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# Cu dimer diffusion on strained Cu(001)

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## ABSTRACT

Cu dimer diffusion energy barrier on strained Cu(001) surfaces has been studied with nudged elastic band method (NEB) and embedded atom method (EAM). Dimer exchange and hopping mechanisms are chosen as the initial diffusion paths in the NEB method. It is shown here that the dimer exchange is dominant on tensile surfaces and the dimer hopping is dominant on compressive surfaces. For most strain conditions Cu dimer diffusion energy barrier is lower than Cu monomer diffusion barrier. The concerted movement of the remaining adatom toward the hopping adatom lowers the dimer hopping barrier. The adsorption induced relaxation makes the dimer exchange barriers lower than the monomer exchange barriers on tensile surfaces. Transition state theory is used to calculate the diffusion frequencies as a function of temperature. No surface crowdion is observed on the shear strained surfaces for the dimer diffusion.

## 1. Introduction

Surface diffusion has attracted scientific interest for a long time. It has been recognized that surface diffusion of adparticles is the key problem in most dynamical processes on surfaces such as chemical reactions and epitaxial thin film growth [1–6]. Field ion microscopy (FIM), an instrument introduced in the early 1950s, provides important insight into the surface diffusion at atomic level [7,8]. In the computational materials science field, *ab initio* calculation, semi-empirical potential calculation, transition state calculation, molecular dynamics (MD) simulations, and kinetic Monte Carlo (KMC) simulations are used to study the surface diffusion of adparticles and thin film growth [9–31], which provides more detailed information and a more complete picture of the surface diffusion.

In the heteroepitaxy thin film growth, the film is normally strained because of the lattice mismatch between the substrate and the thin film. The subsequent thin film growth happens on this strained surface. It is important to understand how surface strain affects the surface diffusion in order to simulate this thin film growth [1,32,27,11,10,33,20,21]. Our previous results show that the energy barriers for monomer diffusion and the dominant diffusion mechanism are dependent on surface strain in the Cu/Cu(001) system [20]. As a result, the adatom diffusion rates are also dependent on the surface strain. During the early stages of thin film deposition, two diffusing adatoms may meet each other and form a dimer. This dimer continues to diffuse on the surface and form a cluster or island after meeting more monomers. Therefore, in order to understand the nucleation and growth of islands during the early stages of thin film growth, it is interesting to investigate the strain effects on the dimer diffusion.

It has been proposed that dimer hopping and exchange are the main dimer diffusion mechanisms on the fcc metal (001) surfaces [15,34] (see Fig. 1). In dimer hopping, one adatom in dimer hops over a neighboring bridge site to one of its nearest neighbor sites along a $\langle 011 \rangle$ direction. This hopping atom is the “hopping atom” or “diffusing atom”. The other adatom in the dimer atom moves concertedly near its original position during the hopping process and it will not hop to other hollow site, which is the “remaining atom”. In dimer “exchange” or “kick-out” mechanism, one dimer adatom displaces a substrate atom in one of the $\langle 001 \rangle$ directions (see Fig. 1). The displaced atom is the “exchanged” or “kicked out” atom.

In this work, the strain effects on Cu dimer hopping and exchange on Cu(001) surfaces are studied. The strain effects on the reverse hopping are also discussed in this paper. The strain dependent energy barriers for dimer diffusion are compared with the energy barriers for monomer diffusion. From the strain dependent energy barrier calculations, the dominant dimer diffusion mechanism under certain strain is analyzed. Finally, the frequencies of the diffusion events are calculated with the transition state theory and the classical harmonic approximation.

## 2. Computational details

The nudged elastic band method (NEB) [35,36] is used to predict the dimer diffusion paths and estimate the energy barriers

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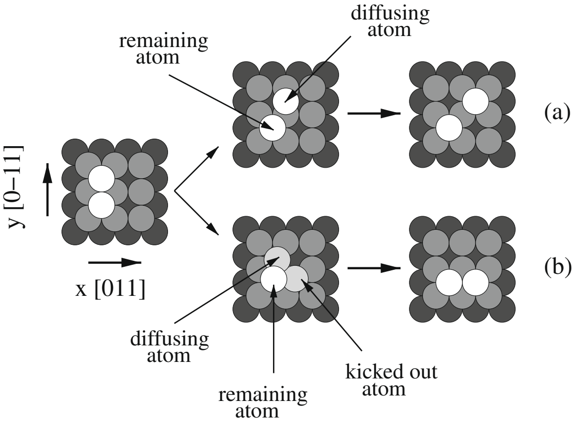

**Fig. 1.** Schematic of dimer diffusion pathways: (a) dimer hopping mechanism and (b) dimer exchange mechanism.

for the dimer diffusion. Dimer hopping and exchange are chosen as the initial paths in the NEB calculations. Compared with DFT calculation, EAM potential calculations can provide generally satisfactory results for surface diffusion on Cu(001) [14] and it can save computing time. Therefore, in this work, atomic scale total energy calculations employ the embedded atom method (EAM) interatomic potentials for Cu developed by Foiles et al. [37]. Force calculations are carried out using the code XMD [38] coupled to our own implementation of the nudged elastic band method. The calculations employ a six-layer slab of atoms composed of 2402 atoms ($6 \times 20 \times 20 = 2400$ substrate atoms and one ad-dimer). Periodic boundary conditions are applied in the $\hat{x}$ and $\hat{y}$ directions and the surfaces are free to relax in the (001) direction. The $\hat{x}$ and $\hat{y}$ axes are in the [110] and [−110] directions respectively (see Fig. 1). Uniform strain states in the range $-0.04 \leqslant \varepsilon_{xx},\ \varepsilon_{yy} \leqslant 0.04$ are considered in this work. NEB calculations are converged completely with respect to cell size. Typically, the path in configuration space is simulated by 15 discrete images. Forces on the images are converged to better than 0.01 eV/Å, and the quoted energy barriers are computed to an accuracy of better than 0.05 eV.

## 3. Result and discussion

### 3.1. Dimer hopping

#### 3.1.1. Dimer hopping results

The energy barriers for dimer hopping are calculated as a function of surface strain and compared with the energy barriers for monomer hopping (see Fig. 2a). Similar to the adatom hopping on strained surface [20], the energy barrier for dimer hopping increases with increasing tensile strain, but the slope of the dimer hopping barrier surface is steeper than the slope of the monomer hopping barrier surface. It suggests that dimer hopping barrier is more sensitive to the surface strain than monomer hopping barrier is. Another observation is that the two energy surfaces cross each other, shows that the dimer hopping barriers are lower than the monomer hopping barriers on compressive surfaces and dimer may diffuse faster than monomer under certain strain condition.

A dimer reaches a meta-stable state in which the two adatoms are at the second nearest neighbor positions after a dimer hopping. The ad-dimer may continue to hop to one possible equilibrium state and the two dimer atoms become the nearest neighbors (see Fig. 1a in a reverse order). The energy barrier for this reverse hopping is significantly lower than the barrier for dimer hopping under the same strain. The energy barriers for dimer reverse hopping are plotted as a function of surface strain in Fig. 2b. The energy barrier for reverse hopping also increases with increasing tensile strain.

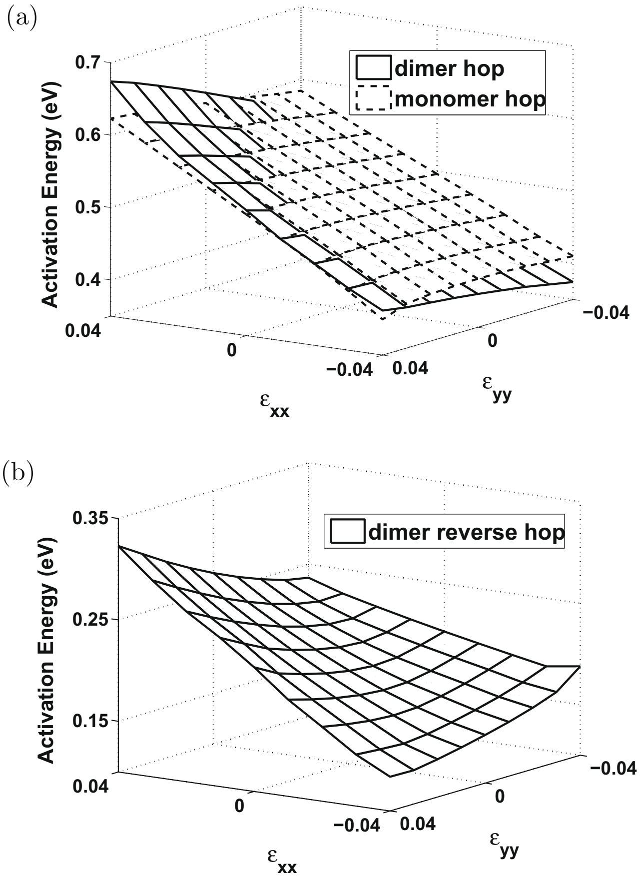

**Fig. 2.** (a) The dimer and monomer hopping energy barriers as a function of surface strain and (b) the reverse dimer hopping energy barriers as a function of surface strain.

#### 3.1.2. Discussion

The difference between dimer hopping and monomer hopping is discussed in this part. Some parameters are defined first for further investigation. The total system energy along the diffusion path for hopping process can be written as:

$$E^{1h} = E_s^{1h} + E_{ds}^{1h}, \tag{1}$$

$$E^{2h} = E_s^{2h} + E_{ds}^{2h} + E_{rs}^{2h} + E_{rd}^{2h}, \tag{2}$$

$E^{1h}$ is the total energy of the monomer hopping system along the diffusion path which includes the adatom and the slab. $E_s^{1h}$ is the energy of the slab without the adatom, which is used to describe the slab deformation along the diffusion path. $E_s^{1h}$ can be calculated by removing the adatom without relaxing the slab. Because the energy of a single isolated atom is zero in EAM potential, the energy difference between system energy and slab energy is the adatom bonding energy to the slab. $E_{ds}^{1h}$ is *the diffusing atom/the slab* bonding energy along the diffusion path in monomer hopping system. $E^{2h}$ is the total energy of the dimer hopping system along the dimer diffusion path. $E_s^{2h}$ is the slab energy without any adatom in the dimer hopping system along the dimer hopping path. Similarly, the slab energy is calculated by removing the adatoms from the system without structure relaxation of the slab. $E_{ds}^{2h}$, $E_{rs}^{2h}$ and $E_{rd}^{2h}$ are the interaction energies between *the diffusing atom and the slab, the remaining atom and the slab*, and *the diffusing atom and the remaining atom* along the dimer hopping path, respectively. The adatom-slab