

## Structural Analysis for the Stress Variation of ta-C film with Deposition Energy: A Molecular Dynamics Simulation

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Molecular dynamics simulations are performed on the atomic origin of the evolution of residual stress in tetrahedral amorphous carbon (ta-C) film using the empirical Tersoff potential. The densities of and residual stresses in the amorphous films generated by molecular dynamics simulations were found to be in good agreement with the corresponding experimental results. A radial distribution function analysis shows that the peak at approximately 2.1 Å found in high-stress configurations, which is referred to as a satellite peak, is closely linked with the variation of the residual stress in ta-C film.

**Keywords:** tetrahedral amorphous carbon, structural analysis, molecular dynamics simulations

### 1. INTRODUCTION

Amorphous carbon thin films are widely used in industry due to their superior optical, physical and chemical properties. Among the various types of amorphous films, tetrahedral amorphous carbon (ta-C) thin films have attracted much attention as they exhibit high hardness and good optical transparency [1-3]. To widen the applicability of ta-C films, the high amounts of residual compressive stress should be reduced as this type of stress can cause the bending of the substrate or delamination of ta-C film from the substrate [4].

In addition, it is generally known that residual compressive stress shows a maximum at a certain bias voltage [1]. This can be interpreted as the kinetic energy of incident carbon atoms during deposition. Given that variations in the densities and  $sp^3$  fraction with the deposition energy show the characteristics of residual stresses, it has been assumed that the densities and/or  $sp^3$  fractions of ta-C films are correlated with the residual stresses. However, the correlation between the residual stresses and densities and  $sp^3$  fractions of ta-C films and its atomic origin are not well understood. Thus, in-depth studies of the evolution of the stress and other

physical properties of ta-C film are required *at the atomic level*.

The experimental research is limited in terms of understanding the evolution of local atomic structures and its correlation with global residual stresses during the growth of ta-C film because no experimental method exists that accurately facilitates the identification of the local disordered atomic structure. Alternatively, atomistic simulations based on reliable interatomic potentials have been considered as powerful tools for investigating the local atomic structures of ta-C films.

One of the most important factors in an atomistic simulation involves the proper handling of the interactions between atoms. In studies of atomic interactions in amorphous carbon films, atomistic simulations contend with either first principle [5-7], tight-binding [8,9], or empirical potentials [10-14]. Simulation studies on ta-C films can also be classified into two categories according to how the amorphous film is generated - by quenching or deposition. The quenching method is widely used to study the local atomic structures and bonding characteristics of amorphous films. However, this method cannot provide information regarding the evolution of the residual stresses with various deposition energies. In order to understand the stress evolution during the growth of ta-C films, a more realistic approach should be used.

Kaukonen and Nieminen [11], using the Tersoff inter-

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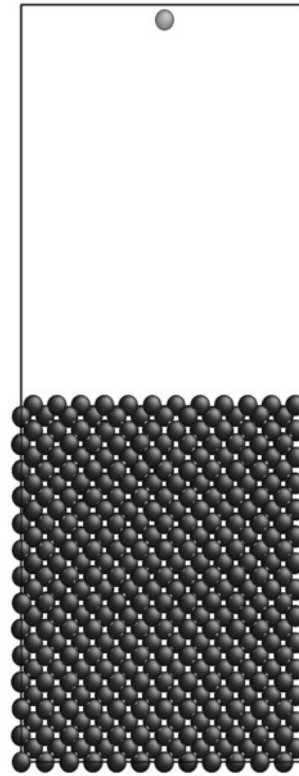
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atomic potential [15], studied local atomic structures and residual stresses in amorphous carbon films with various deposition energies through the radial distribution function, the density, and the coordination number. They reported that the variations of the densities and stresses showed behavior that was similar to that found when investigating the deposition energy. However, they did not consider the atomic origin of the stress evolution in detail. Through tight-binding molecular dynamics simulations, Uhlmann and Frauenheim [8] reported that energetic ions can penetrate into quenched amorphous carbon film and that 30 eV was a critical deposition energy for penetration into the sub-surface. They also reported that tensile stress is dominant at the surface region while compressive stress is dominant in the bulk region. However, they only focused on the details of single atom deposition. Wang and Ho [9] also studied the structure of amorphous carbon films generated by quenching from high-density high-temperature liquid carbon using tight-binding MD simulations. They found a small peak (satellite peak) between the first and second major peaks at approximately 2.1 Å. They also estimated the bond angle distribution that spans from 90 to 130 degree, implying that a large number of distorted bonds exist in the films. However, they did not correlate their results to the residual stress of amorphous films. Marks et al. systematically studied the atomic structures of amorphous carbon films using the Stillinger-Weber potential [6] and the environment-dependent interatomic potential (EDIP) [10]. In spite of their suggestion that the residual stresses depend on the growth process, they did not deal with the relationship between the residual stresses and the deposition energy as it pertains to the atomic structure in detail.

The present study focuses on the relationship between the atomic structure of ta-C films and stress variations of the deposition energy. Amorphous films were generated with several different deposition energies and their atomic structures were analyzed by statistical methods that included radial distribution functions. According to the molecular dynamics simulations conducted in this study, variation of the residual stresses was closely related to the number density of the distorted bond angles of the carbon atoms. The distorted bond angles of the carbon atoms were related to a meta-stable satellite peak at 2.1 Å in the radial distribution function (RDF). Two types of local atomic configurations with high and low stresses, respectively, were identified according to their local environments.

## 2. COMPUTATIONAL DETAILS

In order to investigate the evolution of local atomic structures and the residual stresses during the growth of amorphous carbon films, the molecular dynamics technique is used. This technique simulates the motion of each atom by numerical integration of Newton's equation of motion with



**Fig. 1.** Initial atomic configuration of the molecular dynamics simulation of carbon deposition.

the velocity-Verlet algorithm [16]. The inter-atomic interactions are described using the three-body empirical potential for carbon suggested by Tersoff [15].

The initial calculation condition is shown in Fig. 1. The amorphous carbon films were produced on a diamond (001) surface by bombardment of 3,000 neutral carbon atoms with prescribed incident kinetic energy.

The kinetic energies of the deposited carbon atoms varied from 10 eV to 100 eV. The lateral dimension of the diamond substrate was  $21.4 \times 21.4 \text{ \AA}^2$  and the height was 25 Å. All substrates were equilibrated at 300 K for 0.3 ps. The deposited atoms bombarded the substrate at a normal angle with respect to the surface plane. The horizontal position of the incident atom was selected randomly and was situated 8.56 nm above the substrate surface. The time interval between two consecutive atoms hitting the substrate was 0.6 ps to 2.0 ps, resulting in an ion flux of approximately  $0.2 \times 10^{30} / \text{m}^2 \text{ s}$ . The temperature of the substrate was rescaled to 300 K following the atomic rearrangement caused by the bombardment of the carbon. Although the carbon flux in this simulation was unrealistically high, the time interval was selected such that the atomic structure relaxes to a steady state within that interval to minimize the effect of the unrealistic deposition flux. The thermal diffusion of carbon atoms was neglected because the binding energy of carbon atoms, which functions as the

diffusion energy barrier, is high while the substrate temperature is low. A periodic boundary condition was applied to the lateral directions of the substrate, in both the  $x$  and  $y$  directions. One atomic layer at the bottom of the substrate was fixed to simulate the bulk substrate. The time step was set at 0.2 fs.

### 3. BOND ORDER ANALYSIS METHOD

Carbon atoms that constitute amorphous carbon films have various types of bonding characteristics depending on the atomic environments of their  $sp^1$ ,  $sp^2$ ,  $sp^3$ , and  $sp^4$  hybrids. Understanding the bond nature and the distribution of the carbon atoms in the films is crucial to reveal the origin of the residual stress from an atomic viewpoint. A widely used method of determining the bond characteristic from an atomic structure utilizes the number of atoms within the first nearest neighbor. Generally, the number of carbon atoms within the first nearest neighbor has a range of distribution from one to six. As 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 must be developed.

The assumptions made when determining a new type of bond order are 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, as a dangling bond has not been observed experimentally in a-C film except at 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 this distance has not been observed in films generated from simulations. Fourth, when atom  $i$  has as its neighbor atom  $j$  and when atom  $j$  has as its neighbor atom  $i$ , atom  $i$  and atom  $j$  have at least a single bond.

Based on these assumptions, it is possible to calculate the total number of single bonds in the ta-C films and 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 identical to  $4 \times$  (total number of atoms), can be calculated. The second and third assumptions mentioned in the previous paragraph generate equality between the total number of bonds and the sum of the single and double bonds in a system. Therefore, the following constraint equations are obtained for the total numbers of valence electrons and for the single and double bonds in ta-C films:

$$2X + 4Y = Z \quad (1)$$

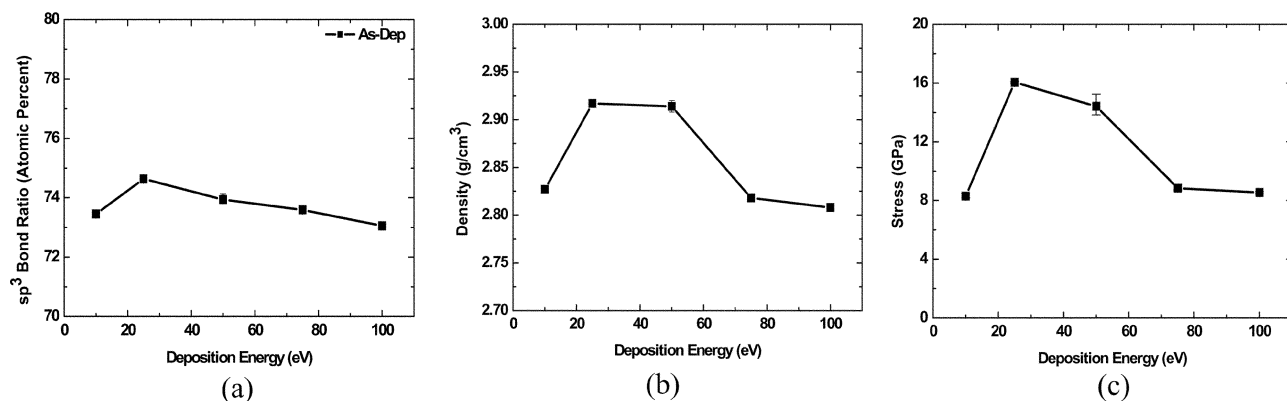
$$X + Y = L \quad (2)$$

where  $X$ ,  $Y$  and  $L$  are the total numbers of single and double bonds and the total number of all bonds, respectively. Here, the new method to count the total number of  $sp^2$  and  $sp^3$  bonds do not provide the atom-specific bond order. Upon development of a more sophisticated model to calculate the number of bonds for each atom, the method will give information in greater detail concerning the bond characteristics of ta-C films when combined with partial RDF analysis.

### 4. RESULTS AND DISCUSSION

The average thickness of the amorphous carbon films grown in molecular dynamics simulations was 4.5 nm. As transient regions such as the surface or interface between the substrate and the film have physical properties that differ from the intrinsic properties of ta-C films, the transient regions were excluded from the calculation of the density and residual stresses of the film.

Figure 2(a) shows the variation of the  $sp^3$  bond ratio in ta-C films with the deposition energies. After increasing the kinetic energy of the deposited atoms, the maximum ratio was obtained at 25 eV, which is consistent with the density variation. However, the extent of the change in the bond ratio with the deposition energies is not prominent. Figure 2(b) shows the densities of amorphous carbon films grown at

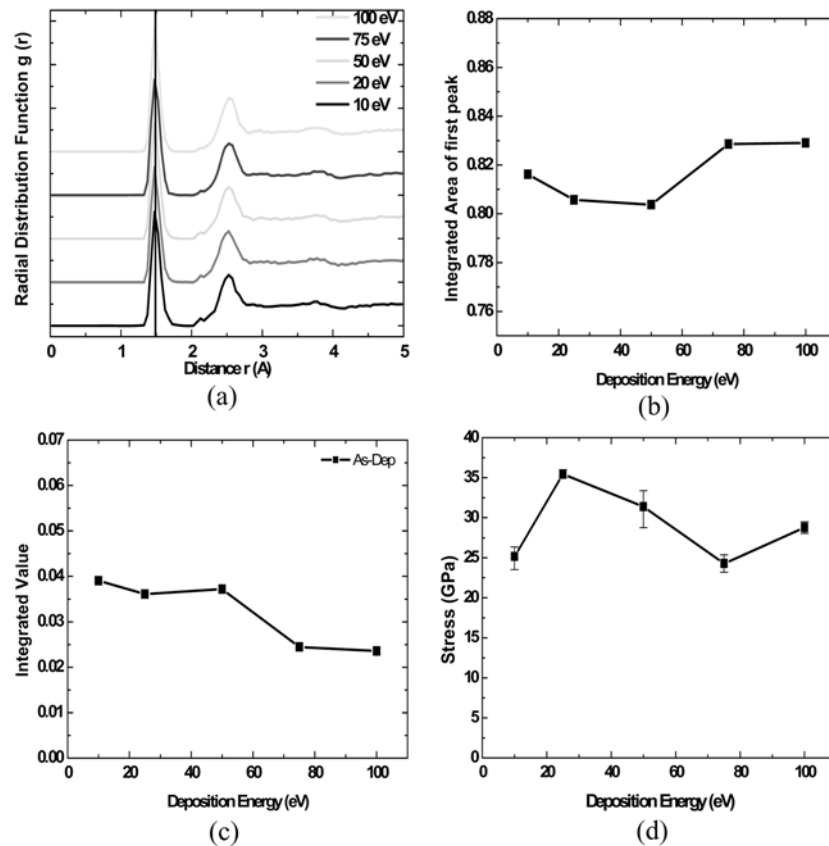


**Fig. 2.** (a)  $sp^3$  bond ratio, (b) densities, and (c) stresses of amorphous films created in molecular dynamics simulations with various deposition energies.

several different deposition energies. The calculated densities vary from  $2.808 \text{ g/cm}^3$  to  $2.917 \text{ g/cm}^3$  in a manner that is consistent with the experimentally observed values for ta-C films [17]. The densities did not increase monotonically as the deposition energy increased. The highest density ( $2.917 \text{ g/cm}^3$ ) was obtained at a deposition energy of 25 eV. The density variation with changes in the deposition energy is correlated with the residual compressive stress shown in Fig. 2(c). This relationship between the film density and the residual stress has also been found elsewhere [11,18]. The variations of the density and the residual stress with changes in the deposition energy can be understood qualitatively. The deposition of energetic atoms on the substrate results in two opposing effects [17]. The first involves a decrease of the interatomic distances and deviation of the angles between the bonds from their equilibrium values. The accumulation of the reduced bond distances and the deformed bond angles may cause the compressive residual stress. This effect is dominant at low deposition energies. The other effect involves the relaxation of the decreased interatomic distances and/or the deformed bond angles to equilibrium. When energetic atoms collide with the surface, an energy transfer occurs that causes local melting of the carbon atoms

on the surface. The quenching following the local melting induces stress in the amorphous carbon structure. The competition between these two effects determines the final stress state of the films. Detailed analysis of the atomic configuration leads to a deeper understanding of the relationship between the atomic structures and the origin of the residual stress.

Figure 3(a) shows the radial distribution functions (RDFs) of amorphous carbon films grown at several incident kinetic energies. The first peak around  $1.49 \text{ \AA}$  corresponds to the distance between the first nearest neighboring atoms. Considering that the equilibrium distance of  $\text{sp}^3$  and  $\text{sp}^2$  bonds are  $1.54 \text{ \AA}$  and  $1.42 \text{ \AA}$ , respectively, atoms in the films are in a mixed state of compressive or tensile stress state as determined by the local atomic configuration. The overall stress state between the first-nearest neighboring atoms is the result of the relative abundance between the  $\text{sp}^2$  and  $\text{sp}^3$  bonds in the films. The calculated overall stress state considering only the first-nearest neighbor atoms was in a compressive state, implying that the decrease of the  $\text{sp}^3$  bond distance dominates the elongation of the  $\text{sp}^2$  bond distance. However, whether or not the decreased bond length can explain the stress variation with incident energies remains unclear. The



**Fig. 3.** (a) Radial distribution functions (RDFs) of ta-C films generated by several different deposition energies, (b) Normalized number density of atoms centered at the first peak observed around  $1.49 \text{ \AA}$  from the center, (c) Normalized number density of atoms centered at a satellite peak around  $2.1 \text{ \AA}$ , and (d) Average stress of high-stress configuration atoms with an interatomic distance of  $2.1 \text{ \AA}$ .

peak positions were not a function of the deposition energy [Fig. 3(a)]. The vertical line in Fig. 3(a) was inserted for guidance. Hence, the first peak position cannot explain the stress variation with the deposition energy. The integration of the RDF curve from 1.3 Å to 1.8 Å, whose meaning is the average number of atoms in the specified distance region, was also conducted, as shown in Fig. 3(b). The integrated values show behavior that is in contrast to the stress variation with the deposition energy. Therefore, the stress evolution with the deposition energy does not have a correlation with the decrease of the nearest-neighbor distance but does with atoms in a region at a specific distance from an atom.

A small peak was observed around 2.1 Å in Fig. 3 (a). This is referred to here as a satellite peak. As a satellite peak has not been found in equilibrium, it is considered to be a meta-stable configuration [14]. The existence of the satellite peak is a matter that is still being debated. Tight-binding and classical molecular dynamics simulations support the existence of the satellite peak [8,11], whereas first principle calculations and the environment-dependent interatomic potential do not [7,10]. Though a first principle calculation is believed to provide the most reliable result, the number of atoms used in the first principle calculation is limited to less than 100 atoms; hence, it does not sufficiently include all meta-stable configurations in an amorphous environment. In order to understand the variation of the satellite peak, the RDF curves were integrated from 2.0 Å to 2.15 Å. The integrated values are shown in Fig. 3(c). The integrated value appears to decrease with the deposition energy. In order to understand the atomic configurations that correspond to the satellite peak, the local structure of the atoms tagged as the satellite peak was investigated. It was found that two different atomic configurations contribute to the formation of the satellite peak.

Figure 4 shows a schematic diagram of the two atomic configurations. The atomic configuration of Fig. 4(a) has high stress and common neighboring atoms tagged as C. Due to the existence of the tagged C atom, the angle among the three atoms ranges from 80° to 95°, which is much smaller than that of sp<sup>3</sup> configuration of 109.5° and that of the sp<sup>2</sup> configuration of 120°. Due to the distortion of the bond angle, the configuration of Fig. 4(a) has a high compressive stress of approximately 30 GPa. A satellite peak configuration with a high-stress state [Fig. 4(a)] is referred to as a high-stress (HS) configuration. In the configuration of Fig. 4(b), two atoms with a distance 2.0 Å to 2.2 Å have no common neighbor. The stress at this configuration corresponds to the average stress of the film. This atomic configuration without a common nearest neighbor is termed a low-stress (LS) configuration. Figure 3(d) shows the average stress of the HS configuration atoms. The average stress in the HS configurations varies from 25 GPa to 35 GPa with a maximum deposition energy of 25 eV. Additionally, it shows

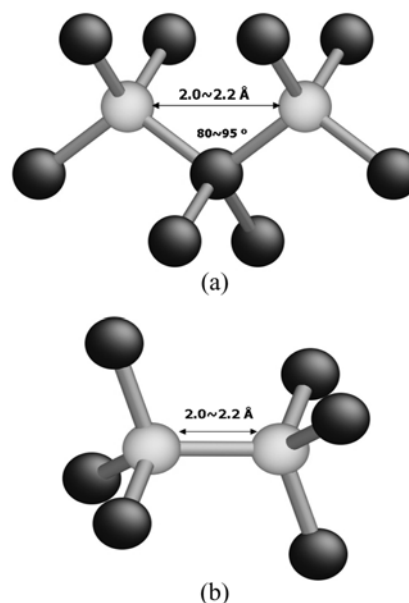


Fig. 4. Two representative atomic configurations corresponding to the satellite peak: (a) a high-stress state and (b) low-stress configurations.

good correlation with the variation of the total average stress of the film with the deposition energy.

## 5. CONCLUSION

The densities and residual stresses of amorphous carbon films generated by deposition in molecular dynamics simulations were found to be in qualitative agreement with those obtained from experiments. The density and residual stress showed maximum values at a deposition energy of 25 eV. The decreased bond length that leads to compressive residual stress in ta-C films was not a major cause of the variation of the residual stress with deposition energies in ta-C films. The stress evolution in ta-C films was in good agreement with the intensity of the meta-stable satellite peak observed in the RDF curve; this was due to two different types of local atomic configurations of the HS and LS configurations.

In the HS configuration, two atoms in the satellite peak had a common nearest neighbor atom and the resulting bond angle was approximately 90°. On the other hand, in the LS configuration, two atoms in the satellite peak did not share any common nearest neighbor.

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