Vol 17 No 11, November 2008
1674-1056/2008/17(11)/4260-08

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Deposition mechanism of nano-structured single-layered C_{36} film on a diamond (100) crystal plane*

Chen Ming-Jun(陈明君)†, Liang Ying-Chun(梁迎春),
Yuan Yi-Jie(袁屹杰), and Li Dan(李 旦)

Center for Precision Engineering, Harbin Institute of Technology, Harbin 150001, *China*

(Received 19 March 2008; revised manuscript received 15 May 2008)

The Brenner–LJ potential is adopted to describe the interaction between C_{36} clusters and diamond surface, and the deposition mechanism of multi-C_{36} clusters on the diamond surface is also studied by using the method of molecular dynamics simulation. The simulation results show that the competition effects of two interactions, i.e. the interaction between cluster and cluster and the interaction between cluster and crystal plane, are studied, and then the influence of these competition effects on C_{36} cluster deposition is analysed. The finding is that when an incident energy is appropriately chosen, C_{36} clusters can be chemically adsorbed and deposited steadily on the diamond surface in the form of single-layer, and in the deposition process the multi-C_{36} clusters present a phenomenon of energy transmission. The experimental result shows that at a temperature of 300K, in order to deposit C_{36} clusters into a steady nano-structured single-layered film, the optimal incident energy is between 10 and 18 eV, if the incident energy is larger than 18 eV, the C_{36} clusters will be deposited into an island nano-structured film.

Keywords: C_{36} clusters, Brenner–LJ potential, nano-structured single-layered film, competition effect

PACC: 6148, 6185, 4630, 0630M

1. Introduction

Since this special kind of cage structure of C_{60}, i.e. fullerene,[1−3] was discovered in 1985, it has been studied extensively because of its unique structure and particular optical, electric, magnetic and mechanical properties. In 1998, Zettl [4] first synthesized C_{36} solid and found it to be very different from C_{60} in property. For example, C_{36} molecule takes on a higher stability, higher critical temperature of super-conduction transition, much stronger van der Waals force between C_{36} molecules than C_{60} molecules, etc. These prominent properties imply that C_{36} material possesses a very broad field of application and research. Therefore, it is necessary to study the deposition of C_{36} clusters into a nano-structured film on a diamond surface theoretically and experimentally, and it has already become one of the most concerned research hotspots in this field now.

Experiments and simulations have shown that the C_{36} structured films that have been obtained so far are all of island growing mode.[5−11] However, we consider that the island structured film is just a product under a certain condition of parameter values. If we choose appropriate values of parameters such as incident energy, incident angle and so on, we can expect that C_{36} clusters can be deposited into a steady nano-structured single-layered film on a diamond surface, and this nano-structured single-layered film of C_{36}-diamond composition has a more profound and lasting application value. Therefore, the mechanism of depositing C_{36} clusters on the diamond (100) crystal surface is investigated in this paper. By studying the effects of competition in the interactions between clusters and clusters and between clusters and diamond surface, the factors affecting the deposition mechanism, such as incident energy and so on are analysed. Finally the conditions under which a nano-structured single-layered C_{36} film can be generated on the diamond surface will be obtained. The research can provide theoretical and experimental guidance for manufacturing nano-structured single-layered films of C_{36}-diamond composition.

*Project supported by New Century Elitist Supporting Program Foundation by the Ministry of Education of China (Contract No NCET-06-0332) and the National Natural Science Foundation of China (Grant No 50405011).
†Corresponding author. E-mail: chenmingjunok@yahoo.com

2. Computational model

In the previous simulation experiments on C_{36} cluster structured film, most researchers used only the Tersoff or Brenner potential to simulate the interaction among carbon atoms in the system. Although the two potential functions can perfectly describe the interaction between diamond and carbon-fullerene atoms (caused by the influence of short-range force), they cannot describe the influence of the van der Waals Force before carbon-fullerene fully contacts the diamond surface (caused by the influence of long-range force). To efficiently and objectively simulate the process where C_{36}clusters deposit on the diamond (100) crystal plane, we adopt the Brenner–LJ (Lennard-Jones)[12] potential to describe the interactions among atoms. Compared with the sophisticated quantum mechanical approach, it is surely less accurate and cannot be used to calculate the electronic structure. However, our molecular dynamics (MD) simulation based on this potential could deal with a larger-size system with a few thousands of atoms even on a personal computer and obtain the dynamical properties simultaneously. And it has also been successfully applied to studying properties of isomers of C_{20}[9], C_{36},[13] C_{60},[14] fullerene, the reaction between nano-tube tip and semiconductor surface,[15−20] etc. In the fitted potential function, the LJ potential function deals with the influence of long-range force, and the Brenner potential function treats the influence of the short-range force. The calculation formulas are as follows:

$$E = V_{\text{Brenner}}(r_{ij}) + V_{\text{vdW}}(r_{ij}), \tag{1}$$

$$V_{\text{Brenner}}(r_{ij}) = \sum_i \sum_{i>j} [V_{\text{R}}(r_{ij}) - B_{ij} V_{\text{A}}(r_{ij})], \tag{2}$$

where V_{Brenner} is the energy expression of Brenner potential function, V_{R} is the repulsive pair potential term of interaction between the internal atoms, V_{A} is the attractive pair potential term of interaction between the internal atoms, r_{ij} is the distance between two atoms, B_{ij} is the many-body bond order term.[21] and V_{vdW} is the van der Waals energy. The detailed expressions are as follows:

$$V_{\text{vdW}} = \begin{cases} 0 & r_{ij} \le r_{\text{s}}, \\ C_{3,k}(r_j - r_k)^3 + C_{2,k}(r_j - r_k)^2 + C_{1,k}(r_j - r_k) + C_{0,k} & r_{\text{s}} \le r_{ij} \le r_{\text{m}}, \\ 4\varsigma[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6] & r_{\text{m}} \le r_{ij} \le r_{\text{b}}, \end{cases} \tag{3}$$

In this simulation system, ς=4.2038×10^{-3} eV, σ=0.337 nm, r_{b}=1.00 nm, r_m=0.340 nm, r_{s}=0.228 nm, $C_{3,k}$=106.623, $C_{2,k}$=131.782, $C_{1,k}$=53.834, $C_{0,k}$= 7.277, r_k=0.709 nm.[22,23]

In this simulation system, the diamond substrate is composed of eight layers of 144 carbon atoms, the whole substrate is divided into three parts: the first part that consists of two layers of atoms in the bottom, which are mounted to simulate an infinite substrate of the crystal in the whole dynamic simulation process; the second part that consists of two layers of atoms on the top, which are completely acted on by the force-field determined by the potential function, and it is permitted to move along with the whole dynamic process; the third part that is composed of four layers of atoms in the middle, which follows the action law of potential function, and the temperature of the substrate is kept around 300K by Bredeson speed standardization[24] to make sure that the system is a canonical assembly. At the initial stage, the C_{36} cluster is 1nm above the crystal plane of the diamond, and there are no interactions of long-range force and short-range force between the C_{36} cluster and the diamond surface. Numerical integration of the system dynamic equation is realized by using the Verlet algorithm[25] in time steps 0.5 fs. In each simulation event the system has a 2.5 ps relaxation at the beginning so that the speed of each atom can be adjusted to the speed in the given system, and then begin to record up till 3 ps since C_{36} clusters and the diamond surface start to interact. If the record time is too long, structure changes will not be seen clearly in the simulation.

3. Experiment and analysis

Whether the C_{36} clusters can be deposited into a steady nano-structured single-layered film on the diamond surface is mainly dependent on the two kinds of competition mechanisms. One is the competition among the clusters, the other is the competition between clusters and the diamond surface. In addition, it is also influenced by the values of parameters concerned in the deposition process. Therefore, we make an intensive analysis of the two kinds of competition mechanisms. And then we study the feasibility, i.e. whether the C_{36} clusters can be deposited into a steady nano-structured single-layered film in this paper.

3.1. Analysis of two kinds of competition mechanisms

To analyse the competition mechanisms between clusters, and between cluster and diamond surface in the deposition process, we suppose that a C_{36} cluster has already been adsorbed on the diamond surface when a second cluster impacts on that diamond surface, and if the distance P between two clusters is in the action range of long-range force or short-range force mentioned above, the two clusters will interact with each other. Consequently the normal deposition on the diamond surface is interrupted, which is the phenomenon where the deposited cluster exerts an influence on the deposition process of the depositing cluster. This phenomenon is referred to as competition effect. Therefore, in this paper we define the incident area, where the competition effect can take place between the second cluster and the first deposited cluster. The area is a circle taking the centre of the first deposited cluster as its centre, and its radius can be obtained by measuring the change in inner energy when one molecule approaches to another. Through analysing the simulation system, we obtain the maximum distance of action, 0.62 nm; the experimental mode is shown in Fig.1.

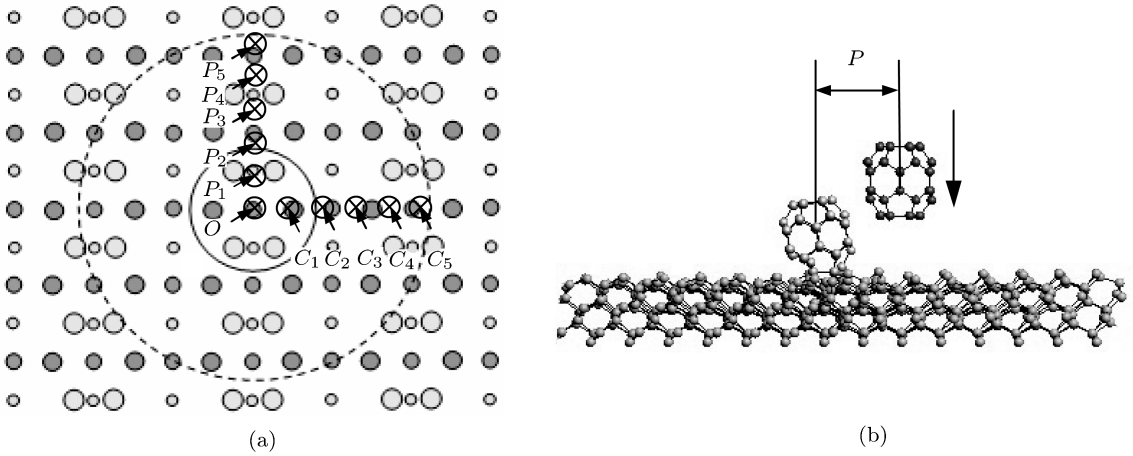


Fig.1. The schematic diagrams of clusters deposition simulation, where panel (a) shows the top view of diamond (100) surface, which has adsorbed one cluster and an incident area of a second cluster, with the solid line circle showing the adsorbed cluster, and the dash line circle representing an incident area of a second cluster, the small circles cross inside showing the impacting point of second cluster; panel (b) shows the side view of diamond (100) surface.

Firstly, we perform a deposition experiment on each of the six points, i.e. O, P_1–P_5. In these series of impacting events we obtain four kinds of deposition results as shown in Fig 2. From Fig.2 we can see obviously that only depositions in Figs.2(c) and 2(d) are meaningful for forming a steady nano-structured single-layered film. From the deposition experiment we find that the formation of these two kinds of deposition effects is related closely to not only the incident area, but also the incident energy. When C_{36} molecule impacts at point O as shown in Fig.1(a), no matter how large the incident energy of the second cluster is chosen to be, it cannot have the deposition effect as indicated in Fig.2(c) or 2(d), when the incident energy is more than 70 eV, bonds begin to form between clusters: the higher the incident energy, the more bonds will form. The process may be explained as follows:

(1) When the second C_{36} molecule impacts at

point P_1, bonds begin to form between the two clusters under the incident energy of 70 eV. With the incident energy increasing up to 80 eV, bonds form among the first cluster, the second cluster and diamond surface simultaneously.

(2) When the second C_{36} molecule impacts at point P_2 and the incident energy reaches 50 eV, the second cluster contacts the first cluster transitorily, then starts to deform and slide onto the diamond surface, thereby forming bonds. Subsequently we carry out different simulation experiments with different increasing incident energies, but the deposition effect cannot be obtained as shown in Fig.2(d).

(3) Finally we perform the deposition simulation experiment starting from points P_3, P_4 and P_5. By analysing the deposition events, we can obtain the deposition effect like that obtained from point P_2, and only the bonding threshold is different from those at other points when the second C_{36} cluster is bound to the diamond surface. The bonding threshold values are 45 eV at point P_3, 36 eV at point P_4, and 32 eV at point P_5.

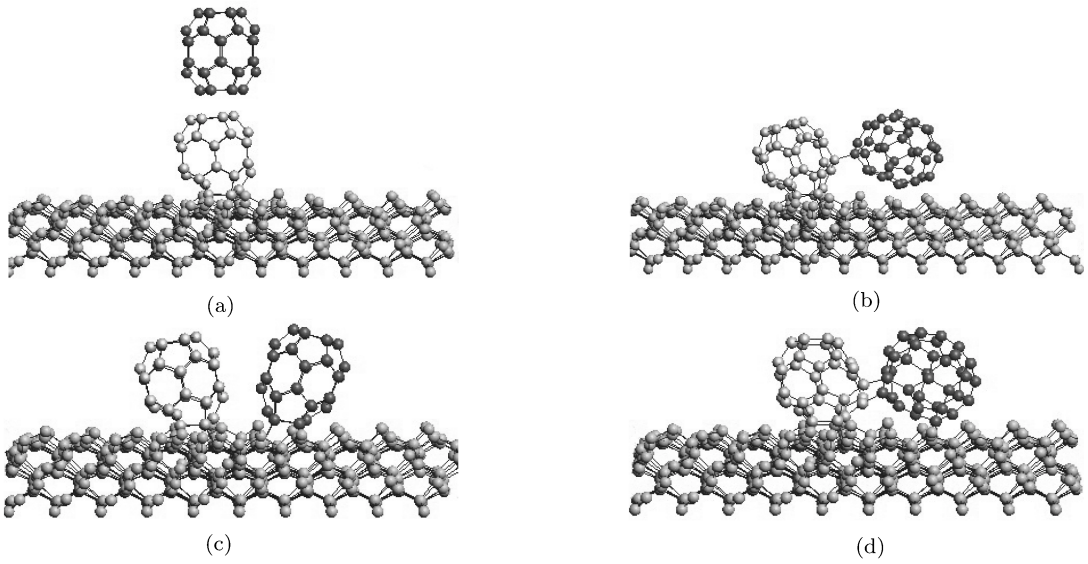


Fig.2. Four different deposit results.

From a series of deposition experiments we find that as the distance between the second cluster and the first cluster increases, the influence of the interaction between cluster and cluster on the deposition process weakens. Figure 3 shows the influence of these two kinds of interactions between clusters and between cluster and diamond surface at points P_1 and P_3 with an incident energy of 70 eV.

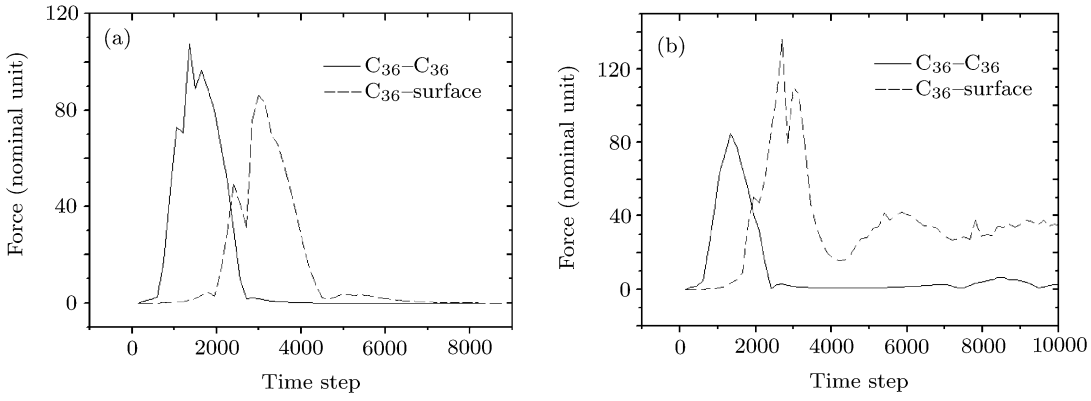


Fig.3. The interaction forces between cluster and cluster and between cluster and surface during the deposition, where panel (a) is for impact point P_1, panel (b) for impact point P_3, with the incident energies in (a) and (b) each being 70 eV.

From Fig.3(a) we can see clearly that the interaction force between cluster and cluster is much larger than that between cluster and diamond surface, implying that at point P_1 the competition effect between cluster and cluster is more prominent. From Fig.3(b) we can see that at point P_3 the competition effect between cluster and cluster is considerably smaller than that between cluster and diamond surface. From the analysis we find that the competition effect of interactions between cluster and cluster and between cluster and diamond surface is dependent mainly on the distance between depositing clusters. Figure 4 shows the tendency of change in deposition action affected by the interaction force between clusters. And from the experiment we can also find that different incident energies at the same impact point can lead to the change in the interactions of these two kinds. To analyse the inner influence laws, because at point P_1 the competition effects between cluster and cluster and between cluster and diamond surface are the most prominent, we choose the incident energies to be 60, 70, 80 and 90 eV to make statistic analysis of the impact events, and the results are shown in Fig.5. We find that with the incident energy increasing, the influence of cluster–cluster competition decreases. This law indicates the favourable condition for depositing steady nano-structured single-layered films on the diamond surface.

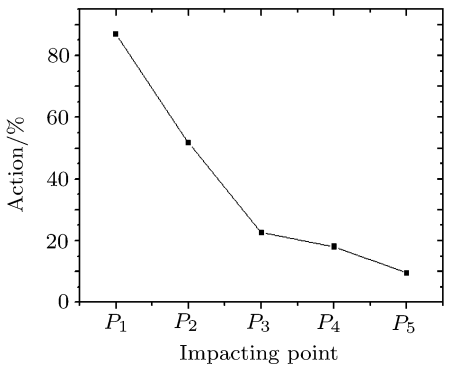


Fig.4. The action of interaction forces between cluster and cluster at different impact points.

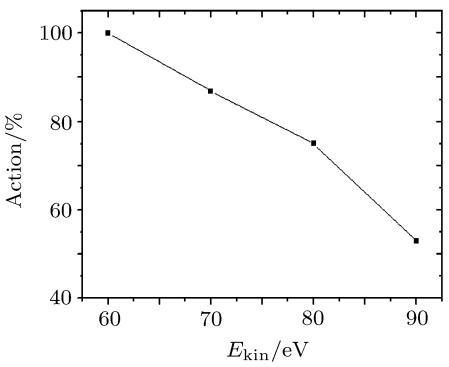


Fig.5. The action of interaction forces between cluster and cluster at different incident energies.

3.2. Deposition threshold

We have known the incident deposition threshold of single C_{36} molecule, but if multi-clusters composed of C_{36} molecules impact at the same time, there must be the interaction between clusters. The molecular interaction between clusters will lead to the change in the incident energy required by C_{36} cluster when it deposits on the diamond surface. To analyse the inner influence, let two C_{36} clusters impact on the diamond surface; the deposition process is shown in Fig.6. From Fig.6 we can see that while the deformation of the first cluster is not restored completely, the second cluster exerts another force on the first one; as a result when the incident energy of the second cluster is just 45 eV, bonds begin to form between the two clusters and have an energy much lower than the 70 eV mentioned above, under which the bonds can begin to form between the free cluster and the deposited cluster.

Now we analyse the deposition circumstance where four C_{36} clusters are on a line in the vertical direction. We find that the first C_{36} cluster impacting on the diamond surface begins to form bonds with diamond surface at an incident energy of 19 eV; when the incident energy is 23 eV, bonds begin to form between two clusters impacting first on the diamond surface and have an energy much lower than the incident energy threshold of two free impact clusters. At this time it puts up a kind of energy transmission phenomenon that when multi-C_{36} clusters impact, the interaction between clusters will make it easier to form bonds between each other or deposit on the diamond surface. When the number of impacting clusters increases again, the threshold does not change too much. It also proves that C_{36} cluster is a sort of elastic molecular cluster.

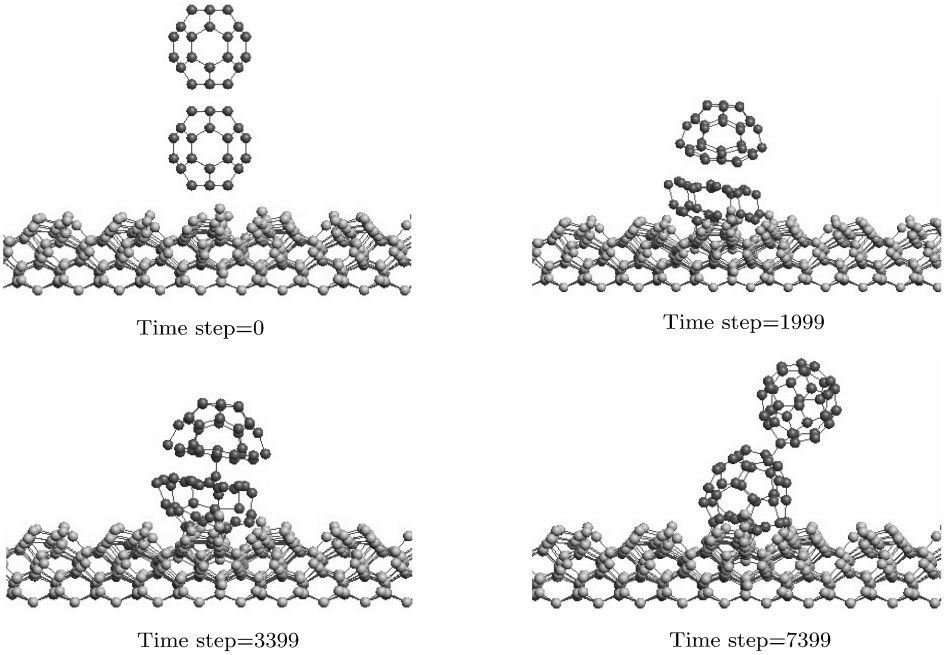


Fig.6. Atomic positions when two free C_{36} clusters impact on the diamond surface.

4. Feasibility analysis of steady nano-structured single-layered film deposition

We have known some characteristics and key parameters of deposition for one or more clusters . Now we carry out a calculation and analysis to see whether C_{36} clusters can be deposited into a steady nano-structured single-layered film on the diamond surface. On a certain condition of incident energy, those clusters that first contact the diamond surface can deposit on the substrate. Now the point is whether the clusters subsequently impacting on the diamond surface slip off the incident area of surface that has already been occupied by the first deposited cluster, and then deposit on the substrate or bounce back from it. To test and verify this point, we perform the simulation of the three C_{36} molecules impacting on the diamond surface. The impacting model is shown in Fig.7(a); two of the three C_{36} clusters are located at the same level; the other C_{36} cluster is positioned over the two clusters, initially it is on the their central line (see Fig.1(a)) and overlaps them largely in the vertical direction, so that when the three C_{36} clusters deposit on the diamond surface, the two clusters below can first deposit on the substrate and the cluster above impacts on them subsequently. For the case where the incident energy is 60 eV, the final deposition effect is shown in Fig.7(b). The experimental results show that the C_{36} cluster above cannot generate bonds with the two below, and finally bounces back from the substrate surface.

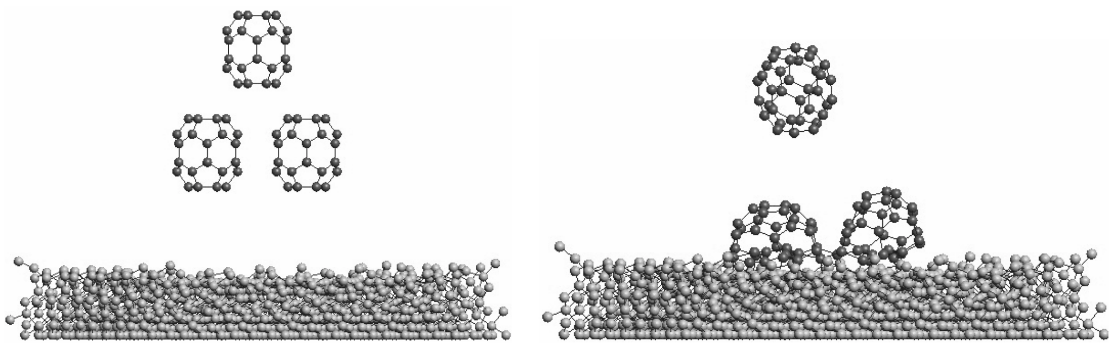


Fig.7. The initial state (a) and final state (b) of three C_{36} clusters deposited on the diamond surface.

Finally we perform the simulation of deposition experiment of three layers of C_{36} clusters with 9 C_{36} clusters in each layer. Clusters keep a distance from each other without interaction between them, and present random impacting postures. Thus we can simulate the random impacting postures of C_{36} clusters as the circumstance of actual deposition. The simulation results are shown in Fig.8. From the simulation results it follows that when the incident energy is higher than 18 eV, bonds form between the first layer of C_{36} clusters and the second layer of C_{36} clusters, however, when the incident energy is lower than 10 eV, there appear most of C_{36} clusters in the first layer not bonding to the diamond surface, which implies that the optimal incident energy for the deposition is between 10–18 eV.

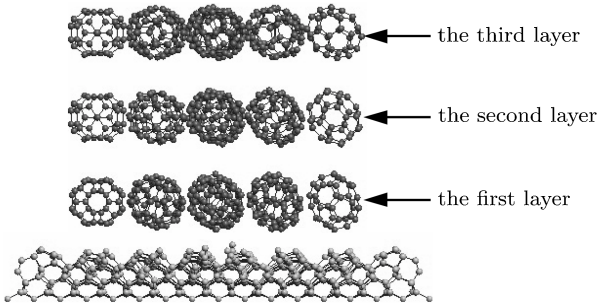


Fig.8. The model of single film experiment.

Figure 9 shows the deposition effects in the case where the incident energy is 15 eV. And to see more clearly the second and third layers of clusters are hidden here in the figure. From Fig.9 we can see that all of the 9 C_{36} clusters can deposit on the diamond surface ideally. To analyse the stability of the deposited single-layered film, we plot the bond angle distribution of the first layer of chemically adsorbed C_{36} clusters in Fig.10. From Fig.10 we can see clearly that the bond angle has peak values around 109° and 120°, showing that the adsorbed C_{36} clusters retain the features of free-cage sp^2 and sp^3 hybridizations as well as indicating that nano-structured single-layered film has a very steady structure.

For the case where the incident energy is higher than 18 eV, there appears the island film growth. The analysis above indicates that it is feasible to deposit steady nano-structured single-layered films, and the optimal incident energy for the deposition ranges from10 to 18 eV; if the incident energy is higher than 18 eV, the island growing mode will occur as mentioned in the literature.

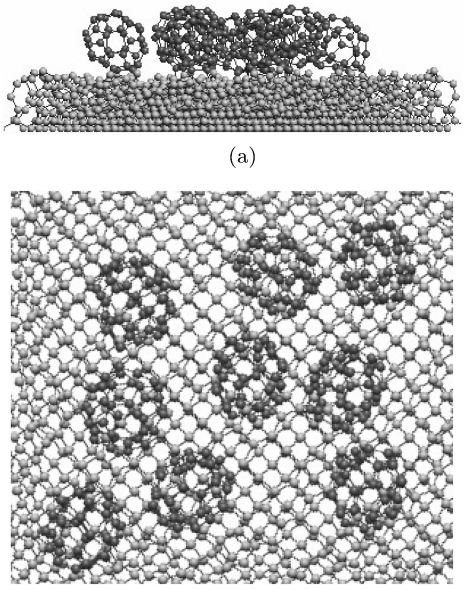


Fig.9. The single film experiment, where (a) is for front view and (b) for top view.

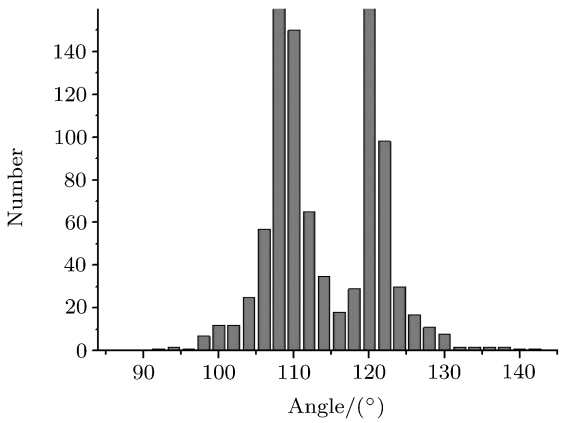


Fig.10. The bond angle distribution of C_{36} clusters in a single-layered film.

5. Conclusions

(1) When multi-C_{36} clusters simultaneously, the competition effect of interactions between cluster and cluster and between cluster and surface is related to the incident energy and the distance between clusters; when the distance is short, with the incident energy increasing, the influence of cluster–cluster competition action will weaken. This law indicates the condition favourable for depositing a steady nano-structured single-layered film on a diamond surface.

(2) When multi-C_{36} clusters are impacting simultaneously, the interactions between clusters will lead

to a change in threshold of bond formation, and at the same time it puts up a kind of energy transmission phenomenon, implying that multi-C_{36} impacting and the interactions between C_{36} clusters will make it easier to form bonds between clusters or deposit the C_{36} clusters on a diamond surface.

(3) It is feasible that C_{36} clusters are deposited into a steady nano-structured single-layered film on the diamond (100) crystal plane. The deposition simulation results show that the optimal incident energy ranges from 10 to 18 eV, at which C_{36} clusters can be deposited into a steady nano-structured single-layered film on the diamond surface; if the incident energy is higher than 18 eV, the deposited film is of island growing mode.

References

[1] Popescu M 2006 *J. Optoelectron. Adv. Mater.* **8** 755
[2] Lorinczi A, Popescu M and Sava F 2004 *J. Optoelectron. Adv. Mater.* **6** 349
[3] Hu Y H and Sinnott S B 2003 *Surf. Sci.* **526** 230
[4] Zettl A 1998 *C_{36}, a New Carbon Solid* (Berkeley: University of California at Berkeley) p771
[5] Heath J R 1998 *Nature* **363** 730
[6] Grossman J C, Cote M, Louie S G and Cohen M L 1998 *Chem. Phys. Lett.* **284** 344
[7] Collins P G, Grossman J C, Cote M, Ishigami M, Piskoti C, Louie S G, Choen M L and Zettl A 1999 *Phys. Rev. Lett.* **82** 165
[8] Cote M, Grossman J C, Cohen M L and Louie S G 1998 *Phys. Rev. Lett.* **81** 697
[9] Du A J, Pan Z Y and Ho Y K 2002 *Phys. Rev.* B **66** 035405
[10] Du A J, Pan Z Y and Huang Z 2002 *Int. J. Mod. Phys.* B **16** 3971
[11] Du A J, Pan Z Y, Ho Y K, Wang Y X and Xu Y 2001 *Nucl. Instrum. Meth.* B **180** 153
[12] Brenner D W, Shenderova O A and Harrison J A 2002 *J. Phys. Condens. Matter* **14** 783
[13] Gao J, Lin Z Z and Ning X J 2007 *J. Chem. Phys.* **126** 174309
[14] Li P and Ning X J 2004 *J. Chem. Phys.* **121** 7701
[15] Smith R and Beardmore K 1996 *Thin Solid Films* **272** 255
[16] Xia Y Y, Mu Y G, Xing Y L, Tan C Y and Mei L M 1997 *Phys. Rev.* B **56** 4979
[17] Garg A, Han J and Sinnott S B 1998 *Phys. Rev. Lett.* **81** 2260
[18] Han Q, Xin H and Yao X H 2008 *Acta. Phys. Sin.* **57** 329 (in Chinese)
[19] Wang L, Wang J B and Zhang H W 2007 *Acta. Phys. Sin.* **56** 1506 (in Chinese)
[20] Chen M J, Liang Y C, Li H Z and Li D 2006 *Chin. Phys.* **15** 2676
[21] Brenner D W 1990 *Phys. Rev.* B **42** 9458
[22] Chen M J, Liang Y C, Yuan Y J and Li D 2007 *Chin. J. Chem. Phys.* **20** 637
[23] Moller M A, Tildsley D J, Kim K S and Quirke N J 1991 *Chem. Phys.* **94** 8390
[24] Berendsen H J C, Postman J P M and Gunsteren W F V 1984 *J. Chem. Phys.* **81** 3684
[25] Verlet L 1967 *Phys. Rev.* **159** 98