Impact-energy dependence of atomic mobility in diamondlike carbon film growth

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In this paper, the deposition of energetic C_2 clusters on silicon and diamond surfaces is investigated by molecular dynamics simulation. The impact energy ranges from 0.5 to 60 eV in order to compare with experiments of diamondlike carbon (DLC) film synthesis by femtosecond (fs) pulsed laser deposition. The influence of the impact energy on the deposition dynamics as well as the structure of the synthesized films is addressed. Simulations show that at the earlier stage of the deposition, the mobility of surface atoms, especially the recoil atoms, is enhanced at elevated incident energies, and contributes to the smooth growth of DLC films. Our results are consistent with experimental observations.

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I. INTRODUCTION

There has been great interest in the field of deposition and characterization of diamondlike carbon (DLC) films due to their unique properties of high hardness, wear resistance, chemical inertness, and potential application as protective coatings.[1–5] The processes employed to obtain such films include cathodic arc, ion beam deposition, pulsed laser deposition (PLD), etc. A common feature of these techniques is that the deposition is energetic, i.e., the carbon clusters (atoms) arrive onto the surface with energy significantly greater than that represented by the substrate temperature.

Recent investigation of PLD experiments showed that the films deposited by femtosecond (fs) pulsed lasers have a higher fraction of sp^3 bonds than those produced by a nanosecond (ns) pulsed laser. Further investigation elucidated that the plasma plume generated by fs pulsed lasers contains mainly lower-mass carbon clusters (C and C_2), and has high kinetic energy, which is favorable to DLC film growth.[6,7] Moreover, the structure properties of nanostructured films assembled from supersonic carbon-cluster beams have been studied.[2] Transmission electron microscopy (TEM) of the assembled films shows large porosity at lower incident energy (0.1 eV/atom) and the film density is increased with increasing impact energy. It is highly desired to study how the incident energy affects the structure of assembled C films.

In this paper, the impact-induced chemisorption of small carbon clusters, C_2, was studied by molecular dynamics (MD) simulations. The impact energy (E_{in}) ranged from 0.5 eV to 60 eV per cluster in order to compare with fs PLD and supersonic cluster-beam-deposition (SCBD) experiments. The main purpose is to investigate the temporal mobility and migration of adatoms on the surface in order to understand the incident-energy dependence of the film morphology at low substrate temperature.

II. COMPUTATIONAL MODEL

The simulation model is similar to that in Refs. 8–10. The semiempirical many-body Brenner (no. 2) potential[11] and Tersoff potential[12] were used to describe the interaction between C-C, C-Si, and Si-Si atoms in the MD simulation. The structure of the C_2 cluster was first simulated. The binding energy of C_2 was calculated to be 6.017 eV, which agrees well with a previous calculation.[13] The silicon and diamond surfaces we employed were composed of 10 layers with 64 atoms per layer. The bottom two layers were held fixed to simulate a thick substrate. The velocity scaling method of Berendsen *et al.*[14] was applied to the middle four layers in order to maintain a constant substrate temperature, which was set at 100 K. Parallel to the surface, periodic boundary conditions were applied. The incident molecule was initially placed at a sufficient distance above the surface where the interactions between the molecule and surface atoms were negligible. Then, it was projected in the normal direction onto the surface, which was equilibrated at a constant temperature. The trajectories of all atoms in the system were determined by integrating the equations of motion according to the leapfrog algorithm with a time step of 0.5 fs.

First, the monoenergetic C_2 clusters were modeled to drop one after the other on the same Si surface to simulate the initial fabrications of cluster assembled films. The orientation and impact position of C_2 were chosen randomly to mimic the experiments. Experimentally, the deposition rate is varied around 10^{17} to 10^{18}/(atoms/s)/cm^2. However, a MD simulation is very time consuming and cannot calculate the time scale as in experiments. It is known that for the covalent cluster assembled films, it is difficult for diffusion to occur during the growth process and the transient impact dynamics plays a leading role, especially at low temperature.[8] The theoretical deposition rate is thus arranged to be low enough to warrant that the next cluster impacted after the full relaxation of the former one. In our previous study, it was observed that the dynamic process of single-cluster deposition was almost completed within 1 ps when the impact energy was below 100 eV.[10] Therefore, the time interval between two successive impacts was set to be from 2 to 6 ps, depending on the impact energy of C_2 clusters. These parameters are corresponding to a very high deposition rate, varying in the range of 10^{23}–10^{25} (atoms/s)/cm^2, similar to that in Ref. 2. Despite this difference, the MD study does provide insight into transient dynamic process during cluster deposition.[2,8,15]

TABLE I. Mean density of the assembled C_2 films at different impact energy.

Impact energy (eV)	0.5	2	5	15	30	60
Density[a] (g/cm^3)	1.82	2.24	2.38	2.87	3.00	3.17

[a]The density of graphite is 2.22 g/cm^3, and the density of diamond is 3.51 g/cm^3.

To explore the growth mechanism of DLC films at an atomic scale, single C_2 clusters were then deposited on a diamond surface with defects. It was expected to elucidate the dynamics of cluster deposition, since the C-C interaction dominates the growth process of the film. The atomic mobility as well as the lateral migration of surface adatoms, which was strongly dependent on the impact energy, was studied by statistics calculations.

III. RESULTS AND DISCUSSION

A. Assembling of DLC films by C_2 cluster deposition

In order to study the influence of the impact energy on the film morphology, the deposition of a monoenergetic C_2 cluster beam on a silicon (001)-(2×1) surface was first simulated and the initial fabrication of the formed films was studied. The impact energy varied from 0.5 to 60 eV/cluster. For each energy value, over 1400 carbon atoms were deposited on the surface. Six different "C_2 films" were thus synthesized, where all the deposition parameters were the same except the impact energy. The structure characteristics of these films were analyzed quantitatively. The mean densities of the simulated films for the six incident energies were calculated and are displayed in Table I. The data were extracted from the "bulk" part of each adlayer. The statistics were accumulated over 1200 deposited C atoms and averaged over 20 times during the MD simulation. Furthermore, the neighbor number (NN) distributions of C atoms in the adlayers are

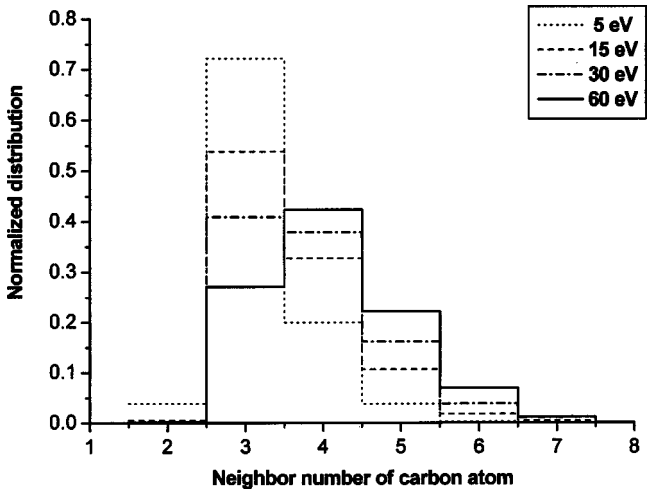

FIG. 1. The neighbor-number distribution of atoms in C films synthesized at the impact energies of 5, 15, 30, and 60 eV. Each has over 700 C_2 clusters deposited.

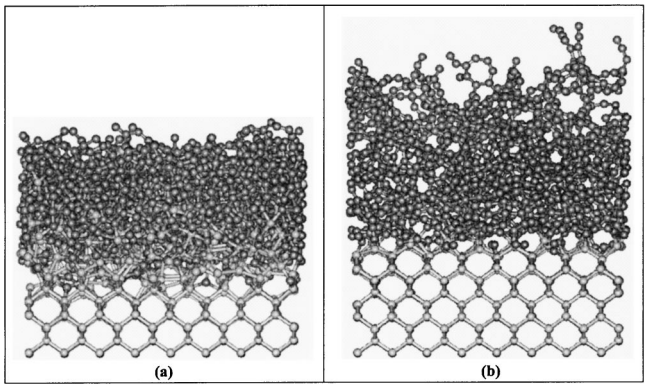

FIG. 2. Atomic configurations of carbon films synthesized of C_2 clusters (gray circles) on a Si substrate (hollow circles) at the impact energy of 60 eV (a) and 0.5 eV (b). Each has 735 C_2 clusters deposited.

calculated by cutting the nearest distance of 1.77 Å, which is obtained with the same statistics and exhibited in Fig. 1.

Table I shows that the higher the impact energy, the higher the density of the deposited film. When the impact energy of C_2 is 2 eV, the density of the assembled film approaches that of graphite (2.22 g/cm^3). Correspondingly, its NN distribution peaks at three, also having the same value as that of graphite. At 15 eV, the density is close to the intermediate value between that of graphite and diamond, and the proportion of four NN's is about 45%, which is much larger than that at 5 eV. At 30 eV, the density is further increased, and the proportion of C atoms having four NN's is about 65%. At 60 eV, the film density reaches that of diamond, and the proportion of carbon atoms having fourfold coordination is dominant ($>70\%$). Our results are in reasonable agreement with TEM measurements in the SCBD experiment,[2] where a cluster beam of mass distribution at 0.1 eV/atom was deposited. The relative lower density in the experiments may attribute to the cluster size effect.[2,8] It also supports the fs PLD experimental findings that the synthesized film is more graphitelike at lower incident energy and more diamondlike at relative higher incident energy. It indicates the higher impact energy is suitable to grow high-quality DLC films.[6,7]

To compare the film morphology, Fig. 2 presents the side view of atomic positions of the grown samples with the 735 C_2 cluster deposited, where the impact energies were 60 eV (a), and 0.5 eV (b), respectively. It is shown that sample (a) is more homogeneous, showing a small density fluctuation in the bulk region, and is more compact. Sample (b), unlike the former case, is no longer homogeneous. Rather it displays density fluctuation and is highly porous. These results are consistent with those of atomic force microscopy (AFM) measurements,[1,5] which shows the film roughness increasing with decreasing impact energy. Furthermore, it was found that smooth surfaces and diamondlike properties are obtainable for $E_{in}\geqslant 30$ eV/atom.

To explain the energy dependence of the film character, Cuomo *et al.*, proposed that in this energy regime (1 to 100 eV) the subsurface interaction become significant.[1] The subplantation model proposed by Lifshitz *et al.* suggested that

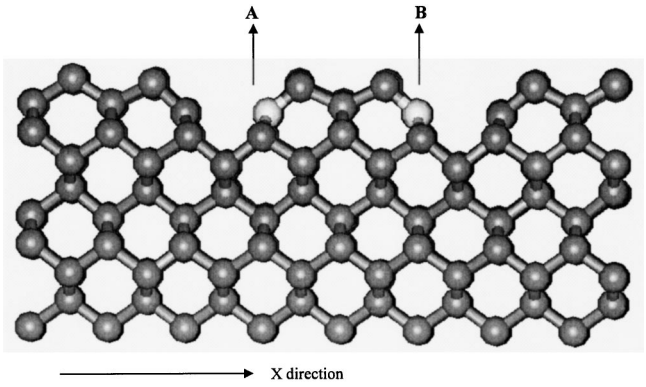

FIG. 3. Side view of the $8\times8\times10$ diamond (001) surface with two rows of vacancies. The two grooves of defects are perpendicular to the X direction.

subsurface internal growth plays a leading role in DLC film synthesis.[5] However, there have been few reports of quantitative studies of the subsurface atomic interaction and how it affects the film structure. During the fabrication process we observed that at low E_{in} the vacancies formed would affect the film morphology to be porous. This is because a local potential barrier existed nearby and the atomic mobility is too low to fill up the vacancies. The porous structure was known to be related to surface roughness and lower density of the films. Therefore, it is highly desirable to investigate quantitatively the mobility and migration of surface atoms induced by cluster impact on the surface, especially a surface with defects. A new simulation model was thus designed and is discussed below in Sec. III B.

B. Statistical study of atomic mobility and migration during C_2 deposition

To explore the atomic-scale growth mechanism of energetic C_2-cluster deposition, single C_2 clusters were deposited on a diamond surface, which has two rows of artificial vacancies (Fig. 3). The simulations were arranged such that the impinging position of C_2 on the surface was limited to the area between line A and B, shown in Fig. 3. Both the orientation and the impact position of the incident C_2 cluster relative to the surface were chosen randomly. The results were compared under the same collision geometry but different impact energy. The statistics were accumulated over 400 clusters at each E_{in}, which ranges from 2 to 60 eV.

To examine the potential barrier caused by defects, the potential energy of a C atom placed at a fixed distance 1.54 Å (diamond bond length) above the surface (Fig. 3), which was assumed to be rigid for simplicity, was first calculated. The potential energy as a function of x and y coordinates parallel to the surface was depicted in Fig. 4. It is shown to be sensitive to the surface structure and there is a potential barrier around the region of vacancy. The maximal value of the barrier is about 2.9 eV. It has to be noticed that the real value may be much larger than that in the above calculation because the cluster may be closer to the substrate and the surface may be damaged and have more defects during cluster impacting. Surrounding atoms that can fill up the vacancy must have enough kinetic energy to overcome the potential barrier.

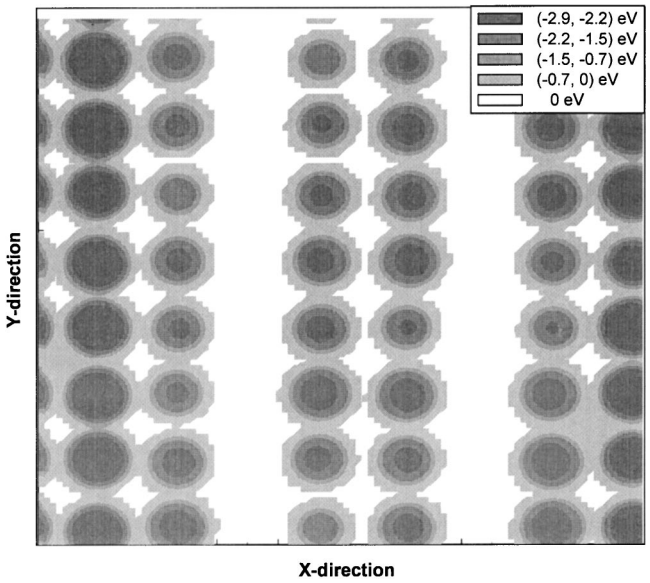

FIG. 4. Map of the surface potential energy for a carbon atom placed at a fixed distance 1.54 Å (diamond bond length) above the surface (see Fig. 3) and moving along the X and Y directions parallel to the surface.

The C_2 cluster was then deposited on the surface at 2, 5, 15, 30, 45, and 60 eV impact energy. Following the subsurface theory, the depth distribution of C_2 on the surface (Fig. 3) was calculated. It was observed that at lower energy, cluster atoms mainly remain on the surface. With increasing energy, more cluster atoms penetrate into the surface. The mean depths of projectiles were found to be -1.3 Å (above the surface) and 1.0 Å for the cases of 2 eV and 60 eV, respectively. Even at 60 eV, the surface reconstruction and atomic migration caused by cluster impact mainly occurred at one or two layers near the surface. This indicates that the implantation of cluster atoms does affect the film structure partly.[1]

TABLE II. Statistical result of transverse migration of cluster and recoils along the X direction.

Impact energy (eV)	2	5	15	30	45	60
Number of impact atoms per cluster with $\Delta X > b_0$,[a] N_{pmx}	0.10	0.19	0.37	0.32	0.38	0.40
Number of recoil atoms per cluster with $\Delta X > b_0$, N_{rmx}	0.01	0.04	0.08	0.23	0.42	0.70

[a] b_0 is diamond bond length (1.54 Å).

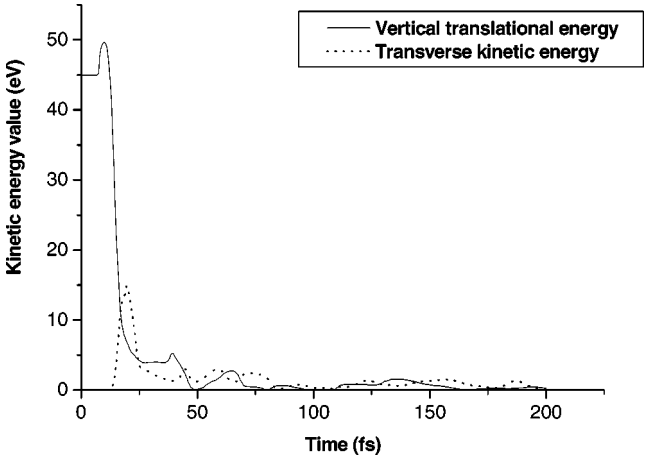

FIG. 5. The time evolution of the vertical kinetic energy and transverse kinetic energy of a C_2 cluster during deposition. The incident energy is 45 eV.

However, the effects are not very sensitive to the impact energy, and are therefore insufficient to explain the energy dependence of the film morphology shown above (Fig. 1 and Table I). Following the trajectories of cluster atoms we found that the migration distance of cluster atoms parallel to the surface was even larger than that in the normal direction, especially at higher E_{in}. Furthermore, the distance is strongly dependent on the incident energy. As an example, at 60 eV some cluster atoms moved $5b_0$ ($b_0=1.54$ Å is bond length of diamond) away from their impact position on the surface, whereas their penetration depths were only around $0.62b_0$. To get smooth films, the atoms on the surface must have enough migration distance along the X direction so that they can probably be trapped in a vacancy. The number of cluster atoms having transverse migration along the X direction larger than b_0 ($\Delta X > b_0$), N_{pmx}, was calculated and is presented in Table II. Also shown in Table II is the number of recoil atoms having the same transverse migration distance ($\Delta X > b_0$), N_{rmx}. Table II shows that below 15 eV, N_{pmx} is increased rapidly with increasing the energy. Above 15 eV, it has less change because more energy is dissipated by the collision with surface atoms. Consistently, N_{rmx} steeply increases as the energy is increased. Above 45 eV, the number of recoil atoms with $\Delta X > b_0$ is larger than the number of projectile atoms with $\Delta X > b_0$. This indicates that the recoil atoms play a more important role in filling vacancies when the impact energy is above 45 eV. Therefore, by increasing the impact energy the lateral spread of atoms both on the surface and in the subsurface is enhanced, and the synthesized C films will consequently be dense and smooth.

The probability of atomic migration on the surface is known to be dependent mainly on two factors. One is the surface potential barrier and the other is the atomic mobility. The time evolution of the kinetic energy of a C_2 cluster during deposition is exhibited in Fig. 5. The incident energy is 45 eV. At about 10 fs, the vertical translational energy of the C_2 cluster, $E_V = m(v_{1z}^2 + v_{2z}^2)/2$, reaches the maximum value, 50 eV, where m is the mass of a carbon atom and v_{1z} and v_{2z} are vertical velocities of the two atoms of a C_2 cluster. Soon

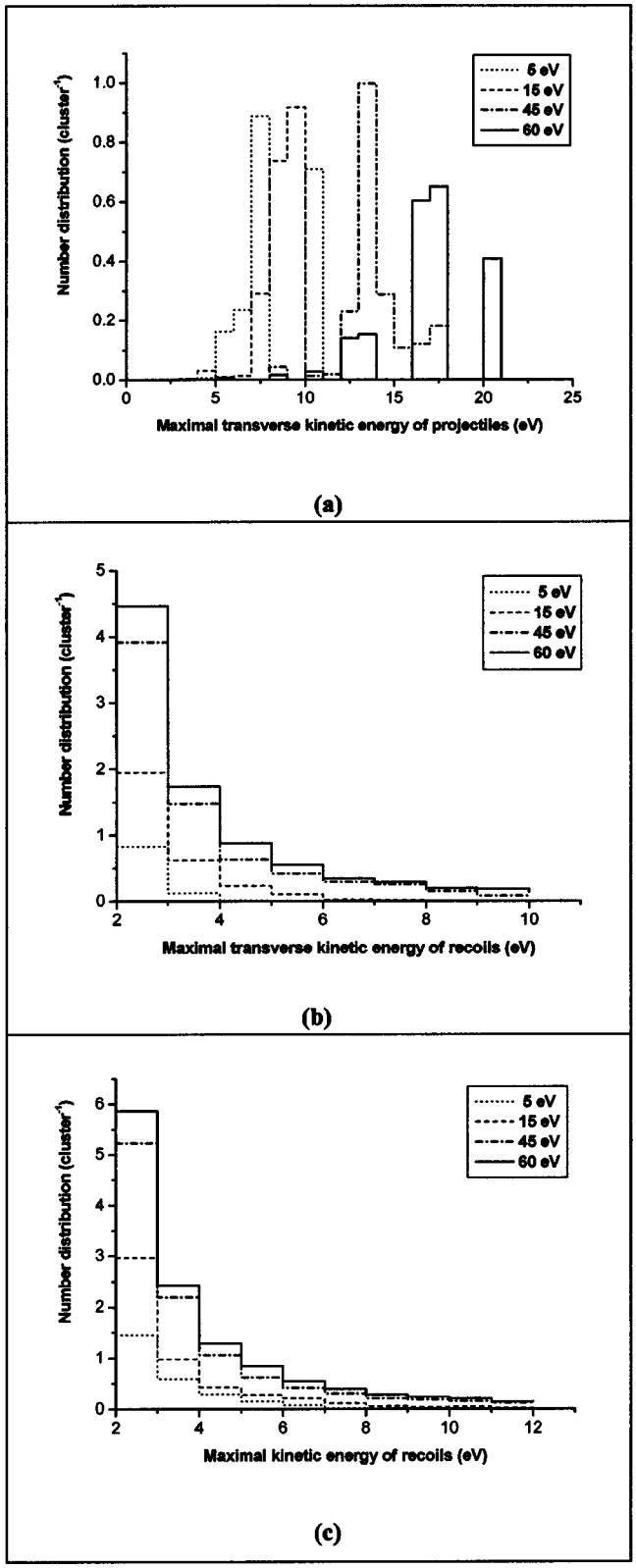

FIG. 6. Transverse kinetic energy distribution of cluster atoms (a) and recoil atoms (b), and the kinetic energy distribution of the recoils (c). See the text for the definition of the transverse kinetic energy.

the energy is transferred to the kinetic and potential energy of the substrate. At about 20 fs, the transverse kinetic energy (E_T), $E_T = m(v_{1x}^2 + v_{1y}^2 + v_{2x}^2 + v_{2y}^2)/2$, reaches the maximum value, 15 eV, where v_{1x}, v_{1y}, v_{2x}, and v_{2y} are the transverse velocities of the two atoms of a C_2 cluster along the X and Y directions, respectively. It is defined as the kinetic energy of cluster atoms corresponding to the momentum parallel to the surface. Around the same time, the kinetic energy of recoil atoms reached the maximum value, too. At about 500 fs, the kinetic energies of both projectiles and surface recoils approach the minimum value and a quasiequilibrium adsorption configuration is thus formed. For each cluster deposited, we followed the trajectory of the cluster atoms as well as the recoils produced and picked the maximum transverse kinetic energy E_T of every moving atom. The distribution of maximum E_T is exhibited in Fig. 6. It shows that both the value of the maximum E_T and the number of moving atoms are strongly dependent on the impact energy. Above 15 eV, almost all projectiles have E_T larger than 7.5 eV (the cohesive energy of diamond is 7.37 eV), which make projectiles have a large transverse motion. This is consistent with Table II. Above 45 eV, the number of recoils having E_T larger than 3 eV is over three times higher than that at 15 eV. At 60 eV, the maximum E_T reaches 20 eV for projectiles and close to 10 eV for recoils. Corresponding to each C_2 impact, over four recoils have energy higher than 3 eV. A similar trend was observed for the kinetic energy distribution of recoils [see Fig. 6(c)]. It can be understood that at higher E_{in}, clusters and recoils have enough lateral kinetic energy to overcome the potential barrier and migrate a large distance. Finally they may reside on the energetically favored adsorption site. The films thus formed become more dense and smooth. At lower E_{in}, the lateral kinetic energy of projectiles is too low to cross the potential barrier. As a result, the formed film may have low density and coordinate number as shown in Table I and Fig. 2. Therefore, we conclude the transient mobility, especially the mobility of recoils, which was observed at the earlier stage of the cluster impact, takes a leading role in DLC film growth.

IV. CONCLUSION

The deposition dynamics of the low energy C_2 clusters and the initial fabrication of films assembled by C_2 on silicon surfaces were studied by MD simulation using the Brenner and Tersoff potentials. The impact energy ranged from 0.5 eV to 60 eV. The effect of the impact energy on the film morphology was investigated by studying the atomic mobility. Our main results can be summarized as follows.

The impact energy plays a significant role in the film structure synthesized by energetic carbon cluster deposition. At lower E_{in} samples are dominated by threefold coordination, and they are porous. Above 45 eV, fourfold coordination is dominant and the densities are close to that of diamond.

The impact induced mobility and the lateral migration of surface atoms, especially the mobility of recoils, which is caused by collision cascades, take a leading role in DLC film growth. The recoil mobility is enhanced greatly as the impact energy is increased.

Our results support the experimental observation that the films assembled from projectiles (mainly C_2 and C) having relatively high kinetic energy may have a high fraction of sp^3 bonds.[6–7] The results are also partly consistent with the earlier theoretical model that in the energy regime of 1–100 eV, subsurface interactions become significant.[1,5] In addition, the present simulation makes clear that the surface mobility, especially the mobility of recoil atoms, caused by energetic impact, dissipates the incident kinetic energy and promotes the smooth growth of films.[15]

The MD simulation conducted was limited to the earlier stage of the film growth, where the collision dynamics take a leading role. The thermally activated diffusion has not been included and needs to be further studied.

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