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Atomistic simulation of Pt trimer on Pt(1 1 1) surface

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Abstract

The diffusion of Platinum trimer on Pt(1 1 1) is studied at different temperatures by molecular dynamics (MD) simulation. The structure stability is studied by cluster binding energy. The interaction between adatoms and surface atoms is discussed based on the calculated phonon density of state of Pt trimer. The diffusion coefficients of Pt trimer are derived from mean square displacement of cluster's mass-center, which is obtained by long simulation times ($\simeq 0.2$ μs) and tracing of interstitial atoms on surface. Then the diffusion prefactor and migration energy are deduced from Arrhenius relation. The calculated results are in reasonable agreement with experiment. In addition, using the diffusion prefactor and migration energy, the efficiency of Pt trimer as a critical nucleus for three-dimensional growth of thin films is discussed.

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1. 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 for crystal and thin-films growth [1,2]. Over the years, several theoretical methods [1], such as static calculation [3–6], MD [7–9], kinetic Monte Carlo [10] have been used to study the cluster diffusion. 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 calculation at finite temperature both reveal the diffusion mechanism and give the corresponding diffusion migration energy and prefactor, and should be the first choice.

The trimer is the smallest cluster that can have a one-dimensional or a two-dimensional structure. The trimer may be as the seed of three-dimensional growth of thin films due to its structure stability. So a quantitative understanding of trimer diffusion is essential to the investigation of the crystal and thin-film growth. Also FCC(1 1 1) surface is extremely stable in temperature, and it is therefore possible to study the diffusion phenomenon over a relatively wide range of temperature.

In the present work, the dynamical behavior of Pt trimer on Pt(1 1 1) surface is studied. The phonon density of state (DOS) of the trimer is calculated to study the interaction between adatoms and surface atoms. The trimer diffusion character is studied by static and dynamics simulation, and the mobility of Pt trimer is discussed according to the calculated diffusion prefactor and activation energy.

2. Simulation approach

In order to perform the MD simulations, we use a modified analytic embedded atom potential (MAEAM), which have been described in details for FCC metals [11]. The model parameters for Pt are listed in Table 1. For the present purpose it is

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Table 1
Model parameters of the many body potential for Pt, n is dimensionless, F_0, α and k_i are in eV

n	1.43
F_0	4.40
$\alpha\ (\times 10^{-5})$	-7.45
k_c	0.75
k_0	-31.40
k_1	-13.39
k_2	10.53
k_3	-17.91
k_4	98.63
k_{-1}	-46.66

important to note that the MAEAM has been shown to give a good description of the surface energies, interlayer relaxation, cluster properties and the surface phonons of various metals surfaces [11–13].

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 free surfaces perpendicular to (1 1 1) plane are obtained by fixing the dimensions of the super-cell size to a value twice as large as the thickness of the crystal in the direction normal to the surface. The system is large enough that finite size effects can be ignored. In the present MD simulations, the six-value Gear predictor-corrector algorithm and Nosé constant-temperature technique [14] are employed, except for a series of bulk calculations in the constant temperature, constant pressure (NPT ensemble) controlled by Andersen method [15] in order to determine the lattice constant at each simulated temperature, used for properly constructing simulation box. A 2D atomic cluster with three atoms is deposited on the top of the surface layer of the slab. Under the conditions of constant volume and constant temperature (NVT ensemble), these surface systems are equilibrated to the desired temperatures. Afterwards, the systems are left undisturbed in 0.1–0.2 μs constant-energy simulations during which the coordinates of the adatoms are stored for follow analysis.

In experiment, the diffusion coefficient for cluster can generally be obtained by measuring the mean-square displacement of the cluster's mass-center [16]. In present simulation once the system is in thermodynamical equilibrium, the positions of interstitial atoms on surface for every 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:

$$D = \lim_{t\to\infty} \frac{R^2(t)}{4t} \tag{1}$$

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

$$\langle R^2(t)\rangle = \langle (x(t)-x(0))^2 + (y(t)-y(0))^2\rangle \tag{2}$$

In order to have reasonable statistics, the quantity MSD is averaged over a number of time origins. Then the prefactor D_0 and migration energy E_m are calculated from the Arrhenius relation for the diffusivity:

$$D = D_0 \exp\left(-\frac{E_m}{K_B T}\right) \tag{3}$$

In present work, simulations are performed of 0.1–0.2 μs (depending on the temperature) in the temperature range from 500 to 700 K, with a time step of 5 fs. The purpose is to obtain reliable statistics for the determination of diffusion coefficient.

The phonon density of state ($S(\nu)$) of the trimer is calculated using the Fourier transform of the velocity auto-correlation function [17].

$$S(\nu) = \sum_{j=1}^{N} \int_0^\infty e^{i2\pi\nu t} \langle v_{j\alpha}(t) v_{j\alpha}(0)\rangle \, dt \tag{4}$$

where $v_{j\alpha}$ is the component of the velocity of the jth atom in the direction α ($\alpha = x, y, z$ denotes the cartesian axes).

3. Results and discussion

Previous theoretical studies have proved that the stacking fault energy is a key parameter in determining the cluster mobility on surface [18], so we first calculate the stacking-fault energy of Pt(1 1 1) surface using the Grujicic's method [19]. The calculated stacking-fault energy is 96 mJ/m^2, which is in agreement with experimental data (110 mJ/m^2) [20]. In addition, the single Pt adatom on the Pt(1 1 1) surface is also considered. In Fig. 1 the Arrhenius diagram of the single adatom diffusion coefficient is presented. From which, we deduce the diffusion migration energy (E_m) and prefactor (D_0) of 0.19 eV and 5.1×10^{-3} cm^2/s, compared to the experimental values of 0.260 ± 0.003 eV and $2.0(\times 1.4^{\pm 1}) \times 10^{-3}$ cm^2/s [2]. These results indicate that the potential provides a rather good description of the dynamics properties for the Pt adatom on Pt(1 1 1) surface.

On FCC(1 1 1) surface, there exist two binding sites, which are called FCC and HCP sites. The FCC or HCP site

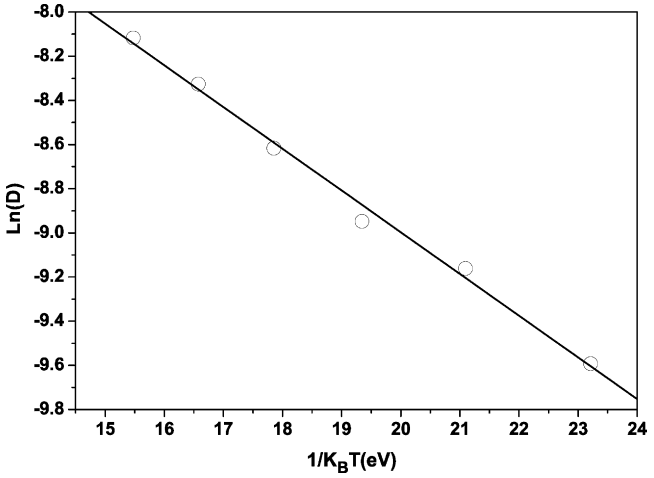

Fig. 1. Arrhenius plot of the diffusion coefficients for Pt adatom. The open circle is the calculated data, and the solid line is Arrhenius fit to the molecular dynamics data.