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Cubic boron nitride synthesis in low-density supersonic plasma flows

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We report on the growth of cubic boron nitride films on {100} silicon using a low density, supersonic plasma jet generated by a direct-current arc discharge expanded to low pressures. The arc discharge was operated on source gas mixtures of nitrogen and argon, with boron trichloride injected downstream of the expansion nozzle. The films were analyzed by infrared absorption and x-ray photoelectron spectroscopy. Phase selectivity was obtained by the application of a negative bias to the substrate so as to bombard the surface with energetic ions during deposition. The deposition process was found to be highly sensitive to substrate temperature and substrate bias voltage.

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Recent advances in the chemical vapor deposition (CVD) of diamond films¹⁻³ have prompted studies expanding CVD methods to the deposition of other metastable or refractory ceramics. In recent years we have developed a process of diamond film deposition using low-density, supersonic arcjet flows.⁴⁻⁸ The successful application of these arcjets to diamond synthesis led us to explore the possibility of synthesizing other refractory materials, in particular, cubic boron nitride (c-BN), boron carbide, and carbon nitride.⁹ In this letter we present an experimental investigation of c-BN growth on {100} silicon in low density, supersonic plasmas generated by an arcjet operating on mixtures of nitrogen (N₂) and argon (Ar) with boron trichloride (BCl₃) injected downstream into the expanding plasma plume.

As with carbon, boron nitride can exist as both hexagonal and cubic phases.¹⁰ Like diamond, c-BN is a chemically resistant, electrically insulating material possessing a high hardness and is used in applications where carbon-based materials are limited by oxidation.¹¹ c-BN has a wide, direct bandgap and can be doped with silicon or beryllium to form high-temperature n-type or p-type semiconductors.¹² It is nonreacting with ferrous metals at temperatures as high as 1500–1600K. There have been many reports in recent years of the use of low-pressure physical and chemical vapor deposition methods to synthesize c-BN films.¹⁰ Among these methods are laser ablation,¹³ low pressure plasma,^{14,15} sputtering,¹⁶ and ion-beam strategies.^{17,18} In all cases the deposited c-BN films have nanocrystalline structure and often contain a mixture of *sp*² and *sp*³ bonds, unlike the high quality, well developed growth habits now routinely observed in diamond synthesis. The observed differences between the CVD of diamond and c-BN are in part attributed to the fact that in synthesizing diamond graphite is easily etched by atomic hydrogen, thereby kinetically hindering its growth under conditions of large supersaturations of atomic hydrogen. In contrast, hexagonal boron nitride is not selectively etched by atomic hydrogen. An alternative means is therefore necessary to destabilize the hexagonal phase and to create an environment that favors c-BN growth. We have found that c-BN can be stabilized and grown in a low density, supersonic plasma jet at temperatures above ~500 °C

and with increased ion energy due to substrate biasing of –60 to –90 Volts.

The experimental facility used for the CVD of these thin films has been described in detail in previous publications⁴⁻⁸ and is only briefly described here. An arc discharge operating on N₂/Ar mixtures and in the 1-2 kW power range was expanded to low densities by way of a converging-diverging nozzle. BCl₃ was injected into the dissociated jet, and the reactive plasma impinged onto a thermally controlled {100} silicon substrate. The volumetric flow ratio of BCl₃ to N₂ was typically in the range of 0.1%–1%. Through a sequence of surface reactions which are not yet well understood, species containing boron and nitrogen condensed to form thin boron nitride films. The plasma source and substrate were mounted in a vacuum vessel capable of achieving an ultimate pressure of approximately 10⁻² Torr. During film deposition, pressures were in the range of 0.2–1 Torr. The substrate temperature was measured with a thermocouple in contact with the back surface of the wafer through a hole in a water-cooled copper mandrel onto which the wafer was mounted. The measured temperatures were expected to be approximately 50°C lower than the surface temperature owing to the finite heat conduction through the 0.5 mm thick wafer. The experimental setup allowed for the application of a negative bias to the substrate (negative in relation to the arcjet ground). In the deposition of c-BN, the negative bias is believed to lead to energetic ion bombardment and therefore subplantation and/or selective sputtering.^{19,20} This increased energy and momentum transfer to the surface during deposition is believed to increase the local density of the boron nitride and stabilize *sp*³ bonding.

Experiments were performed by varying operation parameters until a window of growth was found where the cubic phase could be stabilized. Initial studies at low substrate temperature (less than 400 °C) and no substrate bias resulted in growth of only hexagonal boron nitride (h-BN). Through further experiments it was determined that the c-BN could be deposited at elevated substrate temperatures (500–650 °C) with an applied substrate bias (–60 to –90 V) and with an N₂/Ar ratio of 1:1. These films consisted mainly of c-BN. The growth boundary between h-BN and c-BN with this reactor was quite sensitive to both substrate temperature and bias voltage. This was not surprising since previous researchers have discovered the same sensitivity in other CVD methods.^{17,18}

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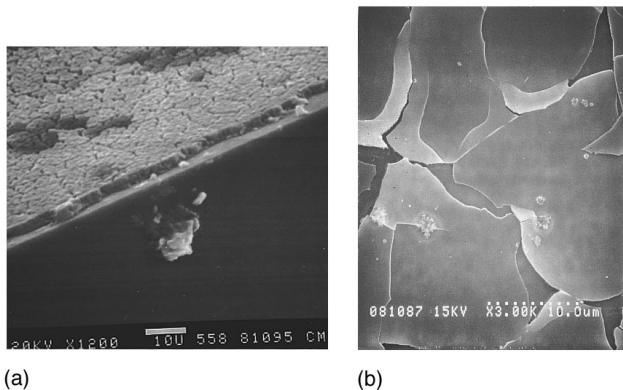


FIG. 1. Scanning electron micrographs of boron-nitride films: (a) typical h-BN film; (b) typical c-BN film.

Figure 1 shows representative SEM images of both h-BN and c-BN films. The cross-sectional view of the h-BN film shown in Fig. 1(a) reveals a “cauliflower-type” morphology. The top-view of a typical c-BN film as shown in Figure 1(b) reveals a tendency for film cracking and delamination which we attribute to the presence of a compressive film stress. The absence of any distinct morphological features indicates that the c-BN is amorphous or nanocrystalline with grain sizes less than 100 nm.

The films were characterized by Fourier transform infrared spectroscopy. Both the cubic and hexagonal phases of boron nitride have very characteristic infrared (IR) transmittance and reflectance spectra. These spectra are dominated by the Brillouin zone-center c-BN transverse optical (TO) mode at 1055 cm^{-1} , the h-BN longitudinal optical (LO) mode at 770 cm^{-1} , and the hBN (TO) mode at 1383 cm^{-1} .²¹ The presence of the silicon wafer must be considered when the IR transmittance spectra are evaluated because of the possible presence of silicon oxide (SiO_2) at the BN/silicon interface or on the back side of the silicon wafer. SiO_2 has an absorption feature very near the c-BN absorption peak at 1072 cm^{-1} .²² An improper account of the presence of SiO_2 may lead to an overprediction or misinterpretation of the amount of c-BN present in the film. It may be desirable to use IR reflectance spectroscopy at low grazing angles, rather than near-normal IR transmittance spectroscopy, so as to be more sensitive to the BN layer and less sensitive to SiO_2 that may be present at the interface. We chose to study the IR transmittance spectra and correct for the presence of SiO_2 . Only minor corrections resulted for the films containing mostly c-BN. Corrections were performed by subtraction of a reference spectrum. The silicon wafer used for this reference was exposed to plasma conditions similar to the c-BN growth conditions with the exception being that no BCl_3 was present and no BN film was grown on the wafer. In order to estimate the relative volumetric fractions of the cubic and hexagonal phases we formulated a theoretical transmittance spectrum of the model BN/Si system using optical constants taken from the literature.^{23–26} Total film thickness and the volumetric ratio of c-BN to h-BN were varied as parameters until agreement between the measured and calculated transmittance spectra was obtained. Details of the IR transmittance simulation will be provided in a future paper.²⁷

Figure 2 shows representative IR spectra of both the

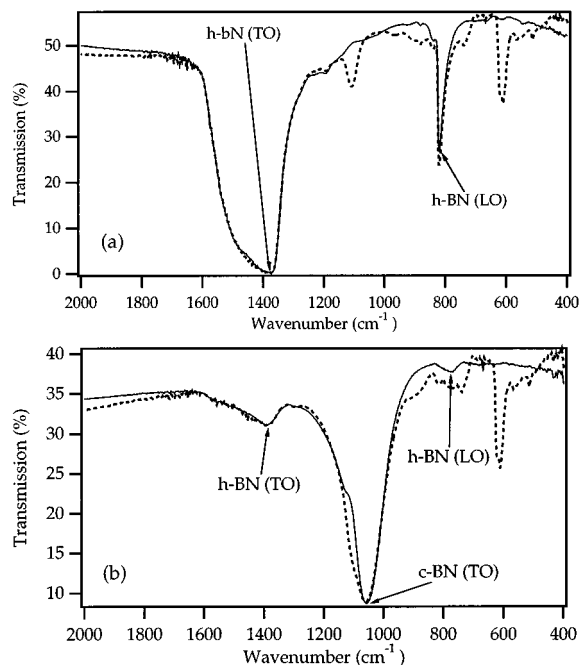


FIG. 2. Infrared transmittance spectra of deposited h-BN (a) and c-BN (b) films. The solid lines are of spectra corrected for silicon dioxide interference. The dashed lines are uncorrected spectra.

h-BN and c-BN films. Fig. 2(a) is an IR transmittance spectrum of a film grown with no substrate bias and a substrate temperature of approximately $600\text{ }^\circ\text{C}$. This spectrum is dominated by the LO and TO absorption features of h-BN. There are no discernible features associated with c-BN. Based on this and the x-ray photoelectron spectrum presented below, we conclude that this film is almost entirely h-BN. Also shown in Fig. 2 are the spectra before correction for the presence of SiO_2 . We see that the SiO_2 correction is minor and will have little effect on the general conclusions that can be drawn from these data. Figure 2(b) is an IR transmittance spectrum of a film grown with the same process conditions as in Fig. 2(a) but with a negative 60 Volt bias applied to the substrate. The effect of ion-bombardment is very apparent. In this case the spectrum is dominated by the c-BN absorption feature and shows very little absorption associated with the h-BN LO and TO modes. From our IR transmittance simulation, we predict this film to be $> 80\%$ c-BN by volume. Other experiments with various bias voltages were performed, and it was found that the cubic phase cannot be stabilized below approximately -40 V .

The elemental composition and film structure were also analyzed by x-ray photoelectron spectroscopy (XPS). It has been shown previously that the hexagonal and cubic phases of boron nitride have discernible features in both XPS and Auger spectroscopy.²⁸ Both h-BN and c-BN have bulk plasmon (BP) loss peaks at approximately 25 and 27 eV respectively, away from the B(1s) and N(1s) peaks. However, due to the difference in bonding between h-BN (sp^2) and c-BN (sp^3), only h-BN has a π plasmon loss peak at approximately 9 eV away from the B(1s) and N(1s) peaks. We use the presence of this feature as a “fingerprint” to further confirm the presence or absence of sp^2 bonding in the film.

XPS spectra of typical h-BN film deposited at low temperature ($300\text{ }^\circ\text{C}$) and without a substrate bias are shown in

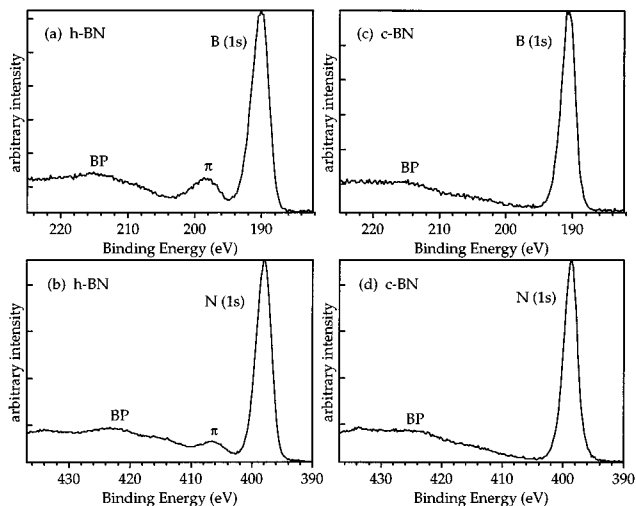


FIG. 3. XPS spectra (vicinity of N(1s) and B(1s) peaks) of typical films: charts (a) and (b) are spectra for h-BN; (c) and (d) are spectra for c-BN.

the top charts of Fig. 3. A survey scan of the film (not shown) was taken to determine the elemental composition. XPS analysis confirmed that the boron/nitrogen ratio is approximately 1:1 with some surface contamination of carbon ($\sim 7\%$) and oxygen ($\sim 3\%$). The amounts of C and O were greatly reduced when the surface was bombarded with energetic (5 keV, 10 mA) argon ions. The high resolution scans of the B(1s) and N(1s) peaks shown in charts (a) and (b) of Fig. 3 were obtained prior to argon-ion exposure so as to not disrupt the nature of the bonding in the films. The B(1s) peak is centered at 191 eV and the N(1s) peak is at 398 eV, in good agreement with values in the published literature.²⁹ The bulk plasmon and the π plasmon loss peaks are present at ~ 25 eV and ~ 9 eV, respectively, away from the 1s peak in their expected positions for h-BN. The presence of the π plasmon peak and its relative intensity is consistent with that observed for a h-BN standard. This result, together with the infrared absorption data, supports the conclusion that these films are predominantly composed of h-BN.

Figure 3 also shows XPS spectra of a typical ($>80\%$ by volume) c-BN film. All of the c-BN films grown with substrate bias voltages of -60 to -90 V and substrate temperatures on the order of 500 - 650 °C had similar XPS spectra. Survey scans indicated a B/N ratio of 1:1 with C ($\sim 10\%$) and O ($\sim 10\%$) surface contamination. Once again, these contaminants could be greatly reduced by exposure to energetic argon ions. Charts (c) and (d) in Fig. 3 show high resolution scans of the B(1s) and N(1s) peaks. The B(1s) is centered at 191 eV and the N(1s) is at 399 eV. Both peaks have satellite bulk plasmon loss features at ~ 25 eV away from the main peak. However, it is apparent that there is no π plasmon peak for either the B(1s) or the N(1s) features, in contrast to what was seen in the h-BN films. This observation, together with the infrared absorption data, confirms that the films are composed mainly of the cubic phase.

To summarize, we have demonstrated the usefulness of low density, supersonic plasma jets in the synthesis of films composed mainly of c-BN. The films appeared to be nanocrystalline in morphology and had a substantial degree of compressive stress which lead to delamination and stress-

relief cracking. An assessment was made of the relative volume fraction of sp^2 and sp^3 bonding by infrared absorption spectroscopy. Films deposited under conditions in which a negative substrate bias of 60 - 90 V was applied, and at temperatures greater than 500 °C, had a substantial cubic content ($> 80\%$). A further confirmation of the phase quality of these cubic films was the absence of the π plasmon peak in the XPS spectra that is an identifying feature in films that are predominantly hexagonal in phase.

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