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# Atomic self-diffusion behaviors relevant to 2D homoepitaxy growth on stepped Pd(001) surface

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ABSTRACT

Using molecular dynamics, nudged elastic band and modified analytic embedded atom methods, the diffusion behaviors of Pd adatom on stepped Pd(001) surface have been investigated. Lower than 975 K, Pd adatom just hops along the perfect [110]-direction step. The diffusion dynamics equation is derived from the Arrhenius law between 875 and 975 K, and the corresponding migration energy and prefactor are 0.76 eV and $5.2 \times 10^{-2}$ $cm^2/s$ respectively, which shows that they adhere to the step in case of adatom moving to the step. The adatom diffuses across the perfect step with an Ehrlich–Schwoebel barrier of 0.09 eV by exchange mechanism. Our calculations show the kink at step can markedly decrease the static energy barrier across the step with a negative Ehrlich–Schwoebel barrier, and it contributes to form layer-by-layer growth model in the epitaxial experiment. Our calculations show that the kink can also markedly improve the adatom's mass transport of interlayer, contributing to the formation of the compact film. Lastly, a quantitative result at 300 K shows that the kink affects tremendously the diffusion mobility of adatom near it, which indicates that the kink plays a key role in the formation of the compact and uniform film on Pd(001) surface in an epitaxial growth experiment.



## 1. Introduction

One of the challenges in recent studies of nanomaterials is the understanding of microscopic processes which control thin film growth, and this is not only a necessary task if we are to build materials of choice by design, but it is also a daunting task [1]. Atomic level processes in thin film growth involve complicated diffusion dynamics behaviors giving rise to an abundant variety of surface morphologies. In this wide field, the study of growth in the submonolayer regime is most worth paying attention due to the large impact of the initial dynamics on the resulting film structure. In an epitaxial growth experiment if atoms or molecules are deposited on a surface at a constant deposition rate, then they diffuse on various structural surfaces to meet other adspecies, resulting in nucleation of aggregates or attachment to already existing islands [2,3]. According to the Terrace Step Kink (TSK) model, the film surface consists of the terrace, step, kink, and so on. The atomic dynamics diffusion behaviors at the terrace, step and kink are a key for atom mass transport on the surface. If surface diffusion on terrace is not sufficient, it is impossible to gain the compact film. Moreover the diffusion dynamics behaviors of adatoms across a step play a crucial role in the crystal growth modes. If adatoms descend easily from an upper terrace to a low terrace, the growth mode is likely layer-by-layer. If having the positive Ehrlich–Schwoebel (ES) barrier [4,5], adatoms cannot easily descend from an upper terrace to a low terrace, and the growth is likely to proceed with formations of 3D model. On the other hand, the shape of the growing two-dimensional islands depends on how fast is the mobility of adatom along steps [6–8].

For atomic diffusion relevant to nucleation and early stage of thin film growth, a great many experiments based on field ion microscope (FIM), scanning tunneling microscope (STM), low energy electron microscopy (LEEM) and quasi-elastic helium atom scattering have been devoted to the determination of surface diffusion coefficients [9]. By using FIM, the dynamics behaviors of adatom or clusters can directly be derived from the Arrhenius law according to the diffusion coefficient as a function of temperature. However, it only can measure some highlighting or hard materials, such as Re, W, Pt, Ir, and so on. STM measures indirectly the dynamics behaviors of adatoms based on the nucleation theory, although it is much more successful in looking at soft materials for example Cu and semiconductors than FIM. In other measurement techniques, such as helium atom scattering, work function determination can also measure the dynamics diffusion behaviors of adatoms. However, these experimental methods which may have the atomic spacial resolution find it very difficult to gain the detailed diffusion processes in transition state because of the very low time resolution (no more than $10^3$ Hz).

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Multi-scale modeling which has become popular these days remains as yet a challenge. Nonetheless, the field is advancing fast. Based on macroscopic continuum mechanics the films are treated as elastic solids [10]. Models based on mean field theory and rate equations [11] make more explicit reference to microscopic processes through scaling laws. Not just as a useful complement, the theoretical calculation even can obtain some results which the experiment methods cannot arrive at. For example, the first principles can calculate the static diffusion barriers on complex surface, even under the stress field [12–14]. Molecular dynamic (MD) simulation not only traces the dynamical trajectories of adatom and clusters on various complex surfaces, but also gives the available diffusion mechanisms directly, especially for more complicated diffusion processes, such as detailed steps during the nucleation [6,8,15,16]. In atomic level, kinetic Monte Carlo (KMC) simulations have been used successfully to study qualitative, even quantitative behavior of growth in limited cases in long time scale [17,18], whose rates are ideally obtained from first principles and MD calculations [19,20]. Although a lot of experimental and theoretical results are now available on the dynamic diffusion behaviors of adatom and clusters on perfect surfaces, rather little is known about the dynamic behaviors of adatom nearby the step. Based on the TSK model, the diffusion behaviors of adatom nearby the step play a key role for the surface morphologies of film in epitaxial growth experiment.

Palladium (Pd) is a rare metal, which has wide application in catalysis and hydrogen storage [21–23]. However, there is a considerable lack of studies about nucleation and growth mechanism that controlled the surface morphology which significantly affects the catalytic capability itself [24–26]. In this series of papers, the atomic self-diffusion dynamics behaviors relevant to nucleation and growth mechanism on perfect Pd(001) and Pd(111) surfaces had been studied [27,28], and the corresponding diffusion mechanisms had been discussed. In this study, we investigate atomic self-diffusion behaviors relevant to 2D homoepitaxy growth on the stepped Pd(001) surface with the combination of MD method, nudged elastic band (NEB) method and a modified analytic embedded atom method (MAEAM) developed from the analytic embedded atom method by Hu [29]. Finally, we analyze quantificationally the impact of the step and kink on Pd(001) surface in an epitaxial growth experiment at T = 300 K.

## 2. Computational methodology

In this paper, the interactions among Pd atoms are described by the MAEAM potentials. The corresponding details and parameters can be found in Refs. [29–31], and MAEAM potentials have been successfully applied in the calculations of nanoparticles and bulk materials [29,32–35]. Recently our researches [32,36,37] have indicated clearly that the MAEAM combined with the MD simulations is a powerful tool for studying the phenomenon of the self-diffusion on the metal surface. Using identical Pd MAEAM potential parameters and MD simulations, the migration energy ($E_m$ = 0.62 eV) of the single Pd adatom on Pd(001) surface has been deduced from the Arrhenius law in the range from 600 to 900 K [27], which is in good agreement with the experimental result ($E_m$ = 0.60 eV) [38], and the diffusion dynamics behaviors about 2D clusters on Pd(111) surface, the surface energy and the vacancy migration energy [28] are in good agreement with other theoretical data [39–41]. These results indicate that Pd MAEAM potential parameters can provide a reasonable description of surface dynamics properties.

Our systems which are shown in Fig. 1 are the Pd(001) slabs with enough thickness in the z direction, normal to the surface. On the surface plane, where periodic boundary conditions have been applied, the size of the slab is 12 rows and 16 columns, as illustrated in Fig. 1(a). The top layer of slab consists of a smaller terrace of 8 columns, delimiting a step along [110] direction on Pd(001) surface, as shown in Fig. 1(b). And then, half of the atoms in the rightmost atomic column are removed on the top layer, forming a typical kink, as illustrated in Fig. 1(c). The slabs used here are large enough so that the finite size effects, which have been tested, can be ignored in the present cases. The six-value Gear predictor–corrector algorithm and the Nosé constant-temperature technique are employed during the MD simulations. For diffusion dynamics behavior of Pd adatom along compact [110] direction, an adatom is placed on the step of the slab first, under the conditions of constant temperature and constant volume (NVT ensemble), and then the MD simulation at desired temperature is done. The classical equations of motion are solved by the standard Verlet algorithm with a time step of 2 fs. Data are recorded after a thermalization of 10,000 steps, which are enough to achieve equilibration. After that the simulation is performed for a considerable number of steps, of the order of $10^7$, in order to accumulate reliable statistical data.

In the present work, the static energy barriers ($E_s$) of atomic diffusion are calculated by using quenched MD and the NEB method [42,43]. At 0 K, quenched MD consists of canceling the velocity of a particle whenever its product with the force acting on the particles is negative. The NEB method allows one to find the minimum energy path for a rearrangement of a group of atoms from a given initial position to a given final position and to estimate the static energy barriers of a diffusion process. The initial and final states are determined from quenched MD simulation. $E_a$ is defined as $E_a = E_{sad} - E_{min}$, where $E_{sad}$ and $E_{min}$ are the total system energy with the adatom or dimer at the saddle point and at the initial or final site, respectively.

## 3. Results

### 3.1. Self-diffusion dynamic behavior along the [110]-direction step

When a Pd adatom is placed at the step of slab, the adatom vibrates in fourfold equilibrium site because of the thermal fluctuations. Movement of the adatom away from the step at the low temperature range is very difficult because it requires breaking more bonding with surrounding atoms. Essentially, this is a process where a two-dimensional cluster containing (N + 1) atoms dissociates a cluster containing N atoms and a dissociated adatom, and the adatom needs to overcome binding coming from the cluster except for spanning the surface saddle, which requires much higher energy. If an adatom always diffuses along the [110]-direction step in a certain temperature range, the self-diffusion dynamics behavior can be derived from the Einstein equation and Arrhenius law.

A Pd adatom is placed at the step of slab as shown in Fig. 1(b). MD simulations are performed in the temperature range from 875 to 975 K with the interval of 25 K, and the simulation time varied from 20 to 30 ns according to the simulation temperature. The lower end of the range corresponds to the limit for appropriate diffusion mobility by way of economizing computation time, while the upper end of the onset of the surface disordering, such as the disordering of step atoms, spontaneous creation of adatom-vacancy of step atoms, adatom away from the step, and so on. The detailed analysis of the trajectories shows that Pd adatom diffuses along the [110]-direction by bridge hopping mechanism in the temperature range from 875 to 975 K, in contrast to the simple exchange mechanism with the substrate atoms on Pd(001) terrace [27,44–46]. With simulation temperature increasing, when $T$ = 1000 K, a little diffusion events away from the [110]-direction step appear by exchange mechanism with substrate atoms, and the exchange direction is along the [001]-direction. The diffusion dynamics equation between 875 and 975 K is shown in Fig. 2; the corresponding prefactor and migration energy are $5.2 \times 10^{-2}$ cm$^2$/s and 0.76 eV. Compared with the adatom's prefactor ($D_0$ = 6.2–8.7 × $10^{-1}$ cm$^2$/s) and migration energy ($E_m$ = 0.63 eV) on Pd(001) terrace, not only is the migration energy along the [110]-direction step more than 0.13 eV, but also is the prefactor lower than 1 order of magnitude. Therefore, the adatom diffusion is more difficult along the step than on Pd(001) terrace at the same temperature. In other words, once a Pd adatom