

## Fluctuation microscopy studies of medium-range ordering in amorphous diamond-like carbon films

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In this letter, we report fluctuation microscopy studies of medium-range ordering in amorphous diamond-like carbon films and the effect of annealing on this ordering. Annealed and unannealed diamond-like carbon films have almost identical short-range order. Our fluctuation microscopy results, however, indicate the presence of medium range order or clustering in the films on a lateral length scale that exceeds 1 nm. Within the clustered regions, the dominant local ordering appears to be diamond-like, and graphite-like ordering is not observed. Thermal annealing up to 600 °C leads to an increase in diamond-like clustering with no onset of graphite-like clustering. However, after high temperature annealing up to 1000 °C, graphite-like clustering becomes apparent as a result of the conversion of diamond-like carbon to graphite-like carbon. The results on the as-deposited films and films annealed up to 600 °C suggest that a spontaneous medium range ordering process occurs in diamond-like carbon films during and subsequent to film growth, and this may play an important role in stress relaxation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1713048]

Hydrogen-free amorphous diamond-like carbon films have stimulated great interest because of their useful properties, such as high hardness, chemical inertness, thermal stability, wide optical gap, and negative electron affinity.<sup>1</sup> Consequently, they may have various potential applications in mechanical and optical coatings, MEMS systems, chemical sensors and electronic devices.<sup>2</sup> Amorphous diamond-like carbon films often contain a significant amount of fourfold or  $sp^3$  bonded carbon, in contrast to amorphous carbon films prepared by evaporation or sputtering which consist mostly of threefold or  $sp^2$  bonded carbon.<sup>3</sup> Structural configurations of these threefold and fourfold carbon atoms determine the properties of these amorphous diamond-carbon films. Although the ratio of threefold and fourfold carbon has been studied with Raman spectroscopy,<sup>4</sup> electron-energy-loss spectroscopy (EELS),<sup>5</sup> and nuclear magnetic resonance,<sup>6</sup> there is a lack of knowledge regarding key questions such as the spatial distribution of the threefold and fourfold carbon atoms in the film, and what local structures those threefold and fourfold carbon atoms take. Conventional diffraction techniques only yield the radial distribution function (RDF) which is essentially a two-body correlation function describing short-range order. The above structural issues however involve atomic arrangements beyond short-range order.

Fluctuation microscopy utilizes a phenomenon called speckle patterns.<sup>7</sup> Speckle patterns are generated by interference under coherent scattering conditions. In a transmission electron microscope (TEM) dark field image, the intensity of

each pixel is only contributed by electrons scattered by a small cylindrical column of atoms,<sup>8</sup> whose radius is defined by the resolution and whose height is the sample thickness. Therefore, the intensity fluctuation is directly related to the local structure change in each small volume of the sample. To the first order approximation,<sup>9</sup> the intensity fluctuation across the whole image is given by:

$$\langle I^2(\mathbf{k}) \rangle - \langle I(\mathbf{k}) \rangle^2 \propto \left\langle \sum_{i \neq j, l \neq m} \exp[i\mathbf{k} \cdot (\mathbf{r}_{ij} - \mathbf{r}_{lm})] \right\rangle - \left\langle \sum_{i \neq j} \exp[i\mathbf{k} \cdot \mathbf{r}_{ij}] \right\rangle \times \left\langle \sum_{l \neq m} \exp[i\mathbf{k} \cdot \mathbf{r}_{lm}] \right\rangle, \quad (1)$$

where  $k$  is the momentum transfer value at which the dark-field image is taken.

Equation (1) shows that the intensity fluctuation involves two pairs of atoms. By measuring the intensity fluctuation in TEM dark-field images as a function of the momentum transfer value  $k$ , atomic correlation involving two pairs of atoms can be extracted. Any local structure correlation beyond a length scale defined by the resolution may be detected. This technique allows experimental access to medium-range order structures of amorphous materials that were inaccessible before. In this letter, we report our fluctuation microscopy studies of amorphous diamond-like carbon films.

Amorphous diamond-like carbon films were fabricated by pulsed-laser deposition using a KrF laser (248 nm) and a graphite target. The deposition was performed at room tem-

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perature on to a polished Si(100) wafer up to a final thickness of 30 nm. The films are hydrogen free and contain about 80% fourfold ( $sp^3$ ) carbon with the rest being threefold ( $sp^2$ ) carbon. In this letter, we will present results from as-grown samples (no annealing after the growth) and samples that were annealed after growth at two different temperatures. The annealing condition consisted of heating in vacuum at  $<1 \times 10^{-5}$  Torr for a period of 30 min at 600 or 1000 °C. Prior electrical and mechanical measurements have shown great differences in properties following postdeposition annealing in this temperature range.<sup>10</sup>

Plan-view TEM samples were made from the films by core drilling and chemical etching in  $\text{HNO}_3:\text{HF}:\text{CH}_3\text{COOH}$  (5:3:3). The film thickness under TEM observations is about 30 nm. Electron diffraction patterns were taken for each sample. The maximum  $k$  was  $22.4 \text{ \AA}^{-1}$ .

To understand the short-range order in those films, we first measured the reduced radial distribution function from diffraction patterns. Small angle scattering was cutoff before the Fourier transform was performed in order to remove the strong electron dynamical effect. This cutoff should not affect our results because small angle scattering does not contribute to the term that yields the radial distribution function.<sup>11</sup> An edge smooth function was applied when the Fourier transform was performed. This procedure reduces artificial oscillations in the resultant radial distribution function. The RDF is an ensemble average of the short-range order structures (2–5 Å) of the whole sample.<sup>11</sup> It cannot provide information on local structure changes at length scales larger than 5 Å, i.e., the medium-range order structures.

All experiments were conducted on a JEOL-4000EX microscope that had been setup for automated fluctuation microscopy data collection at the Electron Microscopy Center at Argonne National Laboratory. During an experiment, a series of dark-field images were taken on an area of the sample as a function of the tilting angle of the electron beam through reciprocal space. The same process is typically repeated for several different areas to gain good statistics. Normally a few hundred images are taken in a single experiment. The images were then processed by a script, removing distortions and applying Wiener filtering. The intensity fluctuation was eventually obtained as a function of the momentum transfer value. This variance function of  $k$  is directly related to a pair–pair correlation function that defines medium-range order at the nanometer scale.

Results of radial distribution functions are presented in Fig. 1. The average bond length is  $1.52 \text{ \AA}$  and the average bond angle is  $72.6^\circ$ . Up to 600 °C, there are no pronounced differences between radial distribution functions for the unannealed and annealed samples (after 1000 °C annealing, there are significant differences that are due to graphitization, discussed below). Figure 1 shows that short-range order information characterized by the RDF is not able to give account to property changes that occur in the diamond-like carbon films at the lower anneal temperatures.

Fluctuation microscopy results, however, reveal a clearer picture. Our results are presented in Fig. 2. The variance peaks at  $4.9$  and  $8.5 \text{ nm}^{-1}$  are signatures of medium-range order or clustering on a length scale of about 1 nm, which is

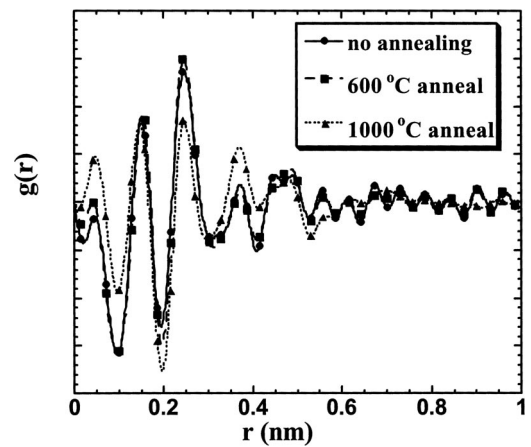


FIG. 1. Measured reduced distribution functions for a film without annealing and films annealed at 600 and 1000 °C. For films annealed up to 600 °C, the short range order is similar.

approximately the electron coherence length used in these measurements. The peak height is a function of the annealing temperature. When annealing was done at 1000 °C, an additional peak shows up at  $2.9 \text{ nm}^{-1}$ , indicating a new ordered structure not present in the lower temperature films. Each peak corresponds to a type of local structure or ordering, represented by a narrow range of  $k$  values. The width of the peak, which is defined by the two minima of the peak, is proportional to the size of this structure unit, i.e., a large well-ordered structure would be represented by a narrow peak. Therefore, the fact that the width of the peaks is not changing indicates that the *size* of the local structure units is not changing. The height of a peak is proportional to the *number* of the corresponding structure units in the sample. Therefore, the variance versus  $k$  plot indicates that the number of structural units, i.e., clusters, is increasing as the sample is annealed up to 600 °C.

From solid state nuclear magnetic resonance measurements performed on amorphous diamond-like carbon films prepared in the same fashion as the films described here, it is known that both  $sp^3$  and  $sp^2$  chemical bonds are present in the material.<sup>12</sup> About 80% of the bonds are  $sp^3$  (fourfold coordinated carbon) from the as-deposited condition through annealing temperatures up to 600 °C.<sup>12</sup> At temperatures

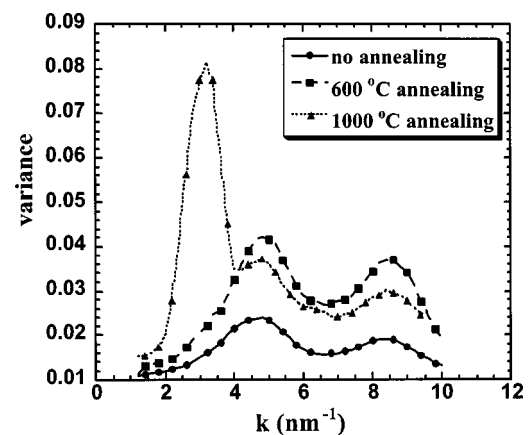


FIG. 2. Plots of the variance as a function of  $k$  for amorphous diamond-like carbon films with or without annealing. The medium range order, indicated by the peaks, is increased after thermal annealing. New structural ordering shows up in the 1000 °C annealed film.

higher than 900 °C, the majority of the bonds are  $sp^2$ .<sup>12</sup> The peak positions in Fig. 2 for the as-deposited and 600 °C annealed films are in approximate agreement with broad peaks, not shown, that were obtained from the calculated diffraction from a theoretical 64-atom cell of amorphous diamond-like carbon.<sup>13</sup> These peak positions are related to local structures adopted in the amorphous network and are dominated by the majority-phase diamond-like component in the material.

After 1000 °C annealing, a new sharp peak forms. This peak is in good agreement with the (002) reflection of graphite, which arises from the interplanar spacing of graphite sheets. It is well-known that high temperature annealing leads to graphitization in diamond-like carbon films.<sup>12,14–16</sup> This is characterized by an increase in three- to fourfold carbon ratio determined by solid state NMR, EELS, near edge x-ray absorption fine structure, or the appearance of a Raman signature that is characteristic of glassy carbon (a disordered carbon material consisting of nearly 100% three-fold coordinated carbon). Therefore, we identify the peak at  $2.9 \text{ nm}^{-1}$  with the presence of disordered graphite sheets in the film, similar to what is observed in glassy carbon. Importantly, the absence of this peak in the lower temperature films is a direct indication that graphite-like ordering is not present in as-deposited or low temperature amorphous diamond-like films.

The experimental results lead to several conclusions: (1) low temperature annealing (up to 600 °C) produces measurable changes in structure in the amorphous diamond-like carbon films, (2) the dominant effect of annealing at 600 °C is to increase the concentration of locally ordered structure units that have local diamond-like ordering, (3) these units are heterogeneously distributed through the sample at a length scale comparable to or greater than 1 nm, (4) 600 °C annealing does not tend to increase the size of these structure units (the peaks do not become narrow), (5) annealing at 1000 °C introduces distinct structural changes with the most pronounced being the presence of sheet-like, (002)-like, graphitic ordering in the sample with relatively large domains (a narrow peak), but this graphitic ordering is not present at lower temperatures. The change in local ordering that is apparent in amorphous diamond-like carbon following low temperature annealing has also recently been reported in a solid state NMR study.<sup>6</sup> Interestingly, the existence of het-

erogeneous ordering (or clustering) in amorphous diamond-like carbon films was also reported in a transmission electron microscopy study.<sup>17</sup> Taken together, these studies suggest that pronounced structural rearrangements may occur in amorphous diamond-like carbon films at modest temperatures, i.e., with low activation energies, while still retaining an amorphous structure that looks nearly identical by RDF analysis (Fig. 1). This finding suggests why stress relaxation may be unexpectedly facile in this system.<sup>10</sup>

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<sup>1</sup>J. Robertson, *Prog. Solid State Chem.* **21**, 199 (1991).

<sup>2</sup>J. P. Sullivan, T. A. Friedmann, and K. J. Hjort, *MRS Bull.* **26**, 309 (2001).

<sup>3</sup>J. Robertson, *Adv. Phys.* **35**, 317 (1986).

<sup>4</sup>A. C. Ferrari, B. Kleinsorge, G. Adamopoulos, J. Robertson, W. I. Milne, V. Stolojan, L. M. Brown, A. LiBassi, and B. K. Tanner, *J. Non-Cryst. Solids* **266–269**, 765 (2000).

<sup>5</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>6</sup>T. M. Alam, T. A. Friedmann, P. A. Schultz, and D. Sebastiani, *Phys. Rev. B* **67**, 245309 (2003).

<sup>7</sup>J. M. Gibson and M. M. J. Treacy, *Phys. Rev. Lett.* **78**, 1074 (1997).

<sup>8</sup>P. B. Hirsh, A. Howie, R. B. Nicholson, and D. W. Pawshley, *Electron Microscopy of Thin Crystals* (Butterworths, Washington, DC, 1965).

<sup>9</sup>X. Chen, J. M. Gibson, J. Sullivan, and T. Friedmann, Symposium W, Materials Research Society Spring Meeting, 16–20 April 2001.

<sup>10</sup>J. P. Sullivan, T. A. Friedmann, and A. G. Baca, *J. Electron. Mater.* **26**, 1021 (1997).

<sup>11</sup>S. R. Elliot, *Physics of Amorphous Materials* (Longman, 1990).

<sup>12</sup>T. M. Alam, T. A. Friedmann, and A. J. G. Jurewicz, in *Thin Films: Preparation, Characterization, Applications*, edited by Soriaga *et al.* (Kluwer Academic/Plenum, New York, 2002), pp. 277–289.

<sup>13</sup>P. A. Schultz and E. B. Stechel, *Phys. Rev. B* **57**, 3295 (1998).

<sup>14</sup>T. A. Friedmann, K. F. McCarty, J. C. Barbour, M. P. Siegal, and D. C. Dibble, *Appl. Phys. Lett.* **68**, 1643 (1996).

<sup>15</sup>S. Anders, J. Diaz, J. W. Ager, R. Y. Lo, and D. B. Bogy, *Appl. Phys. Lett.* **71**, 3367 (1997).

<sup>16</sup>A. C. Ferrari, B. Kleinsorge, N. A. Morrison, A. Hart, V. Stolojan, and J. Robertson, *J. Appl. Phys.* **85**, 7191 (1999).

<sup>17</sup>M. P. Siegal, D. R. Tallant, P. N. Provencio, D. L. Overmyer, R. L. Simpson, and L. J. Martinez-Miranda, *Appl. Phys. Lett.* **76**, 3052 (2000).