

FIRST PRINCIPLES TOTAL ENERGY STUDY OF THE MORPHOLOGICAL INSTABILITY OF Mo(111) INDUCED BY ULTRATHIN FILMS OF Rh

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By using first principles total energy calculations, the surface energies of (100), (110), (111) and (211) surfaces of Mo before and after adsorbing ultrathin films of Rh have been presented. The results show that in the case of clean Mo surfaces Mo(111) is stable against faceting to Mo(211), Mo(110) and Mo(100), while after adsorbing one physical monolayer of Rh, the surface energies of all the four surfaces decrease, and Mo(111) can facet to {211}, but not to {110} and {100} surfaces.

1. Introduction

Faceting is the transformation of a planar surface into a hill and valley structure which exposes patches of small facets oriented in directions different from that of the original surface (Fig. 1). Following the changes in morphology and structure of the surface due to faceting, the physical and chemical properties of solid may change accordingly. Recently, experiments have been carried out to study the effect of ultrathin metal overlayers on bcc(111) metal surface.¹ It was observed¹ that atomically rough but stable Mo(111) and W(111) surfaces undergo remarkable reconstruction from a planar morphology to a faceted surface upon annealing to $T \geq 700$ K when they are covered by films of certain metals (Pd, Pt, Au, Rh, Ir) with the thickness greater than one *physical monolayer* (defined as the coverage of the adsorbed atoms needed to cover all the substrate atoms). The faceted morphology comprises mainly three-sided pyramids of {211} facets. Experiments

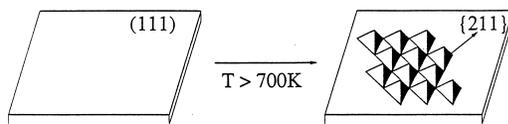


Fig. 1. The faceting of the bcc(111) surface.

show that there seems to be a rather universal critical coverage of approximately one physical monolayer for these metal overlayers induced faceting occurred.

It has been known that all four low index surfaces {111}, {110}, {100} and {211} appear on the Wulff plot of clean Mo² (Fig. 2). In the present work, using first principles total energy calculations, we report the morphology of Mo(111) induced by Rh overlayers, i.e. the possibility of faceting from Rh/Mo(111)

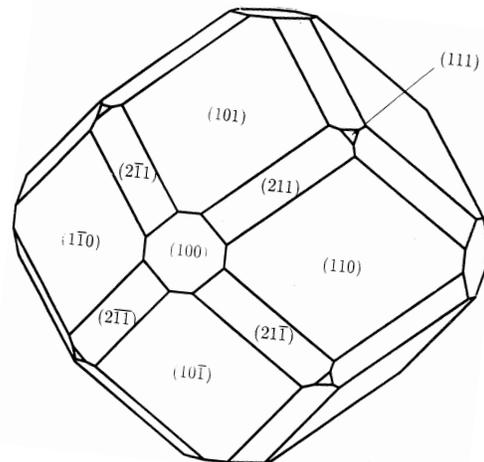


Fig. 2. Wulff plot for clean Mo.

to the other three low index surfaces $\{110\}$, $\{100\}$ and $\{211\}$. We find that after adsorbing one physical monolayer of Rh, the (111) surface can facet to $\{211\}$, but not to $\{110\}$ and $\{100\}$.

2. Method of Calculation

The first principles calculations are carried out within the framework of LDA.³ For Rh/Mo(111) systems, a standard slab model consisting of 11 layers of the bcc Mo substrate and additional pseudomorphic overlayers of adatoms Rh on both sides of the slab is adopted. The separating vacuum region is about 10 Å. The wave functions are expanded in 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.⁴ Norm-conserving pseudopotentials are used.⁵ This approach has been successfully applied to study many transition metal surface problems,⁶ including the overlayer induced faceting of Mo(111) and W(111) surfaces.^{7–9} The \mathbf{k} points are sampled on a uniform grid of not less than 64 points in the surface Brillouin zone. The atomic coordinates are relaxed within a (1×1) surface unit cell by minimizing the Hellmann–Feynman forces. The Broyden algorithm for updating the force matrix is used to predict the atomic coordinates during the relaxation process.¹⁰ The convergence with respect to the screening potential and forces are accelerated by a model based on superposition of atomic charge density.¹¹

3. Results and Discussion

The total surface energy of the bcc(111) surface is given by $\sigma_{111}N$, where σ_{111} is the surface energy per surface unit cell and N is the total number of lattice points on the topmost layer of (111) surface. If the (111) surface facets to another orientation $\mathbf{b} = [hkl]$, the surface energy after faceting is $\sigma_b \frac{A_{111}}{A_b \cos(\theta)} N$; here σ_b is the surface energy per surface unit cell of the \mathbf{b} orientation, A_{111} and A_b are the areas of surface unit cell of the [111] and \mathbf{b} orientation, respectively, and θ is the angle between \mathbf{b} and [111]. The change in surface energy due to faceting from (111) surface to $\{hkl\}$ surface is given by

$$\Delta E = \left(\sigma_b \frac{A_{111}}{A_b \cos(\theta)} - \sigma_{111} \right) N. \quad (1)$$

Faceting from (111) to $[hkl]$ is thermodynamically favorable if $\Delta E < 0$, i.e.

$$\Delta\sigma = \sigma_b \frac{A_{111}}{A_b \cos(\theta)} - \sigma_{111} < 0. \quad (2)$$

These equations are applicable to both the clean Mo surface and those covered by Rh. The surface formation energy of a clean surface per atom (σ) can be determined by $\sigma = \frac{1}{2}(E_{\text{slab}} - nE_{\text{bulk}})$, where E_{slab} is the total energy of the slab and nE_{bulk} is the total cohesive energy of the corresponding substrate atoms in the bulk environment which is determined in a separate calculation. The surface formation energy per surface atom of the combined bimetallic system (A on B) can be defined as

$$\sigma_{A/B} = \frac{1}{2}(E_{A \text{ on } B} - n_B E_{\text{bulk},B} - n_A E_A), \quad (3)$$

where $E_{A \text{ on } B}$ is the total energy of the slab with A adsorbed on B, while $n_A E_A$ is the total energy of the corresponding overlayer A in the bulk environment. σ and $\sigma_{A/B}$ are orientation-dependent and $\sigma_{A/B}$ also depends on the overlayer coverage.

The surface formation energies of Mo before and after adsorption of Rh films in the (100), (110), (111) and (211) orientations are calculated. The results are shown in Fig. 3. For convenience, the coverage is described by the number of physical monolayers. Zero coverage stands for clean substrate surface. The points show the calculated values.

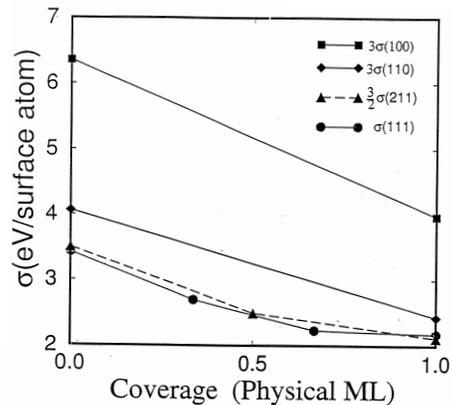


Fig. 3. Surface formation energies per substrate atom for Rh on (100), (110), (211) and (111) surfaces of Mo. The surface formation energies for (100), (110) and (211) are scaled by a geometric factor respectively.

3.1. Possibility of faceting from (111) to {100}

The thermodynamical condition of faceting from (111) to {100} is

$$\Delta\sigma = 3\sigma_{100} - \sigma_{111} < 0. \quad (4)$$

In Fig. 3, the surface formation energies for (100) surface (diamonds) are scaled by a factor of 3. For clean surfaces, σ_{100} , σ_{111} are 2.117 eV and 3.425 eV, respectively. $3\sigma_{100}$ is greater than σ_{111} , as shown in Fig. 3 (coverage = 0). The thermodynamical condition of faceting from (111) to {100} is not satisfied. Therefore, Mo(111) cannot facet to {100}.

After adsorption of Rh, the surface formation energy is lowered for both (111) and (100) orientations (see Fig. 3). When the coverage of Rh reaches one physical monolayer, σ_{100} and σ_{111} become 1.324 eV and 2.177 eV, respectively, and $3\sigma_{100}$ is still greater than σ_{111} . Therefore, Rh/Mo(111) cannot facet to {100} either.

3.2. Possibility of faceting from (111) to {110}

For faceting from (111) to {110}, the thermodynamical condition (2) becomes

$$\Delta\sigma = 3\sigma_{110} - \sigma_{111} < 0. \quad (5)$$

In Fig. 3, the surface formation energies for the (110) surface (squares) are also scaled by a factor of 3. For the clean surface, σ_{110} is 1.354 eV; $3\sigma_{110}$ is also greater than σ_{111} . This means Mo(111) is stable against faceting to {110}.

When the coverage of Rh reaches one physical monolayer, σ_{110} decreases to 0.810 eV, and $3\sigma_{110} > \sigma_{111}$. This means that the surface energy anisotropy of (111) and {110} surfaces is still not big enough to compensate the energy increase due to the area increase induced by faceting from (111) to {110}. Thus, Mo(111) cannot facet to {110} even after the adsorption of one physical monolayer of Rh.

3.3. Possibility of faceting from (111) to {211}

For the faceting from (111) to {211}, The thermodynamical condition (2) becomes

$$\Delta\sigma = \frac{3}{2}\sigma_{211} - \sigma_{111} < 0. \quad (6)$$

In Fig. 3, the surface formation energies for (211) surface (triangles) are scaled by a factor of 3/2. σ_{211} is 2.335 eV with no Rh adsorption. $\frac{3}{2}\sigma_{211}$ is higher than σ_{111} . Therefore Mo(111) cannot facet to {211}.

The surface formation energy of (211) surface is also lowered by adsorption of Rh. From Fig. 3, it can be seen that at one physical monolayer coverage of Rh $\sigma_{211} = 1.411$ eV, and $\frac{3}{2}\sigma_{211}$ becomes lower than σ_{111} . This means that the surface energy anisotropy of (111) and {211} surfaces is big enough to compensate the energy increase due to the area increase induced by faceting from (111) to {211}. That is, the faceting transformation from (111) to {211} orientations is energetically possible after the adsorption of one physical monolayer of Rh. However, the surface energy difference between the {211}-faceted phase and the (111) planar phase is only 0.06 eV. The faceted and unfaceted phases are thus nearly degenerate in energy. Due to thermodynamic effects, the two phases should coexist, i.e. {211} facets will appear and should coexist with (111) planar surface on Rh/Mo(111) when the coverage of Rh reaches one physical monolayer if the faceting is kinetically accessible.

The total energy calculations can only tell us whether a faceting transformation is thermodynamically possible or not. The onset and the limit of such transformations would be governed by kinetics. As discussed in Ref. 7, there is an activation barrier to the nucleation and growth of pyramidal facets, which depends on the surface energy anisotropy and the surface formation energy. The smaller the surface energy anisotropy and the bigger the surface formation energy, the higher the activation barrier. Compared with completely faceted systems⁷ such as Pd/Mo(111), for Rh/Mo, the decrease of the surface formation energy is also substantial, but the surface anisotropy is much smaller. So the activation barrier for the nucleation and growth of {211} pyramidal facets is higher for Rh/Mo(111) than that for Pd/Mo(111). The annealing can increase the mobility of the surface atoms so that the surface phase transition can be kinetically promoted and accomplished. It is natural that the onset annealing temperature of faceting induced by Rh on Mo(111) should be higher than that by Pd in order to overcome the higher activation barrier and make the Mo and Rh atoms transport to form pyramids with {211} facets.

4. Summary

In summary, by using first principles total energy calculations the surface energies of (100), (110), (111) and (211) surfaces of Mo before and after adsorbing ultrathin films of Rh have been calculated. It is found that for clean surfaces, Mo(111) is stable against faceting to the other three low index surfaces {110}, {100} and {211}; all of them, as well as {111}, appear on the Wulff plot. After being covered by Rh, the surface formation energies of all the four surfaces decreased; this means that Rh wets Mo(111), Mo(110), Mo(100) and Mo(211). When the coverage of Rh reaches one physical monolayer, the thermodynamic condition of faceting from (111) to {110} or {100} is still not satisfied, therefore Rh/Mo(111) cannot facet to {110} and {100}; however, the surface energy of the {211}-faceted phase becomes lower than the (111) planar phase, and Rh/Mo(111) can facet to {211}. Due to the small surface energy difference between the {211}-faceted phase and the (111) planar phase, {211} facets should coexist with the (111) planar surface and the onset annealing temperature for Rh to induce {211} facets on Mo(111) should be higher.

Acknowledgments

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