

# Growth of adhesive cubic phase boron nitride films without argon ion bombardment

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## Abstract

Previously, in situ bombardment of massive ions ( $\text{Ar}^+$ ,  $\text{Kr}^+$ , etc.) was considered to be necessary for the formation of c-BN films. Because of the accumulated stress, bombardment of massive ions has led to the formation of c-BN films with poor adhesion. Here we show that c-BN films can be grown without involving bombardment of massive ions. This is achieved by using plasma-assisted pulsed-laser deposition (PLD) in pure  $\text{N}_2$  RF plasma. Furthermore, we show that c-BN films can be grown in a vacuum ( $\sim 10^{-5}$  mbar during growth) by PLD without auxiliary ion source. We show that these are possible at a reduced deposition rate. Energetic growth species initiated by PLD and the pure  $\text{N}_2$  plasma is sufficient to form adhesive c-BN films at moderate deposition rate as long as the energy transfer rate per growth species is sufficient.  
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## 1. Introduction

Cubic phase boron nitride (c-BN) films have many desirable properties such as extreme hardness comparable to diamond, high thermal conductivity, wide band gap ( $\sim 6$  eV) and higher resistance to oxidation and ferrous metals than diamond [1]. In the past two decades, it was reported that ion bombardment was necessary for growing c-BN films, especially with massive ions of Ar or Kr [1–6]. However, poor adhesion was generally observed which hindered the applications of c-BN films. Implantation of Ar or Kr ions into the deposited films is expected to cause structural damage and stress, especially at high ion energy conditions [7]. This is one of the reasons for the poor adhesion.

In addition, c-BN films are found to delaminate in a unique manner. In general, c-BN films were grown with a microstructure consisting of  $\text{sp}^2$  and  $\text{sp}^3$ -bonded phases [1–3]. The c-BN phase is not directly grown on the substrate but on top of a BN interlayer. This interlayer consists of a  $\text{sp}^2$  bonded turbostratic (t-BN) layer and an amorphous BN (a-BN) layer next to the substrate. A significant difference in mechanical properties and internal stress occurs between this interlayer and the c-BN film

on top [8]. This is also one of the reasons for poor adhesion of c-BN films where mechanical failure occurred near the boundary of the  $\text{sp}^2/\text{sp}^3$  phases.

Previously, we have reported the successful growth of the c-BN films in pure  $\text{N}_2$  plasma by RF plasma assisted pulsed laser deposition (PLD) with a novel laser light source (5th harmonic generation of Nd:YAG lasers, wavelength  $\lambda \sim 213$  nm, pulse duration  $\sim 3$  ns) [7,9]. We found that c-BN films grown in  $\text{N}_2$  plasma are more adhesive than those grown with the addition of Ar ions [7]. In this work, the growth of c-BN films in pure  $\text{N}_2$  plasma by the same technique was attempted, however, with a commonly accessible laser—the 4th harmonic generation of Nd:YAG laser ( $\lambda \sim 266$  nm, pulse duration  $\sim 6$  ns). As will be discussed, this is theoretically more challenging. In addition, we found that energetic BN growth species generated by laser ablation in a vacuum is sufficient for the growth of c-BN films without auxiliary ion bombardment from other ion sources.

## 2. Experiments

In the first approach, c-BN films were prepared by RF (13.56 MHz) plasma-assisted PLD. The target was a hot-pressed hexagonal boron nitride (h-BN, 99.99%) pallet of  $0.75 \times 0.75 \times 0.1875$  in.<sup>3</sup> The base pressure for the PLD chamber can be as high as  $10^{-7}$  mbar. The RF power was

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capacitively coupled on a Si (100) substrate to generate plasma in a pure  $N_2$  ambient at a pressure of  $2 \times 10^{-2}$  mbar. By this means, a negative dc bias voltage was induced on the substrates, which initiated a bombardment of positive ions during the deposition of BN films. The growth temperature was maintained at 600 °C as controlled by a proportional-integration-differentiation (PID) system. In the second approach, c-BN films were deposited by PLD in a vacuum. The experimental setup and parameters were similar to those described above. RF plasma was not used in this case.

### 3. Results and discussions

#### 3.1. Theoretical guideline: effect of laser wavelength and laser pulse energy

During laser ablation, electric field generated on the target surface is represented by  $E = [2I/c\epsilon_0]^{1/2}$ , where  $I$  is the irradiance of laser in  $W/m^2$ ,  $c$  is the speed of light, and  $\epsilon_0$  is the electric permittivity in vacuum [10]. Ionic species are generated inside the laser plasma and accelerate away from the target surface with kinetic energies as high as a few tens of eV [11]. Absorption of the laser light by the laser plasma will occur only when the plasma index of refraction,  $n(\omega)$  is complex. According to the relation  $n^2(\omega) = 1 - [\omega_p/\omega]^2$ , a complex  $n(\omega)$  will occur when the plasma frequency is larger than the laser frequency ( $\omega_p > \omega$ ) [10]. Plasma heating will happen when the laser light is absorbed by the laser plasma. This will lead to the melting of the h-BN target and generate h-BN clusters that will then be transferred to the substrates. The transfer of h-BN clusters will prevent the effective growth of c-BN films. Thus,  $\omega_p$  must be minimized especially when lasers with relatively long wavelengths (low  $\omega$ ) are used for PLD.

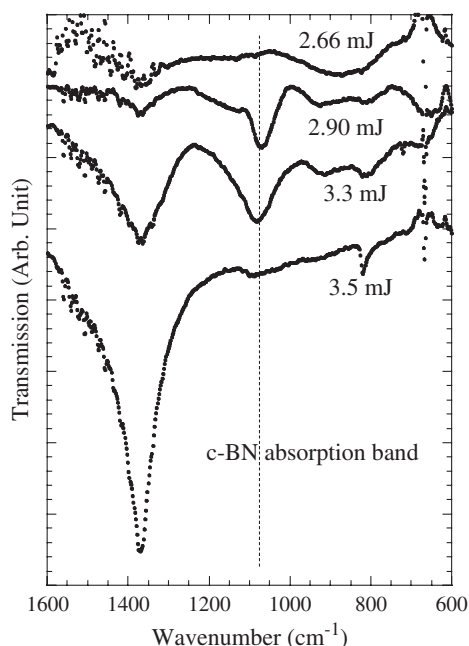


Fig. 1. FTIR spectra of c-BN films prepared at a constant substrate biasing of  $-500$  V in pure  $N_2$  plasma at various pulsed laser energies.

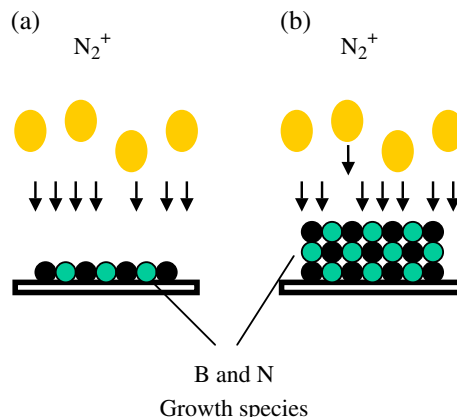


Fig. 2. Schematic of ion-assisted BN film deposition at (a) low and (b) high deposition rates.

According to the relation  $\omega_p = [N e^2 m_e \epsilon_0]^{1/2}$ , where  $m_e$  is the mass of electron and  $N$  is the electron density,  $N$  must be minimized, which can be obtained by keeping the laser energy or irradiance low. In short, laser pulse energy must be minimized for growing c-BN films by PLD, especially when the laser wavelength is relatively long.

#### 3.2. Growth of c-BN films at fixed bias voltage

By following this theoretical guideline, we have attempted to grow BN films at low pulse laser energies. First, we have grown BN films at various laser pulse energies while keeping the substrate bias voltage at  $-500$  V. All these films were deposited for 4 h with the growth conditions mentioned in Section 2. The BN films are characterized by the transmission mode of Fourier transform infrared (FTIR) spectroscopy. The IR absorption due to the entire BN film can be detected as shown in Fig. 1. Two absorption bands at  $\sim 1380$  and  $\sim 780$   $cm^{-1}$  represent the in-plane (B-N) and out-of-plane (B-N-B) stretching modes of the  $sp^2$ -bonded BN phase, respectively [1–9]. The c-BN absorption band appeared at  $\sim 1080$   $cm^{-1}$  [1–9].

As shown, when laser pulse energy of 2.6 mJ is used, no significant BN films are deposited. This means total resputtering occurred. BN film deposited on the substrate is resputtered away by the ion bombardment initiated by the substrate biasing. As we increase the laser pulse energy to 2.9 and 3.3 mJ, the c-BN phase begins to grow, as indicated by the IR absorption at  $\sim 1080$   $cm^{-1}$ . Only h-BN phase is deposited at higher deposition rate (laser pulse energy = 3.5 mJ). We explain these results by referring to a schematic illustration in Fig. 2. At constant negative bias voltage (an equivalent to a constant RF forward power to the plasma), the ionic density in the  $N_2$  plasma is constant for all these cases. Thus the total energy transfer from the ion bombardment to the growth surface is the same for all these films. However, the quantity of growth species on the substrate surface is lower for cases with lower laser energies (lower deposition rates). Thus the energy transfer rate per growth species is higher at lower deposition rate. When the acquired energy is sufficient, c-BN films are grown. Otherwise (say for the case with 3.5 mJ) h-BN films will be formed. Our

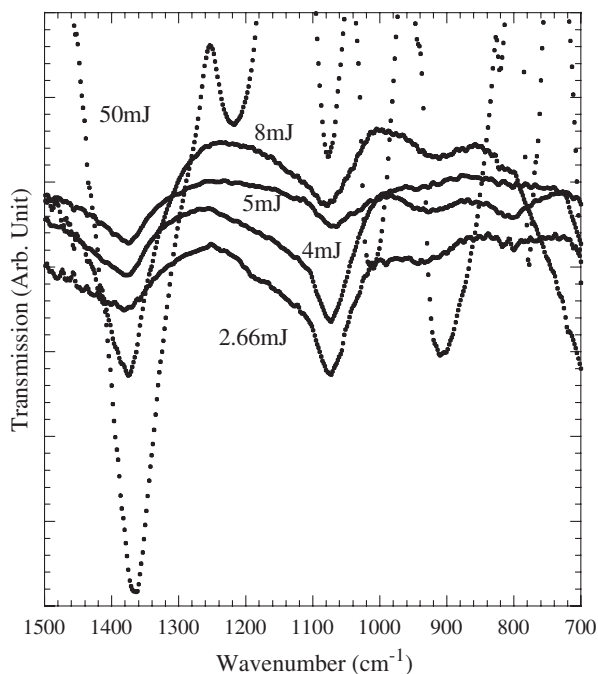


Fig. 3. FTIR spectra of BN films deposited in vacuum at various laser pulsed energies.

results also follow the general phenomenon that c-BN films are formed just before total re-sputtering occurred [1–5].

As a summary, the formation of c-BN films required a balance between the deposition rate and the energy transfer from the ion bombardment, i.e. a window of energy transfer rate per growth species exist for the formation of c-BN films. Our results show that c-BN films can be deposited by pure  $N_2$  plasma if the deposition rate is reduced by the use of low laser pulse energies.

### 3.3. Growth of c-BN films in a vacuum

In the second approach, BN films are deposited for 6 h in a vacuum. As indicated in the earlier discussion, we think that the growth species from the laser plasma has significant ionic density and kinetic energy that could lead to the formation of c-BN films if the deposition rate is optimized. Thus, different pulse laser energies were applied in order to search for an

optimum energy deposition rate that met the energy transfer rate per growth species of c-BN films.

Fig. 3 shows the IR spectra for BN films deposited at various laser pulse energies. As shown, the content of c-BN phase is reduced when higher laser pulse energies are used. The content of c-BN in the films was estimated to be about ~75%, 68%, 50% and 25% for samples deposited at laser pulse energy of 2.66, 4, 5 and 8 mJ, respectively, as referred to the heights of the absorption bands located at  $1080$  and  $1380\text{ cm}^{-1}$  [12,13]. These contents are higher than those reported so far by PLD in a vacuum [14].

This could be explained as follows: higher laser energies will generate growth species with higher kinetic energies. However, higher deposition rates are also initiated. Our results simply show that the energy transfer rate per growth species is reduced with the increase of laser energy. This occurs when the increase of deposition rate exceeds the enhancement of kinetic energy of the growth species. The possible reason is the formation of h-BN clusters from the target, which are then transferred to the substrates.

To verify this, we have attempted to grow BN film by 50 mJ of laser pulse energy. As shown in Fig. 4, the IR spectra is oscillating due to the interference of the IR beams reflected at the top and the bottom surfaces of the BN films as the film thickness is approaching the IR wavelengths. The signal for the c-BN phase could not be determined from this spectrum, but a strong h-BN band at  $\sim 1360\text{ cm}^{-1}$  is clearly shown. We further examine the morphology of all these BN films. As shown in Fig. 4(a), all BN films with c-BN phase have smooth surface morphology as indicated by scanning electron microscopy (SEM). For BN films deposited at 50 mJ, many clusters are observed by SEM and this is explained by the direct transfer of h-BN molten from the target due to laser heating (thermal ablation).

## 4. Conclusion

We have shown that c-BN films can be grown by both plasma-assisted PLD and PLD in vacuum. Our results indicate that adhesive c-BN films can be deposited at moderate ion bombardment without the use of Ar or Kr ions. This is achieved when the deposition rate is reduced to match the moderate

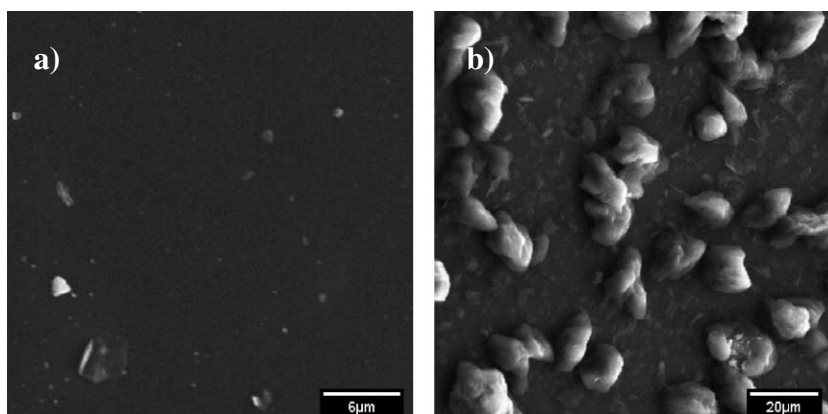


Fig. 4. SEM images (a) c-BN film with smooth surface and (b) h-BN films with clusters.

energy transfer rate of the bombarding ions. A window of energy transfer rate per growth species is observed. A reduced film stress generated by these moderate ion bombardments in our technique is responsible for the good film adhesion.

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