Effects of pressure and temperature on sp^3 fraction in diamondlike carbon materials

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In this work, formation of diamond coating is studied using large-scale molecular dynamics (MD) simulation. The diamond coating is studied to explore how and to what extent the temperature and pressure affects the deposition structure. To analyze the coating results, the radial distribution function and the fraction of diamond (sp^3 bonds) is calculated. It is found that the sp^3 fraction in the deposition structure increases with the temperature and pressure. When the pressure becomes large enough (10 GPa), the effect of the pressure on the coating structure is quite small and the sp^3 fraction tends to be constant.

I. INTRODUCTION

In recent years, the fabrication and characterization of diamondlike carbon (DLC) materials has attracted significant attention because of their special physical, chemical, and mechanical properties. To date, extensive experimental work in this area has been conducted to fabricate diamondlike thin films. Different techniques have been applied for synthesizing DLC, including the mass-selected ion beams,[1] filtered vacuum arc,[2] and laser ablation[3] techniques. A common feature of these deposition methods is that the DLC films with high sp^3 fraction are obtained only by hyperthermal ions. It is important to study the effect of the deposition conditions on structural quality of DLC for much-improved experimental control and optimization.

Numerically, molecular dynamics (MD) simulation and the many-body Brenner–Tersoff potential function have been widely used to simulate the growth of diamondlike materials. Wei et al.[4] studied the deposition of energetic C$_2$ clusters on silicon and diamond surfaces and found that the mobility of surface atoms is enhanced at elevated energies in an earlier stage of deposition. Du et al.[5] investigated the deposition of C$_{20}$ fullerenes on a diamond surface using the many-body Brenner bond-order potential. The deposited C$_{20}$ film showed high sta-

bility even when the temperature was raised up to 1500 K. Jäger and Albe[6] simulated the ion beam deposition of DLC films using MD simulations and calculated the sp^3 fractions. To date, little MD research has been reported about the effects of temperature and pressure on the sp^3 fraction in DLC over a wide range of experimental conditions.

In this work, MD simulations using the Brenner–Tersoff potential are used to study two methods for fabricating diamondlike materials: deposition and compression. To characterize the sp^3 fraction in the simulation results, the variation of the nearest-neighboring distance in diamond and graphite with temperature is first explored. By analyzing the radial distribution function (RDF) and the nearest-neighboring distance among atoms, the sp^3 fraction in the material is obtained. The effect of temperature and pressure on the structural quality of the compression results is evaluated in detail.

II. THEORETICAL BACKGROUND

A. Basis of MD simulation

The basis of MD simulation is to simulate the trajectory of each atom in a system by solving the Newtonian equation. Combined with the potential function, the position, force, and velocity of each atom in the system can be calculated at each time step. In this work, the Tersoff-Brenner potential function is used, which has the form of[7–9]

$$E_b = \sum_i \sum_{j(>i)} [V_R(r_{ij}) - \overline{B}_{ij} V_A(r_{ij})] \quad , \qquad (1)$$

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where V_R and V_A are the repulsive and attractive parts, respectively.

$$V_R(r_{ij}) = f_{ij}(r_{ij})D_{ij}^{(e)}/(S_{ij} - 1) \exp\left[-\sqrt{2S_{ij}}\beta_{ij}(r - R_{ij}^{(e)})\right] \quad, \tag{2}$$

and

$$V_A(r_{ij}) = f_{ij}(r_{ij})D_{ij}^{(e)}S_{ij}/(S_{ij} - 1) \exp\left[-\sqrt{2/S_{ij}}\beta_{ij}(r - R_{ij}^{(e)})\right] \quad, \tag{3}$$

where $D_{ij}^{(e)}$ is the well depth, $R_{ij}^{(e)}$ is the equilibrium distance and the function $f_{ij}(r)$ restricts the pair potential to the nearest neighbors. Detailed information about the terms in Eqs. (1)–(3) can be found in Refs. 7–9.

To calculate force, position, and velocity of each atom based on Eqs. (1)–(3), different methods have been developed in the past. In this work, the widely used Verlet algorithm is used, in which the half-step leap-frog scheme[10] is applied. In the calculation, the time step should be chosen to be much smaller than the typical relaxation time of atomic movement. In our calculation, the time step is set as 0.5 fs.

B. Diamond formation

In this work, two types of diamond formation are investigated: deposition and compression. In the first method, a diamond substrate is used for deposition. The substrate consists of eight diamond layers and is divided into three parts. The bottom part consists of two diamond layers, and the position of each carbon atom is fixed. The top part also comprises two diamond layers, and the atoms will interact with those deposited carbon atoms from the top area. The middle part comprises four diamond layers, and the temperature is kept constant during the simulation. Periodical boundary conditions are applied in the x and y directions (in-plane direction), and the size in these two directions is 14.24 Å. The deposited carbon atoms are first positioned about 3 Å above the substrate. Before the deposition, the atoms above the substrate will be housed in a closed box. During the simulation, equilibrium calculation is conducted to make the atoms in the substrate and the box has the expected deposition temperature and pressure. Once the equilibrium calculation comes to an end, the bottom of the box will be opened to release the atoms, which will start to project to the surface of the diamond substrate.

The other diamond formation studied in this work is compression. Naturally, diamond is formed in a certain range of temperature and pressure. In this simulation, carbon atoms are first positioned randomly in a box. Then one side of the box is gradually moved to compress

the carbon atoms inside to simulate the formation of diamond. The initial size of the box is chosen as 28.5 Å × 28.5 Å × 35.6 Å or 21.4 Å × 21.4 Å × 64.1 Å ($x \times y \times z$). The biggest difference between these two initial boxes is the length in the z direction. Both cases are simulated to study the effect of pressure and temperature as well as the initial box size on the final DLC structure. In the x and y directions, periodical boundary conditions are applied. In the z direction, the 9-3 wall potential function is used to constrain the movement of carbon atoms. This 9-3 wall potential takes the form of $4\epsilon[(\sigma/r)^9 - (\sigma/r)^3]$ where ϵ and σ assume values of 0.01 eV and 1.5 Å, respectively. Different values of ϵ and σ have been tried in this simulation, and very little difference is found for the final DLC structure. When the simulation starts, the top wall begins to move downward at a given speed of 4 m/s and the pressure applied on the top wall is calculated based on the total atom–wall interaction force. If the pressure is larger than a given value, the wall will stop moving downward until the pressure becomes smaller than the given value.

C. Evaluation of sp³ fraction

The sp³ fraction is an important quantity that characterizes the deposition and compression results. A number of methods have been reported to evaluate the sp³ fraction in diamondlike materials, including the nuclear magnetic resonance technique,[11] infrared spectroscopy,[12] spectroscopic ellipsometry,[13] and Raman and x-ray photoelectron spectroscopy.[14] However, most of these methods are experimental and few numerical approaches have been reported. In this work, a method based on the nearest-neighboring distance is developed to calculate the sp³ fraction in the deposition structure. Taking $D_{Diamond}$ as the nearest-neighboring distance among atoms in diamond crystal, $D_{Graphite}$ as the nearest-neighboring distance among graphite atoms, and D_{Mix} for DLC, we have

$$\alpha D_{Diamond} + (1 - \alpha)D_{Graphite} = D_{Mix} \quad. \tag{4}$$

D_{Mix} is determined from the RDF of the DLC coating. It is necessary to point out that the nearest-neighboring distance corresponds to the location of the first peak in the RDF.

III. RESULTS AND DISCUSSION
A. Lattice constant change with temperature for diamond and graphite

For one to calculate the sp³ fraction in the mixture, the nearest-neighboring distance of diamond and graphite structure at different temperatures needs to be known to provide the reference used in Eq. (4). Systematic calculations are carried out to obtain this knowledge about the

temperature dependence of the nearest-neighboring distance in diamond and graphite. Initially, carbon atoms are arranged based on the diamond and graphite structure using the value of lattice constant at 300 K. After 2 ns equilibrium computation, the atomic structure reaches equilibrium state at a specified temperature. The neighboring distance is calculated by averaging the nearest-neighboring distance among all atoms in the system. Figure 1 shows how the nearest-neighboring distance changes with temperature for diamond and graphite. It is observed that the nearest-neighboring distance changes very little from 300 to 1600 K, about 0.42% for diamond, and 1.0% for graphite.

Before conducting systematic simulations, studies are carried out to check, within the computational time of interest, what is the limit of temperature under which stable diamond structure can be obtained. This will provide us with the knowledge about the temperature range to study the formation of DLC. In this work, a number of cases under different temperatures have been studied. Figure 2 shows the atomic configuration at two different temperatures. In the x and y directions, the domain size is 14.24 Å and periodical boundary conditions are applied. In the z direction, the initial size is 28.28 Å with free boundary conditions. Velocity scaling is applied during the first 800 ps to keep the structure in the expected temperature. The total computational time is 2.5 ns. It is found that when the temperature is 2000 K, the structure is still stable and close to that of diamond crystal. However, when the temperature is augmented to 2100 K, the atomic positions become irregular and expand to a much larger space. Therefore, our simulation of diamond deposition will be limited to temperatures below 2000 K.

B. Diamond coating by deposition

Two methods of diamond formation are investigated in this work. Figure 3 shows one of the results obtained by diamond deposition. In this case, both the substrate and deposition (vapor) temperature are set to 1600 K. The time for equilibrium scaling for the vapor is 500 ps.
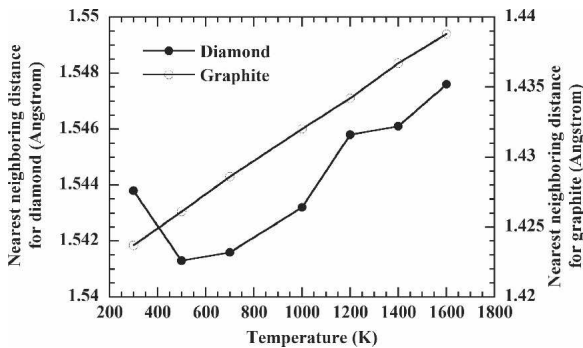

FIG. 1. Variation of the nearest-neighboring distance versus temperature for diamond and graphite.
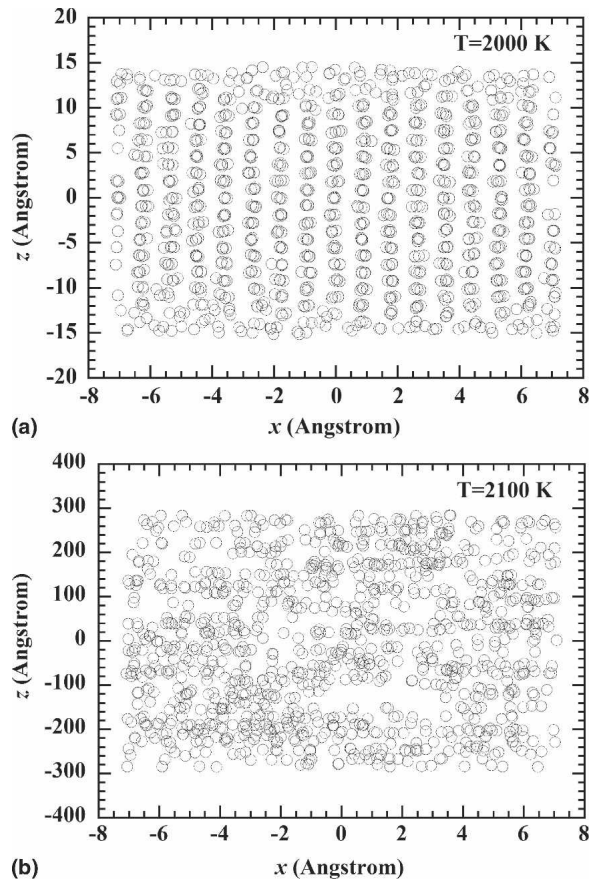

FIG. 2. Configuration of diamond atoms after 2.5 ns equilibrium calculation at temperatures of (a) 2000 and (b) 2100 K.
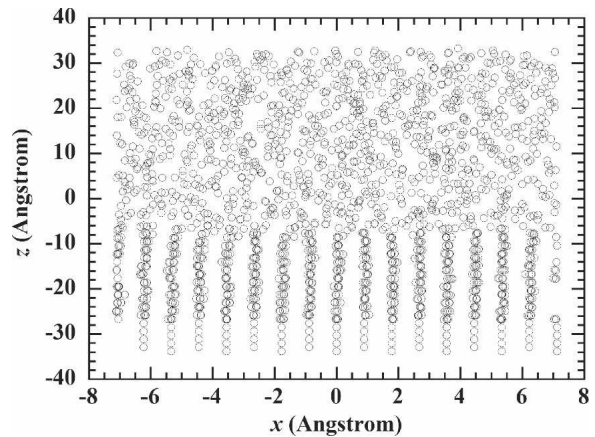

FIG. 3. The atomic configuration of the deposition structure for DLC coating.

After the equilibrium calculation, the carbon atoms start projecting to the substrate. The total computational time (deposition time) is 2 ns. Figure 3 gives the atomic configuration at the end of the calculation (2 ns). In the x and y directions the size is 14.24 Å, and periodical boundary conditions are applied. It is seen that the deposition result has polycrystalline structure. To analyze the deposition

structure, the RDF of the deposited coating is calculated, which is shown in Fig. 4. For comparison, the RDF of pure diamond and graphite at 1600 K is also shown in Fig. 4. This figure shows that the RDF of the deposition does not follow that of either graphite or diamond, confirming its polycrystalline nature. The inset in Fig. 4 shows details of the first peaks of the RDF. It is clearly seen that the deposition structure has subpeaks corresponding to the first peak of the RDF for diamond and graphite. This means the deposition is a mixture of diamond and graphite structure. Using the calculated nearest-neighboring distance at 1600 K and Eq. (4), the sp³ fraction is calculated as 57.9%.

C. Diamond coating by compression

One problem faced in the diamond formation by deposition in Sec. III. B is that when carbon atoms deposit on the substrate, the pressure in the domain will reduce due to the reduction of free C atoms in space. Therefore, it is difficult to precisely study the effect of pressure and temperature on the final structural quality of the DLC coating. Another method of diamond formation studied in this work is compression as outlined in Sec. II. B. The difference between this method and the one used in Sec. III. B is that this method has no solid substrate to facilitate epitaxial growth. Figure 5 shows the atomic configurations at 20 ps and 2 ns and at temperature 1600 K and pressure 7 GPa. The initial size of the box is 28.5 Å × 28.5 Å × 35.6 Å. The top wall moves downward to compress the carbon atoms in the box. At 2 ns, the domain is compressed roughly by 75% in the z direction. Figure 6 shows the RDF of the structure at 2 ns. Similar to the deposition result, the first two peaks are in positions corresponding to the first peak of the RDF for diamond and graphite. This indicates that the final material also has polycrystalline structure. Figure 7 gives the temperature and pressure variation with the compu-
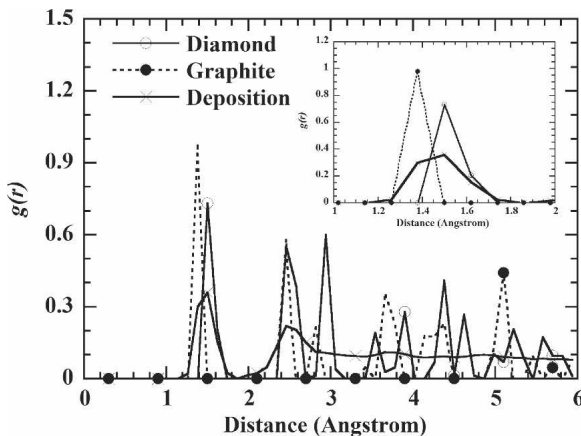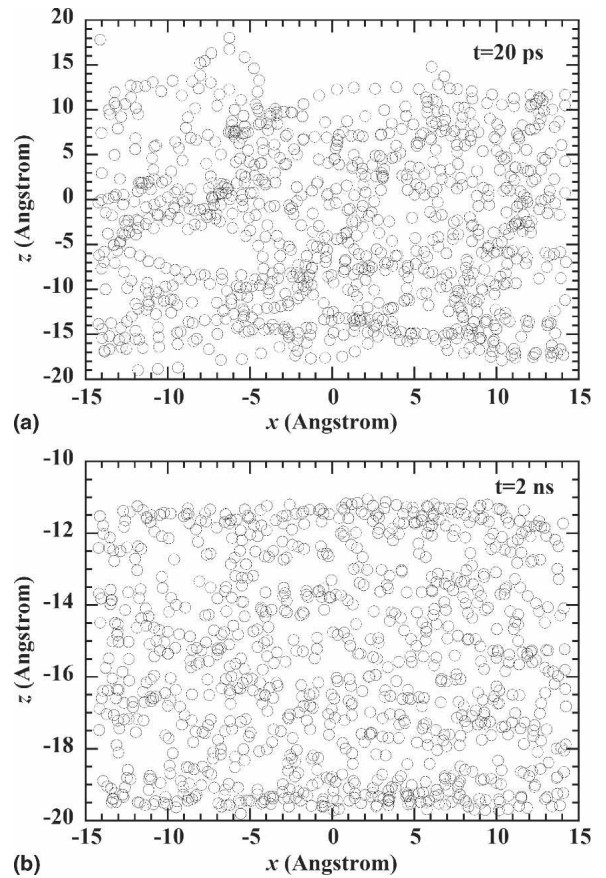
(a)

(b)

FIG. 5. Atomic configurations at (a) 20 ps and (b) 2 ns during compression of carbon atoms.

FIG. 6. Radial distribution function of the structure for diamond coating shown in Fig. 5.
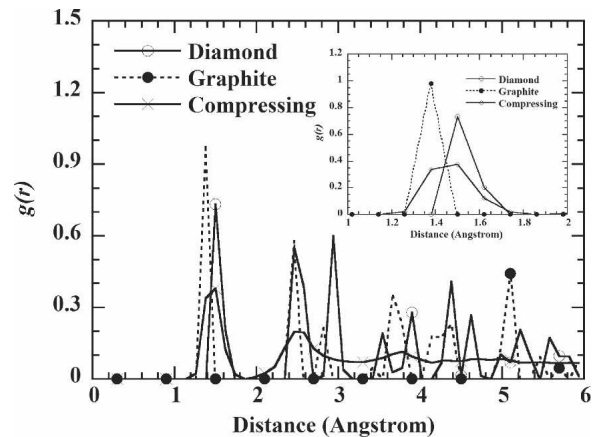
FIG. 4. Radial distribution function of the structure for diamond coating shown in Fig. 3.

tational time to show the conditions in the compression procedure. It indicates the temperature is well controlled to be around 1600 K. Before 0.7 ns, the pressure is increasing while the wall is moving downward. When the pressure reaches the given value (7 GPa), the movement of the top wall is adjusted accordingly to make the pressure fluctuate around 7 GPa.
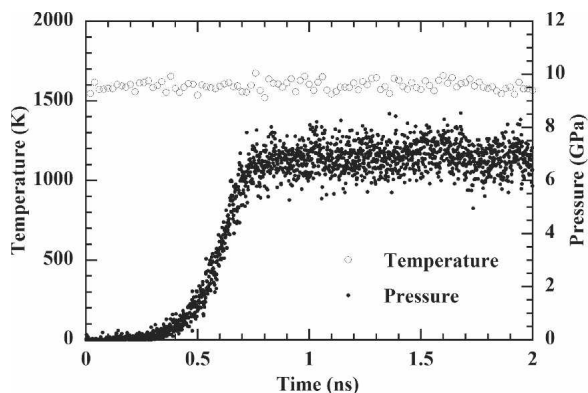
FIG. 7. Variation of the temperature and pressure versus time during compression of carbon atoms.

A longer compression time is also performed by using MD simulation to explore whether the computational time (2 ns) is sufficient to form stable DLC structures. This computation is run for 25 ns to explore whether the sp³ fraction has significant change after the first 2 ns compression. After the initial 2 ns compression, the pressure and temperature in the system are kept at 1600 K and 15 GPa, respectively. Figure 8 presents the change of the sp³ fraction over time. It is observed in our simulation (Fig. 7) that when time is about 1 ns, the pressure reaches the desired value and the top wall does not move anymore. At that moment, the fraction of sp³ bond achieves a pretty stable level, which can be observed in Fig. 8. Then after the top wall stops, although the simulation procedure continues, the fraction does not change much and fluctuates around 40%. It is conclusive that a computational time of 2 ns is sufficient to obtain a stable diamondlike structure.

A number of cases (compression) have been simulated with different temperatures and pressures to investigate the effect of temperature and pressure on the quality of the compressed structure. The variation of sp³ fraction with pressure and temperature is shown in Fig. 9. It is
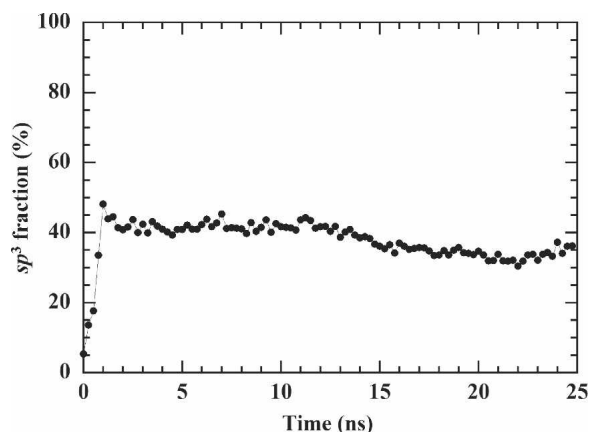

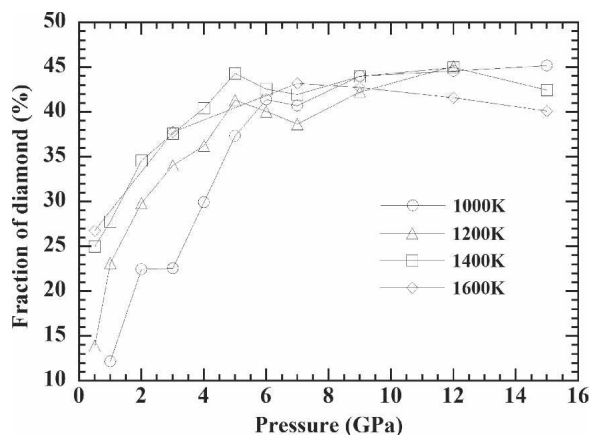FIG. 8. Long-time variation of sp³ fraction during compression at 1600 K and 15 GPa.

FIG. 9. Variation of sp³ fraction with pressure and temperature for DLC formed by compression of C atoms.

seen that the sp³ fraction increases with temperature. For example, at 3 GPa, the sp³ fraction of the diamond coating formed at 1600 K is about 67% higher than that at 1000 K. However, this temperature-induced difference becomes smaller when the compression pressure is increased. Figure 9 shows the fraction of sp³ bond improves with the pressure increasing. When the pressure becomes large enough (larger than 10 GPa), the sp³ fraction tends to be constant, in the range of 40–45%.

IV. CONCLUSIONS

In this work, MD simulations were performed to study the formation of diamondlike materials. Two kinds of the diamond formation: deposition and compression were investigated. The simulation results indicated polycrystalline structure for the diamondlike material. Both sp² and sp³ bonds were observed in the material by studying its RDF. It was found that the sp³ fraction in the simulated structure increased with increase in temperature and pressure. When the pressure became large enough (larger than 10 GPa), the sp³ fraction tended to be constant. Compared with the short compression (2 ns), our long simulation (up to 25 ns) did not show improvement of this sp³ fraction.

NOMENCLATURE

$\overline{B}$, B	empirical bond-order function
D	nearest-neighboring distance among atoms
f	function to restrict the pair potential to nearest neighbors
F	force applied to atoms
E_b	Tersoff–Brenner potential energy
G_C	function associated with bond angles
m	atomic mass
N	number of atoms
r	position of the atom
$R^{(e)}$	equilibrium distance
t	time
V_A	attractive potential energy

V_R repulsive potential energy

GREEK SYMBOLS
α sp^3 fraction
ϕ potential energy

SUBSCRIPTS
i, j index of atoms

ACKNOWLEDGMENT

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