

Plasma deposition of cubic boron nitride films from non-toxic material at low temperatures

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Abstract

Boron nitride has become the focus of a considerable amount of interest because of its properties which relate closely to those of carbon. In particular, the cubic boron nitride phase has extreme hardness and very high thermal conductivity similar to the properties of diamond. The conventional methods of synthesis use the highly toxic and inflammable gas diborane (B_2H_6) as the reactant material. A study has been made of the deposition of thin films of boron nitride (BN) using non-toxic material by the plasma-assisted chemical vapour deposition technique. The source material was borane-ammonia (BH_3-NH_3) which is a crystalline solid at room temperature with a high vapour pressure. The BH_3-NH_3 vapour was decomposed in a 13.56 MHz nitrogen plasma coupled either inductively or capacitively with the system. The composition of the films was assessed by measuring their IR absorption when deposited on silicon and KBr substrates. The hexagonal (graphitic) and cubic (diamond-like) allotropes can be distinguished by their characteristic absorption bands which occur at 1365 and 780 cm^{-1} (hexagonal) and 1070 cm^{-1} (cubic). We have deposited BN films consisting of a mixture of hexagonal and cubic phases; the relative content of the cubic phase was found to be directly dependent on r.f. power and substrate bias.

1. Introduction

Boron nitride has hexagonal and cubic allotropes which are isostructural and isoelectronic with graphite and diamond respectively. Like graphite, hexagonal boron nitride (h-BN) is the stable allotrope under normal conditions whereas cubic boron nitride (c-BN), like diamond, is metastable. They have somewhat similar properties to their carbon analogues, *e.g.* h-BN is soft while c-BN has extreme hardness, chemical inertness, high resistivity, thermal conductivity and transparency. However, with respect to diamond, c-BN is a favourable superhard material that resists oxidation even at elevated temperatures up to about 1600°C .

Thus, because of these desirable properties, the formation of thin films of c-BN has been intensively investigated, motivated by their potential for hard coatings for wear resistance, for high temperature electronic devices and for optical coatings. Recently, significant progress has been made in the experimental techniques for synthesizing c-BN films using various types of chemical vapour deposition (CVD) and physical vapour deposition (PVD). PVD techniques have yielded the most promising results so far. Successful deposition of c-BN films has been reported using ion beam deposition [1–7], ion plating [8, 9], arc-like ion plating [10, 11], r.f.

sputtering [12–15], activated reactive evaporation [16–22] and laser-assisted [23] processes. A number of workers using plasma-assisted chemical vapour deposition (PACVD) have reported success in forming the c-BN, *e.g.* by PACVD thermally activated with a hot tungsten filament [24–28], electron cyclotron resonance (ECR) plasma CVD [29–35], plasma chemical transport [36] and reactive pulse plasma CVD [37–39]. An exhaustive review can be found in two recent papers [40, 41].

All these attempts were successful in producing polycrystalline films of c-BN, although predominantly of a mixed nature with both cubic and hexagonal phases present. Because c-BN crystalline material exists in equilibrium only at temperatures above 2000 K and pressures above 12 GPa, the formation of c-BN thin films is very difficult under more favourable conditions. It appears that most researchers succeeded in the deposition of c-BN if the technique included the input of additional energy from energetic ions during the deposition process. The growth of hard BN films requires ion bombardment during the deposition to form the high temperature, high pressure metastable phase and to remove the soft h-BN phase. In PACVD, the ion acceleration is due to negative self-bias of the substrate by plasma electrons, by the r.f.-driven voltage swings of the plasma potential and, in some cases, externally applied voltage. This paper reports the effects of different plasma excitation, coupled both inductively and capacitively, on the deposited BN films grown in a PACVD system.

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Although c-BN films have been deposited using variation of all the different techniques, many of the so far used source compounds have serious drawbacks, including serious safety problems due to the toxicity and/or highly inflammable nature of the source compounds. Again, to grow BN films at a relatively low substrate temperature, it is better to use some less thermodynamically stable reactants. In a PACVD technique, the average temperature of the gas molecules is maintained at a moderate value while the electron energy is sufficient to break the molecular bonds. This substitution of electron kinetic energy for thermal energy in classical CVD allows deposition at low temperatures.

The reaction material in our system is a borane–ammonia ($\text{BH}_3\text{-NH}_3$) adduct which is an air-stable white crystalline solid at room temperature but is volatile and can be decomposed by the electron energy. It is considerably easier to handle and safer than diborane, boric acid, borazine, boron trichloride or other conventional source compounds.

The present authors have investigated the formation of c-BN films at low temperatures by a r.f. PACVD technique without using any external activation such as a high substrate temperature, hot filament, magnetic field confinement or gas activation nozzle.

2. Experimental details

2.1. Deposition system

The experimental system used in this study is shown in Fig. 1. It consists of a Pyrex glass bell-jar-type chamber with an associated pumping system. The diameter of the tube at the reactant side is 3 in and that at the substrate side is 6 in.

Commercially available (Alfa Products) $\text{BH}_3\text{-NH}_3$ is evaporated outside the reaction chamber by using a resistance-heating system and is introduced in the reactor by using metered nitrogen as a carrier gas. The plasma is generated by using a 13.56 MHz r.f. generator coupled inductively or capacitively with the system.

Mirror-polished silicon substrates were placed onto a heatable, optionally biased or grounded stainless steel support plate. The silicon wafers were etched by 40% diluted HF acid, washed in deionized water and dried. KBr was also used as a substrate to confirm the c-BN IR peak. Further, to minimize surface damage by highly energetic particles, the substrate holder is placed downstream of the plasma zone, corresponding to an indirect PACVD process. The substrate was not water cooled.

The chamber was evacuated by a two-stage rotary pump. The lowest possible value of pressure produced was less than 8×10^{-2} mbar and was monitored with a Pirani gauge calibrated for nitrogen gas.

The temperature of the substrate holder as well as reactant holder was measured with a Chromel–Alumel K-type thermocouple attached to a digital micro-processor indicator.

2.2. Film growth

The chamber was evacuated to a pressure of 8×10^{-2} mbar and flushed with nitrogen gas for about 2 min. The chamber was re-evacuated to 8×10^{-2} mbar. The reactant, $\text{BH}_3\text{-NH}_3$, was heated at 35°C for 10 min to evaporate its water content. After another flush with nitrogen, the base pressure of 8×10^{-2} mbar was attained.

The reactant was evaporated and introduced into the r.f. plasma reactor with the carrier nitrogen gas. The working pressure was maintained constant at 0.7 mbar when the nitrogen flow rate was 6.5 standard $\text{cm}^3 \text{min}^{-1}$. Then BN films were deposited for the desired time.

The film deposition was carried out with three types of plasma excitation: inductively coupled plasma with or without a d.c. substrate bias and capacitively coupled plasma. In an inductively coupled system, the r.f. coil was coupled to the r.f. generator through an impedance-matching network. The substrate was floated or biased by connection to a d.c. supply. In the capacitively coupled system, the r.f. generator was con-

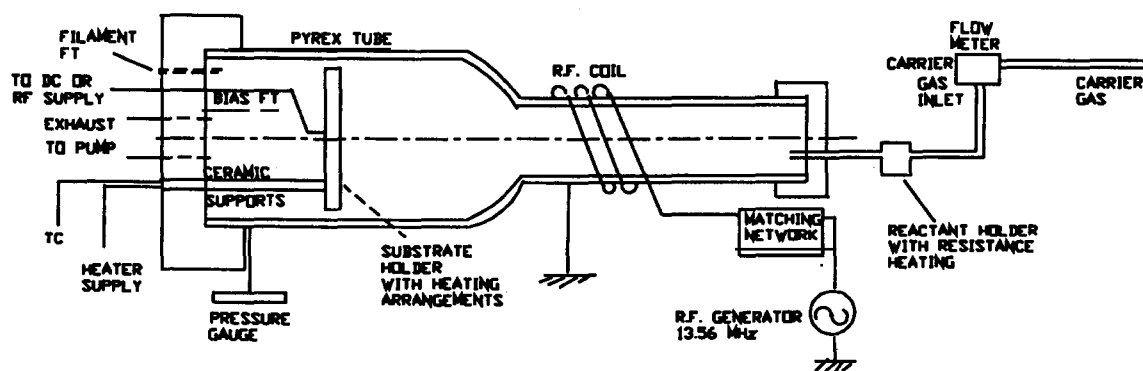


Fig. 1. Experimental system used for the deposition of BN films.

TABLE 1. Deposition conditions

Reactant	Borane-ammonia ($\text{BH}_3\text{-NH}_3$)
Carrier gas	Nitrogen (N_2)
N_2 flow rate (standard $\text{cm}^3 \text{min}^{-1}$)	6.5
Working pressure (mbar)	0.7
r.f. power (W)	0–200
Self-bias voltage (V)	0–900 (negative)
d.c. bias voltage (V)	0–400 (negative)
Substrate temperature ($^\circ\text{C}$)	48–180
Deposition time (min)	45–60
Film thickness (μm)	0.5–1.5

nected to the substrate through a matching network and a blocking capacitor. For the inductively coupled system, the r.f. power was varied from 0 to 200 W. For the d.c. excitation, the negative d.c. bias was varied from 0 to 400 V while the r.f. power was kept constant at 20 W. In the capacitively coupled excitation, the negative d.c. self-bias was varied from 0 to 900 V. The deposition conditions are summarized in Table 1.

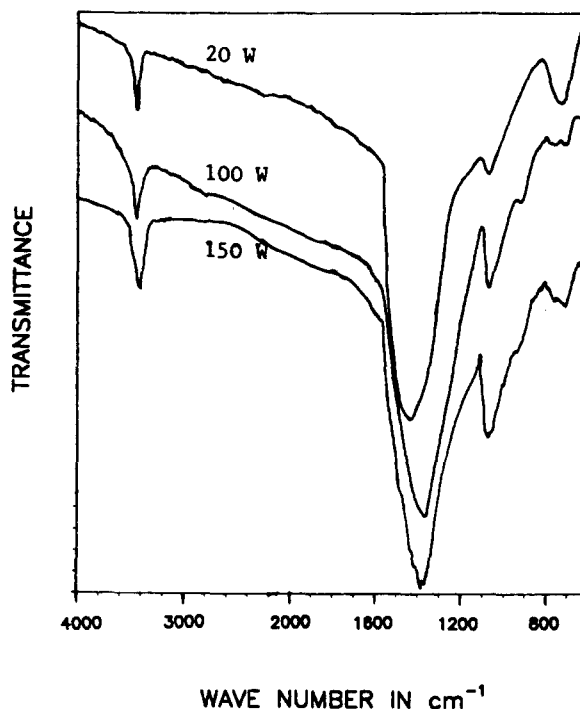
The films were then studied using IR spectrometry which was carried out on a Perkin-Elmer 983G spectrometer in the transmittance mode in the range 600–4000 cm^{-1} , using a bare etched silicon wafer as a reference.

3. Results and discussion

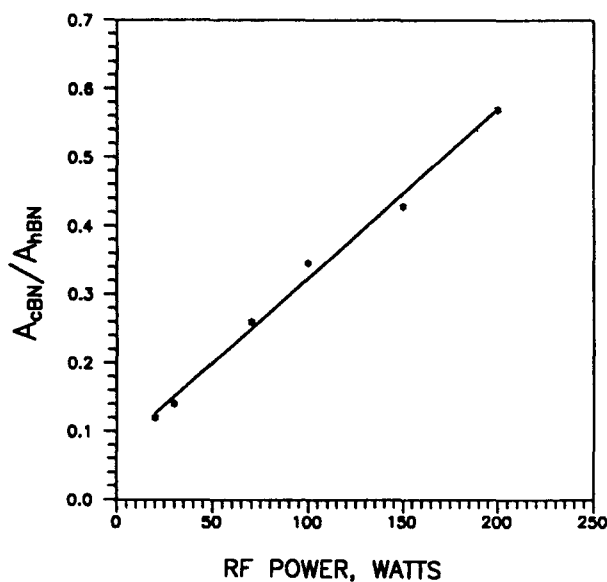
BN films up to 1.5 μm thick were deposited directly on silicon and KBr substrates with a deposition rate about 150 $\text{\AA} \text{min}^{-1}$.

The structural investigation of BN films was mainly based on IR spectroscopy. An IR spectrum of the c-BN crystal shows a strong absorption near 1070 cm^{-1} due to the reststrahlen band (transverse optical mode). The h-BN phase results in a distinct and strong, asymmetrical band near 1365 cm^{-1} , which is attributed to B–N bond stretching (in-plane vibration), and a weaker sharper band near 780 cm^{-1} , which is attributed to B–N–B bond bending (out-of-plane vibration). The relative content of cubic to hexagonal phase was obtained by the intensity ratio of the IR absorption bands at 1070 cm^{-1} and 1365 cm^{-1} respectively, since the absorption intensity is a function of the film thickness. This method was used by other groups also [15, 18, 27]. The intensity was evaluated by the peak height two-point baseline method described in ref. 42.

The IR spectra of most of our films contain a strong absorption band at 1365 cm^{-1} , a medium band at 1070 cm^{-1} and a weaker band at 780 cm^{-1} . Figure 2(a) shows the intensity of the IR absorption band of BN films prepared by varying the r.f. power coupled inductively with the system. No c-BN peak was detected when an r.f. power of less than 20 W was used. As the power was increased, the c-BN peak intensity at



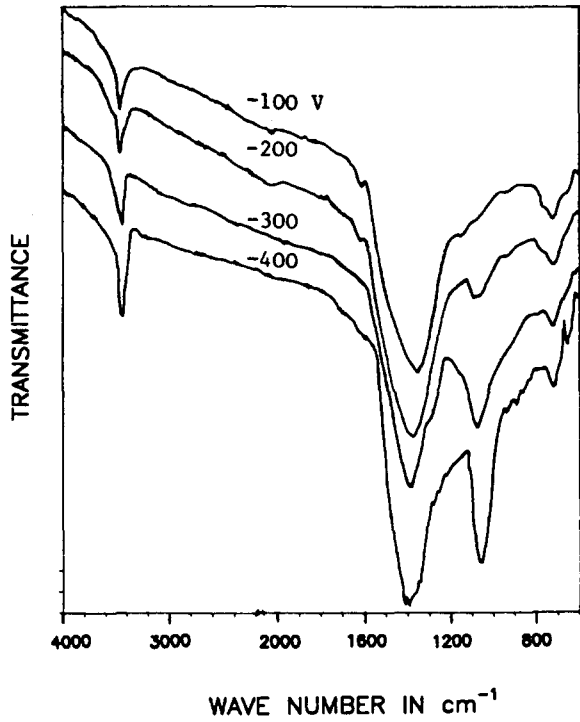
(a)



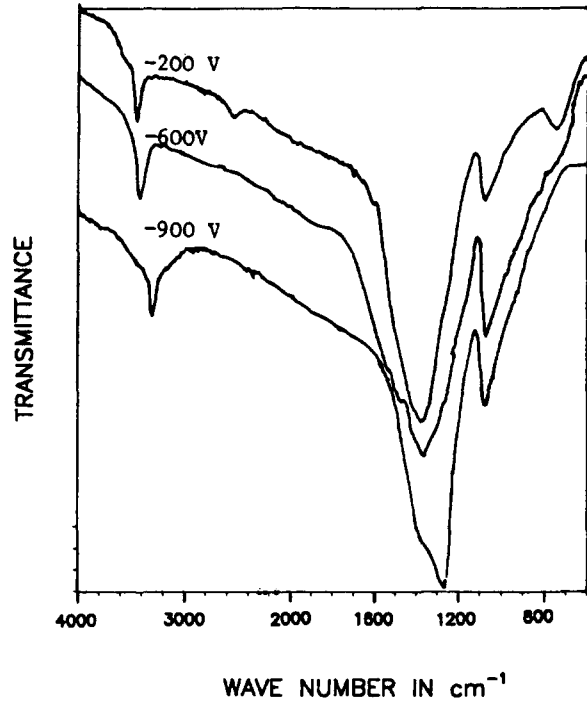
(b)

Fig. 2. (a) IR absorption spectra of BN films prepared by varying the r.f. power coupled inductively with the system. (b) The intensity ratio as a function of inductively coupled r.f. power.

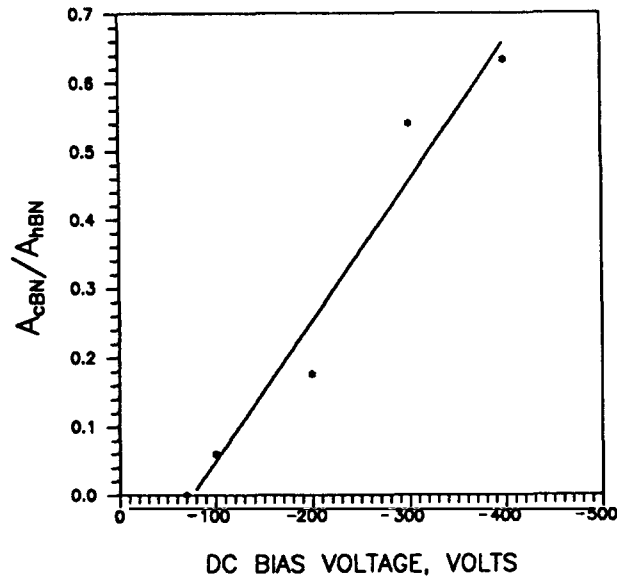
1070 cm^{-1} was increased and became sharper. Although the shape and intensity of the in-plane vibration of h-BN phase did not exhibit any considerable change, the peak was shifted to a lower wavenumber from 1428 cm^{-1} at 20 W to 1365 cm^{-1} at 200 W. The out-of-plane vibrational peak was sharper at lower powers than that at higher powers and also it shifted to a lower



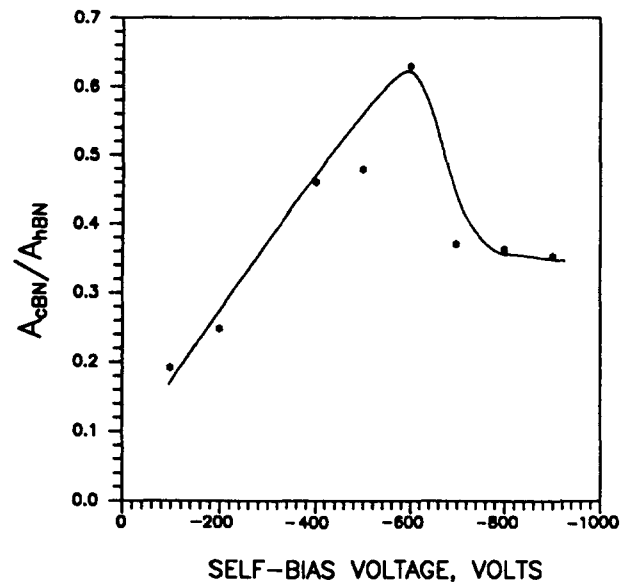
(a)



(a)



(b)



(b)

Fig. 3. (a) IR absorption spectra of BN films prepared by varying the d.c. substrate bias (inductively coupled r.f. power, 20 W). (b) The intensity ratio as a function of d.c. substrate bias.

Fig. 4. (a) IR absorption spectra of BN films prepared by varying the r.f. self-bias voltage at the substrate. (b) The intensity ratio as a function of r.f. self-bias voltage.

wavenumber. This frequency shift indicates a weakened B–N bond and the broadening indicates an average decrease in the ordering of boron and nitrogen atoms to form B–N bonds. This is explained as follows: a high power plasma involves high concentrations of energetic nitrogen ions which etch the hexagonal phase and

increase the volume fraction of the cubic phase, as shown in Fig. 2(b).

Figure 3(a) shows the IR absorption spectra of BN films deposited by varying the negative d.c. bias applied at the substrate. The c-BN peak at 1060 cm^{-1} showed increasing intensity and sharpness with the increasing

bias, but the hexagonal peaks did not show any significant change in peak shift or intensity. Owing to high ionization of the plasma, it was not possible to go beyond 400 V. Figure 3(b) shows the IR absorption ratio as a function of d.c. bias voltage.

In the capacitively coupled system, no c-BN peak could be detected at a substrate bias of less than 70 V. As the bias was increased to 600 V, the c-BN peak near 1070 cm^{-1} increased considerably. The film contained mixtures of hexagonal and cubic phases with a larger hexagonal peak, as illustrated in Fig. 4(a). After 600 V, the c-BN peak is more or less constant. The shape, intensity and peak shift of the out-of-plane and in-plane vibrations of the h-BN phase were found to be dependent on bias voltage. At low voltage, the in-plane vibrational peak was at 1363 cm^{-1} and was split. As the bias voltage was increased, it shifted to a lower wavenumber (1278 cm^{-1} at 900 V), the intensity was decreased and the shape became more roundish. The out-of-plane vibrational peak was very sharp at low voltages. As the bias was increased, it also shifted to a lower wavenumber, became broader and nearly disappeared after 600 V. The c-BN peak exhibited no significant shift but became sharper at higher voltages. This is explained as follows: the shifting to the lower wavenumber and broadening of the peak indicate the decrease in the absorption strength of the lattice vibration of the hexagonal phase. In agreement with ref. 31, these facts show that the ions accelerated by self-bias to the substrate sputter selectively the hexagonal grains which have *c*-axis alignment. The growth of the hexagonal phase is resisted. At the same time, the volume fraction of the cubic phase increases, as shown in Fig. 4(b).

The signal at 1070 cm^{-1} is very close to the Si-O bond vibrational wavenumber 1103 cm^{-1} , which is typical for silicon dioxide film IR spectra. To identify the peak unambiguously, we deposited BN films for all types of plasma conditions on KBr. In addition to the hexagonal peaks, we detected the c-BN peak at 1090 cm^{-1} .

A sharp weak peak at 3430 cm^{-1} was also observed in all our films. This peak is attributed to N-H stretching vibrations, since the N-H peak is sharper than the O-H peak (owing to intermolecularly bonded O-H groups) which also occurs in this region [43]. This N-H vibration was found to be increased slightly with r.f. power and d.c. bias but exhibited no significant change up to 500 V r.f. self-bias beyond which the sharp peak was found to be superimposed on a broad peak. It seems that films grown above 500 V might contain some O-H group. At low substrate r.f. biases, a very weak broad peak at 2519 cm^{-1} , characteristic of B-H stretching, was also observed, but it disappeared after a 300 V r.f. self-bias. No such peak was observed in the inductively coupled system. Since the N-H bond

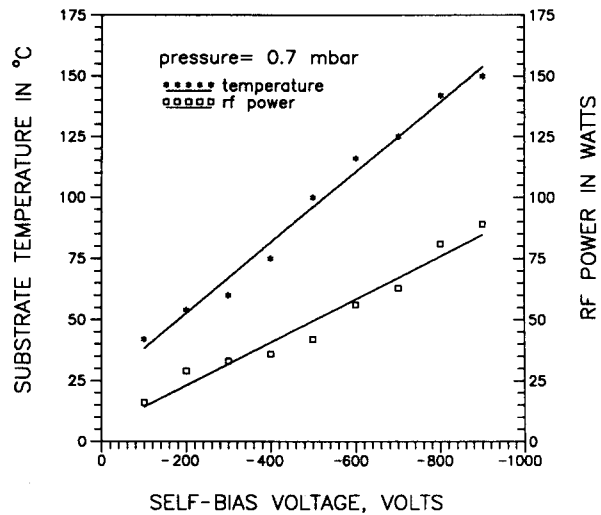


Fig. 5. The relation between the substrate temperature and r.f. power with the r.f. self-bias voltage.

strength is lower than the B-H bond strength (3.2 eV compared with 3.5 eV), removal of nitrogen-bonded hydrogen from the films will be relatively easier.

Figure 5 illustrates the influence of r.f. self-bias on the substrate temperature of the stainless steel substrate; the corresponding r.f. power is also shown. In both coupling systems, the substrate temperature was increased, although the highest temperature did not exceed $150\text{ }^{\circ}\text{C}$. The highest temperature for the inductively coupled system was $115\text{ }^{\circ}\text{C}$ at a r.f. power of 200 W.

The adhesion of the films was strongly dependent on bias voltage and r.f. power. Films deposited at a low bias and a low r.f. power adhered well to the substrates. In contrast, the films, deposited on silicon wafers using a high bias or a high power, tended to debond and break into minute fragments following exposure to atmospheric environments. It is believed that a high residual stress in the films causes this result.

4. Conclusions

We have deposited BN films consisting of a mixture of h-BN and c-BN using the $\text{BH}_3\text{-NH}_3$ adduct as a source material in a PACVD system. The films are likely to contain crystallites of the cubic phase embedded in a predominantly hexagonal matrix. Using only r.f. power or substrate bias, it was not found possible to deposit films which were entirely composed of c-BN, although it was shown that the relative amount of c-BN was directly dependent on r.f. power and substrate bias. The low substrate temperature and non-inclusion of any other particle energy source may not be sufficient to deposit hydrogen-free pure c-BN films in a PACVD

system, as discussed in ref. 40, but films produced by this method may have applications in microelectronics. The study shows that by a suitable choice of another activation source with moderate substrate temperature, the amount of c-BN in the film could be maximized. Further studies are being pursued to modify the existing system to obtain BN coatings consisting entirely of the cubic phase.

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