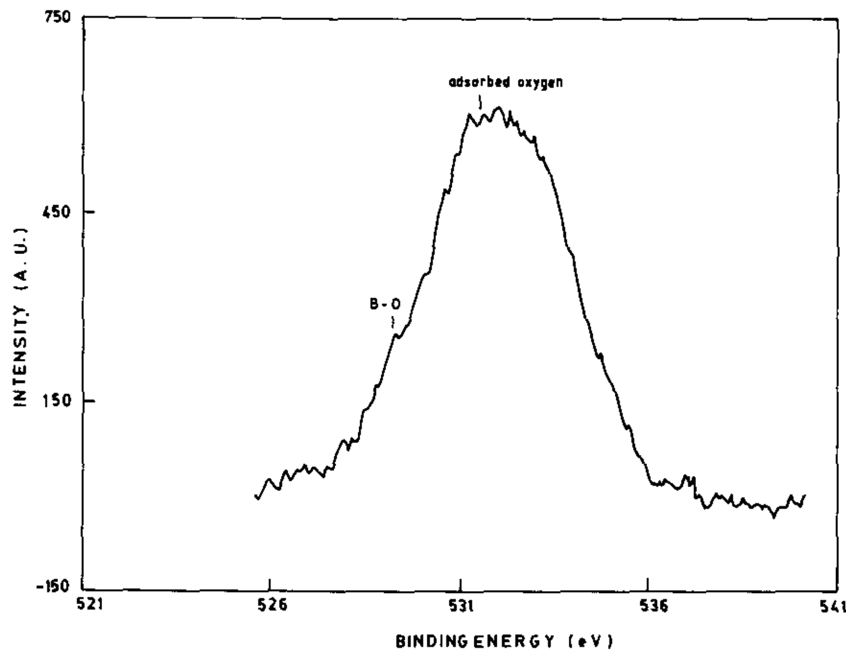

FIG. 6. X-ray photoelectron spectrum from the O1*s* core levels in the BN film.

boron in the presence of nitrogen gas. Films deposited are characterized by XRD, TED, SEM, and FTIR absorption, which confirm the formation of c-BN in the films deposited at 400°C. The chemical analysis of the films is obtained by XPS, which showed that the layers are essentially boron nitride with boron oxide and excess boron. At the moment, it is not possible to explain the mechanism for the formation of c-BN with the limited data available; detailed investigations are underway.

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