

# Prepared Low Stress Cubic Boron Nitride Film by Physical Vapor Deposition

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We present low stress cubic boron nitride (cBN) films with a transition layer deposited on the metal alloy substrates by tuned substrate radio-frequency magnetron sputtering. The films were characterized by Fourier transform infrared spectroscopy and transmission electron microscopy (TEM). The IR peak position of cubic boron nitride at  $1006.3\text{ cm}^{-1}$ , which is close to the stressless state, indicates that the film has very low internal stress. The TEM image shows that pure cBN phase exists on the surface of the film. Several phases of boron nitride were found at the medium implantation dose. It is believed that the transition from the low ordered phases to cBN phase occurred during implantation. © 2002 Elsevier Science (USA)

**Key Words:** cubic boron nitride; IR spectroscopy; internal stress.

## 1. INTRODUCTION

Cubic boron nitride (cBN), a material which has many properties similar to diamond, was first grown by Wentorf in 1957. Its properties of high thermal conductivity, being the second hardest material, wide band gap ( $E_g = 6.4\text{ eV}$ ), low or even negative electron affinity (NEA) (1), and chemical inertness make it a compound of considerable technological interest. In contrast to diamond, cBN is chemically inert against ferrous materials and oxygen at elevated temperature (up to  $1100^\circ\text{C}$ ) and can be easily doped to p- and n-type semiconductors, whereas n-type doping has been difficult for diamond so far. In fact, it has been shown that a cBN p–n junction grown at high pressure and high temperature can operate at  $530^\circ\text{C}$  (2) and can also act as an ultraviolet light emitter (3). However, industrial use will depend on the availability of low cost fabrication methods.

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It is convenient to characterize the phase of BN by the vibrational frequencies of infrared-active phonon modes, which are well known and tabulated (4). In particular, the phase of the hexagonal form of boron nitride (hBN) phase has two modes at  $770\text{ cm}^{-1}$  ( $A_{2u}$  mode) and  $1383\text{ cm}^{-1}$  ( $E_{1u}$  mode), explosive boron nitride (EBN) phase has four peaks in its absorption spectrum at 960, 1250, 1450 and  $1600\text{ cm}^{-1}$ , respectively (5), wurtzite boron nitride (wBN) has a peak at  $1120\text{ cm}^{-1}$  (6), and cBN has a peak at  $\sim 1065\text{ cm}^{-1}$  corresponding to the TO phonon mode. Moreover, the position of the cBN peak depends strongly on the stress in the film. We used Fourier transform infrared spectroscopy (FTIR) to provide information about cBN content and film internal stress.

Recently, there have been many reports on the preparation of cBN films by using a variety of techniques, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods (7–9). All the physical deposition techniques for cBN thin films growth involve energetic ion irradiation of the surface to initiate and sustain the formation the  $sp^3$ -bonded cubic phase (10). Usually the energetic ion bombardment is thought to be responsible for the formation of the cubic phase (11–13). Without ion irradiation, the hBN is formed. However, a high compressive stress is usually produced by this method which results in poor adherence and delamination from the substrates. The position of the c-BN peak depends strongly on the stress in the film. The higher the stress, the larger the shift value of the cBN peak position. The stress value at 25 GPa, which was measured by Ulrich *et al.*, corresponding to the cBN  $sp^3$ -bond IR peak at  $1099\text{ cm}^{-1}$  (14). In the case that the ion bombardment method was used, the cBN peak usually appears in the range of  $1060\text{--}1100\text{ cm}^{-1}$ . The stress is so high in the cBN films that the films are partially peeled from the substrates and not favorable for industrial uses.

Although seemingly unavoidable, energetic ion bombardment of the surface has some negative consequences. It reportedly causes the buildup of stress in the films and

causes structural damage. Thus, eliminating or, at least, significantly decreasing the ion energies required to form the cubic phase is a feasible way to improve film quality. There have been many reports that were used to reduce the internal stress and improve the quality of the cBN film, such as reducing the bias growth (15) and complex heat treatment (16). The internal stress was significantly decreased and the quality of the cBN films was enhanced but the internal stress cannot be eliminated completely by these methods.

In this report, we describe a modification of the radio-frequency sputtering deposition technique that permits the growth of low-stress cBN films on metallic substrates without any ion bombardment. The IR peak position of the cBN films (thickness 700 nm) is at  $1006.3\text{ cm}^{-1}$ , close to the stressless state, which results in excellent adhesion between the cBN films and the substrates. The cBN growth without ion bombardment might be useful to understanding the mechanism of cBN growth.

## 2. EXPERIMENT

The deposition of boron nitride films was performed in a tuned substrate radio-frequency (r.f.) magnetron bias sputtering system with an hBN target (hot pressed from hBN powders of 5 N purity with 50 mm diameter). The cBN films were deposited on the metallic wafers (thickness: 1 mm; diameter: 18 mm). The substrate temperature was kept at  $400^\circ\text{C}$  during the deposition process. The chamber pressures were held at  $2 \times 10^{-3}$  and 1.3 Pa before and after the gas injection ( $\text{N}_2:\text{Ar} = 1:28$ ), respectively. The deposition conditions of the r.f. power  $\sim 150\text{ W}$  and the dc substrate bias voltage  $\sim 200\text{ V}$  (substrate +, target -) were selected here.

The characteristics of the deposited films were measured by Fourier transmission infrared absorption (FTIR) (IFS-66 V type FTIR spectrometer) and transmission electron microscopy (TEM) (Hitachi 8100-IV) prepared to represent selected area diffraction on the surface of films. In TEM experiments, the sample was prepared by backside thinning. In brief, this was the process of using mechanical polishing first and then ion thinning down to  $0.1\ \mu\text{m}$ .

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization

The IR spectra of the BN films, which are deposited on the metallic substrates at different deposition times, are shown in Fig. 1. We can see a broad IR peak at  $1250\text{ cm}^{-1}$  (deposition time: 35 min), which corresponds to the internal vibration modes of EBN, and the peak at  $2000\text{--}2500\text{ cm}^{-1}$ , which belongs to the intermolecular vibration mode. The absorption peaks of the hBN were not

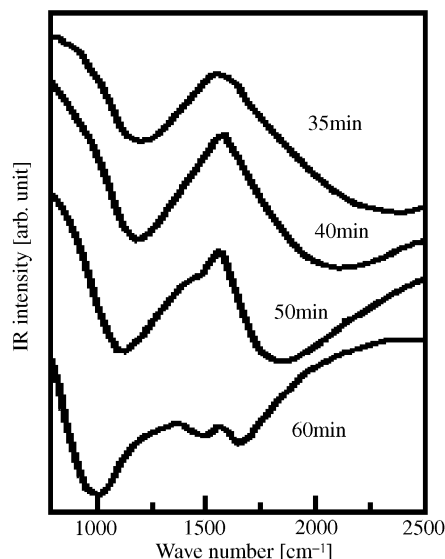


FIG. 1. IR spectra of cBN films prepared at different times.

obviously found, which indicates that the films are EBN. This indicates that EBN was formed from hBN by electron bombardment effect in plasma area. This result is in good agreement with the result of Sokowska *et al.* (17) using electron assisted chemical synthesis EBN. The width of the peak at  $1250$  and  $2000\text{--}2500\text{ cm}^{-1}$  indicates that there are many defects in the films and the grain size is small (15). The sharper IR peak position at  $1224\text{ cm}^{-1}$ , corresponding to EBN and a wide IR  $2000\text{--}2500\text{ cm}^{-1}$  related to the vibration mode of molecular crystal were formed in the sample at a deposition time of 40 min. This indicates that the quality and the percentage of EBN increases with an time increase in. These IR peak positions are shifted down compared to those in the sample at a deposition time of 35 min. This result suggests that some EBN phases began to transform wBN phases. When the deposition time is up to 50 min, a sharp IR peak at  $1120\text{ cm}^{-1}$ , which corresponds to the absorption peak of wBN, has appeared (6). Meanwhile, a tiny peak position at  $1480\text{ cm}^{-1}$  corresponding to EBN and a peak at  $1750\text{--}2000\text{ cm}^{-1}$  corresponding to the molecular vibration were also found. These results showed that the main phase of the films transformed from EBN to wBN. With the deposition time increasing, the peak position of EBN at  $1250\text{ cm}^{-1}$  decreased the least and the peak position of EBN appeared at  $1500\text{ cm}^{-1}$ . The biggest change of the film is that the peak position of the cBN phase appears at  $1008\text{ cm}^{-1}$  compared to the previous samples. The peak position of the molecular vibration mode decreased the least, which indicates that many wBN phases transit to cBN phase. This result is in good agreement with the result of Akashi *et al.* (18) using shock wave dealing with wBN powder in order to synthesize cBN. There is a wide peak at  $1008\text{ cm}^{-1}$  in the

sample deposited at 60 min. This result indicates that there are other phases of BN included at this peak beside cubic phase. In order to analyze all the phases of BN in this sample, the IR spectrum of this sample is analyzed by the soft of peak-fit and the result is shown in Fig. 2. The IR peak position at  $1337\text{ cm}^{-1}$  (B–N stretching) agrees with the vibration mode of the  $sp^2$  bond of hBN<sup>13</sup> and the peak position at  $1130\text{ cm}^{-1}$  is in agreement with the vibration mode of wBN (15). The peak position peaks at 898.3, 1234.8, 1492.5 and  $1645.7\text{ cm}^{-1}$  belong to the internal vibration mode of EBN, whereas the broad peaks at 1784.5 and  $3750\text{ cm}^{-1}$  belong to the external vibration mode of EBN (19). The strong absorption peak value at  $1006.3\text{ cm}^{-1}$  corresponds to the vibration TO mode of the cBN  $sp^3$  bond (20), which is close to the ideal IR peak position (at  $1004\text{ cm}^{-1}$ ) without the internal stress (21).

The cBN films backside thinned were characterized by TEM and the result is shown in Fig. 3. It is seen that the  $d$  values calculated from the diffracting ring at 2.10 (111), 1.82 (200), 1.29 (220) and 1.09 (311) for BN film are in good agreement with those of bulk cBN synthesized by shock wave (18). No obvious evidence was found for the presence of another BN phase. The result indicates that a pure cBN layer exists on the surface of the deposited BN film. These results indicate that the main phase in the film is the cubic phase and there are a few hexagonal, wurtzic, explosive phase and hBN, wBN and EBN are the intermediate composites between the cBN layer and the substrate.

### 3.2. Mechanism of Growth

It is well known that boron nitride is to some extent isostructural with carbon and is known to crystallize in one of four phases: the low-density forms, which are hexagonal (hBN) and turbostratic (tBN) with  $sp^2$  bonds, the metastable high-density phase such as cBN and wBN with  $sp^3$  bonds, and between the low density and high density, explosive (EBN). The molecular structure of EBN was

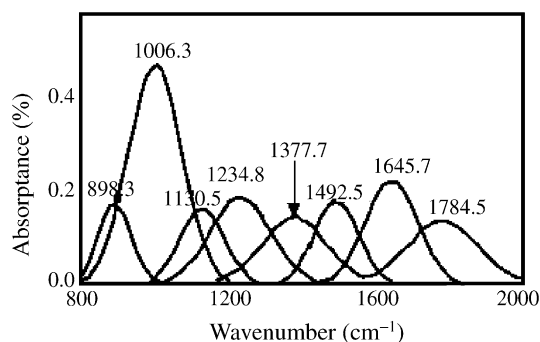


FIG. 2. IR analog spectra for sample of deposition 1 h in the spectra ranging from 800 to  $2000\text{ cm}^{-1}$ .

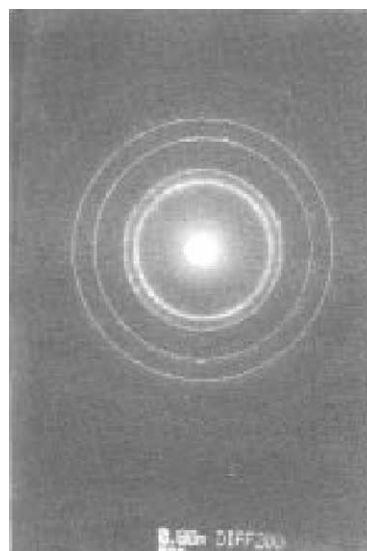


FIG. 3. TEM of BN deposited by 1 h.

modeled using a computer simulation by Olszyna *et al.* (19), containing the  $\sigma sp^3$  and  $\sigma sp^2$  chemical bonds (1:1). The nitrogen and boron atoms are placed parallel to the strongly deformed hexagons shown in Fig. 4. Therefore, it can be concluded that EBN transformed from hBN is easier than cBN and wBN for the lower energies.

During the deposition of BN films, hBN sputtered from the target forms an excitation level by absorbing energy in plasma, and some  $sp^2$  bonds in the hexagonal grid of hBN are changed into  $sp^3$  bonds. EBN was thus deposited on the substrates initially. This result is in good agreement with that of Sokolowska (17). More  $sp^2$  bonds in EBN changed into  $sp^3$  bonds for the electron bombardment with the time increasing, which result in the formation of the wBN phase. wBN is then transformed into cBN because of the effect of electron bombardment. This result is similar to the transition from wBN to cBN by shock wave (18).

The reason for the growth of cBN by r.f. magnet sputtering deposition is that the plasma is of high plasma density, high electron temperature and high electron

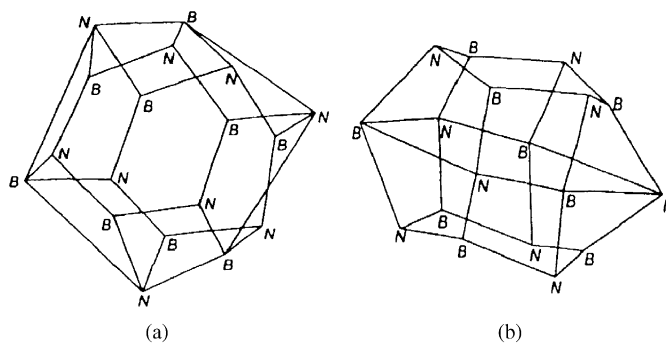


FIG. 4. Structural model of EBN phase.

momentum, which result in a high microscale pressure and temperature on the substrate.

Compared to the effect of shock wave on cBN formation, the electron bombardment may have the same effect on the formation of cBN. Both electron bombardment and shock wave have the same characters of high momentum and low kinetic energy. Less structure distortion in cBN films, which are induced by the electron bombardment than ion bombardment providing the same energies, might lead to low internal stress. From the above analysis, we consider that energy is necessary to disrupt the  $sp^2$ -bonded hBN material, creating local  $sp^3$  bonding sites for the nucleation of the metastable cBN, and the large compressive strain is not a driving force for the hexagonal-to-cubic transition which is in good agreement with the other study (22). This result is also compatible with the result of Fahy *et al.* who found no evidence in the IR-absorption peak shifts to support the theory that cBN nucleates at a time of exceptionally high strain, or that large compressive strain is a driving force for the hexagonal-to-cubic transition (23).

### 3.3. Low Internal Stress

It is well known that FTIR was used to provide information about film stress (15). The lower the IR peak position, the lower the interstress in the film. There have been different results of the peak position of cBN films without internal stress calculated by different theoretic models. The result of Wentzcovitch *et al.* is  $1004\text{ cm}^{-1}$  (21) and that of Fahy is  $1063\text{ cm}^{-1}$  (24). The Wentzcovitch *et al.* result can be confirmed in this experiment and our previous result. Figure 5 is an IR spectrum of the cBN film peeled from substrate which is prepared by the ion bombardment deposition technique described in our previous experiment. The internal stress might be released largely in this sample during the cause of peeling. The peak position at  $1064\text{ cm}^{-1}$  of FTIR indicates that the internal stress in this cBN film was not released completely. The peak of reflection IR absorption at  $1004.7\text{ cm}^{-1}$  in this sample indicates that the surface of this film is close to stressless. If the IR peak position at  $1004\text{ cm}^{-1}$  was assumed as the stress-free value in cBN, the shift of IR peak position with stress should be  $3.8\text{ cm}^{-1}/\text{GPa}$  ( $(1099-1004)\text{ cm}^{-1}/25\text{ GPa}$ ) but not  $1.8\text{ cm}^{-1}/\text{GPa}$  in Ref. (14).

The IR peak position of cBN at  $1006.3\text{ cm}^{-1}$  has a down shift of  $48.7\text{ cm}^{-1}$  compared to the value of bulk cBN of about  $1055\text{ cm}^{-1}$ . This might be caused by the relief of internal stress completely. It is shown that the peak position at  $1055\text{ cm}^{-1}$  is not to produce stress-free value (21). The low internal stress in cBN film shows that the film has weak structural distortion and excellent adhesion. The prepared cBN films with little internal stress and pure cBN phase on the surface can be applied for the corrosion-

resistant coating and the wear-resistant superhard coating.

## 4. SUMMARY

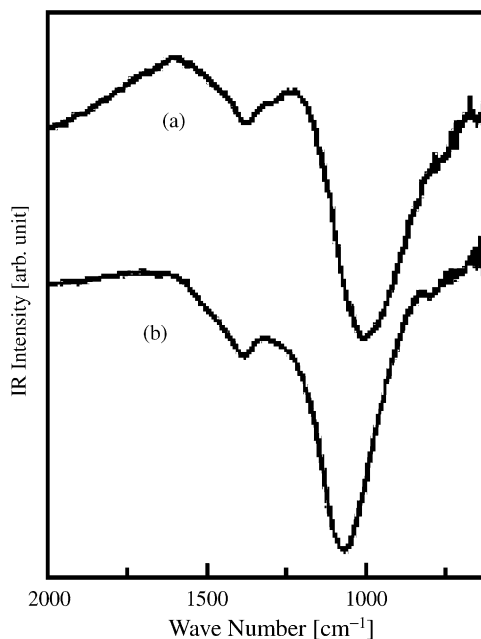
Cubic boron nitride thin films, including hBN, wBN and EBN phases interlayer, were deposited on metallic substrates by tuned substrate r.f. magnetron sputtering. The TEM result shows that the surface of the film is pure cBN. The IR peak position of cBN at  $1006.3\text{ cm}^{-1}$  shows that the film has low stress, which approaches a stressless state and leads to excellent adhesion. During cBN growth production, EBN was formed first, then wBN appeared, and finally cBN formed on the surface. The electron bombardment is thought to be responsible for the transition process and is of the same effect as shock wave on the cubic phase formation. The energy is necessary to disrupt the  $sp^2$ -bonded hBN material, creating local  $sp^3$  bonding sites for the nucleation of the metastable cBN.

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(a) reflection spectrum, (b) transmission spectrum

FIG. 5. IR spectra of cBN films peeled from the substrate.

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