

## Theoretical Study of Noble-Metal (100) Surface Reconstructions Using First-Principles Techniques

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Using first-principles calculations, in conjunction with modeling techniques, we show that the top layer of the Au(100) surface will transform to a close-packed structure while that of Ag(100) will not. Our calculations provide some insight into the microscopic origin of the difference in stability between 4*d* and 5*d* fcc metal (100) surfaces.

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The low index surfaces of 5*d* fcc metals Ir, Pt, and Au exhibit amazingly complex reconstructions not present in the surfaces of the isoelectronic 4*d* transition metals.<sup>1</sup> On the Au(100) surface a  $c(28 \times 68)$  reconstructed pattern showed up in LEED experiments.<sup>1</sup> Subsequent scanning tunneling microscopy<sup>2</sup> and He-ion scattering<sup>3</sup> experiments support the interpretation of the atomic geometry as a contracted hexagonal-close-packed surface layer superimposed on the square lattice of the inner layer substrate atoms. Very similar transformations are observed in Ir(100) and Pt(100). Although numerous theoretical works<sup>4,5</sup> have studied this phase transition, up to now there has been no good basic understanding of the physical mechanism driving this perplexing reconstruction, nor is there a clear explanation of why the reconstruction does not occur on the (100) surfaces of the corresponding 4*d* metals Rh, Pd, and Ag.

Recent experiments indicate that although clear Pd(100) does not reconstruct, the addition of just one monolayer of Pt is sufficient to give a reconstructed top layer.<sup>6</sup> This and the incommensurate nature of the reconstruction suggest that the reconstruction is driven mainly by atomic interactions within the surface layer. Thus, although a complete *ab initio* study of the (100) reconstruction is not feasible because of the huge unit cell of the reconstructed surface, a lot can be learned about the reconstruction by studying the properties of atomic monolayers. For transition metals near the end of the row, the *d* bands are nearly completely filled. Thus the *d* charge distribution is nearly spherical and directional bonding is not important. The main effect of the substrate is to provide an electron background through which the surface atoms on the top layer interact with one another and we can get a very good description of the interactions between the surface atoms by replacing the substrate with a jellium surface of appropriate electronic density. In the present paper, we report the use of *ab initio* calculations to study the energetics of Au and Ag monolayers in isolation and on jellium surfaces. Using the results of these calculations, a two-dimensional Frenkel-Kontorowa-type (FK) model<sup>7</sup>

is constructed to give a detailed picture of the structure of the reconstructed surface. Through our calculations we obtained important physical insights on the basic physics of the reconstruction on the 5*d* transition-metal (100) surfaces.

The first-principles calculations are done within the local-density-functional formalism<sup>8</sup> with the Hedin-Lundqvist form<sup>9</sup> of local exchange correlation. Norm-conserving pseudopotentials<sup>10</sup> are used and the wave functions are expanded in a mixed basis set<sup>11</sup> comprising of plane waves and localized orbitals. This method has been very successful in describing both bulk and surface structural properties of Au<sup>12</sup> and other transition elements. For monolayers and slab calculations described below, 15 *k* points in the irreducible Brillouin zone are used.<sup>13</sup>

Our calculations for isolated monolayers show that it is energetically favorable for both Au and Ag mono-

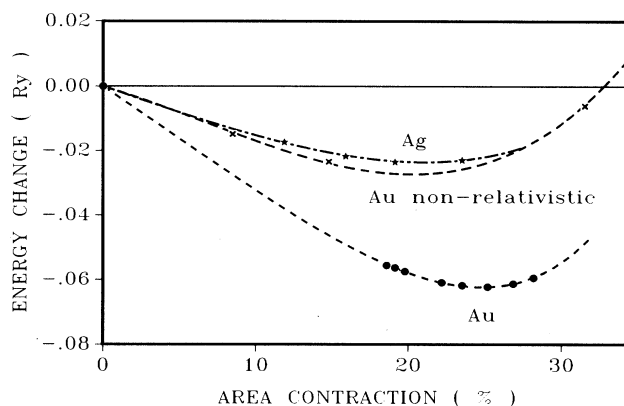


FIG. 1. Energy change per atom for Au and Ag monolayers in close-packed arrangement as a function of the percentage contraction of surface area per atom. Note that the energy gain is reduced substantially if a nonrelativistic potential is used for Au. For Figs. 1–3, the reference point (0%) is the area occupied by one surface atom on an ideal (100) surface.

layers to transform from square to hexagonal-close-packed arrangements and to increase the surface density by reducing the surface area per atom. (For Au, the contracted hexagonal monolayer is 0.37 eV/surface atom lower in energy than the contracted square monolayer and the corresponding number for Ag is 0.23 eV/surface atom.) In Fig. 1, we plot the energy gained by contraction with the layer in close-packed arrangement. Au gains substantially more energy (about 2.5 times) than Ag in the contraction process. In reality, the Au top layer transforms not in isolation but in a nonuniform electron sea provided by the substrate atoms. The simplest way to include this substrate effect is to repeat the calculations with the monolayer placed on the surface of a jellium slab with the appropriate charge density.<sup>14</sup> The energetics of a hexagonal layer of Au and Ag on top of jellium are presented in Fig. 2. The distance of the top monolayer from the jellium edge has been determined by energy minimization for each point on the curves and the energy of the jellium slabs have been subtracted, so that the energy plotted denotes the atomic interactions within the surface layer in the background of a jellium surface. The results are qualitatively the same as those of the monolayer: Both Au and Ag prefer close-packed arrangement with higher atomic density than the (100) square ideal overlayer, but Au contracts more and gains more energy than Ag.

Although the monolayer gains energy by contraction, the reconstruction will not occur unless the energy gained by the contraction and transformation to close-packed structure is greater than the energy lost (the "mismatch" energy) as the top layer loses registry with atoms in the underlying layers. We can obtain a reasonable estimate of this mismatch energy with calculations performed for (100) slabs in which the uncontracted top layer is displaced laterally with respect to the underlying

layer. Specifically, the effect of substrate registry is expressed in the form of a periodic square-lattice potential with energy per surface atom in the form

$$E(\mathbf{R}) = \sum_{\mathbf{G}} W_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{R}}, \quad (1)$$

where  $\mathbf{G}$ 's are the two-dimensional (2D) reciprocal-lattice vectors and  $\mathbf{R} = (x, y)$  is the position of an atom on the top layer. If we truncate (1) beyond the first star of nonzero  $\mathbf{G}$  vectors, we obtain

$$E(x, y) = E_0 + \frac{W}{4} \left[ \cos\left(\frac{2\pi}{a}x\right) + \cos\left(\frac{2\pi}{a}y\right) \right], \quad (2)$$

where  $a$  is the lattice constant of the 2D square lattice. As  $W = E(a/2, a/2) - E(0, 0)$ , it can be obtained from first-principles calculations by computing the energy needed to slide the top layer by  $(a/2, a/2)$ . For Au and Ag,  $W = \frac{1}{2} [E(\text{shifted}) - E(\text{ideal})]$ , where  $E(\text{ideal})$  is the total energy of a five-layer (001) slab and  $E(\text{shifted})$  is that of a five-layer slab with top and bottom layers shifted by  $(a/2, a/2)$ .<sup>15</sup> All interlayer distances are fully relaxed with Hellmann-Feynman forces.<sup>16</sup> Our calculation shows that Ag has a slightly larger mismatch energy than Au (36.8 and 39.3 mRy per surface atom for Au and Ag, respectively). The fact that the energy gained by the top layer transformation is substantially larger for Au than for Ag, while the energy lost in displacing the top layer is actually larger in Ag already offer us a fairly clear indication of why Au reconstructs but Ag does not.

A recent study,<sup>17</sup> based mainly on charge analysis, has questioned the role of  $d$  electrons in the Au reconstruction. Analysis of our results shows that the  $d$  electrons actually play an important role in determining the difference between Au and Ag. For transition metals with a nearly full  $d$  band, a substantial part of the bonding forces between atoms comes from the hybridization of the  $d$  and  $s$  electrons in the solid. This  $d$ - $s$  hybridization is weaker in the  $4d$  transition metals than in the  $5d$  transition metals. The microscopic origin for this difference can be traced to strong relativistic effects in the  $5d$  metals which lowers the energy of the  $s$  states bringing the  $s$  band closer to the  $d$  band and enhances the  $d$ - $s$  hybridization. Another factor is that the better screening and slightly larger core sizes make the  $5d$  electronic states more extended than the  $4d$ . The stronger bonding already shows up in the bulk properties: The  $5d$  metals have stiffer bulk moduli and larger cohesive energies than their  $4d$  counterparts.<sup>12</sup> For the surface, we have repeated our monolayer calculation using a nonrelativistic pseudopotential for Au. The energy gained in contraction of the Au monolayer is substantially reduced when the calculation is done with a nonrelativistic rather than the scalar relativistic pseudopotential (see Fig. 1). Parallel calculations for the other low indexed faces indicated that the missing-row reconstruction for the Au(110) surface is also suppressed for nonrelativistic

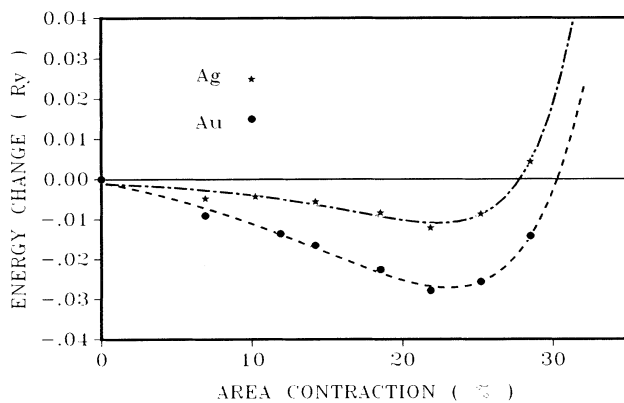


FIG. 2. The energy change per atom for hexagonal Au and Ag monolayers on jellium ( $r_s = 1.9$ ) as a function of the percentage contraction of area per atom.

Au. Since the surface density of atoms changes in the transformation process, the proper quantity that governs the reconstruction is the change in surface energy per unit area, which can be written as

$$S(q) = N[d(q) + qE_s]/(1 - q), \quad (3)$$

where  $q$  is the fractional decrease in area per atom,  $N$  is number of atoms per unit area on the ideal uncontracted surface ( $q = 0$ ),  $d(q)$  is the energy change per atom, in-

$$d(q; \{\mathbf{R}\}) = \sum_{ij} e(\mathbf{R}_i - \mathbf{R}_j) + \sum_i \frac{W}{4} \left[ \cos \left( \frac{2\pi}{a} x_i \right) + \cos \left( \frac{2\pi}{a} y_i \right) \right], \quad (4)$$

where  $\mathbf{R}_i = (x_i, y_i)$  is the position of the  $i$ th surface atom, with the average area per surface atom depending on  $q$  (the fractional contraction) and  $a$  [the surface lattice constant of the original square (100) surface]. The first term describes the energy change due to intralayer interaction and the homogeneous part of the interaction of the top layer with its substrate, while the second term describes the energy change due to a change of registry of the top layer with respect to the underlayers. The 2D FK model describes a situation in which a layer has a different preferred bond length (and in this case, also a different symmetry) with respect to a potential dictated by the underlying layers. The system will find its ground-state configuration by optimizing between the strain energy (first term) and the potential energy (second term). Since our monolayer on jellium calculations include completely the intralayer interaction and the interaction of the top layer with a homogeneous substrate, they should give a good representation of the first term in (4).<sup>19</sup> With a 2D mesh of  $61 \times 61$  atoms, and the total area constrained to correspond to a given contraction  $q$ , the  $\mathbf{R}_i$ 's are relaxed according to Eq. (4) to determine the lowest-energy configurations and the corre-

sponding  $d(q)$ 's, which are then used in Eq. (3) to find the change in surface energy. Results are plotted in Fig. 3. We found it is indeed energetically favorable for Au, but not Ag, to reconstruct. At the energy minimum, the Au layer is basically a hexagonal layer, slightly distorted by the underlying potential, and has a contraction of 21%, which agrees well with experimental results.<sup>20</sup>

We should emphasize that the explicit form of Eq. (4) is one approximation and using our monolayer on jellium results for the first term in (4) is another. However, the final conclusion does not depend on these assumptions. The single most important distinction between Au and Ag is that the top (100) layer of Au gains more energy in contraction and rearrangement. This is mainly due to the more extended nature and stronger participation in bonding of Au  $d$  orbitals which can be traced to relativistic effects and the fact that Au has a bigger core. This distinction is not specific to Ag and Au, and also applies to other  $4d$  and  $5d$  fcc metals, so that it is quite natural for similar (100) surface reconstructions to occur in  $5d$  metals Ir and Pt but not in the corresponding  $4d$  metals Rh and Pd. The encouraging results obtained here suggest that we can use the surface interatomic interactions deduced from our monolayer on jellium calculations to investigate the structure of Au and Ag monolayers on various substrates. We are also considering applications in surface dynamical studies.

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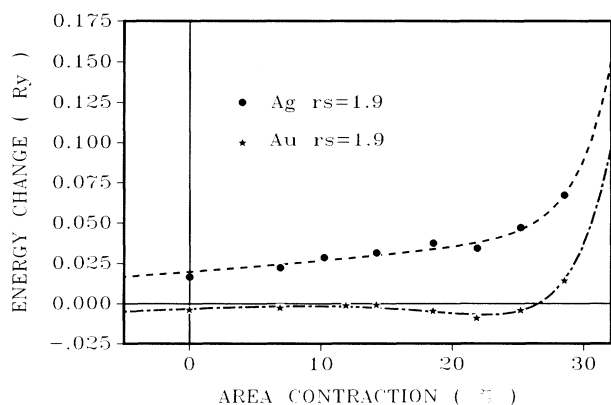


FIG. 3. Surface-energy change (per surface atom) for Au and Ag as a function of the percentage area contraction according to Eq. (3) in the text.

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<sup>10</sup>D. H. Hamann, M. Schluter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

<sup>11</sup>S. G. Louie, K. M. Ho, and M. L. Cohen, *Phys. Rev. B* **19**, 1774 (1979). We used plane waves with kinetic energy up to 12 Ry for both Au and Ag, augmented by local orbitals (Gaussians for Au, numerical functions for Ag) centered at the atomic sites. The shapes of the local orbitals are determined variationally.

<sup>12</sup>K. M. Ho and K. P. Bohnen, *Phys. Rev. Lett.* **59**, 1833 (1987).

<sup>13</sup>Some of the calculations have been checked with 28  $k$  points. Changes are very small except that with 28  $k$  points, the small wiggles in energy versus contraction curve for monolayer on jellium (Fig. 2) disappears.

<sup>14</sup>The jellium densities are determined in two ways: (i) By finding the charge density of Au and Ag at bulk interstitial positions, midway between two nearest neighbors. This gives  $r_s \sim 1.8$  and 2.0, respectively, for Au and Ag; (ii) by putting a monolayer over a jellium slab and varying the jellium density until the charge profile [solved self-consistently and averaged

along a (100) direction] on the monolayer matches that of outermost layer of a slab calculation. This gives  $r_s \sim 1.6$  and 1.76, respectively, for Au and Ag. The densities have been tested and the final results (Au contracts and Ag does not) do not depend on the choice of  $r_s$ . The results plotted in Figs. 2 and 3 corresponds to  $r_s = 1.9$  for both Au and Ag. The thickness of the jellium slab is 11.6 a.u. (about the thickness of three layers of Au or Ag). Few changes are found when results are calculated by jellium slab of thickness 13.6 a.u. The ionic potential due to the jellium is just the Coulomb potential generated by repeated slabs of uniform positive charges. For computational details on treating jellium slabs, see, e.g., S. G. Louie and M. L. Cohen, *Phys. Rev. B* **13**, 2461 (1976).

<sup>15</sup>A seven-layer slab gives  $W = 36.5$  mRy (cf.,  $W = 36.8$  mRy for five layer) for Au.

<sup>16</sup>See K. M. Ho, C. L. Fu, and B. N. Harmon, *Phys. Rev. B* **28**, 6687 (1983), and references therein.

<sup>17</sup>J. F. Annett and J. E. Inglesfield (to be published).

<sup>18</sup>A seven-layer slab gives  $E_s = 52.3$  mRy (cf.,  $W = 51.5$  mRy for five layer) for Au.

<sup>19</sup>The monolayer on jellium results are fitted to two-body potentials in the form of "universal binding curves," see J. H. Rose, J. Ferrante, and J. R. Smith, *Phys. Rev. Lett.* **47**, 675 (1981).

<sup>20</sup>From the variation in relaxation of the interlayer spacings of the slab as the surface layer is laterally displaced, we can estimate the corrugation of the reconstructed surface. We found that the corrugation of the surface layer is about 0.7 Å compared with  $\sim 0.5$  Å from helium scattering experiments (Ref. 3) and 0.47 Å from model simulations (Ref. 5). However, in contrast with Ref. 5 we found that the corrugation is confined mainly to the first layer and decays very rapidly into the bulk.