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The dynamic diffusion behaviors of 2D small Fe clusters on a Fe(110) surface

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Abstract

In this paper, the diffusion behaviors of Fe clusters on a Fe(110) surface have been investigated using molecular dynamics simulations based on a modified analytic embedded-atom method. The stable configurations of Fe clusters are predicted to be close-packed islands configuration for Fe clusters up to nine atoms or even larger in size. The activation energy of surface diffusion exhibits an interesting, oscillatory behavior as a function of cluster size. As compared to the structures with extra atoms at the periphery, compact geometric configurations of Fe clusters (four- and seven-atom clusters) have an obviously higher activation energy. The reason is that for clusters of more than two atoms the diffusion mechanisms of 2D small clusters are achieved by the migration of extra atoms at the periphery.

1. Introduction

On the atomic scale the investigation of the effect of dynamic diffusion behaviors of single adatoms and atomic clusters on the surface aids our understanding of the mechanism of crystal growth and thin film formation. These problems have been intensively studied both experimentally and theoretically. Experimental methods can provide direct microscopic information about the stable configurations of clusters. However, these investigations cannot give conclusive information about the diffusion mechanisms of clusters and thus the theoretical methods are needed. Otherwise, investigations with first-principles methods are not available because of the limitation of the number of atoms for calculation systems. The semiempirical

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many body potential can properly describe the interaction among atoms, and this method provides the most reasonable approach for systematic studies of adatom clusters on surfaces.

The experimental studies have shown that dynamic diffusion behaviors of clusters on surfaces are various and intricate [1–3]. The diffusion mechanisms of single adatoms on metal surfaces are well understood. However the diffusion behaviors of small clusters are still nontrivial [4–6], and the current theoretical research has hardly given a reasonable explanation of the experimental results; thus, it is necessary to investigate the self-diffusion mechanism of 2D small clusters with molecular dynamics simulation. Iron is a very common metal for application. Less work has been done on diffusion in the Fe/Fe(110) system. We refer briefly here to the papers about small clusters on the (110) bcc surface. Davydov [7] calculated the activation energy for bridge diffusion on the (110) bcc crystal plane based on the cohesion approximation. Spišák and Hafner [8] investigated the diffusion of iron atoms on clean W(100) as well as on a Fe/W(100) surface by means of first-principles calculations, and compared the activation energy barriers obtained for the hopping migration process with the exchange migration process. Using a field ion microscope, Tsong [3] calculated the average activation energy of small Pd clusters with two to nine Pd atoms on the W(110) surface, and probed the possible cluster diffusion mechanisms.

In the present work, we investigate the self-diffusion dynamical behaviors of 2D small Fe clusters on Fe(110), and further discuss the diffusion mechanism according to molecular dynamics simulations. The activation energy and pre-exponential factor for self-diffusion of 2D small clusters on an Fe(110) surface are extracted from the Arrhenius relation.

2. Calculation method and model

Semiempirical methods provide the most reasonable approach for systematic studies of adatom clusters on surfaces. The embedded-atom method (EAM) originally presented by Daw and Baskes [9] has proven to be one of the most successful methods for studying defects and surfaces of metals, but its embedded energy and pair potential are not analytical forms, which makes it very difficult to apply this model to alloys systematically. It limits the applications of the method, especially for body-centered-cubic (BCC) and diamond-structure materials. Johnson has developed an analytical EAM model for FCC, BCC, and HCP metals [10, 11]. Considering directional bonding of atoms in a crystal, our group [12–15] developed a modified analytical EAM (MAEAM). Our recent research on Pt trimers on Pt(111) [16] makes it clear that the many body potential combined with molecular dynamics simulation is an effective method for investigating the diffusion dynamics behaviors of clusters on metal surfaces.

We performed our calculations using fifteen 192-atom layers with periodic boundary conditions in the two directions parallel to the surface, and this surface perpendicular to the [110] direction. The slab was free to relax. In our MD simulations the six-value Gear predictor–corrector algorithm and the Nosé constant-temperature technique [17] are employed, except for a series of bulk calculations in the constant temperature, constant pressure (NPT ensemble) controlled by the Andersen method [18] in order to determine the lattice constant at each simulated temperature, used for properly constructing the simulation box. To obtain the stable cluster configurations, the adatoms were initially placed above the four-fold sites of the surface layer of the slab in a bulk type position. During this relaxation, the adatoms moved along the [110] direction and were held fixed parallel to the (110) surface. The substrate atoms and adatoms are relaxed to the most stable configuration, and then the stable configuration of Fe clusters is determined for the following analysis. Under the conditions of constant volume and constant temperature (NVT ensemble) the interactions between Fe atoms are described with MAEAM [19]. The equations of atomic motion are integrated with a fourth-order Gear

predictor–corrector algorithm and a time step of 2 fs. And all of the statistical data are collected from a further 1.5×10^7 time steps, which is sufficient for our calculations.

In our studies, the mean-square displacement is obtained by the trace of an atom or cluster’s geometric center for a period of 10 ns within the framework of MD relaxation, which is sufficient for reaching a relaxation equilibrium. $\langle R^2(t) \rangle$ is the mean-square displacement (MSD) of the mass-center of the cluster and is given by

$$\langle R^2(t) \rangle = \langle (x(t) - x(0))^2 + (y(t) - y(0))^2 \rangle. \quad (1)$$

The coordinate of adatoms on the surface is obtained by recording the positions of atoms for each time step, when the system is in a thermodynamic equilibrium.

The long-time behavior of the mean-square displacement gives us the diffusion coefficient. In experiments, the diffusion coefficient for a cluster can generally be obtained by measuring the mean-square displacement of the cluster’s mass-center (or center of mass) [20]. In the present simulation once the system is in thermodynamic equilibrium, the positions of interstitial atoms on the surface for each time step are recorded for further analysis. In the scenario of two-dimensional random-walk motion, the diffusion coefficient D is calculated using a long-time Einstein relation:

$$D = \lim_{t \rightarrow \infty} \frac{R^2(t)}{4t}, \quad (2)$$

where $\langle R^2(t) \rangle$ is the mean-square displacement (MSD) of the mass-center of the cluster.

In order to have reasonable statistics, the quantity MSD is averaged over a number of time origins. Then the prefactor D_0 and activation energy E_a follow a standard Arrhenius-type analysis:

$$D = D_0 \exp\left(-\frac{E_a}{K_B T}\right), \quad (3)$$

where E_a is the activation energy and D and D_0 are the diffusion coefficient and the pre-exponential factor, respectively.

3. Result and discussion

We are interested in the predictions of the stable configurations for isolated adatom clusters. The stable configurations fall into two categories: linear chains and close-packed islands. For the calculations with adatoms, the adatoms were initially placed at the four-fold sites of the relaxed surface, and all the atoms were relaxed to obtain a lowest-energy configuration. A set of stable configurations and the corresponding binding energy are shown in figure 1.

The binding energy of isolated adatoms is defined as follows [21]. For example, the binding energy of a N -adatom chain is given by

$$E_{CN,B} = (E_{CN} - E_S) - N(E_1 - E_S), \quad (4)$$

and the binding energy of a N -adatom island is given by

$$E_{IN,B} = (E_{IN} - E_S) - N(E_1 - E_S), \quad (5)$$

where E_{CN} and E_{IN} represent the total energy of the slab with a N -adatom chain and a N -adatom island, respectively. E_S represents the total energy of the slab with no adatoms, and E_1 represents the total energy of the slab with one adatom. The calculated one-adatom adsorption energy, $|E_1 - E_S|$, is 3.52 eV.

Will islands continue to be stable for larger Fe clusters? As shown in figure 1, we plot the energies of Fe chains and islands versus the number of adatoms and thus the question can easily

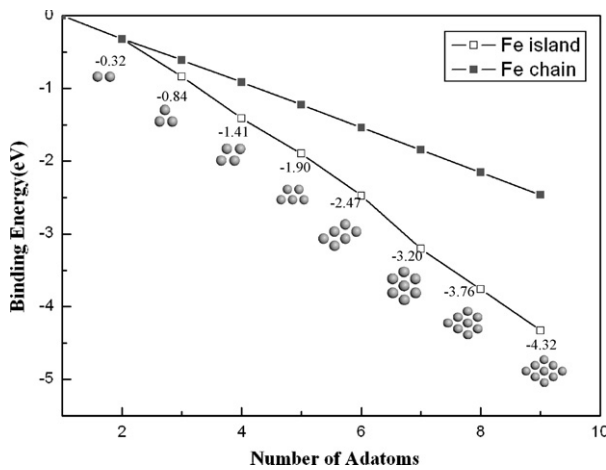


Figure 1. Energies (in eV) of the chain and island configurations shown for Fe clusters containing from two to nine adatoms on a relaxed slab.

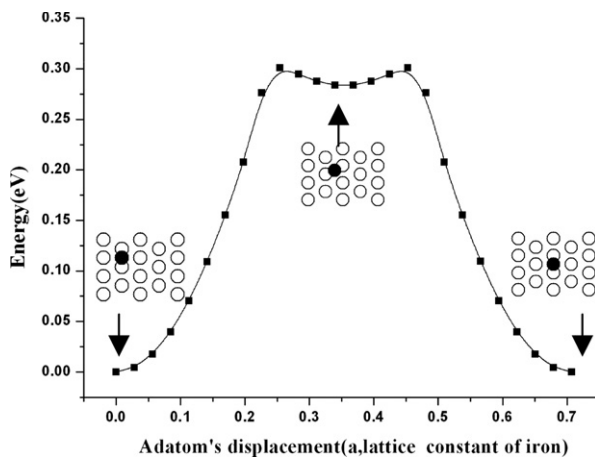


Figure 2. The relation of the increment of system energy with the distance of the single adatom moving along its migration path. Here the open circles represent the top layer atoms. The dark circles are the adatoms.

be answered. The energy of both has a nearly linear dependence on the number of adatoms. From figure 1, it is obvious that islands will continue to have stable configuration compared with chains for larger clusters. To our knowledge, there are no conclusive experimental observations of the stable configurations of Fe clusters on Fe(110). Molecular dynamics simulations predict that linear chains are metastable, and will reconfigure to 2D islands after relaxation.

Fe(110) is the most closely packed surface, because the atomic density of the Fe(110) surface is by a factor of $\sqrt{2}$ higher than that of the Fe(100) surface. The energetically stable configuration for a single Fe adatom on a Fe(110) surface is located in the four-fold site position. The mechanism of diffusion of a monomer is known to be performed by the translation from the four-fold site to the adjacent nearest-neighbor site, and occur by atomic hopping along the most compact direction, i.e. along $[1\bar{1}\bar{1}]$ and $[1\bar{1}1]$ directions. The static energy barrier (E_s) for the Fe diffusion is calculated by the quenching MD method [22]: choose and change a certain freedom according to the diffusion path, then at each fixed increment of this freedom, all the other freedoms of the active atoms are fully relaxed. The energy during the process of the self-diffusion of iron atoms along the $[1\bar{1}\bar{1}]$ direction is shown in figure 2, in which the x -axis represents the x direction of the lattice and the y -axis indicates the energy. It is obvious that the energy curve of self-diffusion is symmetric. However, the saddle point in the diffusing

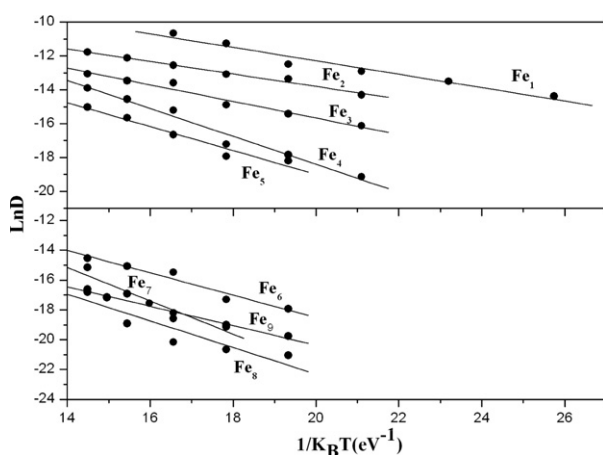


Figure 3. Arrhenius plot used to derive the diffusion parameters for 2D small cluster self-diffusion on Fe(110).

process is not at the middle point of the diffusing path. There are two saddle points in the path. The middle point of the diffusing path is a substable point, at which the energy is 0.28 eV. It is 0.02 eV lower than the energy of the saddle points.

If one ignores the details of the displacement process and focuses only on the motion of a cluster's center of mass, the investigation of the mean-square displacement is essential. From inspection of the mean-square displacements, the nonmonotonic behavior of cluster mobility with increasing cluster size is obvious. This has also been proved experimentally [23] and theoretically [6, 24, 25]. For instance, Wang and Ehrlich [23] have investigated the self-diffusion of Ir clusters on the Ir(111) surface. The calculational binding energy increases sharply from dimers to trimers, drops for tetramers, and then rises again for pentamers and larger clusters, dimer, to trimer, but drops for tetramers, and then rises again for pentamers and larger clusters. In our studies of self-diffusion of Fe clusters, the mean-square displacement of a trimer is 72 \AA^2 at 600 K. The mean-square displacement of a tetramer is 14 \AA^2 at the same temperature, which is a factor of five smaller than that for a trimer. One might expect that tetramers are less mobile than trimers. But, the mean-square displacement of a pentamer is larger than that for a tetramer. This implies that the mobility of the cluster be increased by the addition of an atom to the periphery of the tetramer. The same trend of mean-square displacement is also observed in heptamers and hexamers. At 700 K, the mean-square displacement of a heptamer is only 0.7 \AA^2 . Upon addition of another atom to form an octamer, the cluster becomes more mobile than the heptamer and the cluster's mobility resulting in a mean-square displacement at 700 K of 2.5 \AA^2 for the octamer. These findings have also been confirmed by Shi *et al* [6] for Ag, Cu, and Ni in recent embedded-atom model (EAM) calculations.

An Arrhenius plot for Fe adatoms containing up to nine adatoms diffusing on Fe(110) is shown in figure 3. The activation energy of surface diffusion and the prefactor can be determined from the slope and intercept of the line, respectively.

Although subject to the assumption of a size-independent Arrhenius prefactor, the calculation of the activation energy is useful for examining the mobility of different-sized clusters at different temperatures. The results for the self-diffusion of adatoms of bcc mental Fe on the (110) surface are listed in table 1. As one may notice, D_0 is nearly within an order of magnitude of $10^{-3} \text{ cm}^2 \text{ s}^{-1}$, which is consistent with the results obtained by experiments [20, 26]. The calculated value of E_a for small clusters increases approximately linearly. The exception is tetramers and heptamers, whose self-diffusion activation energy is

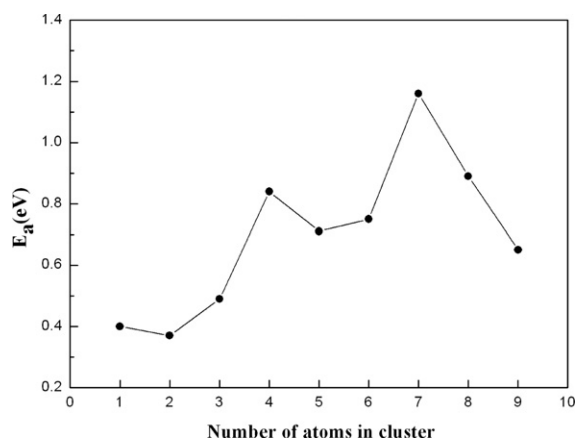


Figure 4. A plot of the activation energy of surface diffusion for Fe clusters on Fe (100). The low mobility of clusters with compact geometric shape causes the activation energy to oscillate as a function of cluster size.

Table 1. Activation energy E_a (in eV) and pre-exponential factor D_0 (in $\text{cm}^2 \text{s}^{-1}$) for Fe cluster diffusion on the Fe(110) surface.

Cluster size (atoms)	Activation energy E_a (eV)	Pre-exponential factor D_0 ($\text{cm}^2 \text{s}^{-1}$)
1	0.40	1.27×10^{-2}
2	0.36	1.59×10^{-3}
3	0.49	2.81×10^{-3}
4	0.84	1.89×10^{-1}
5	0.71	7.71×10^{-3}
6	0.75	2.98×10^{-2}
7	1.16	1.01×10^{-1}
8	0.89	1.18×10^{-2}
9	0.65	6.60×10^{-4}

quite large and a pre-exponential factor that is found to be at least two orders of magnitude larger than others.

Figure 4 shows a plot of the calculated activation energies of surface diffusion as a function of cluster size. The result indicates that the diffusion of Fe clusters on Fe(110) follows the anticipated tendency of increasing activation energy with increasing cluster size. It is surprising that clusters whose atoms are in compact configurations (i.e. four- and seven-atom clusters) have higher activation energies than less compact structures.

In particular, the mean-square displacement yields an activation energy of 0.36 eV for dimer self-diffusion on Fe(110), which is 0.04 eV less than the activation energy for monomers of 0.40 eV. This result suggests that dimer diffusion is faster than the corresponding monomer diffusion. This has been observed previously in FIM studies of Pt on W(110) [26] and Re on W(112) [27]. For Al adatom pairs on Al (100) [28], the first-principles calculations suggested that the pair barrier is lower than the monomer barrier. Considering a dimer on Fe(110), each atom of the dimer has five nearest neighbors. However, a single adatom has only four nearest neighbors. Pauling's bond-order-bond-length correlation [29] indicates that the dimer bonds to the surface will be weaker than those of a single adatom. So the increase of the adatom-adatom interaction energy is compensated by the cost of weakening of the Fe surface bonds. This compensation explains the decrease of the calculated Fe-Fe activation energy as compared

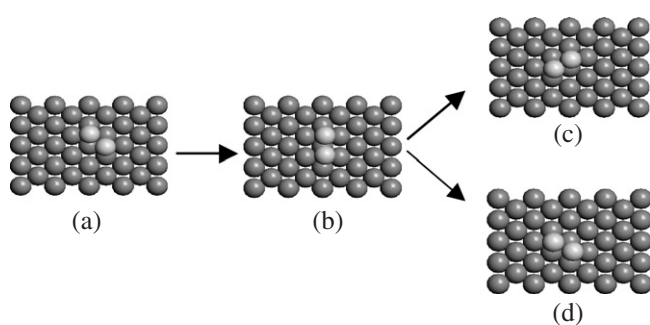


Figure 5. Top views of the structures and diffusion paths for Fe dimers on Fe(110) surfaces.

with a single atom. The result is identical to the calculations of mean-square displacement. The mean-square displacement of a dimer is 377 \AA^2 , which is larger than that for single atom.

The usual assumption is that the activation energy of surface diffusion increases monotonically with increasing cluster size. However, we get the oscillatory nature of cluster mobility as a function of cluster size. Insight into why clusters with compact shapes are less mobile can be gained from diffusion mechanisms of 2D clusters. First of all, we describe the diffusion mechanisms of Fe dimers on Fe(110). One might expect that the elementary step of dimer diffusion is a concerted jump mechanism accomplished by simultaneous hopping of a pair adatoms. However, the behavior of Fe dimer migration is such that when an adatom jumps to a nearest-neighbor site, another atom makes a similar hop as an isolated adatom. Therefore either adatom may then jump in one of two possible directions. This would result in the process of Fe dimer migration being a linear displacement and an orientation change. The reoriented displacement of dimers has been experimentally observed [2]. The possible structures and diffusion paths of dimers on bcc (110) surfaces are summarized in figure 5. Figure 5(b) shows the structure of a transitional state, and the intermediate configuration of a dimer along the [001] direction is not stable. The energy of the substable structure is 0.1 eV, which is larger than that of the most stable configuration shown in figure 5(a). And the energy of transitional state is 0.2 eV lower than that of the saddle points. That is, binding of the atom with the other one over the top of the substrate Fe atom is not favored, so the structure is seldom observed in experiments [3]. The whole process is as follows. First one atom moves to the nearest-neighbor site along the most compact direction, and then the other atom follows the same way. Inspection of figure 5 shows that the reason for the lower barrier for dimers is that the coordination number is higher for the migrating atom when the other atom of the dimer is present. Given that the average bond strength typically decreases with higher coordination number, dimers have weaker bonds with atoms of the surface than monomers. So the mobility of dimers is larger than that of monomers.

In fact, a few experiments have demonstrated the characteristics of surface diffusion. The results suggested that the migration of small clusters is achieved by a jumping mechanism of solitons at the edge of clusters [30, 31]. Molecular dynamics simulations of Fe cluster diffusion on Fe(110) indicate that diffusion occurs by sequential displacements of individual atoms at the edge of the cluster. In addition, the diffusion of extra atoms at the periphery leads to the increasing mobility of the cluster. As one might expect, the tetramer is less mobile than the trimer. However, upon addition of another atom to form a pentamer, the cluster again increases the overall mobility of the cluster and decreases the activation energy. This is consistent with the results from the mean-square displacements. As for clusters with compact geometric shapes, the energy required to break an edge atom free from the cluster is higher. However, the energy to move the peripheral atom from the cluster with less compact structures is significantly less.

It is clear that the activation energy of clusters with compact geometric structures is greater than that of those with less compact shapes.

4. Conclusion

The stable configuration and diffusion mechanism of Fe clusters of up to nine atoms on Fe(110) have been studied using MAEAM. It is noted that the most stable configuration for Fe is 2D islands for all numbers of adatoms. Oscillations in the activation energy of surface diffusion as a function of cluster size would be also somewhat surprising in that when the cluster becomes a tetramer or heptamer, there is a noticeable increase in the activation energy of surface diffusion. The study of diffusion mechanisms of Fe clusters on a Fe(110) surface provide more details of self-diffusion on Fe(110). Molecular dynamics simulations show that the diffusion mechanisms of atomic clusters may be due to the migration of extra atoms at the periphery of Fe clusters. The relatively low mobility of clusters with compact geometries is attributed to the higher activation energy required to detach an atom from the cluster's periphery.

Acknowledgments

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