Possible faceting transformation of Mo from (111) to {110}

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Abstract

It is well-documented that the (111) surfaces of Mo and W are unstable upon the adsorption of ultra-thin overlayers of some fcc metals and transform to {112} type facets. Using first principles total energy calculations, we found that it is also thermodynamically allowed for Mo(111) to facet to the {110} orientations upon the adsorption of a coating layer of Pd and Pt. An overlayer coverage of about one physical monolayer would be needed to drive the transformation. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most of the surface science studies of metal overlayers on metal substrate focus on atomically smooth low index surfaces. Recently, the interaction of ultrathin metal overlayers on the rougher bcc(111) surface was systematically studied by Madey and co-workers and others [1-11], and it was found that the (111) surfaces of the bcc metals W and Mo facet to [112] upon the adsorption of ultra-thin overlayers of certain fcc metals such as Au, Pd and Pt. The surface energies of the Mo [12] at various orientations have been studied and the clean (111) surface is found to be just marginally stable with respect to faceting to the [112]. Overlayer-induced faceting of bcc(111) is thus quite conceivable, since chemisorption may increase the surface energy anisotropy, driving the (111) surface to be thermodynamically unstable. It is, however, surprising that only some metal overlayers can facet bcc(111) and some do not, and there seems to be a rather universal critical coverage for these overlayer-induced facetings to occur [1]. These issues have been examined recently by theoretically calculations [12].

There are other interesting issues about the overlayer-induced instability that are worth investigating. For a bcc metal, the (110) surface usually has the lowest surface energy per unit area. Could the (111) surface also facet to {110}? There is experimental evidence to show that it indeed happens, at least in Pd/W(111) (C-H. Nien and T. Madey, private communication), where a careful STM analysis of faceted W(111) with Pd coating identified pyramids with (110) faces. The purpose of this paper is to use first principles local density functional calculations to investigate whether an (111)→{110} faceting transformation is thermodynamically allowed for a few fcc metals on a Mo substrate.
2. Method of calculation

The total energy and force calculations were performed using the local density functional formalism [13,14] and norm-conserving pseudo-potentials [15]. The wave functions were expanded by a mixed-basis set of plane waves with kinetic energy up to 11.5 Ry and Bloch sums of numerical orbitals centered at the atomic sites [16,17]. This mixed-basis approach has been applied successfully to study many transition metal surface problems [18]. We used a repeated slab geometry, with slabs consisting of 11 layers of bcc Mo and additional pseudo-morphomorphic overlayers of adatoms. The slabs are separated by a vacuum of 9.5 Å. For k-point sampling, we used an uniform grid of up to 140 points in the surface Brillouin zones. The atomic coordinates are relaxed within a (1×1) surface unit cell by computing the Hellmann–Feynman forces. A Broyden algorithm for updating the force matrix is used to predict the new atomic coordinates during the relaxation process. The convergence with respect to the screening potential and forces are accelerated by a recently proposed scheme [19].

Let us consider the possible faceting transformation from one orientation [hkI] to another orientation [lkI], assuming that facets of equivalent [hkI] planes can maintain an average orientation of [hkI]. We will use γ and σ to represent the surface energy per unit area and per surface atom, respectively. According to Herring’s theory [20,21], faceting transformation from [hkI] → [lkI] is favorable when

\[
\gamma_{hlI} \geq \frac{\gamma_{hkI}}{\cos \theta},
\]

where \( \cos \theta \) is the angle between the directions [hkI] and [lkI]. It is more convenient to recast this equation in terms of the surface energy per surface atom. Eq. (1) then becomes

\[
\sigma_{hlI} \geq \sigma_{hkI} \left( \frac{A_{hlI}}{A_{hkI} \cos \theta} \right),
\]

where \( A_{hlI} \) is the area of the surface unit cell for the [hkI] surface. For a bcc crystal, this condition reduces to

\[
\sigma_a \left( \frac{\delta_x a \cdot a}{\delta_y a \cdot b} \right) < \sigma_{hlI},
\]

where \( a = [hkI] \) and \( b = [lkI] \), and \( \delta = 1 \) or \( 2 \) depending on whether \( b + k + l \) is even or odd. For the faceting transformation bcc(111) → bcc(110), Eq. (3) becomes

\[
3\sigma_{110} < \sigma_{112}.
\]

For a Mo surface covered with ultra-thin overlayers of \( X \) (where \( X \) can be Au, Pd... etc.), we can define a surface formation energy of the bimetallic system as

\[
\sigma(X/Mo) = \sigma(Mo) + H(X/Mo),
\]

where \( \sigma(Mo) \) is the surface energy of the clean surface, and \( H(X/Mo) \) is the heat of formation of one or more overlayers of \( X \) on substrate Mo (using bulk cohesive energies as references). \( \sigma(X/Mo) \) depends on orientation and overlayer coverage. For an integral number of pseudomorphic layers, \( H \) can be found by calculating the total energy of \( X \) on Mo as:

\[
\frac{1}{2} \left( E_{X(Mo)} - E_{Mo} + E_x \right),
\]

where \( E_{Mo} \) and \( E_x \) are the total energies of a slab of Mo (contains two clean surfaces) and a slab of Mo covered by \( X \), respectively; and the reference energy \( E_x \) is taken to be the energy of the same amount of \( X \) in a bulk environment (these fcc metals do not dissolve in Mo and excess adatoms form three-dimensional islands).

3. Results and discussion

Using first principles calculations we calculated the surface formation energies for Au, Pd, Pt and Ag on Mo(111) and Mo(100) according to Eq. (5); and to see whether it is thermodynamically favorable for a (111) surface to facet to (110), we check whether the Herring condition is satisfied (Eq. (4)). For an easier comparison of the energetics between different surface orientations, we will measure the coverage of the overlayers in terms of the “physical monolayer” [5], which is defined as the number of geometrical monolayers.
needed to shadow the exposed substrate atoms. A physical monolayer corresponds to one geometrical monolayer for (110), and three geometrical monolayers for (111). One physical monolayer for the bcc(111) carries the same number of adatoms as the faceted bcc(110) surface (which makes an angle of \( \cos^{-1}\sqrt{\frac{3}{4}} \) with the (111) substrate), such that no extra overlayer atoms are needed to cover the faceted surface, and no bare substrate will be exposed by the faceting transformation at the physical monolayer coverage.

The scaled surface energies are compared in Fig. 1 for Au, Pd, Pt and Ag. We first consider the clean Mo surface, corresponding to zero overlayer coverage. In that limit, \( 3\sigma_{110} \) is much higher than \( \sigma_{111} \). This means that the clean Mo(111) surface is stable against faceting to (110). We have to emphasize that (110) has lower surface energy per unit area than (111). The Herring condition is not satisfied (\( 3\sigma_{110} > \sigma_{111} \)) because it takes into account the 22% increase in surface area upon faceting. The situation is changed upon the adoption of other overlayers. In general, the overlayer adsorption lowers the surface formation energy and increases the surface energy anisotropy. The surface formation energy for an overlayer-covered substrate includes the interaction of the overlayer atoms among themselves and with the substrate, and is more favorable for the more compact (110) than the (111). If the overlayer–substrate interaction is strong and the coverage is high, it is possible that \( \sigma_{110} \) would eventually become low enough that the system can facet. All the overlayer elements we have considered lowered the surface formation energy of Mo, indicating that they should all wet the Mo substrate, forming two-dimensional coating layers. For Ag, the heat of formation on Mo (relative to bulk Ag) is smaller than other elements considered and there is a relatively small increase in the surface energy anisotropy. Thus, (111) remains stable with respect to faceting to (110). For the case of Au, the heat of formation is larger, leading to a more noticeable drop in the surface formation energy for both orientations and a corresponding larger anisotropy. The surface energy per unit area of (110) is lowered further relative to (111), and \( 3\sigma_{110} \) is catching up with \( \sigma_{111} \), but still failed to satisfy the Herring condition at the saturation coverage of one physical monolayer. For Pd and Pt, the surface energy anisotropy enhancement caused by the overlayer is even larger, to the extent that \( 3\sigma_{110} < \sigma_{111} \) is clearly satisfied at the physical monolayer coverage. In other words, Pd/Mo(110) and Pt/Mo(110) have low enough energy compared with Pd/Mo(111) and Pd/Mo(111) that the system can gain in energy by faceting from (111) to (110) even though the surface area would increase by about 22%.

We now examine Fig. 2 where we show (as the solid lines) the local-density-of-states (LDOS) at the overlayer metal site for Au, Pd, Pt and Ag on Mo(110) (squares) and Mo(111) (triangles) as a function of the overlayer coverage given in the number of physical monolayers. One physical monolayer corresponds to three geometrical layers for (111) and one geometrical layer of (110) (see text). The lines serve as an interpolation between the calculated points.
note that the Herring condition is a thermodynamic condition and, as such, it is a necessary condition. Whether the faceting transformation predicted by the calculations can actually be observed also depends on whether the kinetic barrier of massive atomic transport and a macroscopic change of surface morphology can be overcome. We note that Pd and Pt can drive Mo and W(111) to facet to (112), while Ag cannot [1]. Au can also drive the (111)→(112) transformation but we see here that it cannot drive (111) to facet to (110). In addition, we found that even for Pd and Pt, the systems gain more energy in faceting from (111) to (112) than to (110): (110) has lower surface energy per area than (112) but (112) makes a smaller angle with (111) and thus has a smaller area penalty (only about 6% increase) in the faceting transformation. This is consistent with the recent observation that while (110) facets have been identified on Pd/W(111) after prolonged heating, the majority of the facets seem to be of (112) orientations (C.-H. Nien, T. Madey, private communication). Our results indicate that the extra energy gained by transforming to (112) instead of (110) is less for the case of Pd/Mo than for Pt/Mo. So there should be a better chance of observing (110)-orientated facets on Pd/Mo(111) than Pt/Mo(111).

In summary, we found by first principles calculation that it is thermodynamically possible for Pd/Mo(111) and Pt/Mo(111) to facet to (110). The calculations indicate that the overlayer coverage needed should be about one physical monolayer, and these (110) facets should appear as triangular-based pyramids because of geometrical constraints, and will probably co-exist with a majority of (112) orientated facets of larger sizes. Heating will be required to overcome the various kinetic barriers. It would be interesting to check experimentally if these can actually be observed for Mo.

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References