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## Simulation of Ni cluster diffusion on Au(1 1 0)-(1 × 2) surface

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### Abstract

We have studied the mobility of small Ni clusters on a crystalline surface by molecular dynamics simulation. We chose the anisotropic Au(1 1 0)-(1 × 2) reconstructed surface as the substrate to host the atom clusters. Similar to Au/Au(1 1 0)-(1 × 2), we found that in-channel Ni adatom diffusion takes place by jumping in the trough and on the sidewall, the Ni dimer by leapfrog and concerted jump. However, the Ni trimer can diffuse via rotation. For the larger cluster with a sphere-like shape, we find the cluster can roll on the surface, which can lead to a large diffusion constant.

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**Keywords:** Small cluster diffusion; Rolling mechanism

### 1. Introduction

Studies on how clusters diffuse on a solid surface have drawn an increasing research interest in surface science and materials research. The most common example is the wetting of surfaces and spreading of various films, such as, the spreading of oily films over water surface, which can be realized by our naked eyes. However, the motion of adatom or small cluster on the surface can only be monitored by the modern experimental tools, like field-ion microscopy or STM. The efficient way to study the cluster on the surface is the computer simulation, which can usually provide detailed information of the cluster motion in atomic scale.

Experimental imaging of surface atoms and their motions on a surface by field ion microscopy [1–4] and scanning tunneling microscopy [5,6] have unambiguously revealed various diffusion mechanisms of adatom, dimer and small cluster. For example, Kellogg and Voter demonstrated experimentally that for Pt diffusion on Pt(1 0 0) surface at 175 K, a Pt dimer can migrate 50 times faster than a single atom, and a trimer is as mobile as a single atom [7]. For the large two-dimensional (2D) cluster, to which most of the work were devoted, the diffusion mechanisms are complicated. The cluster gliding as a whole from one position to another, can be considered as the simplest diffusion mechanism, which usually costs a large activation barrier since all the cluster atoms need to overcome a barrier simultaneously [8,9]. A few other mechanisms, the edge diffusion mechanism in which the motion of a loose adatom along the cluster

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edge causes a shift of the center of mass of the cluster [10], the evaporation and condensation mechanism with which the interchange of adatoms between different clusters (and steps) results in the Brownian motion of the clusters [10–12], the dislocation mechanism with which the gliding of dislocation in 2D cluster leads to the motion of the cluster [13–17], all these diffusion mechanisms cost a small diffusion barrier, and have been confirmed in the simulation or in the experiment. Because only one or a small fraction of atoms is involved in these processes of diffusion, the diffusion barrier can be small. Even though, it is hard to explain the large diffusion constant observed for the 3D cluster, where the mechanism is poorly understood.

Lattice mismatch between cluster and substrate can significantly affect the surface diffusion of atomic cluster. The most direct effect of the mismatch is that it can change the shape of the cluster, for instance from 2D to 3D, thus the diffusion mechanism can be totally changed. Our previous simulation showed that a 13-atom cluster interacted with Lennard–Jones potential has the largest diffusion constant on the fcc(1 1 1) surface when the lattice mismatch is as large as 20% [18]. Montalenti and Ferrando found that a Cu dimer tends to diffuse via dissociation–recombination instead of leapfrog as a Au dimer does [19], they speculated that the different stability between Cu dimer and Au dimer is probably related to a size-mismatch effect. Lattice mismatch can also induce a strain between cluster and substrate, which can also change the behavior of the diffusion. Intuitively, compressive strain can decrease the diffusion barrier, and tensile strain can increase the diffusion barrier, this simple picture has been confirmed in metal surface [20]. Very recently, we have proposed a more general formalism for the relationship between the diffusion barrier of an adatom and the external strain [21],  $\Delta E \propto \epsilon \Delta \sigma$ , where  $\epsilon$  is the strain, and  $\Delta \sigma$  is the difference of the intrinsic surface stress induced by the adatom at the saddle and minimum point. However, for the cluster on the substrate with a lattice mismatch, further studies in this direction are justified.

In this paper, we chose the anisotropic Au(1 1 0)-(1  $\times$  2) reconstructed surface as the substrate, and simulate the diffusion of Ni cluster on the surface with a lattice mismatch.

## 2. Details of calculations

We use the Johnson alloy potential [22,23], which was deduced from the embedded-atom methods [24,25], to describe atomic interactions for Ni and Au, in which the total energy  $E_{\text{tot}}$  is defined by

$$E_{\text{tot}} = \frac{1}{2} \sum_{i \neq j} \phi^{ij}(r_{ij}) + \sum_i F^i(\rho_i) \quad (1)$$

with  $\rho_i = \sum_{j \neq i} f^j(r_{ij})$ ;  $f(r) = f_e \exp(-\beta(r/r_e - 1))$ ;  $\phi(r) = \phi_e \exp(-\gamma(r/r_e - 1))$ ;  $F(\rho) = -E_c(1 - \ln x) - x - 6\phi_e y$ ;  $x = (\rho/\rho_e)^{\alpha/\beta}$ ;  $y = (\rho/\rho_e)^{\gamma/\beta}$ ;  $\alpha = 3(\Omega B/E_c)^{1/2}$ , where  $\rho_i$  is the electron density at atom  $i$  due to all other atoms,  $f(r_{ij})$  the electron density at atom  $i$  due to atom  $j$ ,  $r_{ij}$  the distance between atoms  $i$  and  $j$ ,  $F(\rho_i)$  the energy to embed atom  $i$  in an electron density  $\rho_i$ , and  $\phi(r_{ij})$  is a two-body potential between atom  $i$  and  $j$ .  $f_e$ ,  $\phi_e$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  are the parameters.  $\Omega$ ,  $E_c$  and  $B$  are the atomic volume, cohesive energy and bulk modulus, respectively.  $\rho_e$  is the equilibrium electron density at an atom site in a perfect crystal for each type of atoms.  $r_e$  is the equilibrium nearest-neighbor distance in this perfect crystal. The two-body potential for different kinds of atoms is expressed as

$$\phi^{ij}(r) = \frac{1}{2} \left( \frac{f^j}{f^i} \phi^{ii}(r) + \frac{f^i}{f^j} \phi^{jj}(r) \right) \quad (2)$$

To test the validity of the potential in describing the surface properties of a gold surface, we performed MD simulations on the properties of the Au(1 1 0)-(1  $\times$  2) surface. The results show that the surface is stable until 600 K, in agreement with the experimental data in the literature [26]. We have also calculated the structures of isolated  $\text{Ni}_n$  clusters by using the Johnson potential. The obtained ground state structures are very close to the results predicted by the FS potential [27,28], and other known ab initio results [29]. From these calculations, we conclude that the Johnson potential can properly describe the behaviors of Ni clusters on Au(1 1 0)-(1  $\times$  2).

The simulation cell consisted of 11 layers of Au atoms. Each layer contained 320 atoms, except for the topmost layer which contained only 160 atoms due to the missing row. The atoms in the two bottom layers of the cell were kept static to mimic the underlying infinite solid. Periodic boundary conditions were imposed in the lateral direction to mimic an infinite surface.

The simulation temperature  $T = 400$  K, controlled by scaling the velocities of atoms in the two layers just above the static layers [30], was well below the temperature of surface roughening transition which is known to occur at about 650 K. This ensures that the surface structure remained stable during the simulation.

### 3. Results and discussions

To understand the origin of the diffusion processes of Ni clusters on the reconstructed surface, we have first calculated the potential energy surface of Au(1 1 0)-(1 × 2) for a Ni adatom, as shown in Fig. 1, which is obtained by fixing the x and y coordinates of the adatom and relaxing all the other degrees of freedom (d.f.) of the cell. We find that the lowest energy position is in the trough, as labeled by A in Fig. 1. Another two local minimum positions are at the sidewall, labeled by B and C, respectively. Both positions A and C are on the top of the substrate Au atom, only position B is an interstitial position. By calculating the energy difference between the minimum and the saddle point, we get the diffusion barrier  $E_{AA} = 0.21$  eV from A to D along the closed-packed direction. Jumping from A to B needs an activation energy  $E_{AB} = 0.20$  eV, however the diffusion barrier back from B to A is as small as  $E_{BA} = 0.04$  eV. We find the diffusion barrier on the sidewall of the trough is very small,  $E_{BC} = E_{CB} = 0.05$  eV, and  $E_{CF} = 0.08$  eV. Comparing the results for a Au adatom obtained by Montalenti and Ferrando [31], the main features of the

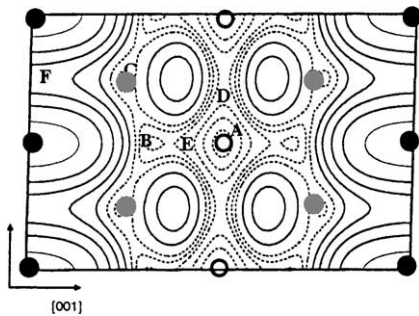


Fig. 1. The contour plot of the potential energy surface for a Ni atom on the Au(1 1 0)-(1 × 2) surface. The filled circles indicate the atoms at the top of the trough, and the open circles indicate the atoms at the bottom of the trough. Labels A, B, C are the minimum energy positions, and E and D are the saddle points.

potential energy surface are similar. But the barriers for Ni atom diffusion are smaller than the barriers for Au adatom. It is also interesting to note that, for Au atom diffusion, jumping from trough to the side wall of the trough ( $E_{AB} = 0.40$  eV) is larger than the barrier ( $E_{AA} = 0.31$  eV), which implies that the Au atom will have relatively larger probability of diffusing in the trough. While for Ni atom, since  $E_{AA}$  and  $E_{AB}$  are comparable, and also the diffusion barriers on the sidewall of the trough is much smaller than  $E_{AB}$ , we can expect Ni adatom can have larger probability to diffuse along the sidewall in comparing with Au adatom.

The complicated potential energy surface leads to a multi-channel diffusion for a Ni adatom on the Au(1 1 0)-(1 × 2) surface. So, on this reconstructed surface, adatom diffusion cannot be considered as one-dimensional problem. Fig. 2 shows a few selected trajectories which show various diffusion paths of the Ni adatom. The first trajectory shows the in-channel diffusion, adatom jumping from one minimum position A to another along the direction of the trough (Fig. 2a). The second one shows the adatom diffusion

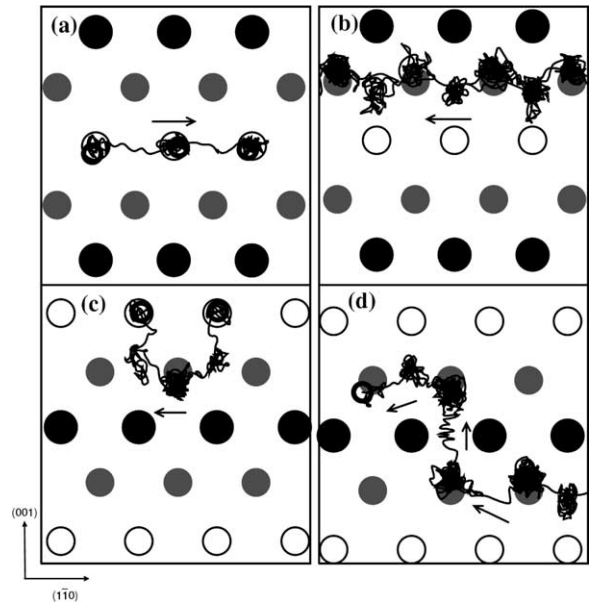


Fig. 2. Selected trajectories for a Ni atom diffusion on the Au(1 1 0)-(1 × 2) surface. The filled, gray and open atoms are for the top, and second and trough atoms: (a) Ni atom diffusion in the trough, (b) diffusion on the side of the trough, (c) diffusion via the local minimum at the side wall, (d) a trajectory shows how a Ni atom diffusion from one trough to another.

on the sidewall (Fig. 2b), from position B to C, then to B, since diffusion barrier on this path is very small, one can expect that diffusion on this path is very fast. Another path is diffusion along the trough but through an intermediate position on the side of wall of the trough (Fig. 2c). Fig. 2d shows that how a Ni adatom climbs up the trough and jumps over, which confirms that at this temperature, diffusion is not a one-dimensional behavior.

The diffusion of the Ni dimer is more complicated. Both the concerted and leapfrog mechanisms have been observed in our simulation [19,32]. What shown in Fig. 3 are a few selected trajectories of Ni dimer diffusion essentially with concerted jumping mechanisms. Both Ni atoms of the dimer, which are at the lowest energy sites, can jump simultaneously from one site to another in the trough (Fig. 3a), keeping the bond direction parallel to the trough. Fig. 3b shows a different diffusion mechanism, one of the Ni atom jumps in the trough and another atom of the dimer jumps concertedly at the sidewall, the bond of the dimer is perpendicular to the trough direction. We discover that both atoms of the dimer can stay on the

side wall, and diffuse on it due to the flat potential energy surface. Fig. 3d shows how a dimer jumps over the trough, from the figure one can see that, first the dimer climbs up to the sidewall, one Ni atom of the dimer rotate around the other which is essentially fixed at a minimum position. When the bond of dimer becomes perpendicular to the trough, two Ni atoms of the dimer across the moft one after the other. As a matter of fact, because of the relatively high potential barrier, such kind of jumping process across the trough does not happen very often in our simulation at  $T = 400$  K. We have also found the leapfrog jumping for Ni dimer, as observed for the Au dimer on Au(1 1 0)-(1 × 2) surface [31], i.e. one atom sits at the minimum position in the trough, and the other atom rotates via the meta-stable position at the sidewall. However, in our simulation, the leapfrog jumping is not as frequent as the concerted jumping. We believe that, lattice mismatch played an important role.

Fig. 4 shows how a Ni trimer diffuses on the Au(1 1 0)-(1 × 2) surface. The equilibrium structure of Ni<sub>3</sub> is a triangle, with two Ni atoms at the bottom of the trough and the third atom near the local minimum

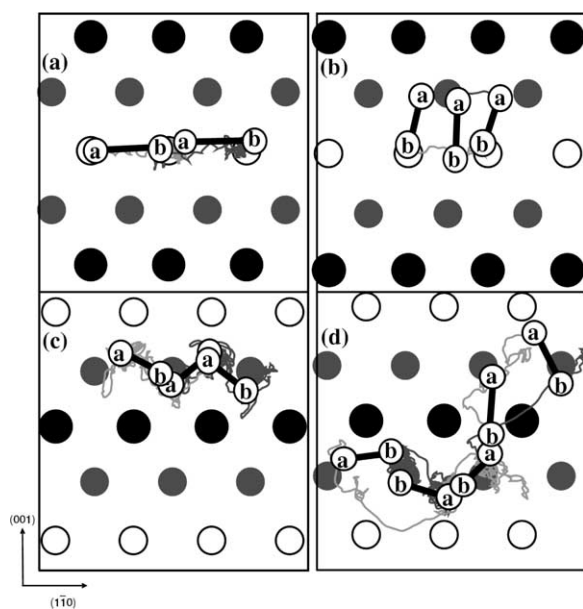


Fig. 3. Selected trajectories for a Ni dimer diffusion on Au(1 1 0)-(1 × 2) surface: (a) the concerted jumping in the trough, (b) dimer diffusion with one atom in the trough and another atom at the side wall of the trough, (c) dimer diffusion on the side wall of the trough, (d) Ni dimer jumping from one trough to another.

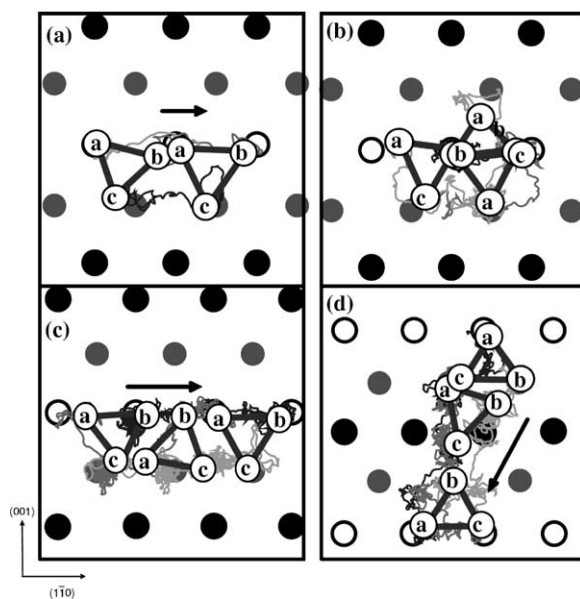


Fig. 4. Selected trajectories for a Ni trimer diffusion on Au(1 1 0)-(1 × 2) surface: (a) translational jumping in the trough, (b) rotation, (c) translational jumping plus rotation, (d) jumping over the trough via rotation and translation.

on the sidewall. When diffusing, the simplest way is the concerted jumping as shown in Fig. 4a, which can be considered as the gliding mechanism of the cluster diffusion. Very similar to the leapfrog in dimer diffusion, we have found the trimer diffusion via the rotation (Fig. 4b). The mass center of Ni trimer moves with the rotation of two atom around the third atom. Comparing with gliding mechanism, rotation mechanism costs a small energy barrier, because only two atoms, instead of three atoms gliding, need to overcome the diffusion barrier. Fig. 4c shows a longer diffusion trajectory with the mixed diffusion mechanism. The trimer first concerted gliding and then rotation. We also find that Ni trimer has a possibility to across the trough via jumping and rotation in our simulation.

Our calculations have shown that clusters with four or more atoms can roll on the surface. Since Ni–Ni interaction is stronger than Ni–Au interaction, Ni clusters on the Au surface prefer a three-dimensional structure, such as Ni<sub>4</sub> is a tetrahedron, Ni<sub>7</sub> is bi-capped pentagon, and also Ni<sub>13</sub> is an icosahedron. An examination of the diffusion trajectories for Ni<sub>n</sub> clusters revealed that sphere-like clusters can roll on the surface, a kind of cluster motion which has not been discussed deeply in the literature. The motion of the cluster can be mixed with gliding, jumping to facilitate the fast cluster diffusion. The overall diffusion constants for Ni<sub>4</sub>, Ni<sub>7</sub> and Ni<sub>13</sub> is about one order magnitude larger than that of other clusters in which rolling cannot be easily activated due to the non-sphere-like shape. It should be pointed out, all the sphere-like clusters move collectively, with neither any internal cluster rearrangement, cluster dissociation, nor atom-exchange between the cluster and the substrate.

Fig. 5 shows how clusters, Ni<sub>4</sub>, Ni<sub>7</sub> and Ni<sub>13</sub>, roll on the reconstructed Au(1 1 0) surface. The first snapshot in Fig. 5a captures the configuration in which atoms a and d rest on two gold atoms at the bottom, and atom c takes the apex position. Between the first and second snapshot, the cluster has rolled to the left with atom c tipping downward and atom a rising to become the new apex. The third snapshot records another rolling motion step with atom a tipping and atom b rising. Fig. 5b shows how Ni<sub>7</sub> cluster rolls in the trough. The right snapshot is a configuration in which one of the apex atom a tipping the bottom atom in the trough, and the another apex atom c is on the top of the cluster and

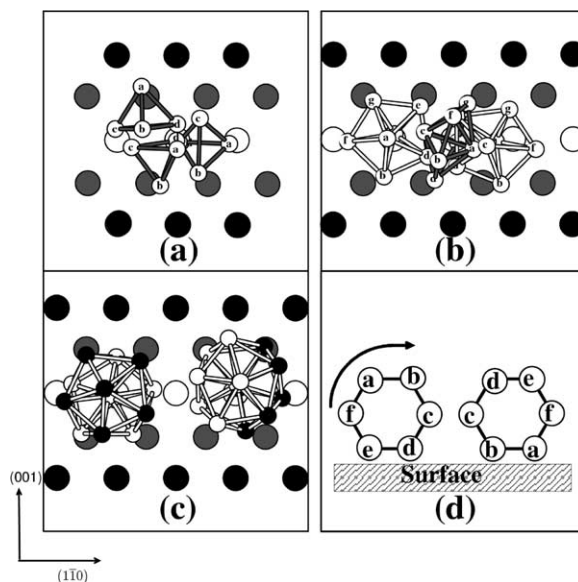


Fig. 5. Representative rolling of Ni cluster on Au(1 0 0)-(1 × 2): (a) rolling of Ni<sub>4</sub> in the trough, (b) Ni<sub>7</sub> rolling in the trough, (c) Ni<sub>13</sub> rolling.

thus does not bind to any Au atom. The bond between two apex atom a, and atom c is perpendicular to the surface, and the pentagon of Ni atoms is on the surface. The middle snapshot, in which the Ni atoms are connected by the gray bonds, clearly indicates a 90° of rotation from the right snapshot, the bond between atoms a and c becomes lying on the surface, the left snapshot shows one more rolling of 90°, with the bond between atoms a and c perpendicular to the surface again. In Fig. 5c, we use the gray and open circular to label the atoms in the Ni<sub>13</sub> cluster, the rolling of the cluster can clearly observed from the two snapshots. Fig. 5d schematically shows the rolling process on the surface.

All these results on the Ni<sub>n</sub> clusters diffusion show that the diffusion mechanism of the cluster is dependent on the size of the cluster. An adatom can diffuse via jumping, but the dimer can glide (concertedly jump) and leapfrog, as reported before. For the Ni trimer, except for the gliding, the rotation of the cluster is a way of motion with a small energy barrier. However, for the large Ni clusters with 3D structure due to the large lattice mismatch between Ni and Au substrate, we find a new diffusion mechanism: rolling. With this rolling mechanism, the cluster diffuses as a



whole, but only one or two atoms needs to overcome the energy barrier. So it facilitates the fast diffusion of cluster, we can believe that the rolling of the cluster is a fast diffusion mechanism, although the clusters diffuse with the mixed mechanism, gliding, rotation and rolling.

#### 4. Conclusion

In summary, we have studied the diffusion behavior of Ni clusters on Au(110)-(1 × 2) by using the molecular dynamics method. We find that the diffusion of Ni cluster on this channel surface is quasi-one-dimensional, since the cluster still has a probability to across the trough in our simulation at  $T = 400$  K. We have also demonstrated that small Ni clusters diffuse on the Au surface as whole without dissociation, due to the strong Ni–Ni interaction. Different clusters can have different diffusion mechanism, jumping, gliding, leapfrog, rotating and rolling. Since rolling mechanism does not need to overcome a large energy barrier, we propose it as the fast diffusion mechanisms for the large cluster.

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