RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 2 15 JANUARY 1987-I

Simulation of Au(100) reconstruction by use of the embedded-atom method

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(Received 3 October 1986)

The embedded-atom method of Daw and Baskes is used to calculate the reconstruction of the Au(100) surface. The state of minimum surface energy for a 5×5 unit cell is attained by adding five atoms to the surface layer, resulting in a 1×5 reconstruction giving a slightly buckled quasi-triangular surface with 20% higher areal atomic density than the truncated surface. These results are compared with experiment and with the recent calculation of Ercolessi, Tosatti, and Parrinello. The experimental results and both calculations agree semiquantitatively.

The gold surface is particularly interesting among the noble metals, since all of the low-index surfaces reconstruct to give close-packed layers.[1] The Au(100) surface has been studied using low-energy electron diffraction,[1] He-ion scattering,[2] and scanning tunneling microscopy.[3] The consensus of these experimental studies is that the topmost layer changes from a truncated fcc (100) arrangement to a slightly rotated and dense-packed triangular structure. This reconstruction has proved quite resistant to theoretical treatment, since it occurs over regions too large for *ab initio* quantum calculations, and is also inaccessible to two-body phenomenological approaches, which do not treat electronic cohesion properly.

A semiempirical procedure for calculating the energy of a large metallic system including many-body cohesive effects was introduced by Daw and Baskes.[4-6] This procedure, called the embedded-atom method (EAM), expresses the structural energy of a metallic system as a combination of pairwise repulsive terms and the energy required to embed the atoms in the local electron density provided by the other atoms of the metal. This procedure takes little longer to calculate than the calculation of simple pair potentials, and thus can be used to study rather large structures. The procedure is based on results from density-functional theory,[5] but the simple implementation of these ideas requires several questionable approximations. Thus it is better to view the final procedure as an empirical fit to an interaction description whose form is based on many-body quantum theory rather than as a fully justified quantum-mechanical entity. The EAM has been used to study many properties of metals, including dislocation propagation,[7] surface segregation,[8] and Pt(110) reconstruction.[9]

The treatment of the cohesive many-body term by the EAM begins with the idea that the total electron density in a metal can be approximated by the linear superposition of the electron densities of the free atoms making up the system. Upon making the further approximation that the electron density near an atom, due to all other atoms, is approximately constant, it becomes possible to express the cohesive energy of the atom in terms of an embedding energy which is simply a function of the background electron density and the atomic species.[5] The pairwise repulsive term is then expressed in terms of a Coulombic $1/r$ interaction where the effective charges of the two atoms are functions of the interatomic separation.

More precisely, the total energy of the system takes the form

$$E=\sum_i F_i(\rho_i)+\tfrac{1}{2}\sum_i\sum_j \phi_{ij}(R_{ij}) \ , \tag{1}$$

where $F_i(\rho)$ is the energy to embed atom i into the background electron density ρ,

$$\rho_i=\sum_j \kappa_j(R_{ij}) \ , \tag{2}$$

and $\kappa_j(R)$ is the electron density of the free atom j at radius R. The pairwise repulsive term takes the form

$$\phi_{ij}(R)=Z_i(R)Z_j(R)/R \ , \tag{3}$$

where the effective charges $Z(R)$ are functions of the atomic species and the interatomic spacing R. Foiles, Baskes, and Daw[6] have recently published a consistent set of functions and parameters which fit Eqs. (1)–(3) to the fcc metals Cu, Ag, Au, Ni, Pd, and Pt; further details on the fitting procedures are available there.

We have used the theoretical structure described above and in Refs. 5 and 6 to model the reconstruction of the Au(100) surface. The initial structure is a 5×5 surface cell with (110)-oriented periodic directions and a thickness of 6 layers [see Fig. 1(a)]. The bottom layer of atoms were held fixed in the equilibrium bulk positions. It was found that the six-layer thickness resulted in effectively decoupling the reconstruction of the top surface from the unrelaxed bottom surface. The energetics of the surface reconstruction were then studied by using a Monte Carlo procedure to generate the minimum-energy configuration corresponding to the initial conditions. The slab is first warmed to about one-half of the melting point, and is then cooled slowly to $T=0$. About 1000 Monte Carlo steps per particle are used to model the cooling process.

When this procedure is applied to the clean, truncated Au(100) surface (described using the EAM and parameters for Au appearing in Ref. 6), the surface atoms are found to shrink together into close-packed strips five atoms wide and separated by a gap [see Fig. 1(b)]. Thus the first layer is trying to reconstruct into a denser layer, while the second layer shows no reconstruction. A series of simulations were then made where a number of adatoms were added to the surface. Upon heating, atoms were absorbed

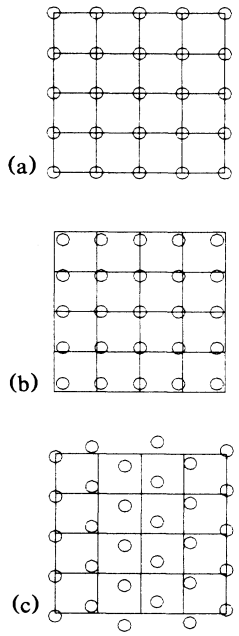

FIG. 1. The top view of the Au(100) surface structure in different stages of reconstruction. (a) is the truncated bulk surface, (b) is the relaxed, but unreconstructed surface, and (c) is the reconstructed surface resulting from absorbing five additional atoms into the surface layer, which is the predicted equilibrium state of 5×5 cell studied. In all cases, the grid represents the unrelaxed locations of the truncated bulk surface.

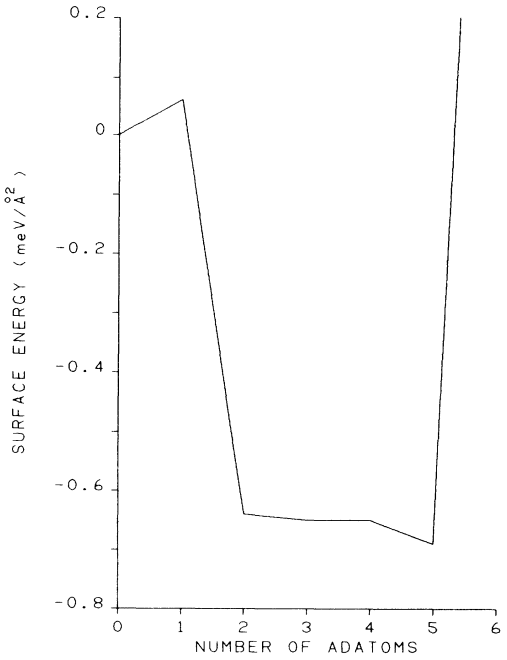

FIG. 2. Differential surface energy (relative to the relaxed truncated surface) for the reconstructed Au(100) surface as a function of adsorbed adatoms. The minimum at $n=5$ represents the equilibrium structure, which is a denser corrugated quasitriangular overlayer, in accordance with experiment.

into the first surface layer with a decrease of surface energy, resulting in a denser packing than the unreconstructed surface. The surface energy was found to decrease until a minimum was found at five adatoms. With six or more adatoms the surface energy increases rapidly (see Fig. 2).

The structure of the surface with 5 adsorbed adatoms, being the predicted equilibrium state, is of considerable interest [see Fig. 1(c)]. The surface layer exhibits a 1×5 reconstruction along a (110) direction, forming a quasitriangular layer 20% denser than the unrelaxed surface layer. The surface layer also shows signs of a small buckling, amounting to about 0.5 Å. This structure is very reasonable as a small-scale model of the reconstructed Au(100) surface, having the correct density and approximate configuration observed in experiments. It is clear, however, that calculations on larger cells might change the details of the structure found for the 5×5 cells. Scanning tunneling microscope studies have suggested that the reconstruction is considerably longer in range, with a unit cell of 26×48 being seen.[3] However, the local structure observed in these experiments agrees with that of our simulation.

It is of interest to compare the present simulation with the related calculation recently published by Ercolessi, Tosatti, and Parrinello (ETP).[10] They used a phenomenological interaction which describes the energy in terms of a pairwise and a many-body term, which includes naturally the effect of the local structure. However, there are many differences in detail between ETP and the present EAM potentials. Despite these differences, however, the predicted reconstructions made by them are quite similar. The values for surface energy differ considerably, with the present predictions being smaller by roughly a factor of 5 (representing a total energy difference of only 1%–2%), but the equilibrium reconstruction and the magnitude of the resulting surface corrugation, as well as the structure of the relaxed but unreconstructed surface, are nearly identical.

The embedded atom method of Daw and Baskes has been used to study the Au(100) surface reconstruction. We find the equilibrium structure of the surface of a 5×5 (100)-oriented unit cell to include a 1×5 reconstruction, yielding a 20% denser triangular overlayer, in good agreement with experimental observations. In addition, the present structural results agree well with the recent work of Ercolessi, Tosatti, and Parrinello using a different phenomenological interaction. The observation that use of different phenomenological interactions yields similar structural predictions suggests that this class of problems is rather robust against analysis using differing potentials, and thus that these semiempirical descriptions of metallic structure and cohesion may have wide application.

This work was performed at Sandia National Laboratories and supported by U.S. Department of Energy Contract No. DE-AC04-76DP00789.

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