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Influential Factors of Low-energy C₃₆ Cluster Deposition on Diamond (100) Crystal Plane[†]

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Brenner-LJ potential is adopted to describe the interactivity between diamond and C₃₆ cluster, and the deposition mechanism of multi-C₃₆ on the diamond surface is researched by molecular dynamics simulation. Through simulative experiments the incident energy, incident point, incident posture, incident angle and other factors are analyzed. Studies discover that the minimal deposition threshold is 20 eV and the maximum is 60 eV with the different incident point locations and incident postures of C₃₆ clusters. When the incident angle is not over 60°, C₃₆ may roll or slip to the region of smaller bonding energy and then bond. So the bonding probability is raised. Research results show that when incident angle is between 0° and 20° and incident energy range is from 30 eV to 60 eV, it is the optimal condition of single C₃₆ cluster deposition on diamond (100) crystal plane.

Key words: C₃₆ cluster, Brenner-LJ potential, Deposition threshold, Bonding probability

I. INTRODUCTION

Since the year 1985 the special cage structure of C₆₀ [1] was discovered, because of its unique structure and special properties in many fields such as light, electronics, magnetism, catalysis, optics and mechanics etc, the carbon tube and carbon rings are researched widely [2-10]. C₆₀ can be tuned from insulating to superconducting by application of an electric field [11]. Single crystals of C₆₀ demonstrated the switching between insulating and superconducting behavior and can be nano switch device or be useful in the fabrication of circuits for superconducting electronics or Josephson junction arrays [11,12]. C₆₀ impacts on the reconstructed diamond (111) surface by binding molecular dynamics simulations, collision experience and three impact regimes are identified, the presence of defects in the C₆₀ enhances its reactivity with the substrate play an important role in deposition processes of the fullerene on semi-conducting surfaces [13]. Small carbon clusters with atom numbers below 24 have been intensively studied with accurate *ab initio* methods. Kent and co-workers studied the energetic stability of structural isomers of C₂₄, C₂₆, C₂₈, and C₃₂ clusters, using diffusion quantum Monte Carlo methods [14]. The DFT method and a valence approximation by the MNDO method has been employed to confirm the most stable isomer of C₃₂ [15], and to investigate the electronic and chemical properties of it, with other small fullerenes, C₃₂ is also prone to

polymerize, and further oligomerization or polymerization of C₃₂ might produce novel one-dimensional polymer structures [16]. In 1998, Zettl research group [17] in University of California in the United States synthesized C₃₆ solid for the first time, and discovered that it had very different properties compared with C₆₀. For example, C₃₆ took on a higher stability, higher critical temperature of super-conduction. The acting force of the van der Waals force between C₃₆'s molecules is far stronger than it between C₆₀'s molecules, etc. These prominent properties of C₃₆ material show us a very extensive field of application and research. Therefore, the deposition mechanism and experiment research on diamond nano-structure film of C₃₆ have become one of the most concerned focus at present in the world.

In the research of carbon-clusters deposition, there are some experimental and simulative reports [18-25]. But chemical-adsorption mechanism of initial nucleation and stability after deposition are unclear. Up to now, there have been fewer reports about the initial nucleation mechanism of C₃₆-diamond nano-composite structures; moreover these researches are not comprehensive. So C₃₆ clusters deposition mechanism on diamond (100) crystal plane is as subject investigated in this paper, and the influence regularity of the incident energy, incident point, incident posture, incident angle of the C₃₆ clusters on deposition effects and the stability after deposition are researched in-depth. At last the optimal deposition initial conditions and ideal energy threshold range is obtained in the C₃₆ clusters depositing process.

II. ESTABLISHMENT OF COMPUTATIONAL MODEL

In the previous simulation test about C₃₆ clusters structure film, most researcher only use Tersoff or Brenner potential to simulate the interaction among carbon

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atoms in the system. Although two potential functions can perfectly describe the interaction among diamond and carbon-fullerene atoms (caused by the influence of short-range force), they cannot describe influence of the van der Waals force before carbon-fullerene fully contact with the diamond surface (caused by the influence of long-range force). To sufficiently and objectively simulate the process that C_{36} clusters deposit on the diamond (100) crystal surface, we adopt Brenner-LJ (Lennard-Jones) [26] potential to describe the interactively acting forces among atoms. In the fitted potential function, the L-J potential function deals with the influence of long-range force and the Brenner potential function deals with the influence of the short-range force, the calculation formulas are as follows

$$E = V_{\text{brenner}}(r_{ij}) + V_{\text{vdW}}(r_{ij}) \quad (1)$$

$$V_{\text{brenner}}(r_{ij}) = \sum_i \sum_{i>j} [V_R(r_{ij}) - B_{ij}V_A(r_{ij})] \quad (2)$$

where V_{brenner} is the energy expression of Brenner potential function, V_R is the repelling pair potential item of interaction among the internal atoms, V_A is the suction pair potential item of interaction among the internal atoms, r_{ij} is the distance between two atoms, B_{ij} is the many-body bond order item [27]. V_{vdW} is the energy of van der Waals. The detailed expressions are as follows

$$V_{\text{vdW}} \begin{cases} = 0 & (r_{ij} \leq r_s) \\ = C_{3,k}(r_{ij} - r_k)^3 + C_{2,k}(r_{ij} - r_k)^2 & (r_s \leq r_{ij} \leq r_m) \\ + C_{1,k}(r_{ij} - r_k) + C_{0,k} & (r_m \leq r_{ij} \leq r_b) \\ = 4\zeta \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] & (r_m \leq r_{ij} \leq r_b) \end{cases} \quad (3)$$

in this simulation system, $\zeta=4.2038$ meV, $\sigma=0.337$ 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 [28].

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 consists of two layers of atoms in the bottom, which are mounted to simulate infinite substrate of the crystal in the whole dynamic simulation process; the second part consists of two layers of atoms on the top, which are completely acted on by the force-field decided by the potential function, and it is permitted to move in the whole dynamic process; the third part consists of four layers of atoms in the middle, which follow the acting law of potential function, and the temperature of the substrate is kept around 300 K by Bredeson speed standardization [29] to make sure the system to be a canonical assembly. In the beginning, the C_{36} is 1 nm above the crystal plane of the diamond, and it is sure that there is no interaction of long-range force and short-range force between C_{36} and diamond. Numerical integration of the system dynamic equation is realized by

Verlet algorithm [30], using calculation step length of 0.5 fs. In each simulation event the system has a 2.5 ps relaxation at the beginning and is made sure that the speed of each atom can be adjusted to the speed in the given system, then begin to record to 3 ps since C_{36} clusters and the diamond surface start to interact; if recording time is longer, the obvious structure changes can not be seen in the simulation.

Because the (100) crystal plane structure of diamond is complicated and in order to discuss C_{36} deposition mechanism more comprehensively, we will discuss A, B, C, D, E five special points, which C_{36} cluster deposit on (100) crystal plane of the diamond, and it's planform is shown as the Fig.1 followed.

III. RESEARCH ON INFLUENTIAL FACTORS OF C_{36} CLUSTERS DEPOSITION ON PLANE OF DIAMOND

Main factors which influence C_{36} clusters depositing on the (100) crystal plane of diamond are discussed such as incident energy, incident point, and incident posture and incident angle.

A. Influences of incident energy

Incident energy is the key factor whether C_{36} clusters can generate chemical adsorption. To obtain critical point of the chemical adsorption incident energy, lots of experiments are done with different incident energy (15-100 eV). At first, point A on the (100) crystal plane of diamond is as the deposition point, and C_{36} cluster keeps the TOP-hexagon down incident posture. It is found that depositing of the C_{36} cluster is very sensitive to the incident energy. According to its deposition status, the incident energy range is divided into four ranges (E_1 , E_2 , E_3 , and E_4). E_1 is below 30 eV, E_2 is 30-50 eV, E_3 is 50-60 eV, E_4 is above 60 eV. When the incident energy is below than 30 eV (E_1), C_{36} can't deposit on diamond surface and bounces from diamond surface after contact it. When incident energy is be-

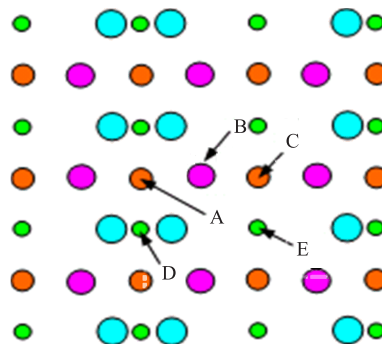


FIG. 1 The planform of (100) crystal plane of the diamond, the largest circles is the first layer atoms on the top, the second largest is the second layer atoms, then the third, the smallest is the fourth layer atoms.

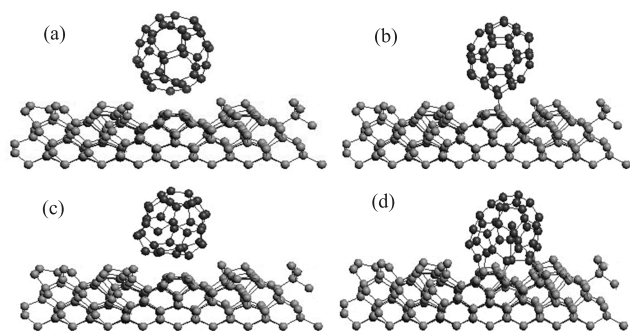


FIG. 2 Influences of the incident energy. (a) $E_{in}=20$ eV, $t=0.75$ ps; (b) $E_{in}=30$ eV, $t=2.25$ ps; (c) $E_{in}=55$ eV, $t=0.75$ ps; (d) $E_{in}=70$ eV, $t=2.25$ ps.

tween 30-50 eV (E_2), C₃₆ generates a chemical bond with the (100) crystal plane of diamond and maintains its free cluster structure after depositing. When incident energy is 50-60 eV (E_3), cluster C₃₆ bonds on the diamond surface, then the chemical bond is tension fracture for the residual energy is too large and C₃₆ bounces from the diamond surface. When incident energy exceeds 60 eV, C₃₆ could deposit on diamond surface, but its cage structure and the diamond surface both come into being many defects. Figure 2 shows the deposition results. All these are in good agreement with reports of Du *et al.* [25].

Because C₃₆ molecule has a cage structure with sp² and sp³ hybridization character, through observing their hybridization content we may analyze structural changes of C₃₆ molecule in the deposition process. In this work, incident energy 35 and 70 eV are taken as investigated samples and the analytical results are shown in Fig.3. For sample with incident energy 35 eV from Fig.3, when C₃₆ cluster does not interact with the diamond surface, its sp³ hybridization content is higher than sp²; as C₃₆ cluster is down depositing, sp² and sp³ hybridization both decrease, and transform into other hybridization form, then their cage structure starts being staved; when sp² hybridization content begins increasing at 0.25 ps and exceeds sp³ hybridization content, sp² hybridization content comes to the maximum at 0.6 ps and at the same time the distortion of the C₃₆ cage structure reach the limit. As C₃₆ cluster depositing continually, sp³ hybridization content increases and sp² hybridization content decreases; sp² and sp³ hybridization content both are restoring to level before impacting after 1.75 s and C₃₆ resumes its free cage structure. This analysis shows that C₃₆ molecules keep their initial structures well after bonding with incident energy 35 eV. For sample with incident energy 70 eV, the change trend of sp² and sp³ hybridization content is basically accordant with 35 eV sample, but the change process is more drastic. This analysis shows that C₃₆ clusters have much more distortion of when incident energy is 70 eV in comparison with 35 eV, and when

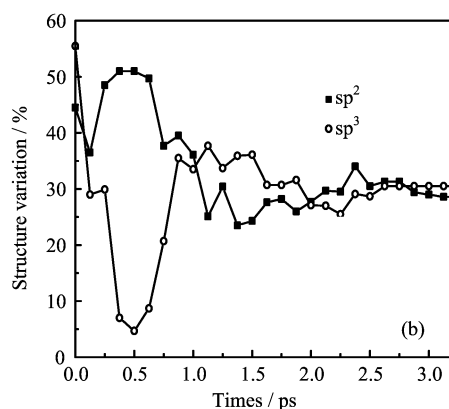
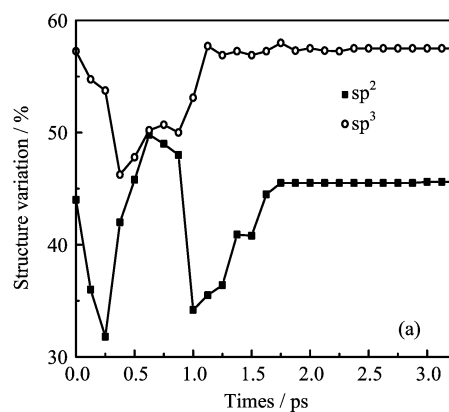


FIG. 3 Content variations of sp² and sp³ hybridization of C₃₆. (a) 35 eV, (b) 70 eV.

the depositing is complete, sp² and sp³ hybridization content of C₃₆ are both below than previous depositing. From above analysis we can conclude that the cage structure of C₃₆ clusters has been destroyed. Through analyzing the changes of the C₃₆ hybridization content of the two samples, this conclusion is correct theoretically in the deposition snapshot.

B. Influences of incident point

In order to discuss the catholicity of C₃₆ deposition, we choose four special incident points B, C, D, E; incident posture of C₃₆ is Top-hexagon down (THD), and obtained deposition thresholds are 30, 35, 38, 32, and 65 eV of A, B, C, D, and E, respectively. At point A, the starting bond threshold as 30 eV is the lowest; at point E, the starting bond threshold is the highest, and the incident energy is reaching to 65 eV. Deposition capability of C₃₆ has great relationship with the deposition location on diamond surface. The bonding threshold is lower in the protuberant region and higher in the low-lying and smoothing region.

TABLE I Physicochemical properties and results of CO chemisorption of the calcined Pt/MgO catalyst

Postures	I	II	III		
			P1	P2	P3
Energy threshold/eV	20	23	39	28	38

C. Influences of incident posture of C_{36} clusters

From a series of experiments to point A, we discover that even if at the same point, different incident postures of C_{36} clusters have a great influence on the deposition threshold. In order to research influences of the incident postures on deposition process, a series of deposition incidents are taken at point A to be separated into three ways of postures (Fig.4). They are Hexagon down posture, Pentagon down posture and line down posture respectively. Here we call them I, II, III posture respectively, and their postures are shown in Fig.5.

The III posture (Fig.5(c)) is C_{36} cluster rotating definite angle on depression angle plane. At point A, obtained deposition thresholds in three ways are shown in Table I. It is found that C_{36} cluster will overturn in the process of deposition in II way and have the similar bonding posture with that in I way. Moreover, its deposition threshold is a little higher than that in I way. Then we still take incident in II way, but incident energy of these clusters is different. Through analysis of depositing snapshot, all deposition clusters generate roll phenomenon. From above analysis we can get a conclusion: C_{36} will more easily deposit in I posture and take on "selective" signs. Namely, as C_{36} clusters don't lose too much energy, they will choose a posture which bonding threshold is lower and has similar energy with them to deposit. At the same time we observe that when C_{36}

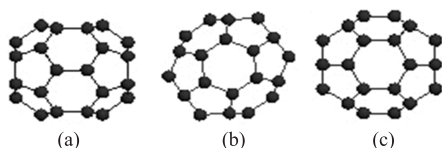


FIG. 4 Elevation view of three incident postures. (a) Hexagon down posture, (b) Pentagon down posture, (c) Line down posture.

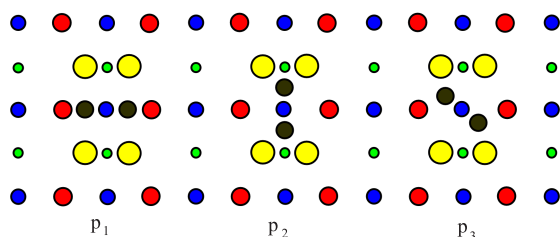


FIG. 5 p_1 , p_2 , and p_3 are projection drawing of two atoms of C_{36} down in III posture on diamond (100) crystal planes.

cluster contact diamond surface, their distortional degree in II posture or I is far less than that under THD condition. So they lose less energy for distortion and the depositing threshold is lower. In the deposition in III posture, even if incident point and contact point of the Fullerene have not change, the depositing thresholds are different with differences of interaction between atoms. Above analysis shows that the influence of incident posture of the C_{36} clusters on depositing thresholds is very large.

D. Influences of incident angles

In macroscopical deposition process, the influences of both incident angles and interaction between clusters may result in that C_{36} contacts with diamond surface with a definite angle. Hence, influence of incident angles must be considered in the simulating process. In order to discuss the influences of incident angles, we choose incident angles, which are 10° , 20° , 30° , 40° , 50° , 60° , 70° , and 80° , and the deposition point is A on the diamond surface. We can't forecast motion track of C_{36} clusters, but we can make sure that the contacting point is on the ridge of the diamond (100) crystal plane. From above experiments we know, C_{36} has similar threshold on the ridge of the diamond (100) crystal plane. So the interference with different depositing location for unpredictable track of C_{36} is avoided.

Firstly, we take the incident energy as 60 eV and incident angles as 60° , 0° respectively to simulate. The three-dimensional velocity curve is as shown in Fig.6. In the experiment with 60° (oblique incident), at 0.295 ps moment in depositing process, C_{36} generates a bond with diamond surface. At 0.415 ps, the bond breaks and lateral velocity is still large and C_{36} slips forward in the horizontal direction on the ridge continually; at 0.715 ps, it forms a bond again; at 1.705 ps, it makes the third bond. By now, the deposition process becomes stable. Through experimental snapshot we observe that after the first bond is broken, C_{36} happens to roll and slip. Due to deposition threshold of its laying down posture is lower, even if its kinetic energy in the vertical direction decreases, C_{36} could bond on the diamond surface, and becomes stable. When C_{36} cluster impacts in 0° incident angle, it bonds with diamond surface and becomes stable after small amplitude oscillating.

Then, we do a series of simulative events with different incident angles and different incident energy. Bond numbers are obtained as shown in Fig.7. From Fig.7 we find that when incident angle range is 0° - 20° and incident energy range is 30-60 eV, the deposition effect is the best, and when the incident angle is above 60° , the deposition effect is quite not ideal or can't bond.

Simultaneously, to discuss the influence of vertical component on depositing process, in which its energy is the same and the incident angle is different, we choose energy component perpendicular to the body as 30 eV. The bond numbers are obtained as shown in Fig.8.

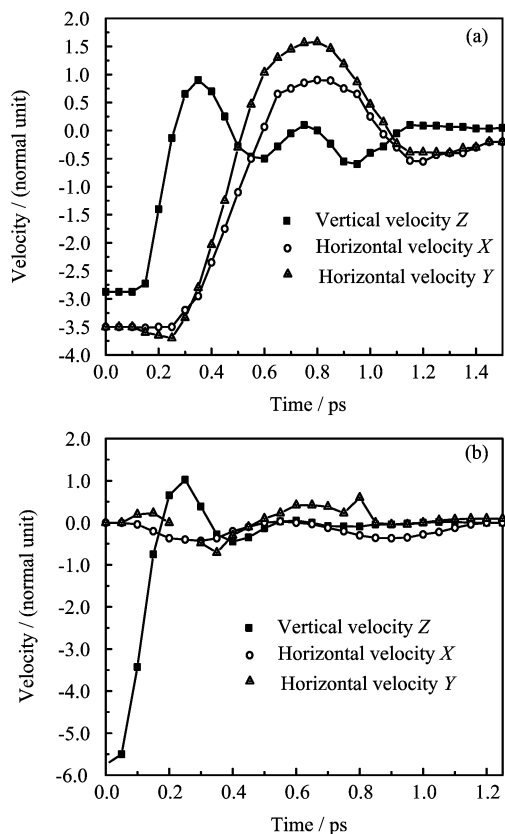


FIG. 6 Three-dimensional velocity curve of C_{36} incident. (a) $E_{in}=60$ eV, incident angle 60° , (b) $E_{in}=60$ eV, incident angle 0° .

From Fig.8 we find that when incident angle is 0° (vertical incident), the bond number is only two; comparably, the bond number is more ideal when C_{36} cluster is oblique incident. After we consider bond numbers and incident energy synthetically, we think that when incident angle is lower than 20° , the depositing effect is ideal. Under oblique incident, at a fixed point, it is determined by vertical component of the incident energy whether bond is formed, but its horizontal component generates some influence on its bonding. If horizontal component is larger, even if vertical component reaches to the bonding threshold and generates chemical bond, this bond may be snapped and bounced away. If horizontal component is larger, even if vertical component is lower than the bonding threshold, because of the rolling and slipping of the C_{36} cluster on diamond surface, it will transform to easily bonding posture or slip into lower bonding threshold region and bond with diamond surface finally. Lots of experimental data are shown that when the incident angle of C_{36} is less 20° , the deposition effect is satisfied.

IV. CONCLUSION

From the simulation above, we can obtain some conclusions as followed: (i) C_{36} is sensitive to incident en-

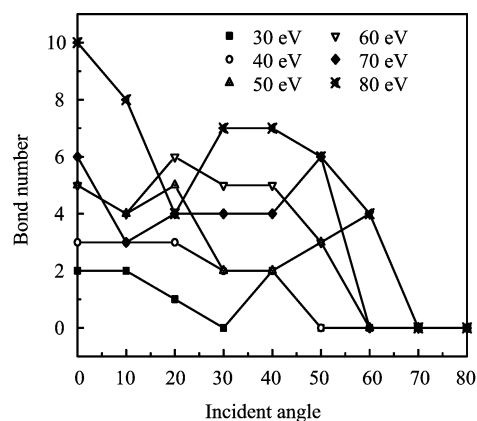


FIG. 7 Bonding status of C_{36} cluster under different incident energy and incident angle.

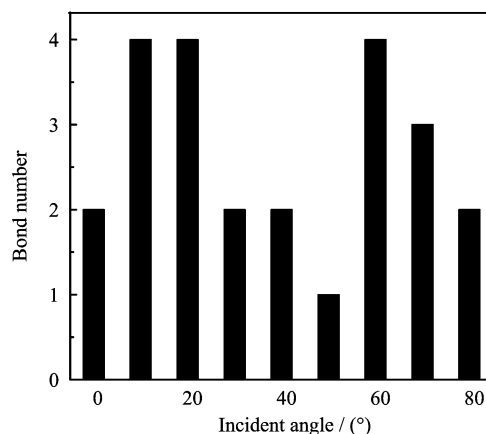


FIG. 8 Bonding status of C_{36} cluster under same vertical component and different incident angle.

ergy when deposits on diamond surface, and to take incident posture THD and point A as an example: when incident energy range is 30 50 eV, C_{36} only can bond on diamond surface and keep original cage structure; (ii) At different incident locations, deposition threshold varies greatly. Take posture THD as an example: on diamond (100) crystal plane, the minimal threshold is 30 eV, but the maximal is 65 eV. The bonding threshold is lower in the protuberant region and higher in the low-lying and smoothing region. (iii) Differences of incident postures can effect on the deposition threshold. When incident direction is parallel with the long axis of C_{36} (III posture), distortion is larger and threshold is higher. On the contrary, when the incident direction is perpendicular with the long axis of C_{36} (I posture), the distortion is relatively smaller and bonding threshold is lower. (iv) Situation of oblique incidence is more complicated. Owing to horizontal component of the incident energy, C_{36} cluster will roll and slip on diamond surface, and transforms to easily bonding posture or slips into lower bonding threshold region and bond with diamond surface finally. Thus the bonding amount or bonding

probability is increasing. But if horizontal component of the incident energy is over large, this generated bond may be snapped and bounced away. (v) Lots of experiment shows that: incident angle 0° - 20° and incident energy 30-60 eV are the optimal initial conditions for C_{36} depositing on (100) crystal plane of diamond.

V. ACKNOWLEDGMENT

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