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## MEDIUM-RANGE ORDER STRUCTURES OF AMORPHOUS DIAMOND-LIKE CARBON FILMS

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### Abstract

In this paper, we have studied medium-range order structures in amorphous diamond-like carbon films with fluctuation microscopy. Medium-range order structures are quantified by a specific form of a general four-body correlation. We name this function as a pair-pair alignment correlation function. By analyzing speckle dark-field images taken over different areas as a function of momentum transfer in reciprocal space, we measured the pair-pair alignment correlation function for both thermally annealed samples and unannealed samples. We have found that thermal annealing introduces medium-range order in amorphous diamond-like carbon films, causing more pairs of atoms to be aligned. These results agree with density-functional simulations. Larger-scale simulations will be needed to fully understand our experimental results.

### Introduction

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[1]. Consequently, they may have various potential applications in mechanical and optical coatings, MEMS systems, chemical sensors and electronic devices. Amorphous diamond-like carbon films often contains significant amounts of four-fold or  $sp^3$  bonded carbon, in contrast to amorphous carbon films prepared by evaporation or sputtering which consist mostly of three-fold or  $sp^2$  bonded carbon. The ratio and the structure configurations of these three-fold and four-fold carbon atoms certainly decide the properties of these amorphous diamond-carbon films. Although the ratio of three-fold and four-fold carbon has been studied with Raman spectroscopy and electron-loss-energy spectroscopy, very little has been understood regarding key questions such as how the three-fold and the four-fold carbon atoms are integrated in the film, and what structures those three-fold carbon atoms take [2]. These questions cannot be simply answered by normal diffraction technique because they involve structures beyond short-range order.

### Theory

Through the history of studying amorphous materials, the radial distribution function (RDF) has played an important role. While it is equivalent to an atomic pair correlation function, its importance relies on the fact that this function can be directly measured from diffraction experiments. The RDF gives good quantitative descriptions of short-range order (2 – 5 Å). However, it is almost impossible to interpret the third and the fourth peaks in the RDF. This is because the number of atoms filling a shell of  $r$  increases significantly as  $r$  increases. At a very large  $r$ , the RDF is approaching to the average number density of atoms. Therefore, the RDF is an ensemble average of the short-range order structures (2 – 5 Å) of the whole sample. It can not provide information on local

structure changes at length scales larger than 5 Å, i.e., the medium-range order structures [3].

For studies of medium-range order structures in the region from 1 nm to 5 nm, either imaging with a resolution of the same order of magnitude or micro-diffraction with a beam size of nanometers is needed. Only transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) can provide this kind of resolution. In TEM or STEM experiments, it is straightforward to measure the fluctuation of intensities in an image, in addition to diffraction patterns. While a diffraction pattern yields two-body correlation functions, this variance function of  $k$  yields information about correlations beyond the two-body correlation.

In TEM imaging mode, what is projected on the detector is actually the wave front of the electron wave that just leaves the sample. Therefore, under coherent illumination, the intensity of each pixel in a dark-field TEM image is contributed only by a small column of atoms from the sample [4]. Fluctuation microscopy utilizes a phenomenon called the speckle. Although speckle has been found in all types of coherent imaging for many years [5], this microscopy technique is relatively new [6]. Speckle patterns are generated by interference under coherent scattering conditions. Since the intensity in a pixel in a speckle image is actually contributed by a small column of atoms, fluctuations in local structures are reflected in fluctuations in the speckle intensity, as shown in figure 1.

### Counting:

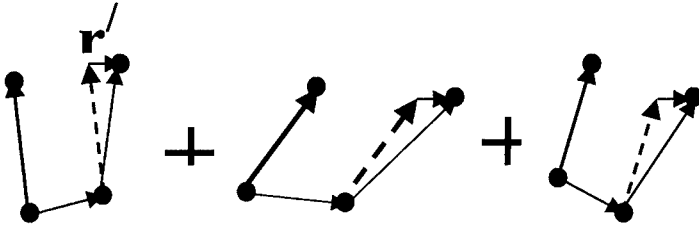


Figure 1 An illustration of the pair-pair alignment function. It counts all atom pairs with the same end vector. These pairs can have varied distances.

The length scale of the sampling column is directly determined by the resolution within the resolution limit of a particular electron microscope. By tuning the resolution, the volume of the sampling column under investigation can be tuned also. Therefore, fluctuation microscopy with varied resolutions will be of great interest in future. With varied resolution, we can study structure changes at different length scales. Hence the scaling behavior of that particular sample can also be studied.

We have for the first time developed a theory to quantify the medium-range order structure [7]. A summary of this theory is the following. A pair-pair alignment function is defined as:

$$G_{2,2}(\mathbf{r}') = \int G_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}') d\mathbf{r}_1 d\mathbf{r}_2 \quad (1)$$

where  $G_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}')$  is a four-body correlation function with  $\mathbf{r}' = \mathbf{r}_3 - \mathbf{r}_1$ ,  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$  give the position of the second, the third and the fourth atom respectively. Therefore, this new function  $G_{2,2}(\mathbf{r}')$  is the number density of an end vector generated by all possible three-body or four-body configurations. This end vector is a summation of two vectors from a three-body configuration or a four-body configuration. The number distribution of this end vector directly yields information regarding three-body configurations and four-body configurations, which contain correlations beyond the two-body correlations revealed by standard diffraction patterns. The meaning of the above function is shown in figure 1.

It is then easy to prove that  $G_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}')$  is actually directly related to the Fourier transform of the intensity fluctuation in speckle images:

$$g_{2,2}(\mathbf{r}) \propto \mathbf{r} \int_{k_{\min}}^{k_{\max}} \mathbf{k} \sin(\mathbf{k}\mathbf{r}) DW(\mathbf{k}) (\langle I^2 \rangle - \langle I \rangle^2) d\mathbf{k} \quad (2)$$

where  $g_{2,2}(\mathbf{r}') = \mathbf{r}' G_{2,2}(\mathbf{r}')$ . This is the function measured in practice. It is a measure of how many pairs of atoms are aligned in a certain volume.

## Experimental details

We use DigitalMicrograph™ to control a JEOL-4000EX microscope in our experiments. A DigitalMicrograph script was written to control the whole experiment. Once an area on the sample is chosen, the script prompts inputs of necessary parameters in the beginning of a session. Then it scans the electron beam through reciprocal space in an interval decided by the operator and takes a dark-field image with each momentum transfer value. Then each dark-field image is saved in a designated folder on the computer attached to the microscope. The same process is typically repeated for several different areas to gain good statistics. Typically a few hundred images are taken in a single experiment.

Another script has been composed to analyze these images. This script opens images in a designated folder on the computer. With each image, it removes distortion caused by modulation transfer in the CCD camera, whose modulation transfer function is pre-measured. Then the script does a Wiener filtering and a frequency filtering. Finally it yields a measured value of the fluctuation of intensity. With the momentum transfer value associated with each image, the intensity fluctuation as a function of the momentum transfer value is eventually obtained. Finally, a Fourier transform is performed on this function to yield the pair-pair alignment function in real space.

## Results

We have studied effects of thermal annealing on the medium-range order in amorphous diamond-like carbon films. Amorphous diamond-like carbon films were

fabricated on a silicon wafer by pulsed-laser deposition using a KrF laser and a graphite target. They are hydrogen free and contain about 70% four-fold ( $sp^3$ ) carbon with the rest being three-fold ( $sp^2$ ) carbon. These films were divided into two groups. One group was processed by thermal annealing while the other stayed in the as-grown state. TEM samples were made from the films by core-drilling and chemical etching. The film thickness under TEM observations is about 30 nm.

Interestingly, thermal annealing caused great property changes in those films. For example, before annealing, the film was under great stress, up to 7 GPa. But after annealing, the stress was released to below 1 MPa. Stress relaxation measurements [8] also showed that the percentage of three fold carbon atoms was increased from 30% to about 37%. Therefore, thermal annealing causes structure changes. Our goal is to understand those changes.

The radial distribution is measured from diffraction patterns. The results are given in figure 2. Figure 2 shows that the annealed and unannealed films have the same short range order structures, although their properties are dramatically different. This verifies our point that short-range order is not enough to give a complete description of amorphous structures.

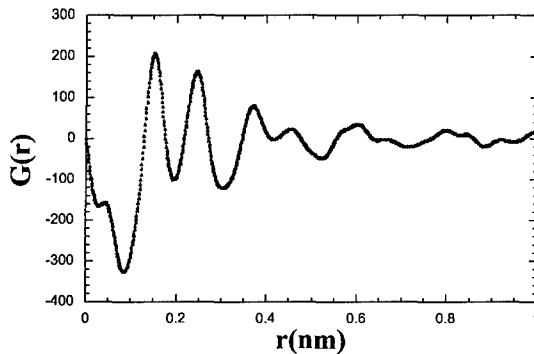


Figure 2. Measured reduced distribution functions show that thermal annealing does not change short-range order while causing great properties changes.

Our results on the intensity fluctuation are plotted as a function of  $k$  in figure 3. This variance function of  $k$  is directly related to a pair-pair correlation function that defines medium-range order at nanometer scale. From the intensity fluctuation function, we can measure the pair-pair alignment function with Fourier transform. Our results are given in figure 4.

There are pronounced differences for annealed and unannealed films, which indicates that there are medium-range order structure changes in these carbon films due to thermal annealing.

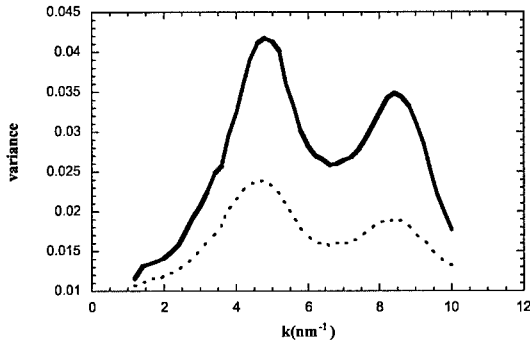


Figure 3. Plots of the variance as a function of  $k$  for amorphous diamond-like carbon films with or without annealing. The solid curve corresponds to the annealed sample and the dotted line is for the unannealed sample. The medium range order, indicated by the peaks, is increased after thermal annealing.

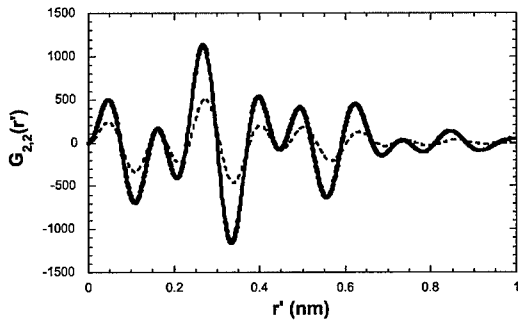


Figure 4. The measured pair-pair alignment function. The solid curve corresponds to the annealed sample and the dotted line is for the unannealed sample. More pairs of atoms are aligned after thermal annealing

For example, the first peak is positioned at around  $0.46 \text{ \AA}$ . From the radial distribution function, we already know that the average bond length is about  $1.51 \text{ \AA}$ . Noticing that  $r'$  is the magnitude of an end vector generated by two pairs of atoms, we can infer that this peak comes from two identical pairs of atoms that are closely parallel from simple geometrical considerations. The length of each pair is the bond length, as

illustrated in figure 1. The magnitude of this end vector, i.e. the position of this peak, directly measures how these two identical pairs of atoms are aligned statistically. The nearer the position is to the origin point, the more parallel these pairs are. On the other hand, the height of each peak is proportional to the number density of the corresponding configuration. The annealed sample has a higher peak than the unannealed one at the same position, which means thermal annealing aligns more pairs. This agrees with electronic property measurements and density functional simulations.

## Discussions

It is interesting to notice that thermal annealing increases the medium-range order in amorphous diamond-like carbon films. The increased medium-range order is correlated to the released stress [8]. This process can be explained well by thermodynamics. Growing films is a non-equilibrium process. During the growth, the system usually does not have time to relax into a minimized free energy state if the growth rate is too high or the substrate temperature is too low. Therefore, the resulted film is highly stressed. Thermal annealing provides the system a channel to relax into a smaller free energy state. Therefore, after thermal annealing, more pairs of atoms are aligned and the stress is released correspondingly.

## Conclusions

We applied fluctuation microscopy technique to study medium-range order in amorphous tetrahedral semiconductor materials. It is shown that this technique is very sensitive to local structure changes in the medium range order and promises solutions to open questions that cannot be answered by current techniques. With this technique, we found that thermal annealing introduces medium-range order in amorphous diamond-like carbon films. A thermodynamic model is suggested to explain those results. Future studies will be focused on modeling and systematic exploration of annealing effects.

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