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A Molecular Dynamics Simulation of Au(001) Surface Reconstruction

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MD 모사법에 의한 Au(001)면의 표면 재배열에 관한 연구

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Abstract – We investigate the Au(001) surface reconstruction, numerically, by Molecular Dynamics (MD) simulation. We find that the top-most layer of Au(001) surface is reconstructed to a contracted hexagonal face, and relaxed about 0.05 Å upward at room temperature. The contraction ratio with respect to a unreconstructed Au(111) surface is about 3.5%. The hexagonal layer is slightly distorted and buckled. The surface corrugation is found to be about 0.28 Å on average. In our earlier work we have predicted the in-plane orientation of the reconstructed layer to be either 0° or 0.7° depending on the size of the cluster. However, we find only 0.0° in this simulation because the size of the cluster corresponding to the 0.7° orientation is larger than the current limitation of MD simulation. These findings are in good agreement with experimental results.

1. Introduction

The structure and dynamic properties of the surfaces are often considerably different from that of the bulk properties. A microscopic understanding of the surface phenomena attracts much attentions because of importance of surface effects in small scale devices (we can never avoid the surface effects in a real application with these small scale devices). The recent advent of many sophisticated surface probing devices such as Scanning Tunneling Microscope (STM) made us possible to probe the surface profile in atomic-scale [1, 2]. Theoretical works [3-5], however, lags a little behind due to the difficulties in the formulation of the atomic interaction and the limitations of current computing power and, consequently, the analysis of the experimental data is difficult in some situations.

Most of low-indexed noble metal surfaces are known to favor the reconstructed surface [6-8]. Among the low-indexed planes, the reconstruction of (001) plane is particularly interesting because: (1) the symmetry of the top-most layer (hexagonal) is completely different from the second layer and below (square lattice); (2) the reconstructed layer has the epitaxial natures. A number of experimental works shows that the top-most layer of the (001) surface favors a contracted and buckled hexagonal layer [9-12]. The most probable reconstruction pattern is the (5×20) but other patterns, between (4×17) and (6×56), have been observed in the experiments [10]. The in-plane orientation is either 0.0° or 0.7°. The physical interpretation of the rotated domain is still controversial among the experimentalist [13] and have been an open question until our earlier works [14] interpreted as the lattice-match effects. We predict-

ed that the in-plane orientation depends on the cluster size. Other properties such as the interlayer spacing have also been predicted correctly in our previous study but the dynamical quantities such as the lattice relaxation could not be studied because of static nature of the calculation. Thus, a purpose of this paper is to investigate the Au(001) surface reconstruction dynamically as a complimentary study of the previous work.

In this paper we employ Molecular Dynamics (MD) simulation technique to study Au(001) surface reconstruction. We find that the top-most layer of Au(001) surface is reconstructed to a contracted hexagonal face and relaxed about 0.05 Å upward at the room temperature. The contraction ratio with respect to the unreconstructed Au(111) surface is about 3.5%. The hexagonal layer is slightly distorted and buckled. The surface corrugation is found to be about 0.28 Å on average. In our earlier work, we have predicted the in-plane orientations of the reconstructed layer to be either 0° or 0.7° depending on the size of the cluster. However, we find only 0.0° in this simulation because the size of the cluster corresponding to the 0.7° orientation is much larger than the current limitation of the MD simulation. Our results are in good agreement with experimental results [7, 9-12].

2. Method

In order to simulate the Au(001) surface reconstruction dynamically we use a usual Molecular Dynamics simulation technique with a modified Verlet algorithm [15]. Since the surface properties of an ordinary two-body additive potential is very different from a realistic one, we use an Embedded Atomic Method (EAM) [16] "Glue" potential [17],

$$E=\sum_{i=1}^{N}F_i[\rho]+\sum_{i}^{N}\sum_{j\neq i}^{N}V_2(|\vec{r}_i-\vec{r}_j|), \qquad (1)$$

where the EAM energy functional, $F_i[\rho]$, is a universal function, $\rho=\Sigma_j^N \rho_j(R_{ij})$ is the sum of electronic charge from neighboring atoms, $V_2(R_{ij})$ is a two-body repulsive potential, and $R_{ij}=|\vec{r}_i-\vec{r}_j|$. The spline fitted parameters for these three functions can be found in the reference [17]. This type of potential predicts an accurate surface energy as well as other surface and bulk properties. Here the potential energy is not in an additive form due to the many-body functional term, $F_i[\rho]$, but the charge density and the two-body potential term are.

Our system consists of two fixed (001) plane and two movable (001) planes containing 441 atoms in each layer. On top of these layers, one movable layer with 289 atoms is placed initially on the lattice points of the (001) surface, i.e., a square lattice. Then the system is annealed for 1000 MD time steps at 1000°K, for 5000 time steps at 500°K, for 2000 time steps at 350°K and for 2000 time steps at 300°K. After the annealing process, the thermodynamic quantities are calculated for another 10,000 time steps. This *"annealing-measurement"* cycle is repeated until the total potential energy is saturated to the minimum energy. The usual periodic boundary condition is not applied in this simulation to avoid the unwanted constrain effects from this boundary. In fact the periodic boundary may not be applicable to this system at all since our system has two different symmetries. (hexagonal symmetry on the top-most layer and square symmetry on the second layer and below).

For the sake of convenience, we use the MD units in the simulation where $\varepsilon=3.78$ eV, $\sigma=2.89$ Å, $t_0=(m\sigma^2/\varepsilon)^{1/2}$ are chosen, respectively, as the units of the energy, the length and time. The one MD time-step is given by $\Delta t=0.001t_0$, and t_0 equals to about 2.13×10^{-13} sec. Here m is the mass of a gold atom.

3. Results

In Fig. 1, we show the adsorption energy per a

top-most layer atom as a function of simulation time. We start with a unreconstructed square lattice at $t=0$ (the energy is marked by a short line with "unreconstructed" in the figure). The system is annealed for the 10,000 time steps following the above mentioned annealing procedure, and then the total adsorption energy is calculated for another 10,000 time steps. Here, the total adsorption energy is defined as the total potential energy, i.e., equation (1), of the system minus the energy without the top-most layer. The annealing and measuring cycle is repeated until the equilibrium is reached. After 120,000 time steps the system is reached an almost equilibrium state (in terms of the energy), and convergency is very slow. The adsorption energy of the reconstructed surface is estimated to be about -3.97 eV. We note that the energy barrier may exist to escape from the unreconstructed configuration to the reconstructed configuration but this barrier will not be presented in the figure because of the annealing procedure during which we did not measure any quantities.

In order to investigate in-plane structure of the top-most layer, we calculate the Fourier transformation of the atomic number density in the top layer, for 10,000 time step, after each annealing procedure. We use an ordinary two dimensional fast-fourier-transformation (fft) routine to perform the transformation, and this atomic number density in the Fourier space is corresponding to the X-ray pattern in a real experiment.

We plot the atomic number density in the Fourier space after 10,000 and 30,000 time steps in Fig. 2(a) and (b), respectively. Fig. 2(a) shows clearly

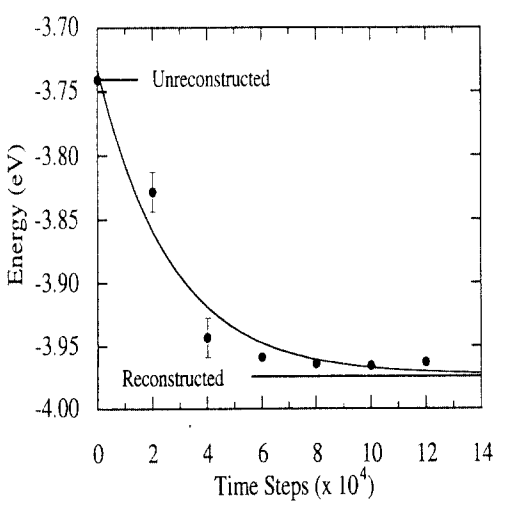

Fig. 1. The adsorption energy per top-layer atom is plotted as a function of the time steps. See the definition of the adsorption energy in the main text.

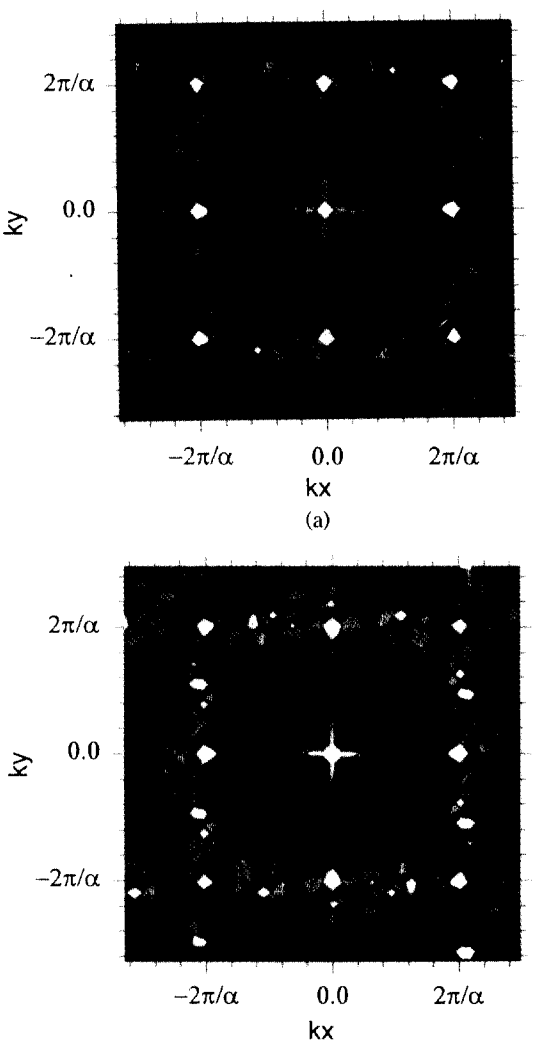

Fig. 2. A density plot for the atomic number density in the Fouier space after: (a) 10,000 time steps; (b) 30,000 time steps. The white spots corresponds to the diffraction points in a real experiment.

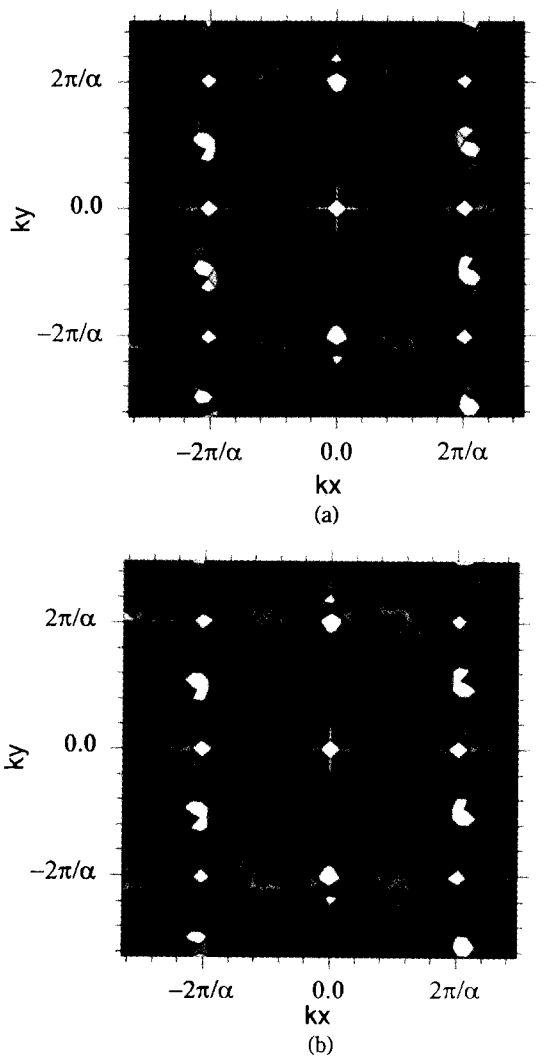

Fig. 3. The same figure as in the Fig. 2 at the: (a) 50,000 time steps; (b) 70,000 time steps.

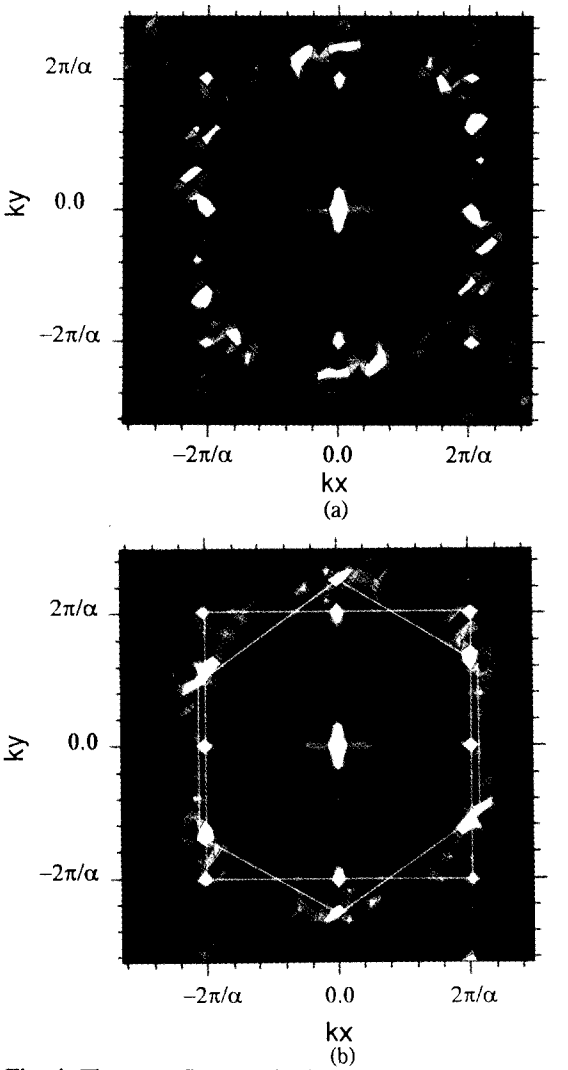

Fig. 4. The same figure as in the Fig. 2 at the: (a) 110, 000 time steps; (b) 130,000 time steps.

the 90° symmetry, i.e., a square lattice with a lattice constant $a=2.89$ Å at room temperature. As the simulation is carried on further to 30,000 time steps, other peaks are showing up but the 60° symmetry, i.e., the hexagonal lattice, is not clear yet. After 50,000 time steps and 70,000 time steps, the hexagonal peaks become evident in Fig. 3(a) and (b), respectively. Finally the hexagonal peaks are clearly visible after 110,000 and 130,000 time steps in Fig. 4(a) and (b). Even after 130,000 time step the square lattice peaks are still visible because the system has not yet reached the true minimum. However, the energy difference between this state and the true minimum state is very small as we can see in Fig. 1 and, consequently, it will take a very long time to reach the true minimum. We will not try to get any closer to the minimum state in this study.

We can also calculate the in-plane lattice constant of the reconstructed surface by measuring the

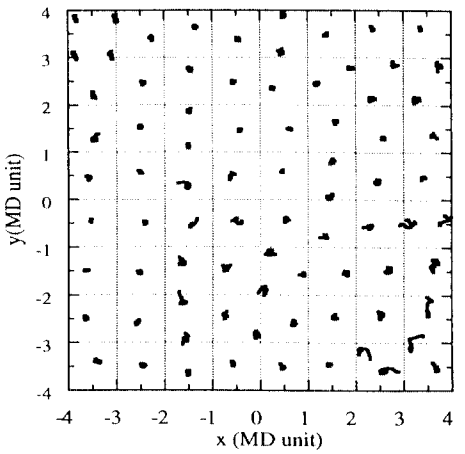

Fig. 5. The atomic motion at the room temperature for 10,000 time steps is plotted after the system evolved 130,000 time steps. The dotted grid lines represent the lattice points of the second square lattice.

Table 1. The energy, the contraction ratio, the interlayer spacing between the top and second layers, the layer corrugation, and the in-plane orientation are listed in the table. Note that there is another in-plane orientation, 0.7° but the size of this orientation is too large to simulate

Paramters	Value
Reconstructed face	Hexagonal lattice
Energy	- 3.96 eV
Contraction ratio	3.5%
Interlayer spacing	2.08 Å
Corrugation	0.28 Å
In-plane orientation	0.0°

peak positions from the density plot in the figures. The square and hexagon in the Fig. 4(b) represents the unreconstructed and reconstructed lattices, respectively. From this measurement we find that the reconstructed hexagonal layer is contracted about 3.5% with respect to the unreconstructed Au(111) layer (a perfect hexagonal layer with a lattice constant equals to 2.89 Å).

The atomic motion for 10,000 time steps after the system has evolved 130,000 time steps is shown in the Fig. 5. Although there are many dislocations and imperfections we can clearly identify this structure as an hexagonal lattice. The dotted grid lines represent the lattice points of the second layer square lattice. We summarize all the parameters we find in this study in Table 1.

4. Conclusion

We have studied the Au(001) surface reconstruction employing Molecular Dynamics simulation technique with EAM type "Glue" inter-atomic potential. We found the top-most layer is reconstructed to a contracted hexagonal layer. The contraction ratio is found to be about 3.5% by a Fourier analysis, and this layer is slightly distorted and buckled. The corrugation of the layer is about 0.28 Å. The interlayer spacing between the top-most reconstructed layer and the second layer is about 2.08 Å which is relaxed upward slightly. The in-plane orientation we found in the simulation is only 0.0°, and no efforts on searching the 0.7° rotated domains were made in this simulation because of the system size limitation that can be simulated by a computer. Our findings are in very good agreement with the experiments and earlier existing theories.

Acknowledgements

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