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Effects of Thermal Annealing on the Atomic Structure and the Residual Stress of Amorphous Carbon Films: A Molecular Dynamics Simulation

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Changes of atomic structure and residual stress of tetrahedral amorphous carbon (ta-C) films were investigated by using a molecular dynamics simulation. Annealing of the ta-C film at 2000 K for 0.5 ns decreased the high level of residual stress of the ta-C film up to 27 %. On the contrary, the mechanical property of the films, which is represented by the sp^3 bond ratio, was seldom changed. Only a 1.7 % decrease in the sp^3 ratio was obtained, which agreed well with experiment. The annealing affected the relaxation of the atomic configuration with high energy, which is referred to as the high-stress configuration of the satellite peak found in the radial distribution function. Since a short-time annealing only reduced the residual stress, this method can be applied when one wants to reduce the residual stress which maintaining mechanical property.

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I. INTRODUCTION

Amorphous carbon films have attracted much attention due to their superior optical, physical and chemical properties. Among these films, tetrahedral amorphous carbon (ta-C) films are widely used for mechanical and optical applications because they exhibit high hardness and good optical transparency [1–3]. However, the applicability of ta-C films has been limited due to high residual stress. The high residual stress results in a bending of the substrates or a delamination of the films from the substrates [4].

Many attempts have been made to reduce the residual stress while maintaining the superior properties. One of them was the addition of a second element. Chhowalla *et al.* [5] reported that addition of boron to ta-C reduced the residual stress. Lee *et al.* [6] reported that the residual stress of the ta-C films with 2.5 at% of silicon was 35 % lower than that for pure ta-C films. The other is a post-annealing to as-deposited ta-C films. Previous studies [7,8] have shown that annealing ta-C films at temperatures up to 600 °C reduced the residual stress essentially to zero while maintaining the hardness of the samples. Friedmann *et al.* [8] obtained a nearly stress-free ta-C film only two minutes of annealing at 600 °C. Considering the short time of annealing, the drastic change in the residual stress is interesting. However, the mechanism of the stress reduction in annealed sample is still not understood.

Recently, Kim *et al.* [9] performed a molecular dynamics (MD) simulation and reported that the residual stress of as-deposited ta-C films was closely related to the population of the high-stress configurations corresponding to the satellite peak observed at 2.1 Å in radial distribution function (RDF). The high-stress configurations were characterized by large distortions of the carbon bonds from the equilibrium configuration. The bond angle of the high-stress configurations was ∼90° while the equilibrium bond angles of sp^2 and sp^3 are 120° and 104.5°, respectively. Since the high-stress configurations are highly distorted, it can be inferred that the configurations are strongly unstable during annealing. The objective of this study is to investigate the effect of annealing on the atomic structure of ta-C films by using a MD sim-

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ulation. It should be noted that the annealing time was limited in a few nano-second due to the intrinsic limitation of the MD simulation. However, the short time of the MD simulation can be justified as follows: The annealing times of the experiments [7,8] were much shorter than the times of conventional annealing experiments, which implies that stress reduction was achieved at an early stage of annealing. The MD annealing temperature was at 2000 K, 1000 K higher than the temperature used in the experiments. Since the higher temperature and the shorter time of annealing correspond to a lower temperature and a longer annealing time, we believe that the calculation performed at 2000 K in this study can reproduced the early stage of the structure change during an annealing experiments.

II. COMPUTATIONAL METHODS

1. Molecular Dynamics Simulation

In order to simulate the deposition and the structural evolution of amorphous carbon films, we use a molecular dynamics technique to simulate the motion of atoms by using the velocity-Verlet algorithm to numerically integrate Newton's equation of motion [10]. The interatomic interactions are described using the three-body empirical potential for carbon suggested by Tersoff [11].

The amorphous carbon films were produced on diamond (001) surfaces by bombardments of 3,000 neutral carbon atoms with a prescribed incident kinetic energy. The kinetic energies of the deposited carbon atoms were varied from 10 to 100 eV. The length and the width of a diamond substrate were 21.4 Å and the height was 25 Å. All substrates were equilibrated at 300 K for 0.3 ps (picosecond). Deposited atoms were bombarded on the substrate at a normal angle with respect to the plane of the surface. The horizontal position of an incident atom was randomly selected at the distance of 8.56 nm above the substrate surface. The time interval between two consecutive atoms hitting the substrate was $0.6 \sim 2.0$ ps., resulting in an ion flux of approximately 0.2×10^{30} /m^{2}s. The temperature of the substrate was rescaled to 300 K after the atomic rearrangement caused by the bombardment of carbon had have finished. Thermal diffusion of carbon atoms was neglected because the binding energy of carbon atoms was high and the temperature was low.

We applied periodic boundary condition to surface normal directions designated as the x- and the y-directions, respectively. The atoms in bottom one layer of the substrate were fixed to simulate the bulk substrate. The time step was set at 0.2 fs (femtosecond). After making ta-C films, we performed an annealing simulation. The annealing was composed of three stages. The first stage was a heat-up process of the ta-C films to 2000 K at a heating rat of 2.4 fs/K of heating rate. In the second stage, the films were annealed at 2000 K for 0.5 ns. Then, the films were cooled down to 300 K at a cooling rate of 0.24 fs/K. In order to analyze the atomic configuration of amorphous carbon films, we used statistical techniques such as the radial distribution function (RDF) [10].

2. Bond Order Analysis

Carbon atoms in amorphous carbon films have various types of bonding characteristics depending on their atomic environments, say, sp^1, sp^2, sp^3 and sp^4 hybrids. Understanding the bond nature and the distribution of carbon atoms in the films is crucial to reveal the origin of the residual stress from an atomic viewpoint, widely used method to determine the bond characteristic from an atomic structure is based on the number of atoms within the first nearest-neighbor distance. Generally, the number of carbon atoms within the first nearest-neighbor distance has a range of distribution from one to six. Since each carbon atom can make only four bonds, a coordination number of five or six is unphysical. Hence, a new method to determine the bond characteristics of each atom has to be developed.

The assumptions made for determining the new type of bond order were as follows: First, atom j within 2 Å from atom i is treated as a neighbor. Second, there is no dangling bond in the film because the dangling bonds have not been observed experimentally in an a-C film, except in the surface region [12]. Third, no triple-bonded carbon atoms exist in the films because the atomic distance between triple-bonded atoms is 1.2 Å and because that distance was not observed in the films generated from the simulation. Fourth, when atom i has a neighbor atom j and, in turn, atom j has neighbor atom i, atom i and atom j have at least a single bond.

Based on the above assumptions, one can calculate the total number of single bonds in the ta-C films and can estimate the total number of valence electrons from the total number of atoms. Assuming that two electrons form one single bond and that four electrons generate one double bond, the total number of valence electrons (Z) , which should be the same as 4 × (total number of atoms), can be calculated. The second and the third assumptions mentioned in the previous paragratph generates an equality between the total number of bonds and the sum of single and double bonds in a system. Therefore, we obtain the following constraint equations for the total numbers of valence electrons and of single and double bonds in ta-C films:

$$2X + 4Y = Z \tag{1}$$

$$X + Y = L \tag{2}$$

where X, Y and L are the total numbers of single, double and all bonds, respectively. Note that the new method to count the total number of sp^2 and sp^3 bonds cannot give

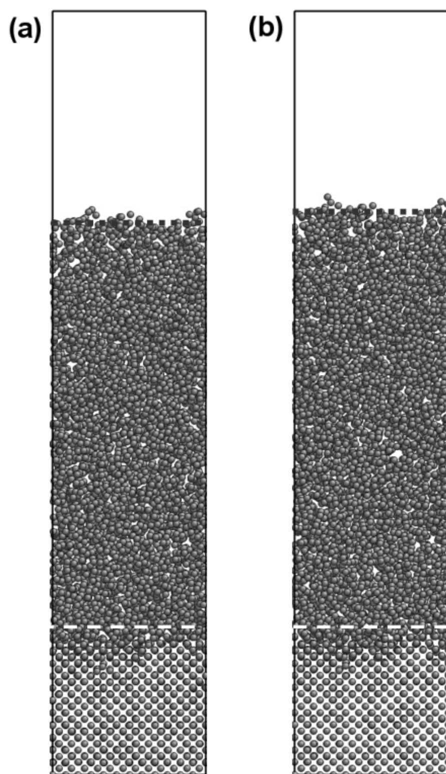

Fig. 1. Thin film morphologies of amorphous carbon films before and after annealing of 2000 K. The as-deposited film was made by deposition at an incident energy of 25 eV. The white dash at the bottom of the figures and the black dots at the top of the films represent the initial position of the substrate and the position of thin film surface, respectively. (a) As-deposited (b) 2000K 0.05 ns annealed sample.

us the bond order of a specific atom. If one can develop a more sophisticated model to calculate the number of bonds for each atom, the method will give more detailed information about the bond characteristics of the ta-C film when combined with the partial RDF analysis.

III. RESULTS AND DISCUSSION

Figure 1 shows the morphology changes of amorphous carbon films. The amorphous film (Figure 1(a)) was made by depositing carbon atoms with an incident energy of 25 eV. The ordered area observed at the bottom of the thin film originates from diamond substrate. Due to the high energy of incident atoms, the surface atoms of diamond were amorphized and the location of the interface was slightly shifted down. The original position is indicated as a white dash. The thickness of the as-deposited amorphous carbon film was estimated to 45 Å. Since the atoms in the top region of the amorphous carbon film have a lower number of bonds and the down-shifted interface region shows the strong character of the diamond substrate, both regions were excluded whenever

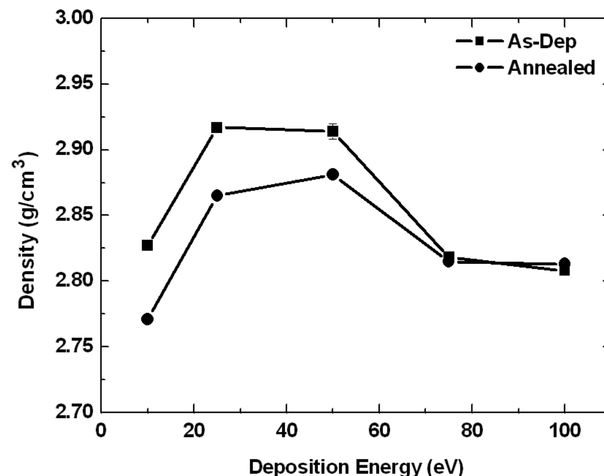

Fig. 2. Density variations of as-deposited and 2000 K annealed samples. The black squares and circles represent the densities of as-deposited and annealed samples, respectively.

bulk properties of amorphous carbon films are needed. The morphology of the amorphous carbon film after 0.5 ns of annealing is shown in Figure 1(b). Compared with the as-deposited film, the appearance of the annealed film was hardly changed. Only the thickness of thin film was slightly increased. The short-time exposure of amorphous thin film to a high temperature did not affect the thin film morphology.

Since the snapshots shown in Figure 1 only give qualitative information on the film's structure, quantitative methods are essential to understand the changes of in the atomic structure. Figure 2 shows the density changes with incident energies before and after annealing. The black squares and circles represent the densities of as-deposited and annealed samples, respectively. The as-deposited sample shows a maximum density at an incident energy of 25 eV. The short-time annealing mainly affected the samples made at lower incident energies. The density decrease was 1.75 % on average. Considering the strong bond between carbon atoms and the short times for annealing, the extent of the density decrease is substantial. This agrees with the increase in the thickness of the amorphous thin films that is shown in Figure 1(b). On the contrary, the annealing did not affect the high-incident-energy samples, such as these at 75 and 100 eV. The samples made at the lower incident energies are thought to have larger populations of highly non-equilibrium configurations that are sensitive to the annealing temperature, which will be explained later.

Since the superior mechanical properties of the amorphous carbon films are closely related to the sp^3 ratio in the films, it is necessary to study the effects of annealing on the variation of the sp^3 ratio. Figure 3 compares the sp^3 ratio between as-deposited and annealed amorphous films. The black squares and circles represent the sp^3 ratio of as-deposited and annealed films. The highest sp^3 ratio of the as-deposited sample was observed at a

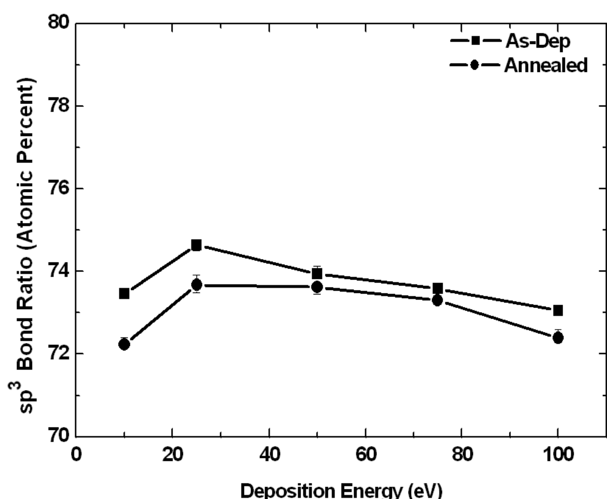

Fig. 3. Changes in the sp^3 ratio during annealing. The black squares and circles represent the as-deposited and annealed samples, respectively.

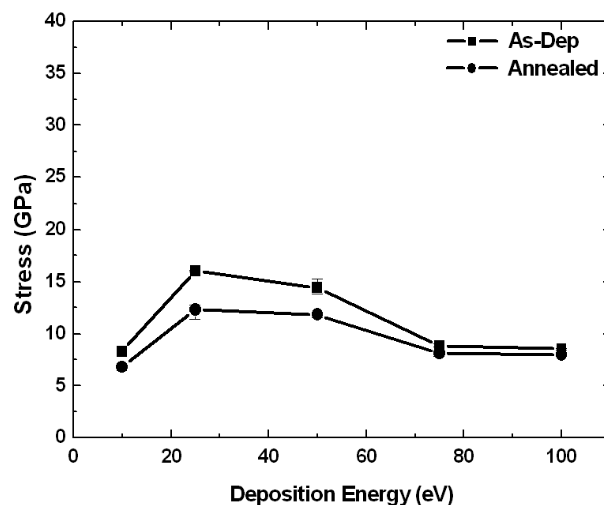

Fig. 4. Residual stress variation with deposition energy of the as-deposited and the annealed samples. The black squares and the circles represent the as-deposited and the annealed samples, respectively.

deposition energy of 25 eV, which is 74.63 %. Though the annealing reduces the sp^3 ratio over all samples studied, the extent of the decrease was 1.3 % at most, which agreed well with the experiment [13]. It can be inferred that the degradation of the mechanical properties of annealed sample was not severe. The annealed sample can retain its superior mechanical properties.

From the analysis of sp^3 bond ratio the short time annealing did not degrade the mechanical properties of amorphous carbon films. The variation of the residual stress is very important. Whether the annealing can reduce the residual stress or not is critical if the applicability of amorphous carbon films is to be widened. The residual stress variation in the amorphous films is shown in Figure 4. The black squares and circles represent the as-deposited and the annealed samples, respectively. The short-time annealing only affects, those deposited at 10 to 50 eV. The annealing did not reduce the residual stress of the higher-incident-energy films, which is related to the population of the non-equilibrium configurations in the films. The extent of residual stress decrease was 23 % for the 25 eV film and 18 % for the 10 and 50 eV films. Since the decrease of sp^3 ratio was only 1.7 %, the extent of the decrease in the residual stress is drastic. Therefore, short-time annealing of amorphous films reduces the residual stress while keeping its mechanical properties.

Annealing drives a high-energy configuration to low-energy. The high-energy configuration reacts more rapidly to thermal effect than the low-energy configuration does. Kim *et al.* [9] pointed that the high-stress (HS) configuration of the meta-stable 'satellite peak' observed in the radial distribution function (RDF) played a crucial role in changing the residual stress in amorphous films. Figure 5 shows the average stress of the HS configuration. The black squares and circles represent the as-deposited and the annealed samples, respectively. Comparing with Figure 4, one finds the average stress of the HS configuration to be approximately two times higher than the total average stress. Therefore, the HS configuration dominates the residual stress in amorphous films. The short-time annealing affected only the low-incident-energy films, which is consistent with the effects of annealing on the densities. The largest reduction was observed for the 25 eV film, which was 27 % on average. The differences in the atomic stress of the HS configuration of the annealed sample were 3 GPa at most while the differences in the as-deposited sample were 7 to 10 GPa. This is due to the fact that the population of the HS configuration was decreased and saturated. On

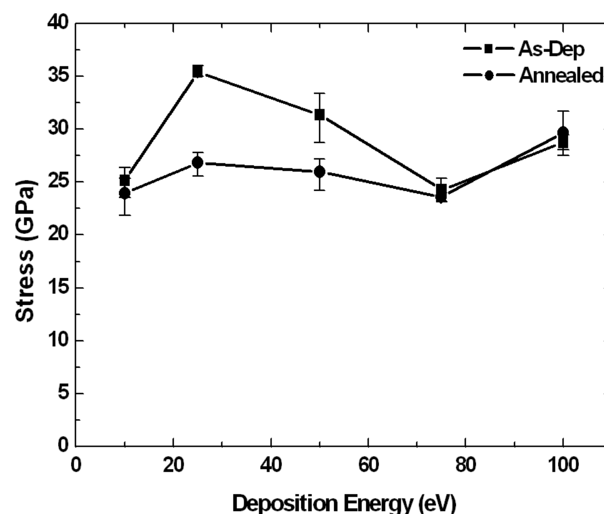

Fig. 5. Changes in the atomic stresses of the high-stress configuration. The black squares and circles represent the as-deposited and the annealed samples, respectively.

the other hand, Sullivan *et al.* [13] attributed the stress reduction to the conversion of sp^3 sites to sp^2 sites. Our result showed that the stress reduction was due to the decrease in the population of the highly distorted bonds that is formed during the deposition process.

IV. CONCLUSION

The effect of a 0.5 ns annealing at high temperature was investigated by using a molecular dynamics simulation with a Tersoff empirical potential. The short-time annealing only affected the atomic structures of samples made at the low incident energies (<75 eV). Only 1.7 % of sp^3 bond ratio was changed during annealing, which implies that the mechanical properties of the amorphous carbon films were retained. On the contrary, the annealing affected the residual stress substantially. A maximum 27 % of the residual stress was reduced. A detailed analysis of atomic structure showed that the non-equilibrium atomic configuration, which is referred to be as a meta-stable, high-stress configuration, was mainly affected by the short time annealing. In a practical point of view, the short time annealing cannot be achieved by using a conventional annealing apparatus. However, laser annealing or some other advanced experimental apparatus can be utilized as a tool for short-time annealing.

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