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Structure character in small-carbon-cluster deposition on diamond surface

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Abstract. Experimentally, hydrogen-free diamond-like carbon (DLC) films were assembled by means of pulsed laser deposition (PLD), where energetic small-carbon-clusters were deposited on the substrate. In this paper, the chemisorption of energetic C_2 and C_{10} clusters on diamond (001)-(2×1) surface was investigated by molecular dynamics simulation. The influence of cluster size and the impact energy on the structure character of the deposited clusters is mainly addressed. The impact energy was varied from a few tens eV to 100 eV. The chemisorption of C_{10} was found to occur only when its incident energy is above a threshold value (E_{th}). While, the C_2 cluster was easily to adsorb on the surface even at much lower incident energy. With increasing the impact energy, the structures of the deposited C_2 and C_{10} are different from the free clusters. Finally, the growth of films synthesized by energetic C_2 and C_{10} clusters were simulated. The statistics indicate the C_2 cluster has high probability of adsorption and films assembled of C_2 present slightly higher SP^3 fraction than that of C_{10}-films, especially at higher impact energy and lower substrate temperature. Our result supports the experimental findings. Moreover, the simulation underlines the deposition mechanism at atomic scale.

PACS. 61.43.Bn Structural modeling: serial-addition models, computer simulation – 79.20.Rf Atomic, molecular, and ion beam impact and interactions with surfaces – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

In recent years, pulsed laser deposition has been used to produce diamond-like carbon (DLC) films, which allows the production of non-hydrogenated DLC films at lower substrate temperature (ST) [1–4]. These films have potential use as protective coatings for magnetic and optical disks and wear resistant applications. Experimental observation showed the DLC films deposited by femtosecond (fs) pulsed laser were superior to that deposited with nanosecond (ns) pulsed laser [1,3]. The former has high microhardness and optical transmittance in the infrared to visible range. Further investigation elucidated that the main components in the plasma plume generated by fs pulsed laser are lower-mass carbon clusters, C and C_2. Whereas, in the latter case, the main component clusters have relatively higher mass, *e.g.* C_{16}, C_{10}, C_4, etc. [1,3]. For the latter, the monocyclic structures are more stable [5]. In addition, it was believed that in the former case, the particles in the plasma plume have relatively higher kinetic energy and more intense flux, which is favorable to have high fraction of SP^3 bond in carbon films [1,3–7].

In this paper, the impact-induced chemisorption of small-carbon-clusters, C_2 and C_{10}, was studied by molecular dynamics (MD) simulations. The impact energy (E_{in}) ranged from a few eV to 100 eV per cluster. In addition, the initial fabrication of films assembled of C_2 and C_{10} (monocyclic) was simulated. The influence of cluster size and the impact energy on the structure character of the adsorbed clusters was mainly addressed.

2 Computational model

The simulation model is similar to that in references [8,9]. The semi-empirical many-body Brenner (#2) potential [10] was used to describe the interaction between C atoms in the MD simulation. The structures of the C_2 and C_{10} clusters were first simulated. The latter has a stable monocyclic structure. The binding energy of C_2 and C_{10} were calculated to be 6.017 and 60.17 eV, respectively, which agrees well with the other calculation [5]. The diamond surfaces we employed were composed of 10 layers

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with 100 and 144 atoms per layer, respectively. The bottom two layers were held fixed to simulate a thick substrate. The velocity scaling method of Berendsen [11] was applied to the middle eight layers in order to maintain a constant substrate temperature. 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 at 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 Leap-Frog algorithm.

To explore the initial stage of carbon cluster (C_2 and C_{10}) assembled films, the clusters were modeled to drop one after the other on the same surface. Experimentally, the time interval between two impacting clusters is millisecond (ms) order of magnitude. But MD is very time consuming and cannot calculate time scale of ms magnitude in the present simulation. For the covalent cluster assembled films, diffusion is difficult to happen during the growth process and the transient impact dynamics plays a leading role, especially at low temperature. At low incident energy studied, the dynamic process of single-cluster deposition was found almost completed within 1 ps. Therefore, the time interval between two successive impacts was set to be 1.5 to 3 ps, respectively, depending on the cluster size. The next cluster impacted after the full relaxation of the former one. To prevent the correlation the impact position as well as the orientation of the molecule relative to the surface were selected randomly.

3 Results and discussion

3.1 Deposition of single C_{10} ring on diamond surfaces

The chemisorption dynamics of C_{10} on diamond (001)-(2×1) surface at room temperature ($T = 300$ K) was first studied. The energy threshold (E_{th}) effect, which is required for chemical bonding, was observed. The values of E_{th} for C_{10} were calculated to be around 5 to 40 eV per molecule, which is sensitive to the impact position as well as the orientation of the cluster relative to the surface. It is a few eV lower with the cluster plane perpendicular to the surface than that with the cluster plane parallel to the surface in general. In the former case, the bonds in C_{10} close to the surface is easy to be broken and form bonds with surface atoms due to the strong local interaction. The dynamic process of a C_{10} ring deposition on the diamond (001) surface at $E_{\mathrm{in}} = 50$ eV is exhibited in Figure 1. The molecule plane was initially perpendicular to the surface and it impacted towards the center of two dimers on the surface. At $t = 50$ fs, it was rotated due to the asymmetry interaction with the surface. Then, bonds were formed between cluster and the surface atoms. At 300 fs, the adsorbed C_{10} was rearranged to be a multi-cyclic bowl-like structure and more bonds were formed between the cluster and the surface, which was kept almost unchanged at the end of this run (3 ps). This feature is quite different from the "memory effect" observed for the fullerene and large C-cluster deposition [9,12,13]. To investigate the effect of impact energy on the adsorption configuration, we varied the impact energy from 10 to 100 eV with the same collision geometry as that in Figure 1. The corresponding adsorption configurations are indicated in Figures 2 and 1. It shows that close to E_{th} (21 eV), the structure of the adsorbed C_{10} is similar to a free-C_{10}. With increasing E_{in} to 50 eV, the adsorbed C_{10} has a multi-cyclic bowl-like structure (Fig. 1). At 100 eV, the ring structure is almost lost in the deposited C_{10} cluster.

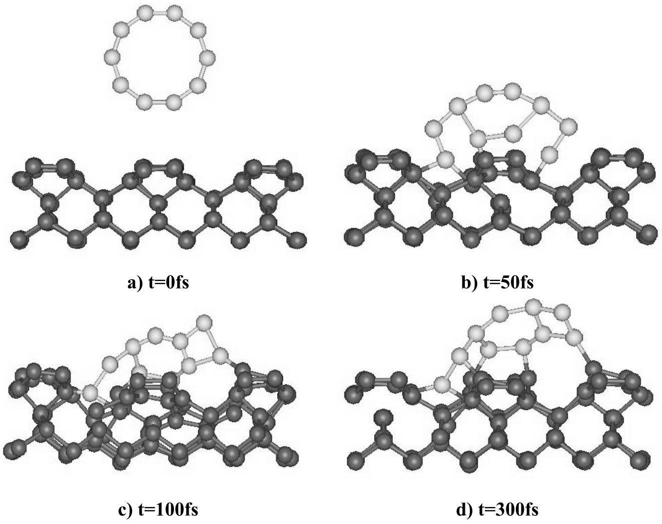


Fig. 1. Snapshots of the atomic positions for a C_{10} cluster impacting on the diamond surface. The cluster is incident normally onto the surface with initial energy 50 eV. (a) $t = 0$ fs, (b) $t = 50$ fs, (c) $t = 100$ fs, (d) $t = 300$ fs. The configuration at 3 ps is almost close to that of 300 fs and therefore, not presented here.

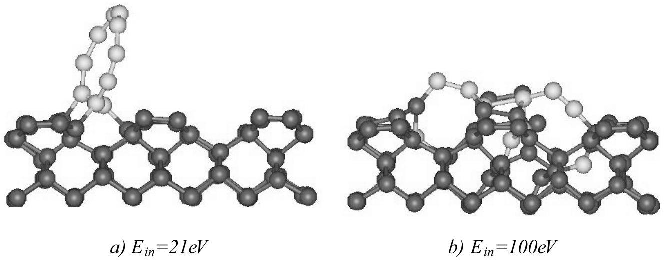
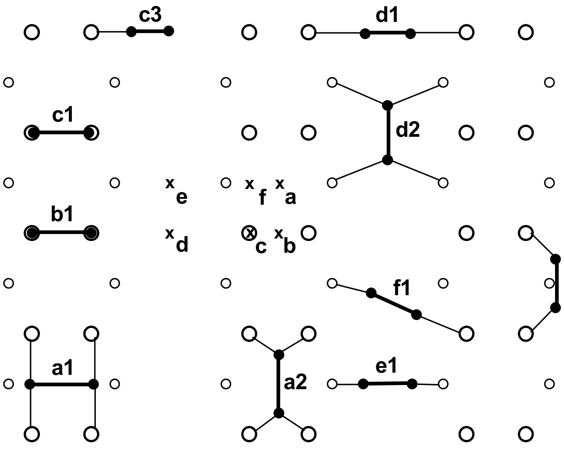


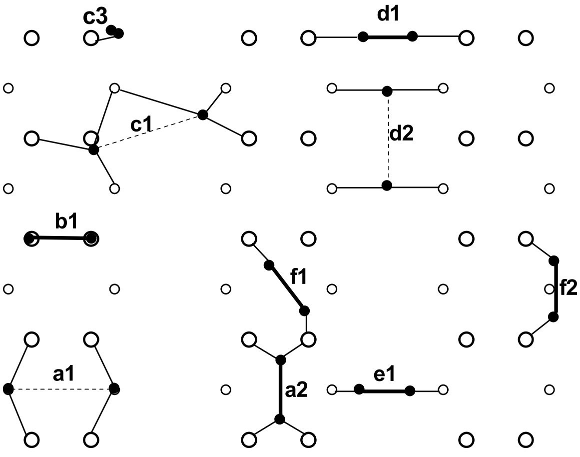
Fig. 2. Snapshots of the final positions (3 ps) of atoms of C_{10} and diamond surface after impact at different energies, E_{in}. (a) $E_{\mathrm{in}} = 21$ eV, (b) $E_{\mathrm{in}} = 100$ eV. The initial structure of C_{10} is a monocyclic as shown in Figure 1a.

3.2 Deposition of single C_2 cluster on diamond surfaces

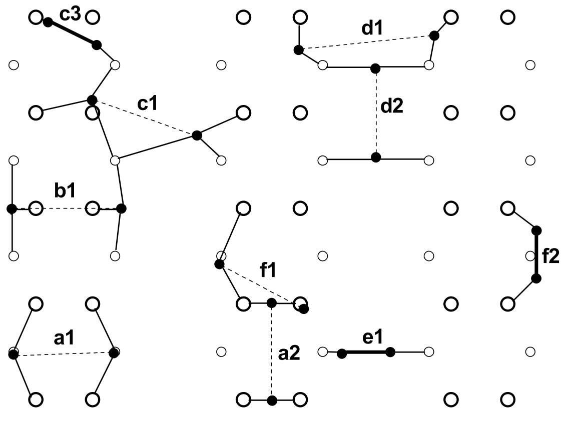
The linear C_2 was then impacted on the diamond (001) surface. It is interesting that even at much lower impact energy, say, 0.01 eV, C_2 is easy to be chemisorbed on the surface. The chemisorption geometry, however, was found



(a) E_{in}=1eV



(b) E_{in}=20eV



(c) E_{in}=30eV

Fig. 3. Schematic illustration of the top view of several typical chemisorption configurations for C_2 on the diamond (001) surface. The hollow circles represent surface atoms. The smaller circles represent atoms in the lower layer. The solid circles represent cluster atoms. The cross symbols (×) show six typical impact positions chosen in this simulation. The thin solid lines are the bonds between the atoms on the surface and that in C_2 clusters. The thick solid lines are the bonds between deposited cluster atoms, and the dashed lines indicate the C_2-bonds broken.

to be dependent on the impact energy strongly. Figure 3 exhibits the typical chemisorption configurations of a C_2 cluster on diamond (001) surface, where a, b, c, d, e, and f denote six typical impact positions chosen. The orientation of the C_2 molecule was chosen along (001), (110), and $(1\bar{1}0)$ direction and the impact energies were 1, 20 and 30 eV. It was observed that with increasing the impinging energy some clusters formed bonds with atoms located at the second or lower layer of the substrate and the probability of the cluster fragmentation was enhanced. At 1 eV, all the bond-lengths in adsorbed C_2 were less than 1.5 Å. While at 20 eV, the bonds within C_2 at sites a1, c1 and d2 were broken and at 30 eV, C_2-bonds at sites a1, a2, b1, c1, d1, d2, and f1, were broken. Furthermore, the dimer opening effect caused by C_2-adsorption, which is the pathway of DLC film growth [14], was found. The probability of dimer opening, corresponding to a C_2 cluster adsorption, is increased with increasing the incident energy. The calculated values, at $E_{\rm in}$ = 5, 20, and 50 eV, are about 0.18, 0.36 and 0.41, respectively. The statistics were accumulated over one hundred events at each energy.

3.3 Assembling of C_{10} and C_2 thin films

Finally, the initial fabrication of "C_2-films" synthesized of C_2 clusters and "C_{10}-films" assembled by C_{10} clusters was simulated by mono-kinetic cluster-beam deposition. The impact energies were selected as 100 eV for C_{10}, and 20 and 5 eV for C_2 for comparison. For each adlayer, more than 800 atoms were deposited. Then the velocity scaling method of Berendsen [11] was applied to the whole system, which lasted around 2 ps for statistical analysis. It was observed that up to 100 eV, the deposited C_{10} clusters were aggregate each other on the surface. The bond-angle and neighbor-number (NN) distribution of the C_{10}-film after 86 clusters deposited at 100 eV are exhibited in Figure 4. The statistics were accumulated over four hundred deposited cluster atoms and data were obtained each 3 fs and averaged over 20 times. It shows the structure of the adlayer presents threefold and fourfold character, and is totally different from the original structure of C_{10}-monocyclic, where the number of neighbors is two and the bond angle is 144 degree for all the atoms in a free C_{10}. Also shown in Figure 4 is the NN and bond-angle distribution of carbon atoms of the "C_2-film" after 400 clusters deposited at 20 eV with the same statistics. The probabilities of four-NN and three-NN are around 0.16 and 0.82, respectively, for the "C_{10}-film". The corresponding values are 0.21 and 0.77 for the "C_2-film". By comparison, the value of four-NN in the C_{10}-film is 24% lower than that in the "C_2-film". In contrast, the value of three-NN in the C_{10}-film is 6.1% higher than that in the "C_2-film". The similar trend was observed in the bond-angle distribution. The peaks at 115° and 120° are relatively higher in the "C_{10}-film". The calculated densities are 2.981 g/cm^3 and 3.173 g/cm^3 for the C_{10} and C_2-film, respectively. Therefore, we conclude the SP^3 fraction in the "C_2-film" deposited at 20 eV is slightly superior to that in the "C_{10}-film" deposited at 100 eV. Furthermore, the influence of

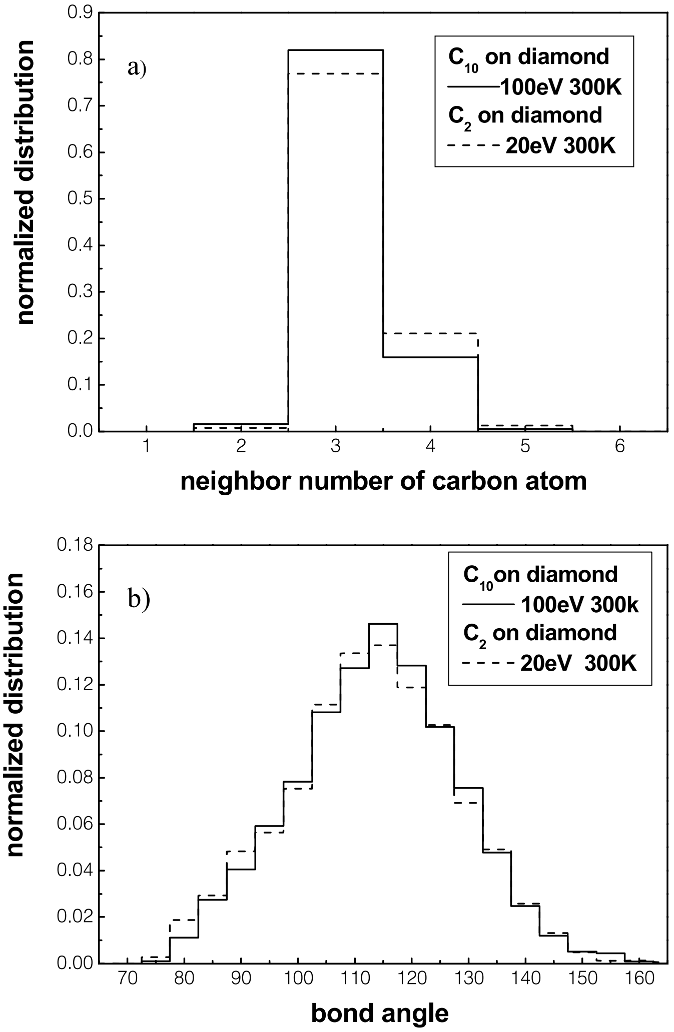


Fig. 4. Comparison of the neighbour-number distribution (a), and bond-angle distribution of carbon atoms (b), between the "C_{10}-film" and "C_2-film". The former has 86 C_{10} clusters deposited and the latter has 400 C_2. The impact energies are 100 eV and 20 eV, respectively. The substrate temperature was set at 300 K.

the impact energy and the ST were studied. The bond angle distributions of the C_2-films assembled with three different conditions are exhibited in Figure 5. It is shown that the bond-angle distribution corresponding to $E_{\text{in}} = 5$ eV is peaked at 115−120°, which presents high SP^2 fraction. It indicates that higher incident energy is suitable to grow DLC films. Figure 5 also shows that at the same impact energy (20 eV), the peak at 110° (SP^3) is enhanced at lower ST (100 K).

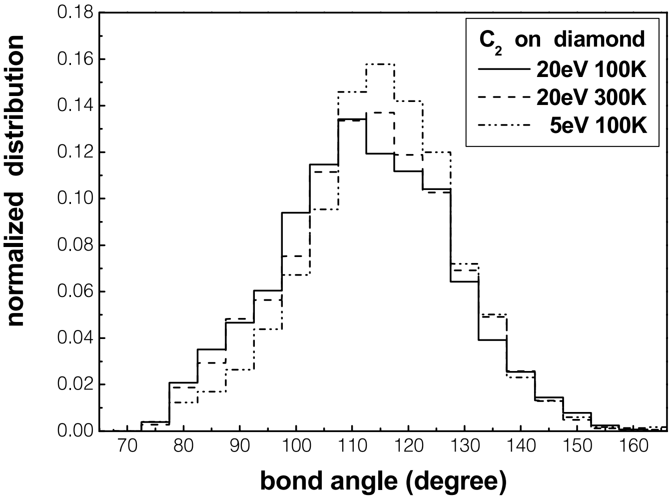


Fig. 5. Comparison between the bond-angle distributions of carbon atoms in C_2-films with $E_{\text{in}} = 20$ eV, $T = 300$ K; $E_{\text{in}} = 20$ eV, $T = 100$ K; and $E_{\text{in}} = 5$ eV, $T = 100$ K.

4 Conclusion

The deposition dynamics of the low energy C_2 and C_{10} clusters and the initial fabrication of films assembled by C_2 and C_{10} on diamond surfaces were studied by MD simulation using the Brenner potential. Our main results can be summarized as follows:

1. the carbon dimer (C_2) is easily to adsorb on the diamond surface even at much lower energy (0.01 eV). However, the energy threshold (E_{th}) was observed for the C_{10} ring adsorption on the diamond surface, which is around 5 to 40 eV depending on the impact position and the cluster orientation relative to the surface;
2. the structure of the adsorbed C_{10} is different from that of the free C_{10} ring. With increasing the incident energy, the difference becomes more apparent;
3. the fragmentation of C_2 and the surface-dimer opening caused by C_2 chemisorption were observed, which are suitable to growth DLC films. Their probabilities are increased with increasing the incident energy;
4. the film assembled of C_2 is slightly superior to that synthesized by C_{10}-clusters especially at higher impact energy and lower ST. The SP^2 fraction is enhanced with decreasing the impact energy.

Our results are in reasonable agreement with the experimental findings that comparing with the ring-structure clusters, the linear C_2 cluster seems more suitable than the former in DLC film growth, especially at relatively higher kinetic energy and lower ST [1–4]. Moreover, the present simulation underlines the deposition mechanism at atomic scale and establishes the rational link between the structure character of the deposited clusters with the beam feature (cluster size and the incident kinetic energy). Owing to the approximation inherent to the MD model and the limitation of computational capability, not only the number of deposited clusters, but also the simulation time are much less comparing with the experiments. Therefore, in order to compare with the experimental results quantitatively the simulation model needs to be further improved in our future study.

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