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Structural stabilities and diffusion of small Fe clusters on Fe (1 1 0) surface: A molecular dynamics study

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ABSTRACT

Using Embedded-atom-method (EAM) potential of iron, structural stabilities of small Fe clusters on a Fe (1 1 0) surface have been investigated by molecular dynamics studies. It is presented that a tetramer and heptamer clusters are more stable than other sizes. These two clusters have high transition energies. They can be a critical nucleus at low and high temperature, respectively. A dimer diffuses more easily with lower energy barrier than single adatom. The trimer's rotation and dimer shearing mechanisms have been investigated in this paper.

1. Introduction

Acquiring a detailed knowledge of the microscopic mechanisms of single atom and small clusters diffusion on a surface is of very importance for the understanding of a number of phenomena such as nucleation and thin film growth. For this reason, extensive investigations have been done on the atomic scale concerning the structural stability and dynamical behavior of small clusters on various surfaces. These studies have shown that dynamic diffusion mechanisms of clusters on surfaces are various and intricate.

Although much valuable information about small clusters diffusion can be obtained experimentally by field-ion microscope (FIM) [1–4], it is difficult to distinguish directly the path of the adatoms diffusion by this technique, especially when diffusion mechanisms are complicated. Therefore, theoretical studies are usually needed. First-principle calculations should be preferred in principle, but in practice it is severely limited by computing power. Therefore, the calculations including molecular dynamics simulation based on semiempirical potentials are usually performed [5–10]. Although the results obtained from the semiempirical potentials, especially some quantitative results are sometimes not completely in accordance with the experiments owing to the impreciseness of the potentials, the semiempirical potentials method is still very effective to study qualitatively the self-diffusion of adatoms and clusters, and it makes large-scale and long-time molecular dynamics simulation be possible. Finite temperature molecular dynamics simulations are very helpful to study adatoms and small clusters diffusion, as they allow tracking the adatoms on the surface. Moreover, it is convenient to find low-energy diffusion path and new diffusion mechanism.

As far as we know, adatoms and small cluster diffusion on body-centered cubic (BCC) metal surfaces has not been studied as extensively as face-centered cubic (FCC) metal surfaces. Recently, we have investigated single vacancy diffusion near the Fe (1 1 0) surface by molecular dynamics method [10]. Chamati et al. [11,12] carried out molecular dynamics simulations using EAM potential to study single Fe adatom and vacancy diffusion properties on Fe (1 0 0) surface. Chen et al. [13] investigated the dynamic diffusion behaviors of 2D small Fe clusters on a Fe (1 1 0) surface by a modified analytical embedded-atom potential. However, they have not presented detailed cluster diffusion mechanisms. It is necessary for studying structural stability and diffusion mechanisms of small Fe clusters on Fe (1 1 0) surface via molecular dynamics in detail.

In this paper, using EAM potential [11] of iron, small Fe clusters' structural stability on Fe (1 1 0) surfaces have been investigated by molecular dynamics methods. It is presented that a tetramer and

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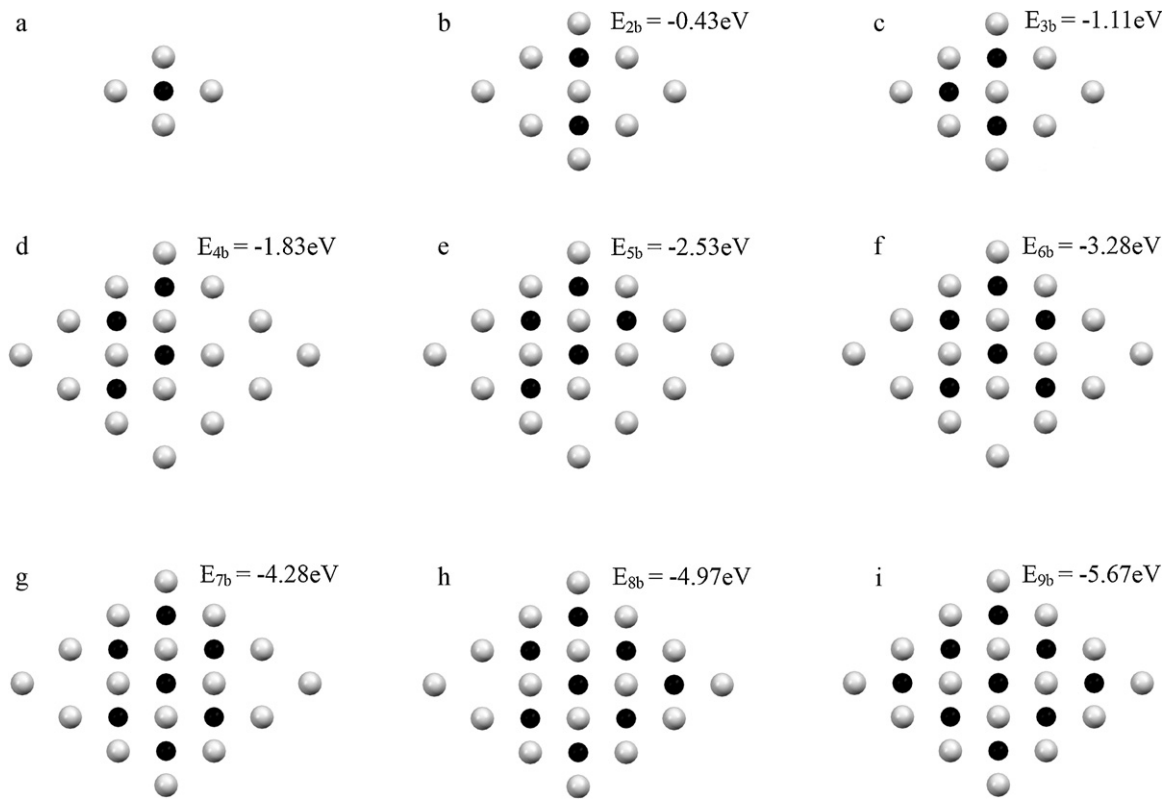

Fig. 1. Binding energies and minimal energy configurations of small Fe adatom clusters on a Fe (1 1 0) surface have been calculated by EAM potential. Light grey and black solid circles represent substrate atoms and adatoms, respectively.

heptamer of Fe cluster on Fe (1 1 0) surface are more stable relatively than others. These two clusters have high transition energies. Because of lower energy barrier, dimers diffuse more easily than single adatom. The dimers' shearing and trimers' rotation mechanisms have been presented in our investigations.

2. Calculation methods

All of our static calculations were performed by using EAM potential of Fe [11]. The EAM potential, partly based on density functional theory (DFT) concepts, gives a realistic description of FCC and BCC metal systems. Although the potential is semiempirical, it can give good results about some properties of BCC Fe and Fe (0 0 1) surface, such as elastic constants, bulk modulus, phonon dispersion curves, vacancy and adatoms diffusion [10–12].

We carried out our calculations by using twenty 200-atom (total 4000 Fe atoms) layers as a substrate eliminating sufficiently small size effect, with periodic boundary conditions in the two directions parallel to the surface. Upper eighteen layers of the substrate with a 20 Å vacuum to eliminate the interaction between its two surfaces are free to relax in three directions. Nevertheless, Fe atoms of the lowest two layers of the substrate are fixed to the BCC lattice positions. For the numerical integration, the Verlet algorithm was employed in our calculations at the constant temperature, constant pressure (NPT ensemble), with a time step of 2 fs. In order to determine the lattice constant at each simulated temperature, Andersen method [14] has been used properly to construct the simulation box.

For a detailed description of the mechanism of adatoms motion through previously defined paths, we carried out molecular static calculations at 0K. The static diffusion barriers and the minimum energy paths of these mechanisms were obtained using the nudged elastic band (NEB) method [15]. It uses both the initial and the final states of the system to calculate a chain of "images" that initially represents the intermediate configurations. The static diffusion barrier is then obtained from the image with the highest potential energy, which can be identified as the saddle point configuration. For calculating binding energies of clusters, we placed initially adatoms at the fourfold sites of the relaxed surface, and all of the atoms were relaxed in three free directions to obtain a lowest energy configuration at 0 K.

3. Results and discussions

3.1. Structural stabilities

To predict the stable configurations of isolated Fe adatom clusters on Fe (1 1 0) surface, we have calculated binding energies of various clusters defined as the following formula [16].

$$E_{nb} = E_n - E_s - n(E_1 - E_s) \quad (1)$$

where E_{nb}, E_n and E_s represent the binding energy of n-atom cluster, the total energy of the substrate with n-atom cluster, the total energy of the substrate, respectively. The single adatom adsorption energy, $E_1 - E_s$, is −3.26 eV, which is consistent with the result that is reported by Chen [13], −3.52 eV.

In Fig. 1, binding energies and minimal energy configurations of small Fe adatom clusters on Fe (1 1 0) surface have been shown in detail. From this figure, we can find that binding energies of clusters have decreasing trend as a function of cluster size. As Chen et al. [13] have reported, compact configurations of adatom clusters are more stable with lower binding energies than other configurations. Our calculation results have similar trend to that of their investigations. However, there is a little difference. All of binding energies of small Fe adatom clusters are lower than the corresponding results that reported in the Ref. [13]. This is contributed to different potentials.