

Near edge x-ray absorption fine structure study of aligned π -bonded carbon structures in nitrogenated ta-C films

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Polarization dependent studies of near edge x-ray absorption fine structure (NEXAFS) show evidence for the presence of aligned π -bonded carbon structures and the formation of a nonplanar CN phase in tetrahedral amorphous nitrogenated carbon (ta-CN) films deposited at room temperature. Moreover, the analysis of NEXAFS data as a function of nitrogen concentration and annealing temperature leads to a comprehensive assignment of the local CN bonding configurations in these ta-CN films and suggests an unusual and almost thermally stable nitrogenated carbon structure. © 2006 American Institute of Physics. [DOI: 10.1063/1.2173046]

I. INTRODUCTION

During the last decade, many attempts have been made to synthesize the crystalline phase of carbon nitride (CN_x) films, based on the theoretically predicted superior mechanical properties of β - C_3N_4 in comparison with those of diamond.¹ On the other hand, tetrahedral amorphous carbon nitride (ta-CN) films having excellent properties such as high hardness, low friction, and chemical inertness,²⁻⁴ have attracted technologically important industries, such as protective coatings for magnetic storage devices and electron field emission devices.⁵⁻⁷ However, to date, there also exists a major difficulty in identifying the local structure of ta-CN films due to the complexity of the different hybridizations present. The Raman and infrared spectroscopies have often been used to determine the structure of CN_x films,⁸⁻¹¹ but the information gathered has been qualitative and limited and therefore, more detailed studies of the local bonding configurations within ta-CN films using near edge x-ray absorption fine structure (NEXAFS) spectroscopy are needed.¹²⁻¹⁹ Despite little or no evidence for a crystalline phase of β - C_3N_4 being established, the debate on the possible substitutional and nonsubstitutional structures of CN_x films continues.²⁰ In parallel, for a long time researchers have attempted to establish aligned π -bonded structures in amorphous carbon films by several means such as thermal annealing, ion irradiation, and nitrogen incorporation.^{20,21} In this way the development of local structures or aligned configurations has been attempted, in which NEXAFS played an important role on supporting these claims.^{13,21} In nitrogenated diamondlike or ta-CN films grown at room temperature, the evidence for oriented graphitic or aligned π -bonded carbon structures is

yet to be established. In this report, using angular dependence NEXAFS analysis we show that even though nitrogen does not form any oriented (or aligned and planar) C=N bonding configurations, an oriented graphitic carbon structure in the films grown at room temperature is very likely. In addition, we propose different features of the structure of hard ta-CN films prepared within a range of nitrogen concentrations at room temperature and demonstrate its thermal stability through vacuum annealing.

II. EXPERIMENT

The ta-CN films containing increasing concentrations of nitrogen ($0 \leq x \leq 12.5$) were deposited using a filtered cathodic vacuum arc (FCVA) technique. An arc current of 80 A under floating conditions was used to synthesize films of a thickness range between 75 and 100 nm. Details of the deposition technique can be found in a previous literature.¹⁰ Following deposition, the highest nitrogen content films (12.5 at. %) were subjected to rapid thermal annealing at temperatures ranging from 500 to 750 °C for 2 min, and then cooled to room temperature by flowing argon gas. NEXAFS measurements were performed at station 1.1 of the synchrotron radiation source facility, at Daresbury Laboratory, UK. The spectra at the C *K* edge and N *K* edges were recorded in the total electron yield mode and were normalized to the signal from a gold covered grid, recorded simultaneously. The resolutions of the beam line were 0.1 and 0.2 eV at the C *K* and N *K* edges, respectively. The jump of the C and N *K* edges at the ionization potential was fitted by an erf function multiplied by an exponential decay function, described by the following equation:¹²

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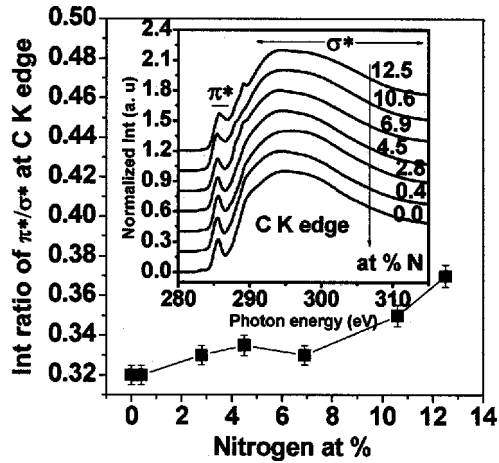


FIG. 1. Intensity ratio of π^*/σ^* peak at C K edge with nitrogen concentration. Inset: Variation of C K-edge spectrum with nitrogen concentration.

$$I_{\text{step}} = H \left\{ 0.5 + 0.5 \operatorname{erf} \left[\frac{(E - P)}{W/C} \right] \right\} \times \{ \exp - [d(E - P - W)] \} \quad E > P + W, \quad (1)$$

where H is the height of the function immediately above the step, E is the independent variable energy, P the position of the inflection point of the step (290 eV), W is the full width at half maximum (FWHM) of the step, d is the exponential decay coefficient, and C is a constant defined by $c = 2\sqrt{\ln 4}$. Although the ionization potential may be different for samples containing very different values of nitrogen, for simplicity it was considered as a constant. After subtracting the respective ionization jumps at both C K and N K edges, the resulting spectra were decomposed into several Gaussian peaks. In particular, the σ^* areas were fitted by asymmetric Gaussian peaks.

III. RESULTS AND DISCUSSION

We have analyzed the effect of (i) nitrogen concentration and (ii) thermal annealing on the structure of ta-CN films. However, we focus our study on the polarization dependence of NEXAFS for ta-CN films having ~ 12.5 at. % nitrogen concentration. The microstructure of these samples was also analyzed by Raman spectroscopy where the narrowing of the G linewidth and the increase of ID/IG ratio with nitrogen incorporation denoted an increase in the sp^2 fraction, as it is related to the bond angle disorder at sp^2 sites.^{8–11,22}

A. Effect of nitrogen concentration

The normalized C K edge spectra of ta-CN films, as a function of nitrogen content, are presented in the inset of Fig. 1. All spectra were normalized at the maximum height for comparison purposes. Two main features are identified in the C K edge spectra: (i) a sharp preedge peak (285 eV $< E < 288$ eV) known as π^* peak, due to the transitions from the orbital $1s$ to different π^* levels and (ii) a broader resonance at photon energy $E > 293$ eV corresponding to transitions from the $1s$ to empty σ^* states of sp^3 , sp^2 , and sp sites. It is quite difficult to distinguish the σ^* states as we have observed (Fig. 1) a broad σ^* feature that arises from a super-

position of the signatures of many different configurations (C–C, C=C, C=C, C=C, C=N, C=N, and C–N) in the matrix. The sharp π^* peak in carbon nitride films principally originates from C=C and C=N bonds.

The intensity ratio of π^*/σ^* peak at the C K edge, as a function of nitrogen content, is shown in Fig. 1. The π^*/σ^* ratio in the C K edge presents the relative contribution from C=C, C=N, C=C (if present), and C=N (if present) to the all possible σ^* states. This ratio is used to estimate the sp^2 domain configurations in amorphous carbon network. The error in the value of π^*/σ^* ratio arises from the uncertainty in the fitting of the π^* and σ^* peaks. For films having low nitrogen content the π^*/σ^* ratio did not change significantly. However, for films containing high nitrogen concentration, we noticed a clear increase in the π^*/σ^* ratio. It appears that for lower nitrogen content (< 7 at. %), the concentration of C=C and C=N relative to C–C and C–N bonds does not vary significantly, which in turn keeps the π^*/σ^* ratio unaffected (Fig. 1). In fact, at the higher N content films, both the sp^2 cluster size and distribution of sp^2 domain in the sp^3 matrix change due to the formation of CN bonds. The increase of π^*/σ^* ratio in the films having 10.6 and 12.5 at. % nitrogens is a signature of the formation of a graphitelike structure. We can also observe (Fig. 1) that the π^* peak width increases at higher nitrogen content films, indicating a fall of sp^3 bonding. The small peak around 289.5 eV in the films with 12.5 at. % N may originate from contamination related to either $1s \rightarrow \pi^*(\text{C–H})$ or $1s \rightarrow \pi^*(\text{C=O})$ transitions.^{12,23}

The normalized N K edge NEXAFS spectra of ta-CN films, as a function of nitrogen content, are shown in Fig. 2(a). From Fig. 2(a) we see that with increasing nitrogen content, the intensity of the π^* peak becomes higher. Two well-resolved peaks, denoted as N1 and N2, are observed in the energy range of 399–403 eV for all films and an additional peak denoted as N3 was clearly observed for the higher N content films [Fig. 2(a)]. These three resonance peaks were previously observed by several authors^{12–17} and seem to be typical in *a*-CN films with moderate nitrogen concentrations. These N1–N3 peaks in the N K edge indicate π^* bonding in three different environments. However, there is no unanimity in their assignment.¹⁸ The assignments, reported in the literature, were mainly based on studying model compounds such as pyridines, pyrroles, and nitrogen molecules. The peaks N1, N2, and N3 are suggested to be due to C=N, C=N, and substitutional nitrogen in graphite, respectively,^{13,17} however, for some cases due to the complex bonding environments in *a*-C:N films these assignments were not very clear.^{14,18} It has also been suggested that the peak N1 is related to the constrained CN bonds, the peak N2 to the pyridinelike double bonds, and the N3 to the presence of nitrogen atoms inside the graphite domains.^{16,24} Alternatively, these three peaks were considered to originate from a pyridinelike structure due to bonding, antibonding, and splitting states.¹² In the following section, we will discuss how these peaks change with N content and try to assign the bonding status of each of them.

The intensity of each π^* peak (N1, N2, and N3) to σ^* peak, as a function of nitrogen content, is shown in Fig. 2(b).

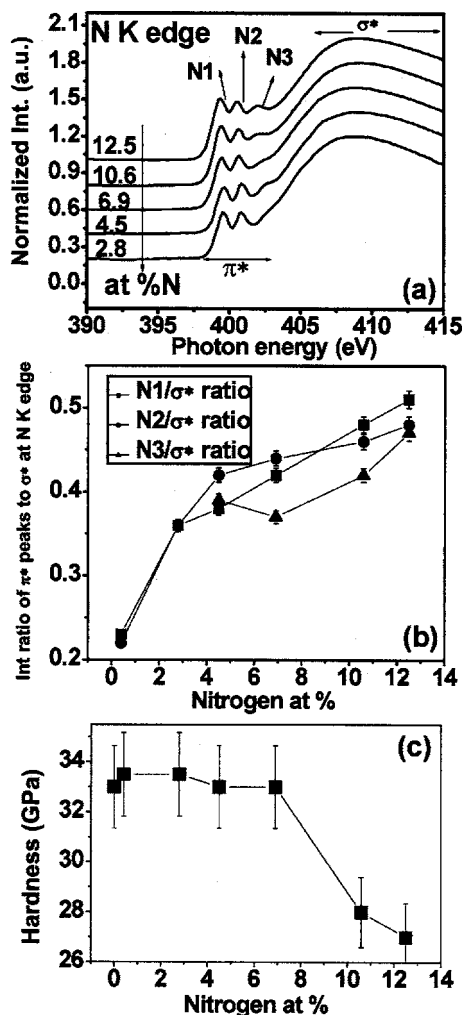


FIG. 2. (a) Variation of N K edge spectrum with nitrogen concentration in the films. (b) Intensity ratio of π^*/σ^* peak at N K edge with nitrogen concentration. (c) Variation of film hardness with nitrogen concentration.

All ratios increase with the N at. % indicating an increase of C=N bonds, graphitelike N substitutional bonds and C \equiv N bonds, if present. An increase of nitrogen concentration, hence an increase of nitrogen related features at the N K edges is responsible for the increase of these ratios. We assign the peak N1 to C=N bonds as reported by several authors.^{13,17} The origin of the peak N2 is difficult to assign, however, it could well be due to pyridinlike orbital splits¹² or N bonded to C with different functionalities.¹⁸ It is well known that the formation of C \equiv N bond is not favorable in lower N at. % films. We ruled out the possibility of the peak N2 being attributed to C \equiv N bonding as it is clear from Fig. 2(a) that the relative intensity of peak N2 to N1 decreases in higher N films, which may not be acceptable if we assign the peak N2 to C \equiv N bond. The peak N3 could be due to substitutional nitrogen in graphite structures or aromatic rings.^{13,17} The peak N3 appears at higher N content films indicating that graphitelike N substitution is not favorable at lower N concentrations. The increase of the intensity ratio of N3/ σ^* indicates the formation of a graphitelike structure at the higher N content films. The decrease of film hardness [see Fig. 2(c)] supports the formation of slightly graphitic structure in these films at high nitrogen concentration. We

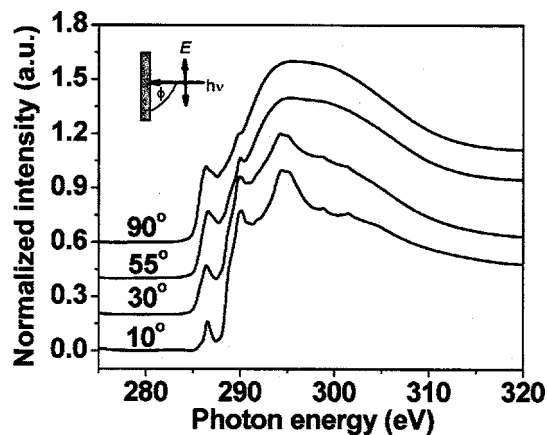


FIG. 3. Angular dependence of the C K edge of a ta-CN film containing 12.5 at. % N.

present more discussions on the assignment of N1–N3 peaks on the basis of annealing experiments in Sec. III C.

B. Angular dependence

A variation of the dipole transition intensity $C1s \rightarrow \pi^*$ or σ^* peak with the angle between the electric field polarization vector E and the normal to the plane of graphitic structure (if any) in the films can determine the spatial orientation of carbon structures (with respect to the incident x-ray beam). Figure 3 presents the angular dependence of the C K edge for CN_x films containing 12.5 at. % nitrogen and Fig. 4 illustrates three representative decomposed C K edge spectra. The direction of the incident beam or the electric polarization vector was varied with respect to the orientation of the thin film specimen and spectra recorded for incident angles (ϕ) between 10° and 90° (Fig. 3, left inset). The increase of the first peak (C1), a signature of graphite π^* resonance, with polarization confirms the presence of oriented graphitic structures in the film, which is aligned almost normal to the

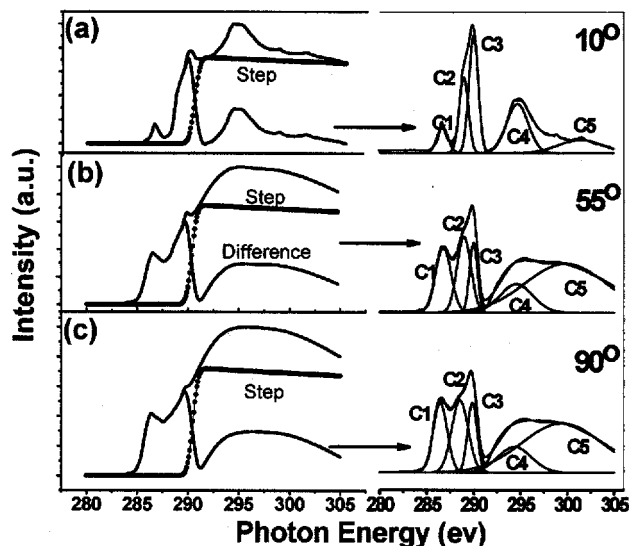


FIG. 4. Deconvoluted C K peaks for angles (a) 10, (b) 55, and (c) 90 deg, respectively, of a ta-CN film containing 12.5 at. % N. On the left compartment the solid line represents the resulting difference curve and the dotted line the fitted ionization step function.

plane of the sample. By increasing ϕ , the intensity of the $\pi^*_{C=C}$ resonance referred as C1 in Fig. 4 increases. At normal incidence of x ray, E is parallel to the substrate surface and along the axis of π^* orbitals. Hence the π^* resonance intensity will be the highest at normal incidence. On the other hand, at glancing angle, E is orthogonal to the π^* orbitals and has only a small projection onto the π^* orbitals, yielding a minimum intensity of the π^* resonance peak. This trend is opposite to the recently reported work for highly oriented pyrolytic graphite (HOPG),^{21,25} namely, an inverse dependence of the π^* intensity with increasing incidence angle.

The second resonance C2 does not correspond to $C=C \pi^*$ but randomly oriented CN. As a result no significant change of the second peak with polarization has been observed. The peak C3 attributed to a σ^* transition of the $C-H$ bonds that would originate from the absorption of hydrocarbon to the surface dangling bonds.²⁶ Since σ^* orbitals are orthogonal to the π^* orbitals an opposite trend of the intensity of the peaks with polarization is observed.

No clear evidence of oriented pyridine structure has been observed from the position and relative intensities of the $N K$ edge π^* peaks (not shown here). Also an absence of any significant polarization dependent variation of the $N K$ edge suggests that nitrogen could be present only within a randomly oriented π -bonded structure or nonplanar carbon structures in these films. As the relative intensity of the $N1-N3$ peaks does not match with a pyridine molecule structure, a very distorted or nonplanar molecular structure is expected. This is ultimately a nondoping configuration.¹⁵ However, it was clearly demonstrated that some amount of graphitization of ta-CN films from Raman and x-ray photoemission (XPS) studies, which resulted in a slight decrease of the film hardness for high nitrogen concentrations [Fig. 2(c)].¹⁰

The presence of the third peak (C3) at the $C K$ edge was not prominent at 0 at. % nitrogen films, which, however, is intensified with nitrogen concentration. Also an opposite angular dependence of C3 peak, which may be assigned to the surface defect,²⁶ compared with the C1 peak can be found. Besides, these results confirm that the C3 peak could be related to the σ^* transition.²⁶ Our angular dependence result clearly reflects that the surface dangling bond σ^*_{C-H} is also not randomly oriented.

C. Thermal annealing

An important property of ta-CN films is its thermal stability, with several studies being carried out on the structural changes taking place during annealing. Observations such as an increase in crystalline content and a relief of compressive stress within the films have been reported.^{8,27} NEXAFS studies on thermally annealed samples could further provide an insight on the local electronic structure of the nitrogenated films.

The normalized NEXAFS $C K$ - and $N K$ edge spectra of a ta-CN film containing 12.5 at. % N as a function of annealing temperature are illustrated in Figs. 5 and 6(a), respectively. One may note that the room-temperature spectrum of

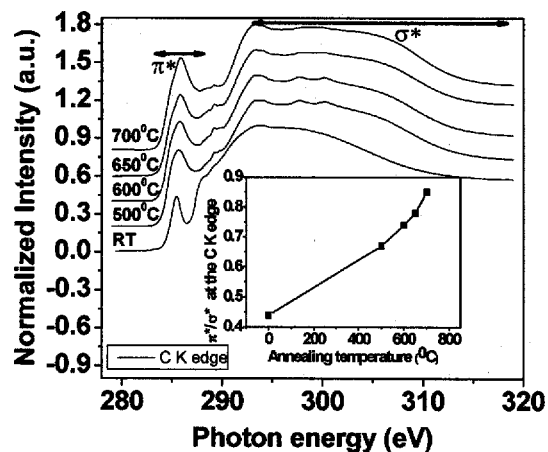


FIG. 5. Variation of $C K$ edge spectra of a ta-CN film containing 12.5 at. % N with annealing temperature. Inset: π^*/σ^* peak intensity as a function of temperature.

the $C K$ edge is not exactly the same as that presented for the 12 at. % N ta-CN film, in Figs. 1 and 3. The surface contamination peak observed at 289.5 eV in Figs. 1 and 3 is absent in Fig. 5. The reason for this inconsistency is that the spectra in Fig. 5 were taken on a different sample, deposited under the same conditions. Plotted in the inset of Fig. 5 is the intensity ratio of the π^*/σ^* peak at the $C K$ edge as a func-

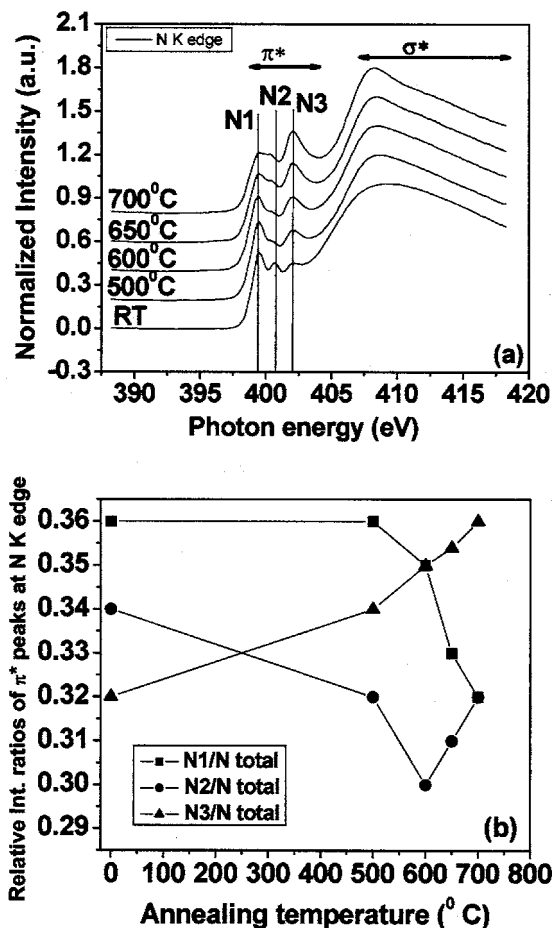


FIG. 6. (a) Variation of $N K$ edge spectra of a ta-CN film containing 12.5 at. % N with annealing temperature. (b) Variation of relative intensity ratios of π^* peak at $N K$ edge with annealing temperature.

tion of annealing temperature. A clear trend has emerged in which the intensity ratio is enhanced as the annealing temperature is increased. This trend can be explained by a lower contribution from the σ^* states due to the decrease in the sp^3 C–C and sp^3 C–N bonds as the temperature is raised. Another reason is due to the increase in the graphitelike CN bonds which have enhanced the intensity of the π^* resonance as well as an increase in the percentage of sp^2 C=C bonds compared with the sp^3 bonds. A shift of 0.3 eV for the π^* peak position was also observed as the temperature increased to 700 °C and is attributed to the formation of a graphitelike structure. We can also see in Fig. 6(a) that the σ^* features become narrower as the temperature is increased, indicating a fall in sp^3 bonding percentage. The tiny peak located at 289.3 eV originates from either $1s \rightarrow \pi^*(\text{C–H})$ or $1s \rightarrow \pi^*(\text{C=O})$ transitions.²⁴ In a recent study we attempt to explain the N1–N3 peaks at the N *K* edge for a batch of similar films.²⁸ From this study N3 has been clearly assigned to the distorted graphitic C=N structure based on the increase of the peak with annealing temperature.

Figure 6(a) shows the evolution of N1, N2, and N3 peaks of the N *K* edge spectra as a function of temperature. In the following section, we will discuss how these peaks change with annealing temperature and try to find out their origin from the temperature behavior. Figure 6(b) shows the relative intensity of each peak (peaks N1, N2, and N3) referred to the total intensity N1+N2+N3 as a function annealing temperature. We can see that several interesting patterns have emerged. As the temperature is increased the relative intensity of the N1 peak decreases, the intensity of N3 peak increases, whereas the N2 peak did not show any well-defined trend. The increase of the relative intensity of N3 peak indicates the formation of graphitelike structure with annealing temperature. The decrease of N1 peak implies that the C=N bond contribution is suppressed by the high temperature. As the temperature is increased the N is driven out of the film, which causes the lowering of C=N bonds and the endorsement of a richer graphitelike structure. By thermal annealing the degree of graphitization in the films increases and a small amount of nitrogen diffuses out from the bonded matrix. This is also supported by the narrowing of the σ^* features at the N *K* edge indicating a clear loss of C–N bonds. Interestingly, the degree of graphitization is not very high up to 500 °C suggesting that these films are almost thermally stable at that temperature.

IV. CONCLUSIONS

In this article we proposed how a modified structure of ta-C films can be obtained by nitrogen addition through an in depth analysis of NEXAFS spectra and proper assignment of the peaks at N *K* edge for a batch of films prepared with different nitrogen concentrations. Nitrogen addition in the ta-C films produces almost thermally stable sp^3 CN or distorted sp^2 CN structures, with some oriented sp^2 C. However, in the present case nitrogen atoms do not contribute to

aligned CN_x structures, contrary to the previous observations.^{20,21} Therefore, present results verify the formation of oriented C=C structure in nitrogenated ta-C films without any high energetic thermal treatment of the films.

- ¹A. Y. Liu and M. L. Cohen, *Science* **24**, 841 (1989).
- ²H. Sjöström, S. Stafström, M. Boman, and J. E. Sundgren, *Phys. Rev. Lett.* **75**, 1336 (1995).
- ³N. Hellgren, M. P. Johansson, E. Broitman, L. Hultman, and J. E. Sundgren, *Phys. Rev. B* **59**, 5162 (1999).
- ⁴H. Sjöström, L. Hultman, J. E. Sundgren, S. V. Hainsworth, T. F. Page, and G. S. A. M. Thunissen, *J. Vac. Sci. Technol. A* **14**, 56 (1996).
- ⁵G. A. J. Amaratunga and S. R. P. Silva, *Appl. Phys. Lett.* **68**, 2529 (1996).
- ⁶W. Xu, T. Fujimoto, L. Wang, T. Ohchi, and I. Kojima, *J. Vac. Sci. Technol. A* **22**, 6 (2003).
- ⁷V. S. Veerasamy, J. Yuan, G. A. J. Amaratunga, W. I. Milne, K. W. Gilkes, M. Weiler, and L. M. Brown, *Phys. Rev. B* **48**, 17954 (1993).
- ⁸A. C. Ferrari, S. E. Rodil, and J. Robertson, *Phys. Rev. B* **67**, 155306 (2003).
- ⁹K. W. R. Gilkes, S. Praver, K. W. Nugent, J. Robertson, H. S. Sands, Y. Lifshitz, and X. Shi, *J. Appl. Phys.* **87**, 7283 (2000).
- ¹⁰S. S. Roy, P. Papakonstantinou, R. McCann, G. Abbas, J. P. Quinn, and J. McLaughlin, *Diamond Relat. Mater.* **13**, 1459 (2004).
- ¹¹R. McCann, S. S. Roy, P. Papakonstantinou, S. C. Ray, and J. A. McLaughlin, *J. Appl. Phys.* **97**, 073522 (2005).
- ¹²D. A. Outka and J. Stohr, *J. Chem. Phys.* **88**, 3539 (1988); S. Bhattacharyya, M. Lübke, and F. Richter, *J. Appl. Phys.* **88**, 5043 (2000); S. Bhattacharyya, M. Lübke, P. R. Bressler, D. R. T. Zhan, and F. Richter, *Diamond Relat. Mater.* **11**, 8 (2002).
- ¹³I. Shimoyama, G. Wu, T. Sekiguchi, and Y. Baba, *Phys. Rev. B* **62**, R6053 (2000).
- ¹⁴I. Jimenez, W. M. Wong, D. K. Shuh, B. C. Holloway, M. A. Kelly, P. Pianetta, L. J. Terminello, and F. J. Himpsel, *Appl. Phys. Lett.* **74**, 2620 (1999).
- ¹⁵S. R. P. Silva, J. Robertson, G. A. J. Amaratunga, B. Rafferty, L. M. Brown, J. Schwan, D. F. Franceschini, and G. Mariotto, *J. Appl. Phys.* **81**, 2626 (1997); J. Robertson and C. A. Davis, *Diamond Relat. Mater.* **4**, 441 (1995).
- ¹⁶M. Mubumbila, B. Bouchet-Fabre, C. Godon, C. Marhic, B. Angleraud, P. Y. Tessier, and T. Minea, *Diamond Relat. Mater.* **13**, 1433 (2004).
- ¹⁷J. M. Ripalda *et al.*, *J. Chem. Phys.* **118**, 3748 (2003).
- ¹⁸S. E. Rodil and M. Muhl, *Diamond Relat. Mater.* **13**, 1521 (2004).
- ¹⁹C. Lenardi, P. Piseri, V. Briois, C. E. Bottani, A. Li. Bassi, and P. Milani, *J. Appl. Phys.* **88**, 1521 (2000).
- ²⁰In *Properties of Amorphous Carbon*, edited by J. Robertson and S. R. P. Silva (INSPEC, IEE, London, 2003); N. M. J. Conway, A. Ilic, J. Robertson, W. I. Milne, and A. Tagliaferro, *Appl. Phys. Lett.* **73**, 2456 (1998); D. G. McCullach, E. G. Gerstner, D. R. McKenzie, S. Praver, and R. Kalish, *Phys. Rev. B* **52**, 850 (1995); S. Bhattacharyya and S. V. Subramanyam, *Appl. Phys. Lett.* **71**, 632 (1997); S. R. P. Silva and J. D. Carey, *Diamond Relat. Mater.* **12**, 151 (2003); S. Bhattacharyya, O. Madel, S. Schulze, P. Häussler, M. Hietschold, and F. Richter, *Phys. Rev. B* **61**, 3927 (2000).
- ²¹E. Cappelli *et al.*, *Diamond Relat. Mater.* (in press).
- ²²J. R. Shi, J. P. Wang, A. T. S. Wee, C. B. Yeo, C. T. Cheng, M. Ueda, S. Tomioka, and J. Ohsako, *J. Appl. Phys.* **92**, 5966 (2002); J. D. Carey and S. R. P. Silva, *Phys. Rev. B* **70**, 235417 (2004).
- ²³G. A. Abbas, S. S. Roy, P. Papakonstantinou, and J. A. McLaughlin, *Carbon* **43**, 303 (2005).
- ²⁴A. J. Papworth, C. J. Kiely, A. P. Burden, S. P. R. Silva, and G. A. J. Amaratunga, *Phys. Rev. B* **62**, 12628 (2000).
- ²⁵S. Banerjee, T. H. Benny, S. Sambasivan, D. A. Fischer, J. A. Misewich, and S. S. Wong, *J. Phys. Chem. B* (in press).
- ²⁶C. S. Lee, J. K. Shin, K. Y. Eun, K. R. Lee, and K. H. Yoon, *J. Appl. Phys.* **95**, 4829 (2004).
- ²⁷A. C. Ferrari, B. Kleinsorge, N. A. Morrison, A. Hart, V. Stolojan, and J. Robertson, *J. Appl. Phys.* **85**, 7191 (1999).
- ²⁸R. McCann, S. S. Roy, P. Papakonstantinou, M. F. Bain, H. S. Gamble, and J. A. McLaughlin, *Thin Solid Films* **482**, 34 (2005).