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Diffusion Dynamics of Cu_x Cluster on Cu(111) Surface

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The diffusion dynamics of small two-dimensional atomic clusters Cu_x ($1 \leq x \leq 8$) on Cu(111) surface were studied using the molecular dynamics simulations and a modified analytic embedded-atom method in the temperature range from 200 K to 800 K. The cluster size and temperature dependence of the diffusion coefficients and migration energies are presented. Our simulations show that the diffusion migration energy of the Cu_7 cluster is the highest and the prefactor for the Cu_7 cluster is almost three orders of magnitude larger than that for single atom diffusion. This conclusion is consistent with the experimental results for similar metals. In addition, the dependence of cluster diffusion on film growth is also discussed.

Key words: Cluster, Molecular dynamics, Surface diffusion

I. INTRODUCTION

A comprehensive understanding of the mechanisms and energetics by which small atomic clusters migrate across the single crystal terraces is of both fundamental and technological importance. In addition to a providing physical insight into the details of adatom-surface and adatom-adatom interactions on surfaces, information on the mechanism and energetics of cluster motion can contribute to a better understanding of crystal and thin-films growth kinetics [1]. Recent investigations of cluster diffusion by field ion microscopy studies [2-5] of compact clusters on the fcc(111) surface have documented several remarkable diffusion behaviors as follows. (i) Edge running and evaporation condensation apparently can be ruled out as mechanisms for diffusion. (ii) The prefactor for diffusion is several orders of magnitude larger than that for single atom diffusion. These unusual experimental observations motivate many detailed theoretical studies [6-14]. Over the years, various diffusion mechanisms of clusters have been found. Despite that, rather less quantitative information is available from theoretical studies about the diffusion properties of clusters. Recently, the diffusion prefactor (D_0) for Ir_7 on Ir(111) was calculated from the local vibrational density of states [7], and the calculated D_0 was of the same order of magnitude as in single atom diffusion. The authors suggested that the high prefactor found in experiments on the diffusion of compact clusters did not arise from one single displacement mechanism characterized by a very high prefactor, rather it came about because a large number of non-equivalent processes, with similar activation barriers, could participate in diffusion of compact clusters. Thus the molecular dynamics (MD) calculations, which includes all diffusion mechanisms and follow the actual dynamical evolution of the system, should be the first choice for a small cluster. In addition, it is worth noting that kinetic Monte Carlo method has been used to study the cluster diffusion. Its current strength lies in investigating a large cluster, but the technique cannot reveal the intervening microscopic processes [15].

In this work, MD simulations are used to investigate the diffusion of 2D clusters with N_c (N_c from 1 to 8) Cu atoms on Cu(111) surfaces in the temperature range from 200 K to 850 K. The diffusion prefactors and migration energies for all studied clusters are calculated. It is of interest to study cluster diffusion on the fcc(111) surface, because it proceeds in a particularly simple manner. In addition, this surface is extremely stable in temperature, and it is therefore possible to study the phenomenon over a relatively wide range of temperature and to study the cluster size and temperature dependence of the diffusion prefactors and migration energies. This allows excellent quality diffusion data to be accumulated for a description of film growth.

II. SIMULATION METHOD

In order to perform the MD simulations, we use a modified analytic embedded atom potential (MAEAM), which has been described in detail for fcc [16,17] metals. This potential has been widely used for both cluster and surface systems, giving reasonably good results as compared to experiments [17,18]. The model parameters for Cu are n=1.12, F_0=2.30 eV, α=-2.88×10^{-5} eV, k_c=0.75, k_0=-24.31 eV, k_1=-16.07 eV, k_2=-6.85 eV, k_3= 4.32 eV, k_4=-8.51 eV, k_{-1}=51.26 eV, respectively.

In our MD calculations, the simulation box contains 21 atomic layers with 192 atoms each, arranged in an FCC lattice. Periodic boundary conditions are applied in the lateral directions, i.e. parallel to the surface. Two

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free surfaces perpendicular to the (111) planes are obtained by fixing the dimensions of the supercell size to a value twice as large as the thickness of the crystal in the direction normal to the surface. All simulations are carried out in constant volume, constant temperature (*NVT* ensemble), except for a series of bulk calculations in constant pressure, constant temperature (*NPT* ensemble) in order to determine the lattice constant at each simulated temperature which is used for properly constructing simulation box. A 2D atomic cluster with 2 to 8 atoms is deposited on the top of the surface layer of the slab. The stable configurations for all clusters are obtained by quenching molecular dynamics [19] which is the fastest way to gain the minimum of the potential energies of the system. The quenching consists in canceling the velocity of a particle each time its product with the force is negative. This procedure is terminated when the system reaches a sufficiently low temperature, in our case 10^{-9} K. Simulations are performed of 1-4 ns (depending on the temperature) in the temperature range from 200 K to 800 K (depending on the cluster size), with a time step of 3 fs, which is sufficient to obtain reliable statistics for the determination of the diffusion coefficient of all clusters.

In experiment, the diffusion coefficient for cluster can generally be acquired by measuring the mean-square displacement of the cluster's mass center [20]. However, that method may not be used to calculate the cluster diffusion coefficient using MD simulations because of the unusually great migration energies for cluster diffusion. The mean-square displacement of cluster's mass center is too small, from which the diffusion coefficient cannot be deduced using the Einstein relation.

In this work, the diffusion coefficients for all clusters are obtained by calculating the jump frequencies [21,22]. The number of hopping events (n) of clusters are counted and used to obtain the jump frequency Γ=n/t. n for cluster is equal to the average of the hopping events for all atoms of the cluster. The diffusion coefficients (D) are related to the jump frequency (Γ),

$$D = \frac{\lambda \Gamma d^2}{2Z} \tag{1}$$

where Z is the dimensionality of the diffusion space (two in our case), λ is the number of jump directions (three for hopping mechanism of fcc(111)), and d stands for the jump distance. The prefactor D_0 and migration energy $E_{\rm m}$ are calculated from the Arrhenius relation for the diffusivity

$$D = D_0 \exp\left(-\frac{E_{\rm m}}{k_{\rm B}T}\right) \tag{2}$$

III. RESULTS AND DISCUSSION

The main purpose of the present work is the study of a 2D cluster with $N_{\rm c}$ (from 1 to 8) atoms of Cu on the Cu(111) surface. In order to ascertain that the potential used describes well the system under study, the single Cu adatom on the Cu(111) surface is first considered. In Table I, we present the computed $E_{\rm m}$ and D_0, along with available experimental and theoretical results. As we can see from Table I, the calculated $E_{\rm m}$ and D_0 are 0.052 eV and 2.46×10^{-4} cm^2/s, respectively, which are in reasonable agreement with the experimental data and other theoretical values [15,23-25].

TABLE I Migration energies $E_{\rm m}$ and prefactors D_0 of the single Cu adatom diffusion on the Cu(111) surface

	$E_{\rm m}$/eV	$D_0/(10^{-4}{\rm cm}^2/{\rm s})$
This work	0.052	2.46
Experiment [24]	0.093	–
Theory [30]	0.04	–
Theory [23]	0.041±0.002	2±0.1
Theory [24]	0.064	4.24
Theory [25]	0.026	3.0

On the fcc(111) surface, there are two types of sites for an adatom. The atom may sit on top of an upward triangle formed by the surface atoms (this is an fcc site) and the adatom sits on top of a downward triangle (in this case, it is an hcp site). The calculation using quenching MD shows that the clusters prefer to bind on fcc sites. This has also been observed for Ir islands on Ir(111) by field-ion microscopy [26]. In addition, the theoretical calculation with the effective medium theory for Pt on Pt(111) also obtained a similar conclusion [11]. The energy-minimized configurations of Cu_x clusters for MD simulation are shown in Fig.1.

It is our aim here to provide some quantitative understanding of the cluster diffusion on the FCC(111) surface. Thus, at each temperature we perform a detailed trajectory analysis to calculate the number of hopping

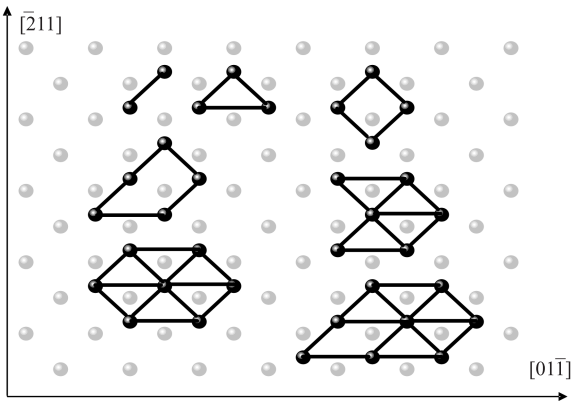

FIG. 1 A schematic picture of the structure of stable small Cu clusters on the Cu(111) surface. The gray balls show the surface atoms. All adatoms stay at fcc sites. The lines joining the adatoms are drawn to show which atoms belong to the same cluster.

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TABLE II The number of hopping events of different atoms in cluster at 550 K. The total simulation time is 2.5 ns. The numbers (1, 2, 3, $\cdots$, 8) denote the different atoms in a cluster

Cluster	Atom labels in a cluster								Average
	1	2	3	4	5	6	7	8	
Cu_2	1923	1938							1930.5
Cu_3	828	836	812						825.3
Cu_4	345	333	337	326					335.3
Cu_5	246	219	195	258	203				224.2
Cu_6	183	147	172	162	155	129			158.0
Cu_7	29	29	27	20	27	28	28		26.9
Cu_8	33	36	29	17	35	22	82	64	39.8

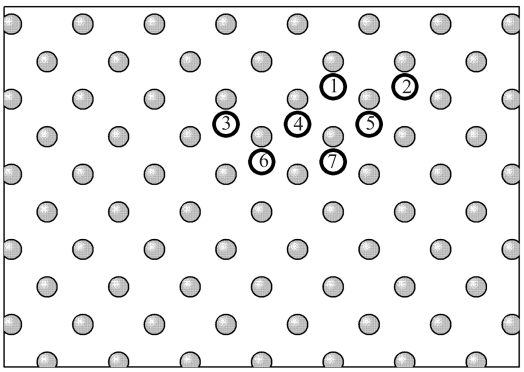

FIG. 2 The dimer shearing along cluster edges for Cu_7 cluster diffusion.

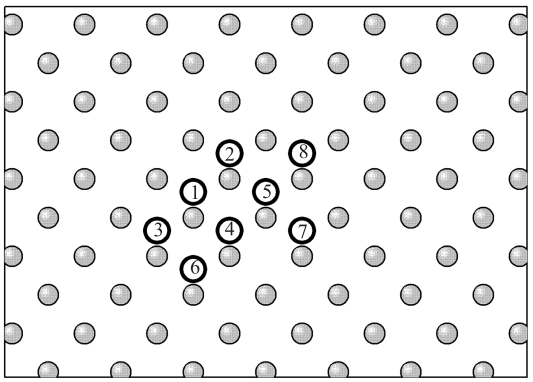

FIG. 3 Atoms (7, 8) move along cluster edges.

events of clusters. The number of hopping events for each atom in clusters at 550 K is listed in Table II. As shown in Table II, in the case of dimer, trimer, and tetramer, the number of hopping events in clusters is almost the same. This shows that the dominant diffusing mechanism for these three clusters is concerted motion. However, the situation is different when the cluster size is greater than 4-atom. Because of periphery diffusion, hopping events for atoms in cluster is no longer equal.

Experiments have shown that compact clusters diffuse by concerted motion and without any change in shape. However, as shown in Table II, the number of hopping events for atom 4, which is the geometric center of the Cu_7 cluster, is much smaller than that for other atoms of cluster. We find that the dimer shearing diffusion mechanism results in the difference. As shown in Fig.2, the upper dimer (1, 2) has moved along the row edge diffusing to the right of the cluster and a distortion of shape for the compact cluster is observed. It should be pointed out that the intermediate distorted states are short-lived and therefore, would probably not be seen in the experiments [8].

For Cu_8 cluster, the number of hopping events for atom 7 and 8 is much greater than that for other atoms, as can be clearly seen in Table II. This indicates that the motion of atoms (7, 8) along cluster edges plays an important role, as shown in Fig.3. In addition, because of the hopping of atom 7 and 8, the average number of hopping events for a Cu_8 cluster is greater than that for a Cu_7 cluster.

To quantify observation we counted the jump frequency, from which the diffusion coefficients for all studied clusters derive. In Fig.4 the Arrhenius plots of the diffusion coefficients for Cu_1 through Cu_8 are shown. We can find that the diffusion coefficients for all clusters follow the Arrhenius law. From these plots, we can obtain D_0 and E_m associated with each cluster, which are given in Table III. Our results suggest that, with increasing cluster size, the D_0 and E_m for these Cu clusters increase monotonically except for the Cu_7 cluster. It is evident that, as the cluster size increases, in general it is difficult to diffuse as a whole. The character is similar to the experimental results of Pt clusters, but is different from that of Ir clusters, which has a sharp dip in the migration energy for Ir_4. From our calculations, unusually high D_0 and E_m for a compact cluster (Cu_7) are obtained. The D_0 for Cu_7 is nearly 3 orders of magnitude greater than that for single adatom, and the E_m is almost 10 times than that for single adatom. These ratios are comparable with the experimental results for other similar metals (Ir, Pt) [2,4,5]. The static calculation using local vibrational density of states [7] found that D_0 is the same order of magnitude as in single atom diffusion. Kürpick suggested that the high

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TABLE III The calculated diffusion prefactors and activation energies for Cu_x clusters

	Cu	Cu_2	Cu_3	Cu_4	Cu_5	Cu_6	Cu_7	Cu_8
$D_0/(10^{-4}cm^2/s)$	2.46	6.24	12.7	20.3	22.7	46.1	561	82.3
E_m/eV	0.052	0.074	0.15	0.21	0.24	0.29	0.48	0.38

TABLE IV The average lifetime of atoms for Cu_1, Cu_7 and Cu_8 cluster at surface site at different temperatures (unit in s)

Cluster	Average lifetime/s							
	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K
Cu_1	3.2×10^{-10}	1.3×10^{-11}	4.6×10^{-12}	3.0×10^{-12}	2.5×10^{-12}	2.4×10^{-12}		
Cu_7	4.4×10^{9}	3.7×10^{-3}	3.5×10^{-7}	3.4×10^{-9}	1.9×10^{-10}	3.1×10^{-11}	8.5×10^{-12}	3.4×10^{-12}
Cu_8	2.4×10^{5}	6.9×10^{-5}	4.6×10^{-8}	1.2×10^{-9}	1.1×10^{-10}	3.0×10^{-11}	1.1×10^{-11}	4.3×10^{-12}

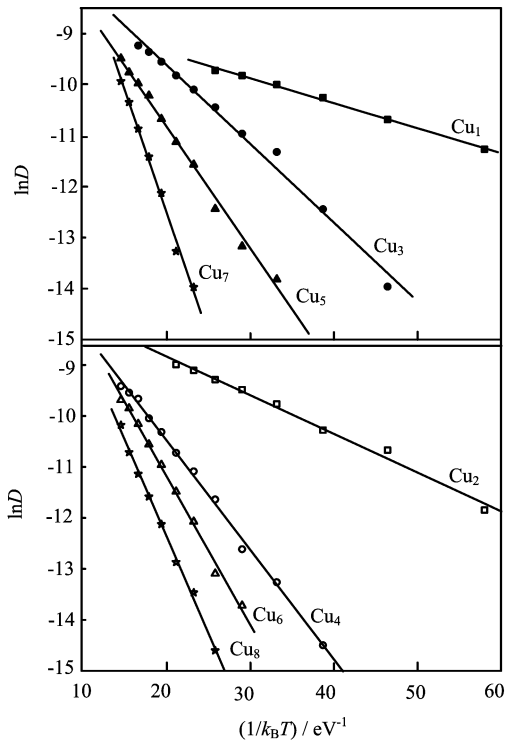

FIG. 4 Arrhenius plots of the diffusion coefficients for Cu_x clusters. The solid lines are Arrhenius fits to the molecular dynamics data.

prefactors found in experiments on the diffusion compact cluster did not arise from one single displacement mechanism [7]. Due to considering all diffusion mechanisms, the MD calculations should be closer to the experiment results.

In order to discuss the implications of our calculated results for film growth, the average lifetimes k (k=1/Γ) of atoms in clusters at surface site are listed in Table IV. When a particle spends at a site a time much longer than the time scale of molecular motion, the atomic motion is a site-to-site hopping [27]. For example, the k is 1.8×10^{-7} s at 50 K for single atom diffusion, 3.2×10^{-10} s at 100 K, and 3.9×10^{-11} s at 150 K. Thus, at 50 K, we can talk about site-to-site hopping, whereas at 150 K the lifetime is so short that that kind of description is inappropriate [11]. If the close-packed Cu_7 cluster is the seed for the onset of fractal growth on Cu(111) [28], for temperatures between 100 and 300 K, there is enough mobility for the single atoms (k=3.2×10^{-10} s) to arrive at the edge of the island and the time between the arrival of atoms at Cu_7 cluster is much shorter than the time in which an atom leaves the cluster, so the size of the islands, at a given total coverage, increases with the temperature. For temperatures above 600 K, the lifetime for Cu_1, at 600 K is comparable with that for Cu_7 and Cu_8, so the departure of atoms in Cu_7 and Cu_8 is no longer negligible and the film growth will become slow.

In order to get deeper insight into the film growth behavior, the thermal stability of the Cu_7 cluster on the surface is also investigated. The order parameter η is calculated using the following relation [9,29]:

$$\eta = R/h \tag{3}$$

where R is the mean cluster radius and h is the height of the center of mass from the substrate. R was obtained by averaging the distance of atoms from a vertical axis passing through the center of mass. The melting transition of clusters would be signaled by an abrupt increase in η. The temperature dependence of the order parameter for Cu_7 clusters is shown in Fig.5. It is clear that the melting temperature of Cu_7 clusters is about 1150 K, which is about 15% lower than the bulk melting temperature in MAEAM. The result is in good agreement with Gallego's calculation [9]. In addition, in order to illuminate the melting process of Cu_7 clusters, the temperature dependence of R and h is also plotted in Fig.5. We find that the melting for Cu_7 clusters is mainly caused by the increasing of R, which indicates that the clusters lose their hexagonal configuration at melting temperature.

IV. CONCLUSION

In the present work, using a modified analytic embedded-atom method and MD simulations, the dif-

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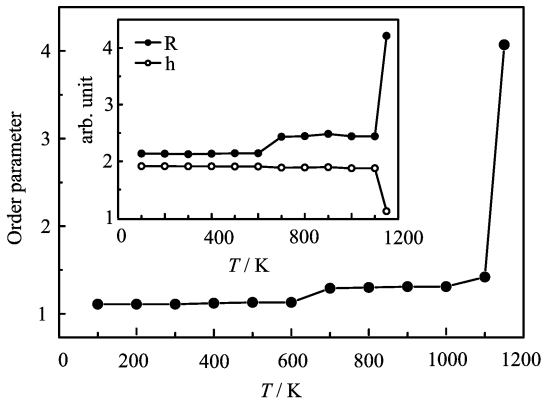

FIG. 5 Temperature dependence of the order parameter for the Cu_7 cluster on the Cu(111) surface. In addition, the temperature dependence of R and h is also plotted.

fusion coefficients are calculated by counting the average number of hopping events for studied clusters. The diffusion mechanisms are discussed according to the average number of hopping events. The calculated D_0 and $E_{\rm m}$ increase with increasing cluster size, except for the Cu_7 cluster. The calculated D_0 for compact clusters is almost three orders of magnitude larger than that for single atoms diffusion, which is consistent with the experimental results for other fcc metals. This suggests that the unusually high D_0 for compact clusters observed from the diffusion experiments is the contribution of all diffusion mechanisms. The dependence of cluster diffusion for thin film growth is also discussed. It is found that the appropriate temperature range for thin film growth is from 100 K to 600 K. Finally, the thermal stability for Cu_7 clusters is investigated by calculating the order parameter. The computed melting temperature of the close-packed cluster is 1150 K.

V. ACKNOWLEDGMENT

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