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Diffusion dynamics of vacancy on Re(0 0 0 1), compared with adatom

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ABSTRACT

Using molecular dynamics (MD) simulations along with our recently constructed modified analytic embedded-atom method, the diffusion dynamics of single vacancy and adatom on Re(0 0 0 1) surface are studied. The diffusion coefficients of Re adatom and vacancy are calculated, and are found to present Arrhenius diagram. The diffusion migration energies (E_m) and prefactors (D_0) are obtained from the Arrhenius relation. The calculated E_m for adatom is in agreement with the recent low-temperature field ion microscope experimental data. The E_m and D_0 show that the vacancy has very low diffusive rate.

1. Introduction

It has been recognized that the properties of vacancy are especially important for the kinetic behavior of metals. The mass transport in metal surface is usually due to the propagation of lattice vacancies, and the study of the microscopic diffusion mechanism of vacancies is a key step to understand how nanostructures are built up on surfaces [1]. The investigations of the motion of Mn atoms on Cu(0 0 1) surface have found vacancy-mediated diffusion mechanism [2,3]. In addition, the investigations have also found that vacancy diffusion was a viable means of mass transport on Cu(1 0 0), Ni(1 0 0) and Ag(1 0 0) surfaces [4–6]. The vacancy might affect surface morphology in film growth [7], although the vacancy might be much less mobile than adatom. All in all, the investigation for vacancy diffusion is essential.

In contrast to many theoretical studies of surface defects diffusion for FCC and BCC metals [5,6,8–17], the studies on adatoms and vacancies diffusion for HCP metallic surfaces are very much limited, mainly due to the lack of reliable interatomic potentials or large computational resources for ab initio. To our knowledge, the self-diffusion of adatom and vacancy on HCP metallic surfaces are only investigated for static, equilibrium potential surfaces [18]. The static calculation cannot find all significant diffusion pathways, thus ignoring possible low-barrier processes, and the diffusion coefficient is intrinsically a dynamic quantity, it is the prefactor which contains the true dynamical information. So the dynamic simulation at finite temperature both reveals the diffusion mechanism and gives the corresponding diffusion migration energy and prefactor, and should be the first choice.

It is our aim here to provide some understanding for the dynamics of vacancy diffusion on HCP metallic surface. To this effect, the self-diffusion of vacancy and adatom on the Re(0 0 0 1) are investigated using molecular dynamics (MD) method. We chose the rhenium because the experimental data can be obtained to affirm the validity of our calculated results [19]. To describe interactions between the atoms in the model systems, the embedded-atom method (EAM) is used. Although less precise than first-principles approaches, the simple potential model is necessary in order to afford the large systems and long simulation times needed to simulate diffusion.

2. Simulation approach

To perform a MD simulation, we employ many-body potentials of the analytic embedded-atom method (AEAM), as developed by

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Hu et al., which has been described detailed in another paper [20]. The potential provides a good description for many-body interaction, and can distinguish the difference between atomic interaction in the bulk and that near the surface without any additional parameter. The AEAM potentials for HCP metals have been used to study the surface anharmonic effects of Be and Mg. The calculated results are in good agreement with the available experimental data [21,22]. In addition, the AEAM potentials for FCC metals have been successfully used for the study of the surface self-diffusion of clusters [23,24]. These investigations indicated that the present AEAM potential provided a rather good description of HCP and FCC metallic surfaces.

In the present work, the simulation box contains 21 atomic layers with 192 atoms each, arranged in an HCP lattice. Periodic boundary conditions are applied in the lateral directions, that is, parallel to the surface. Two free surfaces perpendicular to the (0 0 0 1) 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.

A standard MD technique is used to simulate the positions of atoms by solving numerically Newton's equations of motion using six-value Gear predictor–corrector algorithm [25], and the time step is taken as 2 fs. The MD simulations are carried out in the constant volume and constant temperature (NVT) ensemble, the temperature is controlled via the Nosé–Hoover thermostat [26,27]. At each temperature, a simulation in the constant temperature, constant pressure (NPT) ensemble is necessary in order to find the lattice constant, used to construct simulation box. The self-diffusion of single adatom or vacancy on (0 0 0 1) face is studied by putting one adatom or vacancy on each free surface of slab. Simulations are performed for 10–100 ns (depending on the number of diffusion events observed) in the temperature range from 600 to 2700 K. The number of diffusion events(n) of the adatom or vacancy is counted and used to obtain the jump frequency (Γ):

$$\Gamma = n/t \tag{1}$$

Both the jump frequency and the diffusion coefficient (D) are deduced using the standard results of the transition state theory:

$$\Gamma = \Gamma_0 \exp\left(-\frac{\Delta E}{kT}\right) \tag{2}$$

$$D = D_0 \exp\left(-\frac{\Delta E}{kT}\right) \tag{3}$$

$$D = \frac{\lambda \Gamma d^2}{2z} \tag{4}$$

where z is the dimensionality of the diffusion spacing (two in the present case), λ is the number of jump directions (three for simple hopping on Re(0 0 0 1) surface), d is the distance traveled during one diffusion event and ΔE for the migration energy, while Γ_0 and D_0 are the prefactors.

3. Results and discussions

First, the single vacancy-formation energies (E_f) in the first six layers at 0 K are calculated using quenching MD [28]. The MD simulation at 0 K is somewhat a hard task. In the present work, 0 K is obtained rapidly by quenching method. The quenching procedure consists of canceling the velocity of a particle each time whenever its product with the force acting on the particle is negative. The quenching is terminated when the crystal reaches a temperature lower than 10^{-9} K. The calculated results are plotted in Fig. 1. It can be seen that the E_f converges rapidly to the bulk value. The E_f in the first layer is lower than that in other layers, and the E_f in the second layer is the highest. It is obvious that the fewer coordination of surface atoms leads to the large difference in E_f between the surface vacancy and a vacancy in the second layer. Similar conclusions for FCC [17] and BCC [14] metals have also been obtained.

For adatom on HCP(0 0 0 1) surface, there exist two binding sites, which are called FCC and HCP sites. The FCC or HCP site corresponds to an ABC or ABAB stacking, respectively (see Fig. 2). Our quenching MD calculation shows that the difference in energy between HCP and FCC sites on the (0 0 0 1) surface is very small (less than 0.035 eV, i.e., not really significant), in favor of the HCP site. In subsequent simulations, we assume the two equilibrium sites for adatom on the (0 0 0 1) surface to be equivalent.

The present MD simulations show that the dominant diffusion mechanisms for adatom and vacancy are simple hopping of single adatom or vacancy to a nearest-neighbor equilibrium site, which have been described in other studies for FCC(1 1 1) surfaces [29–32]. The static activation energies (E_s) for the simple hopping mechanism are determined by allowing the migrating atom to relax in a plane perpendicular to the diffusion path at each step. The rest of atoms in the system are allowed to relax in all directions. The E_s is defined as $E_s = E_{sad} - E_{min}$, where E_{sad} and E_{min}

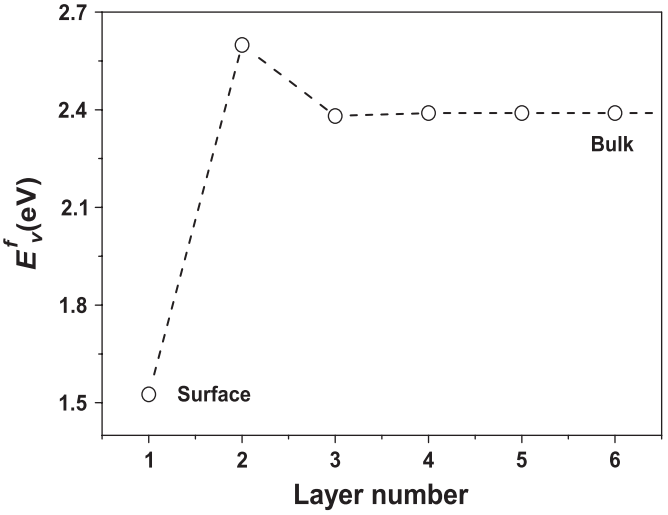

Fig. 1. The vacancy-formation energy as a function of layer number.

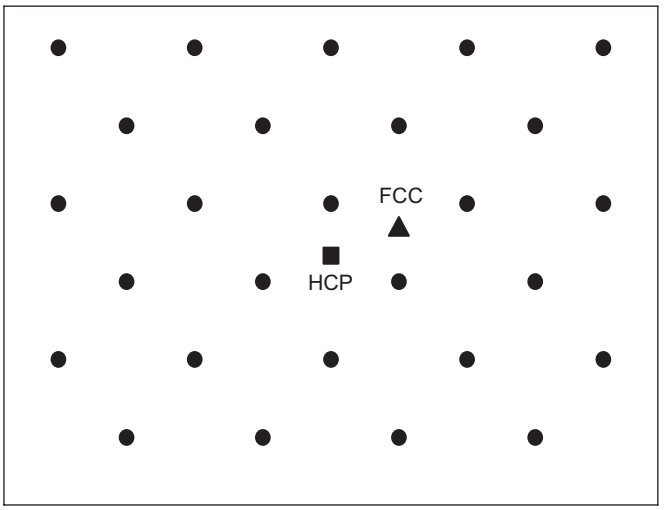

Fig. 2. A schematic picture of the structure of Re adatom on the Re(0 0 0 1) surface. The black circles show the surface atoms. An adatom can bind to an FCC site (black triangle) or an HCP site (black square).