Simulations of C$_{28}$ chemisorption on diamond (001)-(2×1) surface: The comparison between cluster–cluster interaction and cluster–surface interaction

W. J. Zhu$^{a)}$ and Z. Y. Pan$^{b),c)}$
State Key Laboratory for Material Modification by Laser, Ion, and Electron Beams, Institute of Modern Physics, Fudan University, Shanghai 200433, People’s Republic of China

Y. K. Ho$^{d),e)}$
CCAST World Laboratory, P.O. Box 8730, Beijing 100080, People’s Republic of China

Y. X. Wang$^{f)}$
State Key Laboratory for Material Modification by Laser, Ion, and Electron Beams, Institute of Modern Physics, Fudan University, Shanghai 200433, People’s Republic of China

(Received 26 January 2000; accepted for publication 29 August 2000)

In this article, the dynamic behavior of C$_{28}$ chemisorption on diamond (001)-(2×1) surface was investigated by molecular dynamics simulation. The many-body Brenner potential was employed to describe the interaction between carbon atoms. With the incident energy ranging from 25 to 40 eV, the single C$_{28}$ was found to have more than 50% of the probability to be chemisorbed on a diamond surface and to form two C–C bonds with one dimer of the surface. Then the chemisorption of two C$_{28}$ clusters was simulated at the above energy range. The cluster–cluster interaction was found to hinder the next incident cluster to be chemisorbed. Besides, the juxtaposition configuration of two C$_{28}$ on the surface was observed when their impact points were along the same dimer row. For multicluster impacting, when two or three clusters formed a nucleation site, the forthcoming cluster was easily to be adsorbed close to it. The growth of the C$_{28}$ cluster assembled film is typically a three dimensional island mode. Our study also showed that within the energy range the C$_{28}$ clusters retained their cage structure after chemisorption. This is in agreement with experimental results.

© 2000 American Institute of Physics. [S0021-8979(00)03223-0]

I. INTRODUCTION

In recent years, intensified effort has been devoted to the research of cluster assembled materials.$^{1}$ Clusters exhibit specific properties which do not exist in solids and atoms or molecules. Due to the development of the technique in the low pressure inert gas condensation cluster source and the laser vaporization cluster source, clusters of various chemical elements can be produced. The low energy cluster beam deposition (LECBD) is a method to synthesize thin films which maintains the characteristic properties of free cluster (memory effect).$^{2}$ The experimental result suggested that covalent material produced by LECBD such as carbon and silicon showed different structure and some unique properties comparing with conventional amorphous structures (a-C and a-Si). Raman spectra from films assembled by LECBD of free clusters with mass distribution between $n = 20$ and $n = 30$ showed that the randomly stacked carbon clusters form specific nanostructures, which maintained the electronic structure of free clusters and deposited film kept the cage structure of the free cluster.$^{3}$ Of all the small fullerenes, C$_{28}$ is found experimentally to be the smallest.$^{4}$ Kroto proposed that C$_{28}$ cluster is a fullerene cage, chemically reactive, with four preferred active sites (A sites).$^{5}$ Guo et al. concluded that C$_{28}$ could form cage structure and reacts chemically both on the outside and on the inside.$^{4}$ The electronic states and structure of C$_{28}$ hyperdiamond were studied by ab initio method.$^{6,7}$ But much less is known about the dynamics of C$_{28}$ deposition on surface. There were a few theoretical studies on the deposition process of C$_{28}$ clusters.$^{8}$ Structure properties of C$_{28}$ cluster synthesized films, which influence the electronic and optical performance, depend on the deposition condition. The film synthesizing process is strongly affected by single cluster interaction with substrate and the interaction between impacting clusters. Here, we focus our attention on how the competition between cluster–cluster interaction and cluster–surface interaction affects chemisorption dynamics of C$_{28}$ clusters on diamond (001)-(2×1) surface and the initial fabrication of cluster assembled films. Simulation results showed that low incident energy deposited clusters could form covalent bonds with each other and maintain cage structure. This finding supports the random compact stacking mechanism during the LECBD process proposed by Paillard et al.$^{1}$ The calculation model is introduced in Sec. II. Computational results and discussion are given in Sec. III.

$^a$Also at: Institute of Fluid Physics, Chinese Academy of Engineering Physics, Mianyang City, Sichuan Province, 621900, People’s Republic of China.

$^b$Mailing address: Institute of Modern Physics, Fudan University, Shanghai 200433, People’s Republic of China.

$^c$Also at: Ion Beam Laboratory, Shanghai Institute of Metallurgy, Chinese Academy of Science.

$^d$Also at: State Key Laboratory for Material Modification by Laser, Ion, and Electron Beams, Institute of Modern Physics, Fudan University, Shanghai 200433, People’s Republic of China.

$^e$Electronic mail: hoyk@fudan.ac.cn
II. COMPUTATIONAL MODEL

In order to describe the interaction between C28 and a diamond surface, we employed the semiempirical many-body Brenner potential,9 which was developed from Tersoff potential with bond order function correction. The binding energy for this hydrocarbon potential is given as a sum over bonds by

$$E_b = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ V_R(r_{ij}) - B_{ij} V_A(r_{ij}) \right]. \quad (1)$$

In Eq. (1), $E_b$ is the binding energy for the system, $V_R(r_{ij})$ and $V_A(r_{ij})$ are the repulsive and attractive interactions, respectively, and $r_{ij}$ is the scalar distance between atoms $i$ and $j$. $B_{ij}$ is the bond order function which depends on quantities such as atomic coordinate and bond angles and includes nonlocal effects. The Brenner potential was originally derived from the simulation of diamond synthesis through chemical vapor deposition. This potential has been successfully applied to the study of fullerene interaction with semiconductor surfaces, too.11–13 The C28 cage is composed of 12 pentagons and 4 hexagons as shown in Fig. 1. There are four special atoms that form the apexes where three pentagons meet, which are sp$^3$ hybridization. They are termed as A sites. Each A site has a dangling bond, chemically active. The atoms that belong to pentagons and bond with A sites are termed as B sites. Other atoms are named as C sites. Both B sites and C sites are sp$^2$ hybridization, which form hexagon rings. Before processing the simulation, the structure parameters and cohesive energy of a single C28 cage were calculated, which is in good agreement with the quantum simulation.4,8 The results are listed in Table I.

![Geometric representation of C28 cluster structure. A sites are represented by black circles, B sites are represented by deep grey circles and C sites are light grey circles.](Image)

III. RESULT AND DISCUSSION

A. Single C28 cluster interaction with diamond surface

First, the single C28 cluster was dropped on the diamond surface to study cluster–surface interaction. The incident energy was chosen from 5 to 50 eV in steps of 5 eV. In order to study how the anisotropic structure of the surface affects cluster chemisorption and to save computational time, we chose 29 fixed impact points along ⟨110⟩ and ⟨1 10⟩ directions rather than random impacting, which are represented by small circles with cross symbol in Fig. 2(a). The simulation results showed within a specific incident energy range from 25 to 40 eV, the incident C28 clusters have more than 50% chance to be chemisorbed on the diamond surface with their cage structure. In most of the chemisorption configurations, a single C28 cluster forms two bonds with a surface dimer. Meanwhile, the related dimer length is observed to be increased, which supports the dimer opening mechanism proposed by Garrison et al.16 This typical chemisorption configuration is shown in Fig. 2(b).17 However, when the incident energy was less than 25 eV, the chemisorption probability was less than 10%. Most C28 cages rebounded from the surface with unbroken cage structure. When the incident energy exceeded 40 eV, the C28 cages were easily broken and the impact induced defects in diamond substrate appeared. Comparing with our previous simulation,16 C28 was found to be more chemical active than well-known C60. In our previous simulation, we found when the incident energy was about the critical value of 100 eV (1.67 eV/per atom), applied to the middle eight layers in order to maintain the substrate temperature constant at 300 K. Periodic boundary conditions are employed in the two directions parallel to the surface. Before the deposition begins, the system has been relaxed in a 300 K thermal bath for 10 ps allowing it to approach a thermal equilibrium state. The incident direction of the C28 cage is perpendicular to the diamond surface. The incident cluster is assumed to be rotationally and vibrationally cold. The incident cluster is initially located at 3 Å above the diamond surface where the interactions between the cluster and the substrate atoms are negligible. The trajectories are determined by integrating the equations of motion according to the LEAP-FROG algorithm.15

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Brenner Potential</th>
<th>Tight-Binding Potential</th>
<th>LDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A–B bond length (Å)</td>
<td>1.46</td>
<td>1.44–1.46</td>
<td>1.42–1.45</td>
</tr>
<tr>
<td>B–C bond length (Å)</td>
<td>1.44</td>
<td>1.40–1.44</td>
<td>1.40–1.44</td>
</tr>
<tr>
<td>C–C bond length (Å)</td>
<td>1.49</td>
<td>1.47–1.55</td>
<td>1.46–1.57</td>
</tr>
<tr>
<td>$E_b$ (eV)</td>
<td>186.64</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
C$_{60}$ would be chemisorbed on the diamond (001) reconstructed surface. For the present simulation, when incident energy was more than 25 eV (0.89 eV/atom), C$_{28}$ was likely to be chemisorbed on the diamond surface, even with incident energy as low as 5 eV (0.18 eV/atom), chemisorption of C$_{28}$ cluster on diamond surface was observed. This can be understood from the difference between the cohesive energy 6.56 eV/atom of C$_{28}$ and 6.99 eV/atom of C$_{60}$, and the existence of dangling bonds in C$_{28}$.

B. Competition between cluster–cluster interaction and cluster–surface interaction

In the aforementioned study, only the cluster–surface interaction was considered. However, during film synthesis process both cluster–surface and cluster–cluster interaction will take effect together. In order to study the competition effect between cluster–cluster interaction and cluster–surface interaction, a surface is designed with one C$_{28}$ cluster already chemisorbed on a surface dimer (termed as surface A), then a second C$_{28}$ cage is dropped on it. The incident energy of the second cluster is chosen to be between 25 and 40 eV, where a single C$_{28}$ cluster has a high probability of being chemisorbed on the diamond surface without breaking the cage structure. If the second C$_{28}$ had no interaction with the chemisorbed C$_{28}$, the dynamic behavior of the impact could be the same as that of a single cluster studied. Therefore, we limit the impact area of the second cluster to be within a circle centered at the chemisorbed C$_{28}$ with a certain radius. This radius is defined as the impact parameter $p$ if we consider the surface A as a target and the incident cluster as a projectile [see Fig. 2(b)]. In order to determine the maximum value of this radius, two free C$_{28}$ clusters were pushed closer together while their interaction potential energy (IPE) was calculated. It was observed that the two clusters began to interact with each other when the distance between them reached 6.5 Å. Since there is no chemical bond formed during the pushing process, the interaction force is always repulsive. The maximum radius of the impact area of the second C$_{28}$ was set to be 6.5 Å. We chose the same 29 fixed impact points as that in the previously mentioned study. The simulation model is illustrated in Fig. 2. We applied 116 events with 29 impact points and low incident energies of 25, 30, 35 and 40 eV. The impacting C$_{28}$ always rebounded from the surface A when the impact parameter $p$ was less than 3 Å. When $p$ was larger than 3 Å, there was about 15% of events where chemisorption happened. The results showed interaction between two clusters causes the chemisorption rate on surface A to be much less than that (about 50%) on the diamond surface without chemisorbed clusters. It is worthwhile to keep in mind that there are no long-range forces in the Brenner potential. Therefore, the decreasing probability of the chemisorption rate on surface A, caused by repulsion, may be overestimated.

In order to study the dependence of chemisorption configuration on the anisotropic structure of surface A, we used a C$_{28}$ cluster as a probe to scan the surface A and measured their IPE. The height of the C$_{28}$ probe was fixed at 0.5 Å above the surface A. The contour of IPE is illustrated in Fig. 3(a), where the white represents strong interaction and the black represents weak. The profiles along (110) direction (line AB) and (110) direction (line AC) are shown in Figs. 3(b) and 3(c). From Fig. 3, one can see the IPE is much higher when the $p$ is less than 3 Å. Since we kept the cluster probe at a height of 0.5 Å above surface A and considered the whole system as rigid, the IPE should be larger than that of a relaxed system. But, from Fig. 3, one can still conclude that in the area where the $p$ is less than 3 Å the cluster–cluster interaction dominated over cluster–surface interaction. Under this condition, since the interaction between two clusters is repulsive, the interaction between the impacting cluster and the surface is hindered. Within the same energy range, although the impacting cluster compressed the chemisorbed cluster, they did not form new bond. After the incident energy was transferred to the surface through deformation of the chemisorbed cage, the repulsive force pushed the
impacting cluster away from the surface. In the area where
the separation of the two cluster centers is between 3 and 6.5
Å, the dynamics of impact process is more complex. The
cluster–cluster interaction is comparable to the interaction
between the impact cluster and surface. Under this condition,
the impacting cluster first compressed the chemisorbed clus-
ter and the whole incident energy was divided into three
parts. The first part was transferred to surface, the second
part was transferred to the lateral kinetic energy through de-
formation, the rest kept the impacting cluster moving toward
the surface. After that, if the impacting cluster had enough
kinetic energy to open surface dimers it could be chemi-
sorbed on to the surface. For impacting events along \( \langle 110 \rangle \)
direction on surface A, the impacting cluster was pushed
away along line AC (see Fig. 3) due to the interaction with
the chemisorbed cluster. But it was difficult for the impact-
ing cluster to make new bonds with the surface dimer next to
the chemisorbed cluster due to the repulsive cluster–cluster
force. Only when the impact parameter is between 3 and 4 Å,
the impacting cluster retained enough lateral kinetic energy
after the first interaction stage between two clusters (see Fig.
3(c)) and could interact with the surface dimer further away
from the chemisorbed cluster. If the interaction is strong
enough to open the surface dimer, the impacting cluster can
be chemisorbed onto the diamond surface. After the chemi-
sorption had happened, the two clusters had no interaction
between each other. One of the snapshots of this kind of chemi-
sorption process is shown in Fig. 4. Since the surface struc-
ture along \( \langle 11 \rangle \) direction is different from that along
\( \langle 110 \rangle \), the interaction between the impacting cluster and
surface A is different (see Fig. 3(b)). After interacting with
the chemisorbed cluster, the impacting cluster could easily
interact with the surface dimer closest to the chemisorbed
cluster. If chemisorption happened, the impacting cluster
could interact further with the chemisorbed cluster. Under
this condition, it is possible for the two clusters to form
chemical bonds. During our simulation, we observed three

FIG. 3. Contour of IPE of the system where the diamond surface and C28
are considered to be rigid and the height of the C28 cluster above the dia-
mond surface is fixed as 0.5 Å. (a) The top view of IPE \( E_{ip} \), \( E_{ip} = E_{tot} -E_{s} -E_{f} \), where \( E_{tot} \) is total potential energy of the whole system, \( E_{s} \) is
determined as potential energy of the surface A (see Sec. II), \( E_{f} \) is potential
energy of a free C28 cluster. (b) The profile along AB. The origin is the mass
center of the chemisorbed C28 cluster. (c) The profile along AC.

FIG. 4. Snapshots of one chemisorption event along \( \langle 110 \rangle \) direction.
such events. The snapshots of one of these events are shown in Fig. 5.

C. Simulation of initial stage of C\textsubscript{28} cluster assembled film

To explore the microscale growth mechanism of C\textsubscript{28} cluster assembled film, a simulation model was designed as allowing one C\textsubscript{28} cluster after another to drop on the same diamond surface. Actually the time interval between two impacting clusters is millisecond (ms) magnitude in experiments.\textsuperscript{2} But molecular dynamics is very time consuming and cannot calculate the time scale of ms magnitude with this simulation model. For covalent cluster assembled films, diffusion is difficult to happen during the growth process and the transient impact dynamics plays a leading role. The dynamic process of the interaction has been completed within 3 ps. After that, the cluster either rebounds from the surface or keeps a stable chemisorption configuration. To mimic the experimental conditions, the simulation model is arranged such that after one C\textsubscript{28} cluster is chemisorbed on the diamond surface, the trajectory integration lasts 3 ps, then the velocity scaling method is applied for the whole system for 5 ps to obtain a quasithermal equilibrium condition at 300 K. After that the next C\textsubscript{28} cluster begins to drop, the impact positions are randomly chosen and the incident energy is fixed at 35 eV per cluster.

Since the limitation of computational capability exists, we only calculated 35 clusters chemisorbed on the diamond surface. After 20 clusters were chemisorbed on the diamond surface, it was observed only these clusters located on neighbor dimer columns could form bonds with each other which is in perfect agreement with the previous result. In addition, the sites, where two or three clusters already formed bonds with each other, could easily chemisorb more incident clusters. Figure 6 showed that after 35 clusters were chemisorbed, these sites became a kind of nucleation center. Although the diamond surface was not covered up, the third layer began to grow. The chemisorbed clusters were random stacked. However the characteristic cage structure of C\textsubscript{28} was retained. The neighbor number distribution of carbon atoms of the chemisorbed clusters was calculated and the result is shown in Fig. 7. The chemisorbed clusters kept a mean $sp^2$-hybridization that was the same as the free C\textsubscript{28} cluster. This finding supports the atomic force microscopy observa-

FIG. 5. Snapshots of one chemisorption event along (1\bar{1}0) direction.

FIG. 6. Snapshot of 35 chemisorbed clusters on the diamond surface. (a) Top view. (b) Side view.

FIG. 7. Comparison of the neighbor number distribution between the 35 chemisorbed C\textsubscript{28} clusters and 35 free clusters. Dashed line represents the chemisorbed clusters. Solid line represents the free clusters.
tion and Raman spectra of cluster assembled material which showed highly porous nanostructured morphologies. 

**IV. CONCLUSION**

The low energy deposition of C_{28} clusters on diamond (001)-2×1 surface at room temperature was investigated by molecular dynamics simulation using the many-body hydrocarbon potential developed by Brenner. The collision dynamics event was studied in detail. We devised a special surface configuration with a chemisorbed C_{28} cluster to study competition between the cluster–cluster interaction and cluster–surface interaction, as well as the initial fabrication of cluster assembled films.

Our main results can be summarized as follows: Within the incident energy window ranging from 25 to 40 eV, the incident C_{28} clusters can be chemisorbed on the diamond surface without breaking its cage structure and inducing surface defect. Since interaction between two C_{28} clusters is dominating repulsive, chemisorption probability of the second incident clusters is less than that of the first single C_{28} cluster. Due to the anisotropic structure of diamond (001) reconstructed surface, two chemisorbed C_{28} clusters can form bonds with each other and juxtapose across trough between dimer columns, but can not form bonds with each other along dimer column. The juxtaposed clusters can easily develop a nucleation process. The chemisorbed clusters randomly stacked to grow film in a typical three dimensional island growth mode. The film retained the characteristic cage structure as that of C_{28} clusters. The simulation results are in good agreement with related experiments.

Because of the limitation of our computational capability, in this simulation, we only addressed the initial stage of cluster assembled film. Much attention is focused on cluster–cluster interaction and cluster–surface interaction during low energy deposition process. In our further study, we plan to drive more C_{28} clusters and change incident angles so that we can investigate synthesis process involving more than two layers of C_{28} cluster assembled thin film.

**ACKNOWLEDGMENT**

This work was partially supported by National Nature Science Foundation of China under Grant Nos. 19875011 and 19835030.