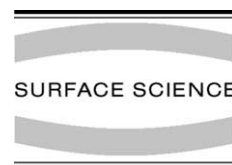




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# Local strain induced anisotropic diffusion on $(23 \times \sqrt{3})$ -Au(1 1 1) surface

Y.B. Liu<sup>a</sup>, D.Y. Sun<sup>a</sup>, X.G. Gong<sup>a,b,\*</sup>

<sup>a</sup> Institute of Solid State Physics, Academia Sinica, 230031 Hefei, China

<sup>b</sup> Department of Physics, Fudan University, Shanghai 200433, China

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## Abstract

Based on the many-body *glue* potential, the adatom diffusion on the reconstructed  $(23 \times \sqrt{3})$ -Au(1 1 1) surface is theoretically studied. We demonstrate that the reconstructed surface is strongly anisotropic for the adatom diffusion. The local strain enhances the adatom diffusion, and leads to diffusion barriers dependent on the direction and position. © 2001 Published by Elsevier Science B.V.

**Keywords:** Surface diffusion; Surface stress; Surface structure, morphology, roughness, and topography

## 1. Introduction

The diffusion of adatom on surface is an important dynamics process in many surface-related phenomena, such as crystal growth, adsorption, corrosion, and surface reconstruction, etc. In past a few years, many efforts had been devoted to experimental and theoretical studies of the diffusion on strain-free surfaces. In the experiment, it was able to directly observe an adatom diffusion on surface by the field ion microscope [1,2] and scanning tunneling microscopy (STM) [3]. On the other hand, theoretical studies had played an important role in understanding the micro-process of the surface diffusion [4–7]. Some diffusion mecha-

nisms had been proposed for strain-free surfaces [8,9]. One can easily expect that the strain can change the diffusion properties of adatom on surface, however, how the strain affects the adatom diffusion on a surface is far from fully understanding.

Recently, a few studies had been performed on the diffusion of adatom on the strained surface. It was found that the strain can have a large impact on the surface diffusion of an adatom. For Si adatom on Si(001), it showed that the diffusion barrier changes significantly with the applied external strain [10]. Brune et al. found that, for Ag diffusion on Ag(1 1 1) surface, the diffusion barrier increases with the increasing of the tensile strain and decreases with increasing of the compressive strain [11], which was also theoretically confirmed by the effective medium theory. By using the first-principles method [12], Ratsch et al. had studied the strain dependence of the surface diffusion, the

\* Corresponding author. Address: Department of Physics, Fudan University, Shanghai 200433, China.

E-mail address: gong@theory.issp.ac.cn (X.G. Gong).

obtained results were in good agreement with the experimental data [11]. All of these theoretical studies are carried out on surface by applied external strain. However, it is well known, many reconstructed surfaces itself involve local strain, which provides an interesting intrinsically strained surface for studying the strain effect on the adatom diffusion.

Gold is the only fcc metal whose (1 1 1) surface reconstructs. Experiments [13–17] have observed  $(22 \pm 1) \times \sqrt{3}$  reconstruction on Au(1 1 1) surface. The reconstructed Au(1 1 1) surface forms an ordered array of boundaries between surface regions with fcc-like stacking and hcp-like stacking. The reconstruction will produce the local strain (stress) in the top layers, and also the existence of the various stacking type from fcc- to hcp-like structure will cause different strain in the different regions on the surface. Thus, studies of diffusion barriers for an adatom on the reconstructed Au(1 1 1) surface will not only provide information on how the adatom diffusing on the reconstructed surface, but also will give us some evidences on how the local intrinsic strain affecting the adatom diffusion, instead of the external strain as studied in other theoretical work.

In this paper, by calculating the diffusion barriers of an adatom on the  $(23 \times \sqrt{3})$ -Au(1 1 1) surface, we find a strong anisotropy of adatom diffusion, the local strain does play an important role in adatom diffusion. In the rest of this paper, we present the calculation details in Section 2, and we show the main results and discussions in Section 3, finally, we summarize the major results in Section 4.

## 2. Simulation methodology

Our calculations are performed on the  $(23 \times \sqrt{3})$ -Au(1 1 1) surface. The simulation cell consists of 12 atomic layers, the atoms in the bottom two layers are kept rigid to mimic the semi-infinite solid, all other atoms are allowed to move, the periodic boundary conditions are imposed along the directions parallel to the surface. Since the reconstructed  $(23 \times \sqrt{3})$ -Au(1 1 1) surface can be considered as 23 atoms on 22 atoms along  $[1 \bar{1} 0]$  direction, our simulation cell contains 23 atoms in

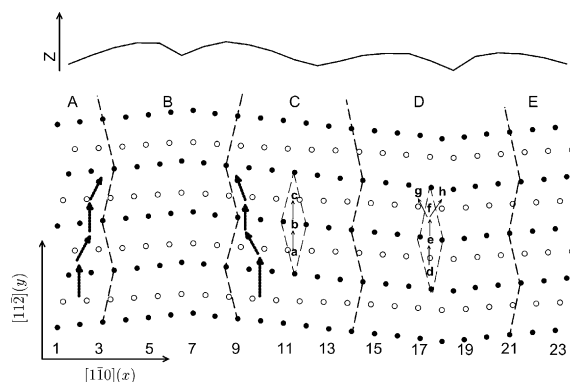


Fig. 1. The schematic show of the top view for the reconstructed  $(23 \times \sqrt{3})$ -Au(1 1 1) surface. The filled circles denote the atomic positions for the top layer, and the open circles denote the atoms in the second layer. Regions marked with B and D are fcc- and hcp-like region separately, A, C, E are the transition regions. The thick arrows indicate the favorite diffusion direction in regions.

$[1 \bar{1} 0]$  direction ( $x$ ) and 12 atoms along  $[1 1 \bar{2}]$  direction ( $y$ ) in the top layer, while each other layer contains 22 atoms in  $[1 \bar{1} 0]$  direction and 12 atoms in  $[1 1 \bar{2}]$  direction.

Fig. 1 schematically shows the atomic structure in the simulation cell. The region marked with D is hcp-like, in which positions of surface atoms are close to hcp sites, the region marked with B is fcc-like, in which positions of surface atoms are close to fcc sites, the regions marked with A, C, E, are transition regions. In those regions atoms are neither at hcp- nor fcc-like position. From Fig. 1, we can see that positions of 23 atoms in the top layer (black circles) vary between hollow sites of fcc and hcp stacking to fit onto 22 atoms in the second layer.

The binding energy of adatom at each position are obtained by fully relaxing the atomic positions. Diffusion barriers are calculated as the binding energy difference between the saddle point and the nearest local energy minimum position. Because of the existence of the anisotropic local distortion, the adatom at each equilibrium position has three different possibilities to diffuse away, as indicated in the D region of Fig. 1, which associates with three different diffusion barriers, i.e.,  $E_y$  along  $y$  direction,  $E_x$  along opposite  $x$ -direction (f–g direction) and  $E_x$  along  $x$ -direction (f–h direction).

In the defect-free surface,  $E_{\bar{x}}$  and  $E_x$  are usually the same, however on the reconstructed surface, the local strain makes  $E_{\bar{x}}$  and  $E_x$  different. In order to get these diffusion barriers, we calculate the binding energy of adatom on the diffusion path. At each position, the adatom is allowed to relax only in the direction perpendicular to the surface, while surface atoms are fully relaxed. The diffusion barrier  $E_d$  is then determined as the energy difference between the equilibrium position and the saddle point.

The interaction between Au atoms is modeled by the so-called many-body *glue* potential [18,19]. This potential can well reproduce many physical properties of the ideal and reconstructed Au surface, and was widely used in studying surface melting and surface reconstruction [20,21]. Most importantly, the glue potential can correctly predict the Au-( $23 \times \sqrt{3}$ ) reconstructed surface to be more stable than the unreconstructed surface, also correctly give the surface energy difference 2 meV/ $\text{\AA}^2$  between the ( $23 \times \sqrt{3}$ ) reconstructed surface and the most stable one ( $11 \times \sqrt{3}$ ). However, our calculation finds that the glue potential gives a diffusion barrier as large as 0.7 eV for an adatom on the unreconstructed surface. Although the soft Au(111) can have a much larger diffusion barrier comparing with other metal (111) surface, the data predicted by the glue potential is still quite large. To see how much the potential has overestimated the diffusion barrier, one needs to perform the ab initio calculation. Fortunately, our present interest is not on the absolute value of the diffusion barrier, but only the general trend of the strain effect on the diffusion barrier.

### 3. Results and discussion

Fig. 2 shows the binding energy of an adatom on the surface at the different positions from the left side to the right side of the simulation cell. One can see an oscillatory behavior from one region to another, binding energies at the different positions are quite different, the largest difference of the binding energy at different positions is up to 0.3 eV. As one can expect from the surface structure, in the fcc- or hcp-like region, the binding energy

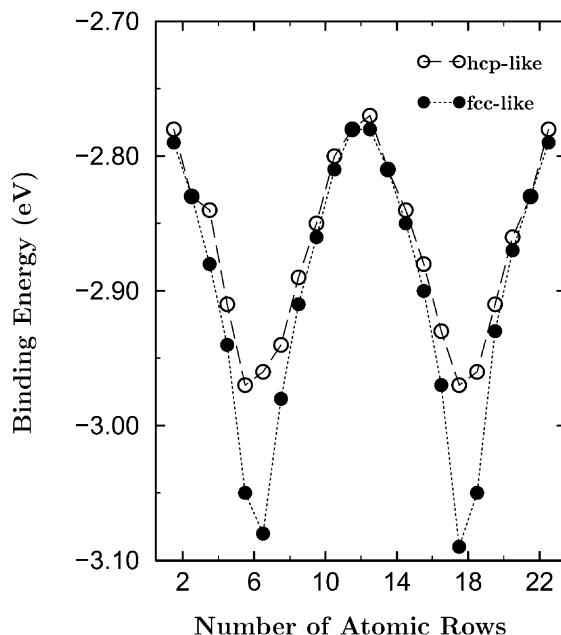


Fig. 2. The binding energy of an adatom at fcc- and hcp-like positions in the whole unit cell of the reconstructed surface (please note: even though in the transition region, there are fcc- and hcp-like positions). The binding energies at fcc-like site are always larger than that at the hcp-like site, which are also strongly position dependent.

shows a maximum, while in the transition region, the local structure of the surface is much different from the ideal fcc (111) surface, thus the binding energy becomes quite small.

On the reconstructed Au(111) surface, although a significant distortion exists, there are still fcc- and hcp-like binding sites for an adatom. Our calculations show that an adatom at the fcc-like position has larger binding energy than that at the hcp-like position, similar to what observed for many metal surfaces [2,3,22], which indicates that the local strain does not change this energy sequence. Diffusion barriers between the fcc-like site and the saddle site are always higher than that between the hcp-like site and the saddle site. However, this difference varies from position to position on the surface, because of the existence of the local strain.

The large difference of the diffusion barrier in different regions indicates the strong anisotropy for the diffusion of an adatom on the reconstructed

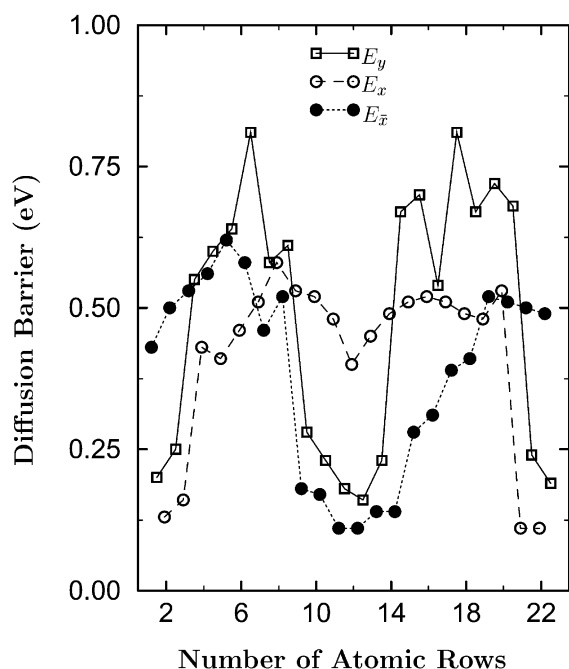


Fig. 3. The diffusion barriers for three different directions at positions in the unit cell.  $E_y$ ,  $E_x$ , and  $E_{\bar{x}}$  are the diffusion barriers along  $y$ ,  $x$  and the opposite  $x$ -direction, respectively. The diffusion of adatom shows strongly direction and position dependent.

$(23 \times \sqrt{3})$ -Au(111) surface. What shown in Fig. 3 is diffusion barriers along three directions at different positions on the surface. We can find that, generally, the diffusion barriers in the transition region are low, while in the fcc- or hcp-like region, the diffusion barriers are high.

The diffusion barriers along the different directions could be much different (see Fig. 3). In the fcc- or hcp-like region, the diffusion barriers are around 0.5–0.70 eV, while in the transition region, the difference of the diffusion barriers along different directions could be a factor of two. These direction dependent diffusion barriers could lead to an important consequence: adatoms will segregate and diffuse in the transition regions. Supposing an adatom on the hcp-like region D (see Fig. 1), since  $E_{\bar{x}}$  is the smallest in this region, the adatom will diffuse into the transition region C, where the diffusion barriers  $E_y$  and  $E_{\bar{x}}$  are quite small. Supposing an adatom on the fcc-like region B, since  $E_x$  is smaller than  $E_{\bar{x}}$  (except one point

near the boundary), the adatom will diffuse into region C, too. If the adatom is at transition region A, it needs to overcome  $\sim 0.3$  eV barrier to jump onto the fcc-like region B, then transition region C. As we can see from Fig. 3, the diffusion barriers in transition regions A, C, and E are small, so we can expect that these transition regions will be channels for mass transportation in the reconstructed Au(111) surface. This anisotropic diffusion and segregation of adatoms provides a good base for the growth of low-dimensional nanostructure.

To qualitatively demonstrate how the local strain affects the diffusion barrier, we define a local strain, the displacement between the fcc (hcp) site on the reconstructed surface and the fcc (hcp) site on the ideal surface divided by the equilibrium interatomic distance. Obviously, this is not the exact strain of the surface, but it is a kind of measure of the strain. Since on the top layer there are 23 atoms which is on 22 surface atoms, the strain should be compressive. The calculated local strain across the unit cell is shown in Fig. 4. It is

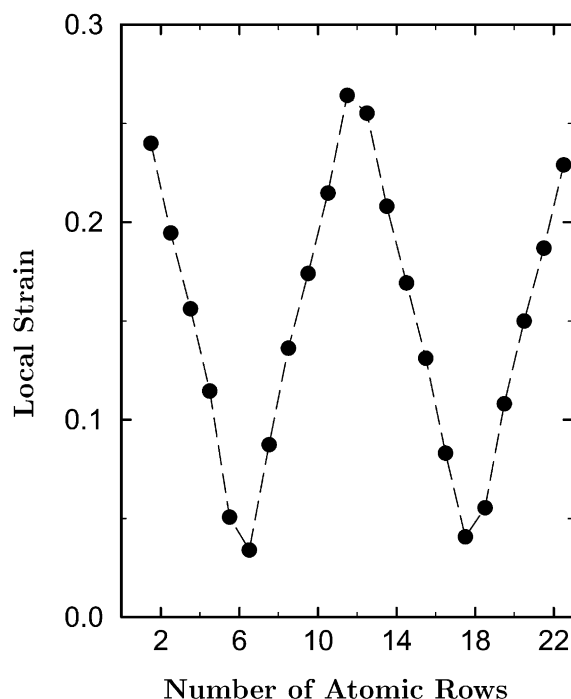


Fig. 4. The local strain on the different positions of the unit cell. A strong position dependent behavior can be observed.

not strange to find that, in the fcc- or hcp-like region, the local strain is small, and in the transition region the local strain is large. We can see that, the largest strain is in the transition regions A, C, and E, where the diffusion barriers are relatively small. This gives us a qualitative picture, the larger the local strain, the smaller the diffusion barriers, which is in consistent with what obtained for homogeneously stained surface [12,23]. Even though, to get an exact relationship between diffusion barrier and the local strain, one needs to have a more accurate definition of the local strain,

our results from the present definition of the local strain can still give a qualitative relationship on the local strain and the diffusion barrier.

To explain the large difference of the diffusion barrier between fcc-like (hcp-like) and transition region, we show structural changes after an adatom is added to a few surface positions (Fig. 5). In the transition region, the existence of the large distortion in the surface causes the potential energy surface soft, adding an adatom can move the surrounding surface atoms away as large as 0.7 Å, as indicated in the lower two panels of Fig. 5, and the binding energy at the local minimum is small, thus the diffusion barrier becomes low. While in the fcc- or hcp-like region, surface atoms are almost in the ideal lattice positions and each atom has a large binding energy, the adatom at the fcc or hcp binding site is also very stable, adding an adatom cannot shift the surface atom to a large extent (as shown in the up two panels of Fig. 5). Thus, the difference of diffusion barrier between fcc-like (hcp-like) and transition region becomes large.

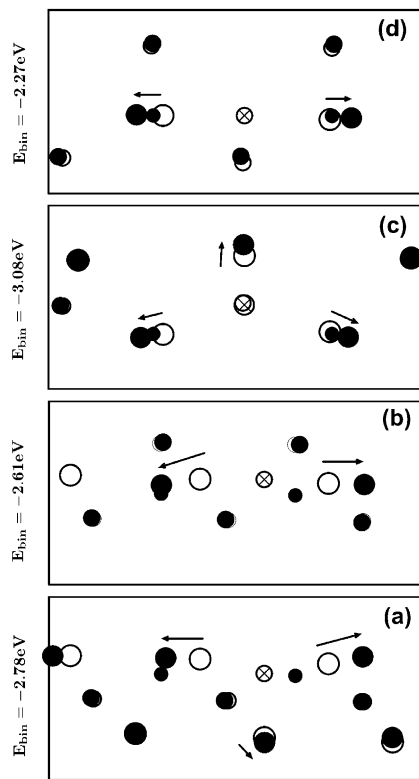


Fig. 5. The schematic showing (top view) how an adatom changes the surface structure at different positions. Panels (a), (b), (c), and (d) show the structural changes when the adatom was added to point e, d, b, and a in Fig. 1. The circles with crosses denote the adatom. The open circles denote the initial positions of surface atoms without adatom, and the filled circles denote the positions of the surface atoms with adatom. The largest filled circles, smallest filled circles and the middle size filled circles represent the atoms in the first layer, the second layer and the third layer, respectively. The arrows denote the direction of the displacement for surface atoms.

#### 4. Summary

Based on the glue many-body potential, we have calculated the diffusion barrier for an adatom on the reconstructed  $(23 \times \sqrt{3})\text{-Au}(111)$  surface. We find that the binding energy of an adatom on the surface varies from positions to positions, the binding energies at the fcc- and hcp-like regions are much larger than that in the transition region. We have observed that adatom diffusion on the reconstructed surface is anisotropic. Diffusion barriers at different regions can be changed from 0.12 to 0.8 eV, also the diffusion is strongly direction dependent. Since the diffusion barrier in the fcc- or hcp-like region is in order of 0.5 eV and there is a tendency for the adatom to diffuse into the transition region, we conclude that the structural transition region is a fast channel for the mass transportation on the reconstructed Au(111) surface. We have also qualitatively correlated the diffusion barriers with the local strain. We find that the intrinsic compressive strain in the reconstructed surface also decrease the diffusion barrier,

in agreement with results in the homogeneously strained surface.

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