

# Chemical sputtering of ta-C: Implications for the deposition of carbon nitride

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The majority of attempts to synthesize the theoretically predicted superhard phase  $\beta$ -C<sub>3</sub>N<sub>4</sub> have been driven towards the use of techniques which maximize both the carbon  $sp^3$  levels and the amount of nitrogen incorporated within the film. However, as yet no attempt has been made to understand the mechanism behind the resultant chemical sputter process and its obvious effect upon film growth. In this work, however, the chemical sputtering process has been investigated through the use of an as-deposited tetrahedrally bonded amorphous carbon film with a high density nitrogen plasma produced using an rf-based electron cyclotron wave resonance source. The results obtained suggested the presence of two distinct ion energy dependent regimes. The first, below 100 eV, involves the chemical sputtering of carbon from the surface, whereas the second at ion energies in excess of 100 eV exhibits a drop in sputter rate associated with the subplantation of nitrogen within the carbon matrix. Furthermore, as the sample temperature is increased there is a concomitant decrease in sputter rate suggesting that the rate is controlled by the adsorption and desorption of additional precursor species rather than the thermal desorption of CN. A simple empirical model has been developed in order to elucidate some of the primary reactions involved in the sputter process. Through the incorporation of various previously determined experimental parameters including electron temperature, ion current density, and nitrogen partial pressure the results indicated that molecular nitrogen physisorbed at the ta-C surface was the dominant precursor involved in the chemical sputter process. However, as the physisorption enthalpy of molecular nitrogen is low this suggests that activation of this molecular species takes place only through ion impact at the surface. The obtained results therefore provide important information for the modeling and growth of high density carbon nitride. © 2001 American Institute of Physics. [DOI: 10.1063/1.1359170]

## I. INTRODUCTION

Plasma-based ion beam deposition techniques are of use in the synthesis of metastable thin film materials owing to their ability to produce well-defined ion fluxes of known composition and energy. To date, this has led to the synthesis of a number of superhard materials including ta-C,<sup>1</sup> ta-C:H,<sup>2</sup> and cubic-BN.<sup>3</sup> Considerable efforts have also been made to deposit another super-hard material, namely the hypothetical compound  $\beta$ -C<sub>3</sub>N<sub>4</sub>.<sup>4-9</sup>

The majority of the ion beam based methods used in carbon nitride deposition have employed the use of a filtered cathodic vacuum arc source (FCVA)<sup>5-7</sup> and either a Kaufmann<sup>8</sup> or Freeman<sup>4,9</sup> ion source for the carbon and nitrogen ion fluxes, respectively. While these sources can produce beams of sufficient energy to overcome the perceived activation barriers for  $\beta$ -C<sub>3</sub>N<sub>4</sub> formation, in all cases the resulting films are both amorphous and nitrogen deficient, with a maximum nitrogen content of approximately 45 at.%.<sup>9</sup> Several authors have postulated that this may be due to the formation of a volatile product such as CN, C<sub>2</sub>N<sub>2</sub>, or N<sub>2</sub> from the growth surface during ion bombardment, although the exact mechanism by which this was thought to

occur remained unclear.<sup>10-12</sup> In light of these observations a more rigorous study of the effect of nitrogen ion bombardment on the growth surface is required before generic growth mechanisms may be elucidated. The aim of this work, therefore, was to determine the effect of nitrogen ion bombardment on a previously deposited carbon target with a view to obtaining an insight into some of the processes involved in the ion beam deposition of carbon nitride.

## II. EXPERIMENT

The tetrahedrally bonded amorphous carbon (ta-C) films were prepared under standard conditions in a filtered cathodic vacuum arc (FCVA) system described previously.<sup>1</sup> Following deposition, the samples were cut into approximately 8 mm square sections before film thickness measurements were performed by ellipsometry (Gaertner Scientific L117). Thereafter the films were treated using a highly ionized low pressure nitrogen plasma produced by a novel electron cyclotron wave resonance (ECWR) source (DN150CF COPRA, CCR GmbH). Previous results from sources of this kind have suggested that when nitrogen is used as the precursor gas, both high plasma densities and high electron temperatures are obtained.<sup>13</sup> Therefore a degree of control of not only the ion energy but also of the composition of the ion

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flux is possible, as these are both intrinsically linked to the plasma density and the electron energy distribution function.

The first series of sputtering experiments investigated the effect of both the ion energy and ion current density on the surface carbon sputter rate and the sputter yield. Each sample was treated with a nitrogen plasma for a period of 1 min. During this procedure the nitrogen flow rate, rf power, chamber pressure, and substrate temperature were all maintained at 10 sccm, 300 W,  $2.5 \times 10^{-4}$  mbar, and 298 K, respectively. However, as the mean ion energy was varied between 50 and 135 eV there was a concomitant decrease both in ion current density ( $0.375\text{--}0.2\text{ mA/cm}^2$ ) and in the  $N^+/N^+ + N_2^+$  flux ratio (0.8–0.5) due to the power balance function of the source. The second set of experiments investigated the effect of a different plasma beam to substrate angles. This was performed in order to determine whether the carbon removal mechanism could be attributed predominantly either to physical sputtering or chemical etching. The beam angle was first varied from normal incidence ( $0^\circ$ ) to  $30^\circ$  and finally  $60^\circ$ . In each case the nitrogen flow rate, incident rf power, and substrate temperature were maintained at 10 sccm, 300 W and 298 K, respectively. In addition, the ion energy, ion current density, and the  $N^+/N^+ + N_2^+$  flux ratio were also fixed at 100 eV,  $0.225\text{ mA/cm}^2$ , and 0.58, respectively. The chamber pressure, however, was slightly higher than in the previous series of experiments ( $4 \times 10^{-4}$  mbar) owing to a slight change in pumping speed within the ultrahigh vacuum reactor. A further set of experiments investigated the effect of substrate temperature (298–691 K) on the surface carbon removal process. As in the previous series of experiments, the ion energy, ion current density,  $N^+/N^+ + N_2^+$  flux ratio,  $N_2$  flow rate, and chamber pressure were maintained at 100 eV,  $0.225\text{ mA/cm}^2$ , 0.58, 10 sccm, and  $4 \times 10^{-4}$  mbar, respectively. Gas-phase analysis was also performed during each of these experiments both by optical emission spectroscopy (Verity Scanview) and by mass spectrometry (Spectra International, Microvision Plus). This was performed in order to determine some of the most important gas-phase precursors and product species involved in the surface carbon loss process. Finally, following plasma treatment of each sample, changes in film thickness were determined by ellipsometry.

### III. RESULTS

Figure 1 shows the variation in sputter rate with energy of the incident ion flux. Despite a reduction in both the ion current density and the  $N^+/N^+ + N_2^+$  flux ratio, the carbon sputter rate was found to rise almost linearly until a maximum of 9 nm/min was obtained at an ion energy of  $\sim 100$  eV. Thereafter, the rate fell dramatically before reaching a value of 5 nm/min at an ion energy of 135 eV. The sputter yield (see Fig. 2) calculated using a surface carbon atom density of  $2.9 \times 10^{15}$  atoms/cm<sup>2</sup> exhibits more pronounced behavior, presumably as it takes into account the source dependant variation in ion current density with ion energy. These results therefore suggest the presence of two distinct ion energy dependent regimes. The first, at ion energies between 50 and 100 eV, is dominated by the ion energy

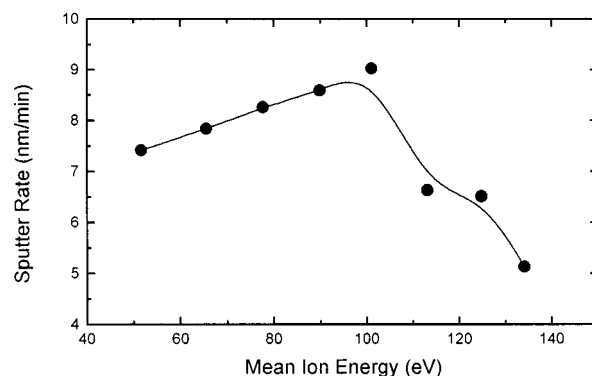


FIG. 1. Variation in the sputter rate as a function of the mean ion energy.

enhanced removal of carbon from the ta-C film surface, whereas the second, at ion energies between 100 and 135 eV, appears to involve the penetration of a significant fraction of the incident ion flux into the ta-C matrix itself. There is also a striking variation in the surface carbon removal rate with a change in the plasma beam to substrate angle. At normal incidence the rate is of the order of 12 nm/min, although this first rises to 13 and then to 15 nm/min as the plasma beam to substrate angle was increased to  $30^\circ$  and  $60^\circ$ , respectively. This confirms the existence of a sputter process as pure chemical etch processes exhibit identical carbon removal rates irrespective of the irradiation angle. Perhaps the most interesting result, however, was the decrease in sputter rate with an increase in substrate temperature from 12 nm/min at 298 K to 1.5 nm/min at 691 K as is shown in Fig. 3. This behavior cannot be explained by a simple physical sputtering mechanism, however, as simple sputtering processes are temperature independent. It is more likely therefore that a chemical sputtering mechanism is responsible whereby an additional chemical precursor is required to enhance the sputter rate. Hence as the substrate temperature and therefore the precursor desorption rate is increased there is a concomitant decrease in the observed sputter rate. This would also explain the anomalous variation in sputter rate with increasing chamber pressure as observed in the first two series of experiments (9 nm/min at 100 eV and  $2.5 \times 10^{-4}$  mbar compared with 12 nm/min at 100 eV and  $4 \times 10^{-4}$  mbar).

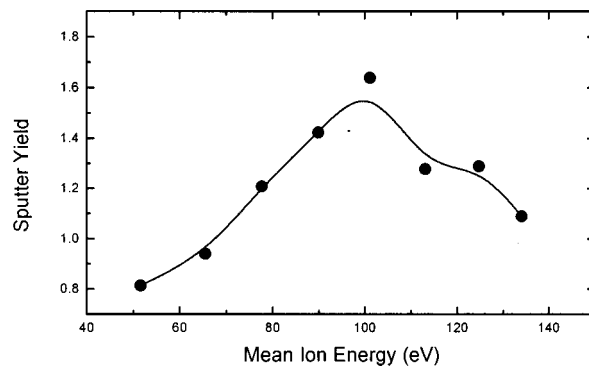


FIG. 2. Variation of the sputter yield as a function of the mean ion energy.

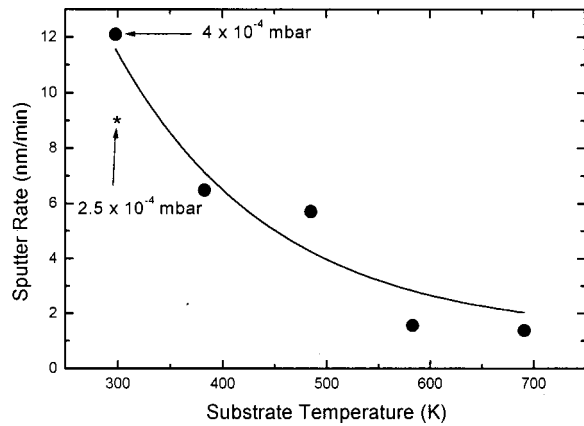


FIG. 3. Plot of the reduction in sputter rate with an increase in substrate temperature.

A representative optical emission spectrum from a nitrogen plasma during sample treatment is shown in Fig. 4. Spectral bands indicative of the presence of atomic nitrogen (625, 645, and 745 nm), the  $N_2^+$  molecular ion (391 and 428 nm), and both the first (540, 590, 660, and 755 nm) and second positive (337, 380, 400, and 420 nm) systems of neutral  $N_2$  were observed for each experiment, in addition to a band associated with the CN violet system (388 nm).<sup>14-16</sup> Following normalization of the N,  $N_2^+$  first negative,  $N_2$  second positive and CN bands (at 675, 391, 400, and 388 nm, respectively) with respect to the  $N_2$  first positive band at 660 nm some subtle variations in the intensity of these transitions and hence species concentrations were observed. These spectral variations as a function of incident ion energy are shown in Fig. 5. If we assume concentrations are monotonically related to emission intensities, then the results indicate a decrease in the atomic nitrogen concentration with an increase in incident ion energy due to the power balance function of the source and therefore this suggests that atomic nitrogen does not play a dominant role in the chemical sputter process. The  $N_2$  second positive intensity was found to mirror that of the  $N_2^+$  first negative system, providing further support to the recent suggestion that the  $N_2$  second positive system can be generated through the radiative recombination of an electron with a ground state  $N_2^+$  molecular ion.<sup>15</sup> In

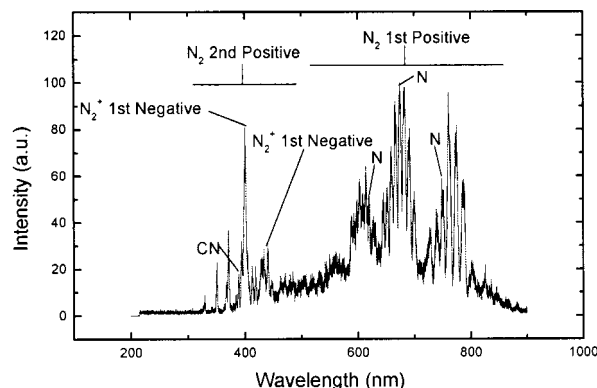


FIG. 4. Representative optical emission spectrum from a nitrogen plasma at an  $N_2$  flow rate, rf power, and chamber pressure of 10 sccm, 300 W, and  $2.5 \times 10^{-4}$  mbar, respectively.

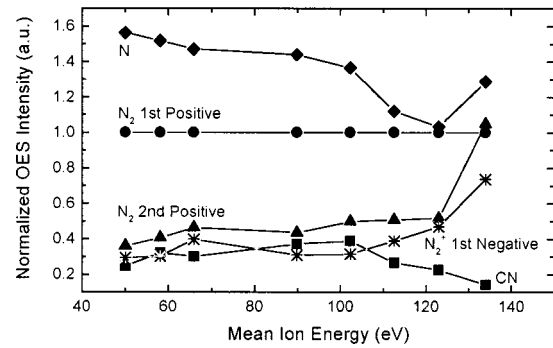


FIG. 5. Plot of the variation in normalized OES intensities for atomic nitrogen, N first positive, N second positive, N first negative, and CN against mean ion energy.

addition, conclusive evidence for the formation of CN as a chemical sputter product was obtained. The CN transition intensity was observed to first increase with ion energy up to a maximum at  $\sim 100$  eV before decreasing again in a manner reminiscent of the sputter rate.

The data obtained from the mass spectrometry of the gas-phase during plasma treatment also provided invaluable information on the nature and relevant concentrations of the chemical sputter products. Under a steady nitrogen flow only peaks associated with oxygen, water vapor, and molecular nitrogen were observed, even at substrate temperatures up to 691 K. However, upon treatment of the amorphous carbon film with the nitrogen plasma, extra peaks at  $m/e$  26, 27, and 52 were detected. These peaks have previously been attributed to the  $CN^+$  or  $C_2N_2^{2+}$ ,  $HCN^+$ , and  $C_2N_2^+$  species, respectively.<sup>10</sup> Figure 6 shows the effect of the incident ion energy on the  $CN^+$  or  $C_2N_2^{2+}$ ,  $HCN^+$ , and  $C_2N_2^+$  partial pressures. The results suggest that HCN is the dominant product species in the gas phase. Similar behavior has been reported previously by Hammer and Gissler and has been associated with the high reactivity of the CN radical with either water vapor or hydrocarbon species adsorbed on the chamber walls.<sup>10</sup> Consequently, both peaks were found to exhibit a slow increase in intensity until a maximum was obtained at an ion energy of  $\sim 100$  eV. Nevertheless, the peak at  $m/e$  52, while exhibiting an intensity over two orders of magnitude lower than that observed for CN, gradually

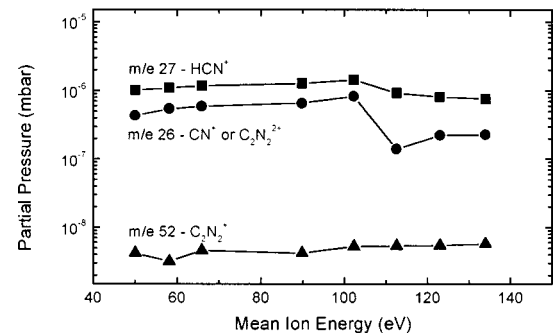


FIG. 6. Plot of the variation in  $HCN^+$ ,  $CN^+$  or  $C_2N_2^{2+}$ , and  $C_2N_2^+$  partial pressures versus mean ion energy.

increased in intensity across the entire ion energy range. This suggests that  $C_2N_2$  is unlikely to be formed through the dimerization of CN in the gas phase but is more probably produced through a direct surface ballistic ejection process.

#### IV. DISCUSSION

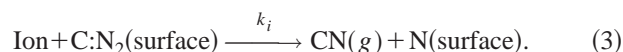
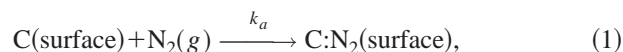
The sputter yield can be defined as the number of ballistically ejected particles per ion incident at the surface. It is determined by the extent of momentum transfer, which takes into account the masses of both the incident ion and the surface bound atom, the angle of incidence at the target surface, the kinetic energy of the ion, and the heat of sublimation of the target material itself.<sup>17</sup> As such it is rather insensitive to the local chemical bonding environment, and for most materials is of the order of 0.1–0.5 at energies below  $\sim 150$  eV.<sup>18</sup> Nevertheless, it increases with an increase in ion energy before it either levels off or falls as the penetration and entrapment probabilities become significant. The experimental results obtained in this work, however, have indicated yields as large as 1.64 at an ion energy of only 100 eV. Such high values are more indicative of chemical sputtering where the plasma supplies both chemical precursors and ion species to the surface. In some cases the damage induced by ion bombardment is sufficient to promote an increase in the reactivity of the surface towards either incident neutral radicals or existing chemisorbed or physisorbed species, hence the observed increase in rate when compared to simple physical sputtering mechanisms.

In the case of a nitrogen plasma, both atomic and molecular nitrogen may become adsorbed at the carbon surface. At low surface coverages atomic nitrogen chemisorption takes place readily owing to the exothermic nature of C–N bond formation, providing that a vacant site is present. Such a surface site is expected to take the form of a dangling bond formed through carbon to carbon bond scission associated with previous high energy ion impact. However, chemisorption also thermodynamically favors the maximization of the coordination between the nitrogen ad-atom and the carbon surface. This is particularly important at high temperatures, as simple Gibbs free energy calculations using both the surface chemistry data reported by Coltrin and Dandy<sup>19</sup> and the CHEMKIN thermodynamic database<sup>20</sup> suggest that the formation of the  $C\equiv N$  surface moiety is thermodynamically unfavorable at temperatures above 250 °C. Physisorption processes are less energetically expensive and result from simple Van der Waals interactions between the nitrogen adsorbates and the carbon surface. As these interactions are relatively weak, the energy released during physisorption is very small and is roughly of the same order as the enthalpy of condensation. Indeed, reported values in the literature suggest an enthalpy of condensation for molecular nitrogen on charcoal of  $\sim 0.13$  eV.<sup>21</sup> Such a small enthalpy change is insufficient to lead to bond cleavage and as a result the physisorbed nitrogen molecule retains its identity. Nevertheless, bond fragmentation can occur when an incident nitrogen ion transfers sufficient energy to raise the internal energy of the adsorbate above its dissociation threshold, which in the case of ground state  $N_2$  is  $\sim 9.9$  eV.<sup>16</sup> This therefore implies that

the physisorbed molecular nitrogen is activated through direct ion impact dissociation.

Experimental evidence presented in this study also suggests that the rate determining step, rather than the desorption of surface bound CN species, actually involves the desorption of physisorbed nitrogen, thus resulting in the depletion of neutral precursors from the surface. Consequently, we observe a decrease in the experimental sputter rate with an increase in substrate temperature and an increase in sputter rate as the chamber pressure and hence the neutral particle density are increased. This latter point may explain why no direct correlation between the atomic nitrogen concentration and the CN peak intensity was observed, either by optical emission spectroscopy or mass spectrometry. This was further illustrated following the construction of a simple empirical model based upon an Eley–Rideal reaction mechanism. It was assumed that the most important reactions in this process were the adsorption and desorption of neutral nitrogen species and the subsequent sputtering of CN units from the surface.

A simplified reaction scheme can be described as follows:



If Langmuir kinetics are assumed then the rate of change of surface coverage  $\theta$  (with an area density  $n'_0$ ) is therefore

$$\frac{\partial \theta}{\partial t} = k_a n_{N_2} (1 - \theta) - k_d \theta - Y_i k_i n_i \theta = 0. \quad (4)$$

Consequently,

$$\theta = \frac{k_a n_{N_2}}{k_a n_{N_2} + k_d + Y_i k_i n_i}, \quad (5)$$

where  $k_a$ ,  $k_d$ , and  $k_i$  are the adsorption, desorption, and ion impingement rate constants,  $n_{N_2}$  and  $n_i$  are the neutral nitrogen and nitrogen ion densities, respectively, and  $Y_i$  is the sputter yield. The rate constant  $k_a$  can be defined by

$$k_a = \left( \frac{1}{4} \right) \left( \frac{8kT}{\pi M_a} \right)^{1/2} \left( \frac{1}{n'_0} \right), \quad (6)$$

where  $k$  is the Boltzmann constant,  $T$  is the gas temperature, and  $M_a$  is the mass of the adsorbate.<sup>22</sup> The rate constant  $k_d$  takes its usual Arrhenius form.

Finally, the ion impingement rate constant  $k_i$  was obtained from

$$k_i = \left( \frac{\mu_B}{n'_0} \right) = \left( \frac{eT_e}{M_i} \right)^{1/2} \left( \frac{1}{n'_0} \right), \quad (7)$$

where  $\mu_B$  represents the Bohm velocity,  $e$  is the charge on the electron,  $T_e$  is the electron temperature, and  $M_i$  is the mass of the ion.<sup>22</sup> As the mass spectrometry results indicated that in the absence of a nitrogen plasma there was no thermal desorption of either carbon or carbon containing species

from the surface, then the flux of CN units leaving the ta-C film as a consequence of ion bombardment can be denoted by

$$\Gamma_{\text{CN}} = Y_i k_i n_i \theta n_0' \quad (8)$$

Hence the vertical sputter rate can be defined as

$$E_v = \left( \frac{\Gamma_{\text{CN}}}{n_C} \right), \quad (9)$$

where  $n_C$  is the atomic density of the film ( $\sim 1.556 \times 10^{29} \text{ m}^{-3}$  for ta-C of density  $\sim 3.1 \text{ g/cm}^3$ ). Under the experimental conditions described earlier,  $n_0' = 2.9 \times 10^{19} \text{ m}^{-2}$ ,  $n_N$  ranges between  $6.68 \times 10^{18}$  and  $1.01 \times 10^{19} \text{ m}^{-3}$  depending upon the chamber pressure, and  $n_i$  is approximately  $6.10 \times 10^{15}$  to  $1.18 \times 10^{16} \text{ m}^{-3}$  depending upon the ion current density. Based upon previous Langmuir probe studies, an electron temperature of 5.6 eV was used,<sup>13</sup> hence  $k_a$  and  $k_i$  values of  $4.10 \times 10^{-18}$  and  $2.15 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$  were obtained. By incorporating the experimental sputter rates at 298 and 691 K and by remembering that the sputter yield is independent of substrate temperature,<sup>17</sup> the desorption rate constants were then estimated retrospectively. This yielded values of 55.7 and  $865.7 \text{ s}^{-1}$  at 298 and 691 K. Furthermore, as desorption processes follow a strict Arrhenius temperature dependence, the activation enthalpy for desorption was calculated through the solution of two simultaneous Arrhenius equations. This yielded an enthalpy of desorption of  $\sim 0.12 \text{ eV}$  which compares well with data previously reported in the literature for molecular nitrogen on charcoal.<sup>21</sup> As further data pertaining to the molecular nitrogen concentration, ion density, and sputter yield were incorporated into the model, close agreement was found between the theoretically predicted and experimentally observed results demonstrating, to a first order, the model's validity. Indeed, the average error observed between the theoretical and experimental sputter rates was of the order of 5%.

The subplantation of nitrogen into the ta-C film was detected through the observation of a maximum in both the sputter rate and sputter yield as a function of ion energy. This maximum was observed at an energy of  $\sim 100 \text{ eV}$  and is indicative of a sharp rise in the ion penetration fraction through a decrease in the collision cross section. Furthermore, it is well-known that the penetration fraction is a function of the energy per incident ion, the penetration threshold, and an empirically determined spread parameter.<sup>23</sup> As such it can be described by

$$f = 1 - \exp\left(\frac{-(E - E_1)}{E_2}\right), \quad (10)$$

where  $E$  is the energy per atomic nitrogen ion,  $E_1$  is the penetration threshold energy, and  $E_2$  is the spread parameter, respectively. Consequently, if we use a penetration threshold intermediate in energy between 100 and 110 eV based upon our experimental results and a value of the spread parameter for ballistic processes in carbon of 16 eV, then the penetration fraction increases dramatically from 0 at an ion energy of 100 eV up to 0.27 at an energy of 110 eV. The net result, therefore, is a decrease in the overall number of ion species

available for the sputtering of carbon from the film surface, hence the experimental sputter rate is appropriately reduced.

## V. IMPLICATIONS FOR THE DEPOSITION OF CARBON NITRIDE

The crystal lattice of  $\beta\text{-C}_3\text{N}_4$  is reputed to consist of sixfold rings of alternating C–N bonds.<sup>24</sup> Random covalent networks, however, contain odd-membered rings which require like atom (C–C or N–N) bonds.<sup>25</sup> As the C–N bond strength is intermediate between the N–N and C–C bond strengths (285 cf. 160 and 356 kJ/mol, respectively<sup>26</sup>) this stabilizes the amorphous phase of carbon nitride with respect to crystalline  $\text{C}_3\text{N}_4$ . Furthermore, as the C–C bond is the most thermodynamically stable bond in an  $sp^3$  hybridized amorphous  $\text{CN}_x$  network this suggests that highly tetrahedrally coordinated carbon nitride will also be nitrogen deficient. One final point pertaining to the low nitrogen content of these carbon nitrides may arise as a consequence of the greater strength of the  $\text{N}\equiv\text{N}$  bond compared with the  $\text{C}\equiv\text{N}$  bond (945 cf. 770 kJ/mol<sup>26</sup>). Coupled with the high volatility of  $\text{N}_2$  compared with CN this accounts for the preferential sputtering of N from the surface during ion bombardment.<sup>4</sup>

The ionicity of the C–N bond is also expected to play a role in determining the crystallinity of ion beam deposited carbon nitride. Solids with ionicities above a critical value of  $\sim 0.43$  have been shown to crystallize following ion bombardment.<sup>27</sup> Therefore as both the Pauling and Cohen ionicities of the C–N bond are very low (0.06 and 0.22, respectively<sup>28,29</sup>) it is expected that amorphous ta- $\text{CN}_x$  rather than crystalline  $\text{C}_3\text{N}_4$  will be deposited through the use of ion beam based techniques.

Our results suggest that high nitrogen content material will only be synthesized if chemical sputtering at the growth surface can be minimized. This can be accomplished by the use of a mass selected ion beam deposition system in order to filter out neutral nitrogenated precursor species and also to provide a monochromatic beam of energy just above the penetration threshold but also below the  $sp^3$  to  $sp^2$  relaxation threshold. Furthermore, substrate temperatures in excess of  $250^\circ\text{C}$  should be used in order to help prevent the formation of the terminal  $\text{C}\equiv\text{N}$  moiety and therefore increase the levels of nitrogen coordination with the remainder of the amorphous network. This type of behavior has previously been reported for the “hot” ( $500^\circ\text{C}$ ) implantation of nitrogen into glassy carbon.<sup>30</sup>

## VI. CONCLUSIONS

The effect of nitrogen ion bombardment on a tetrahedrally bonded amorphous carbon film has been investigated using a high density electron cyclotron wave resonance plasma source. The results indicated that at low ion energies (50–100 eV), the predominant ion–surface interaction involved the chemical sputtering of carbon. This process was controlled principally by the neutral nitrogen density and the ion energy. Furthermore, the sputter rate was observed to decrease with increasing substrate temperature indicating that the carbon loss mechanism was heavily dependent on the surface concentration of weakly adsorbed neutral precursor

tor species. A simple chemical kinetic model was also constructed and indicated that molecular nitrogen physisorbed at the carbon surface was the dominant precursor involved, which suggests that it was activated through ion-impact dissociation at the film surface. The results also indicated that at ion energies in excess of 100 eV there was a sharp increase in both the ion penetration and entrapment probabilities as the experimental sputter rate was observed to fall dramatically after this threshold was surpassed. Consequently, through a combination of low background neutral nitrogen concentrations, ion energies slightly in excess of the penetration threshold and substrate temperatures in excess of 250 °C, it is expected that a window for the synthesis of high density, high nitrogen content carbon nitride will exist.

## ACKNOWLEDGMENTS

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- <sup>1</sup>P. J. Fallon, V. S. Veerasamy, C. A. Davis, J. Robertson, G. A. J. Amaratunga, W. I. Milne, and J. Koskinen, *Phys. Rev. B* **48**, 4777 (1993).
- <sup>2</sup>M. Weiler, S. Sattel, T. Giessen, K. Jung, H. Ehrhardt, V. S. Veerasamy, and J. Robertson, *Phys. Rev. B* **53**, 1594 (1996).
- <sup>3</sup>N. Tanabe and M. Iwaki, *Diamond Relat. Mater.* **2**, 512 (1993).
- <sup>4</sup>S. S. Todorov, D. Marton, K. J. Boyd, A. H. Al-Bayati, and J. W. Rabalais, *J. Vac. Sci. Technol. A* **12**, 3192 (1994).
- <sup>5</sup>J. Koskinen, J. P. Hirvonen, J. Levoska, and P. Torri, *Diamond Relat. Mater.* **5**, 669 (1996).
- <sup>6</sup>L. Wan and R. F. Egerton, *Thin Solid Films* **279**, 34 (1996).
- <sup>7</sup>A. R. Merchant, D. G. McCulloch, D. R. McKenzie, Y. Yin, L. Hall, and E. G. Gerstner, *J. Appl. Phys.* **79**, 6914 (1996).

- <sup>8</sup>C. Spaeth, M. Kuhn, U. Kreissig, and F. Richter, *Diamond Relat. Mater.* **6**, 626 (1997).
- <sup>9</sup>K. J. Boyd, D. Marton, S. S. Todorov, A. H. Al-Bayati, J. Kulik, R. A. Zuhr, and J. W. Rabalais, *J. Vac. Sci. Technol. A* **13**, 2110 (1995).
- <sup>10</sup>P. Hammer and W. Gissler, *Diamond Relat. Mater.* **5**, 1152 (1996).
- <sup>11</sup>W. T. Zhang, H. Sjostrom, I. Ivanov, K. Z. Xing, E. Broitman, W. R. Salaneck, J. E. Greene, and J. E. Sundgren, *J. Vac. Sci. Technol. A* **14**, 2696 (1996).
- <sup>12</sup>J. A. Taylor, G. M. Lancaster, and J. W. Rabalais, *J. Am. Chem. Soc.* **100**, 4441 (1978).
- <sup>13</sup>N. A. Morrison, S. Muhl, S. E. Rodil, A. C. Ferrari, W. I. Milne, J. Robertson, and M. Nesladek, *Phys. Status Solidi A* **172**, 79 (1999).
- <sup>14</sup>R. M. Park, *J. Vac. Sci. Technol. A* **10**, 701 (1992).
- <sup>15</sup>K. J. Clay, S. P. Speakman, G. A. J. Amaratunga, and S. R. P. Silva, *J. Appl. Phys.* **79**, 1 (1996).
- <sup>16</sup>R. P. Vaudo, J. W. Cook, Jr., and J. F. Schetzina, *J. Cryst. Growth* **138**, 430 (1994).
- <sup>17</sup>D. A. Glocker and S. Ismat Shah, *Handbook of Thin Film Process Technology* (Institute of Physics University of Reading, Berkshire, 1995), A3.0.1a.
- <sup>18</sup>P. A. Redhead, J. P. Hobson, and E. V. Kornelsen, *The Physical Basis of Ultrahigh Vacuum* (American Vacuum Society, 1993), p. 186.
- <sup>19</sup>M. E. Coltrin and D. S. Dandy, *J. Appl. Phys.* **74**, 5803 (1993).
- <sup>20</sup>R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia Report No. SAND87-8215B, 1990 (unpublished).
- <sup>21</sup>P. W. Atkins, *Physical Chemistry* (Oxford University, New York, 1990), p. 873.
- <sup>22</sup>M. A. Lieberman and A. J. Lichtenburg, *Principles of Plasma Discharges and Materials Processing* (Wiley, New York, 1994), p. 481.
- <sup>23</sup>J. Robertson, *Radiat. Eff. Defects Solids* **142**, 63 (1997).
- <sup>24</sup>A. Y. Liu and M. L. Cohen, *Science* **245**, 841 (1989).
- <sup>25</sup>J. Robertson, *Diamond Relat. Mater.* **5**, 519 (1996).
- <sup>26</sup>F. A. Cotton, G. Wilkinson, and P. L. Gaus, *Basic Inorganic Chemistry* (Wiley, New York, 1986), p. 9.
- <sup>27</sup>H. M. Naguib and R. Kelly, *Radiat. Eff.* **25**, 1 (1974).
- <sup>28</sup>A. Garcia and M. L. Cohen, *Phys. Rev. B* **47**, 4215 (1993).
- <sup>29</sup>A. Garcia and M. L. Cohen, *Phys. Rev. B* **47**, 4221 (1993).
- <sup>30</sup>A. Hoffman, R. Brener, I. Gouzman, C. Cytermann, H. Geller, L. Levin, and M. Kenny, *Diamond Relat. Mater.* **4**, 292 (1995).