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FIRST PRINCIPLES STUDIES OF OVERLAYER-INDUCED FACETING

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Abstract

Using first principles total energy calculations, we studied the overlayer growth mode and the substrate stability when ultra-thin overlayers of various metals are grown on Mo(111) substrates. In close agreement with experimental results, we found that the growth modes are Stranski-Krastanov, and the overlayers of some metals can induce the substrate to facet. The faceting is basically driven by the enhancement of the surface energy anisotropy due to adsorption, and the interaction with the substrate are stronger for faceting agents than for non-faceting agents. In some cases it is energetically favorable for the substrate to transform to facets of more than one orientation, leading to the possible coexistence of two types of pyramidal facets.

1. Introduction

First principles calculations have made important contributions in understanding the structural, electronic, magnetic, and vibrational properties of surfaces at the atomic scale. On the other hand, the study of surface physics at the "meso" or "macro" scale length are frequently based on the phenomenological approach. The purpose of this article is to review some calculations we have done [1], so as to demonstrate that in some cases, first principles calculations can also provide useful information and insight for problems that involve macroscopic phenomena such as growth and faceting. We will focus on the phenomena of the growth of ultra-thin coating layers of fcc metals on bcc substrates and the subsequently growth-induced faceting of the substrate.

These phenomena have been systematically studied for various metallic overlayers on bcc(111) substrates such as Mo and W [2]. The salient features in these systems are rather generic [2–4]: (1) The clean Mo(111) and W(111) surfaces are stable. (2) Annealing (usually to over 700K) is needed to observe the overlayer induced faceting. (3) The (111) surfaces usually facet to triangular pyramids with [112] orientations. The pyramids are made up of the substrate atoms (Mo or W) coated with a thin wetting layer of overlayer atoms. (4) The growth mode is Stranski-Krastanov. Excess overlayer atoms form 3D islands after the completion of one wetting "physical monolayer". A physical monolayer is defined as the number of geometrical monolayers needed to shadow the exposed substrate atoms. The number of geometrical monolayers contained in a physical monolayer depends on the orientation of the surface and it corresponds to two geometrical monolayers for bcc(112) and three geometrical monolayers for bcc(111). (5) Only some metals like Au, Rh, Pt, Ir, Pd cause faceting. Other metals do not. (6) A critical coverage of approximately one physical monolayer is needed to induce the facet formation.

We will show that these generic features can be understood through a systematic study of these systems via first principles calculations. The theoretical results can also provide new insight into the physics of the problem.

2. Method of Calculation

The first principles calculations are based on the local density formalism [5] and norm conserving scalar-relativistic pseudopotentials [6]. We choose to use a mixed basis-set [7], which consists of Bloch functions constructed from numerical orbitals centered on the atomic sites, augmented by a set of plane waves. These surface systems are modeled by the standard repeated slab geometry. We relax all atomic positions until the system reaches its ground state.

Thermodynamically, the change of the surface formation energy upon the deposition of the overlayer determines the equilibrium growth mode of the overlayer, and the surface energy anisotropy governs the stability of surfaces and is thus relevant for the phenomenon of faceting.

To calculate the surface energy, we first have to determine the atomic positions of the atoms. The surface energy of a clean surface per surface atom, σ, can then be determined by

$$\sigma = \frac{1}{2}(E_{\text{slab}} - nE_{\text{bulk}}), \tag{1}$$

where E_{slab} is the total energy of the slab and nE_{bulk} is the total cohesive energy of the corresponding number of atoms in the bulk environment. The surface energy anisotropy can be determined simply by calculating and comparing the surface energies in the different orientations under consideration.

If the growth is pseudomorphic, the equilibrium growth mode [8] of material A on substrate B can be determined theoretically as follows. We define, for computational purposes, the surface formation energy per surface atom of the combined bimetallic system (A on B) as

$$\sigma_{\mathrm{A/B}} = \frac{1}{2}(E_{\mathrm{AonB}} - n_{\mathrm{B}} E_{\mathrm{bulk,B}}) - E_{\mathrm{A}}, \tag{2}$$

where E_{AonB} is the total energy of the slab with A adsorbed on B, and E_{A} is the reference energy of A (usually taken to be the bulk energy); then the growth mode should be the Volmer-Weber mode (3D island growth) if $\sigma_{\mathrm{A/B}} > \sigma_{\mathrm{B}}$. In that case, the surface formation energy of the combined system (A/B) is higher than that of the clean substrate B. Alternatively, we can also define a heat of formation of A on substrate B as

$$H_{\mathrm{A/B}} = \frac{1}{2}(E_{\mathrm{AonB}} - E_{\mathrm{slab,B}} - 2\mu_{\mathrm{A}}), \tag{3}$$

where $E_{\mathrm{slab,B}}$ is the total energy of the slab with substrate B only, and μ_{A} is the reference chemical potential of A. If the magnitude of the heat of formation of A on B is less than the cohesive energy of A, then A will prefer to bond with A in a bulk environment rather than wetting the substrate B. Growth will proceed with the Volmer-Weber mode. If, however, $\sigma_{\mathrm{A/B}} < \sigma_{\mathrm{B}}$, it is more favorable for A to cover B than to form 3D islands of its own. It is the condition for complete wetting, and A will grow on B in a layer-by-layer mode until the surface energy goes up again. If it takes N ad-layers before the surface formation energy would go up again, the growth mode is Stranski-Krastanov and the substrate should be covered by N overlayers at saturation.

Let us now consider the possible faceting transformation from one orientation $[hkl]$ to another orientation $[h'k'l']$, assuming that facets of equivalent $\{h'k'l'\}$ planes can maintain an average orientation of $[hkl]$. We will use γ and σ to represent the surface energy per unit area and per surface atom respectively. Faceting transformation from $(hkl) \rightarrow \{h'k'l'\}$ is favorable when [10–12]

$$\gamma_{hkl} > \frac{\gamma_{h'k'l'}}{\cos(\theta)}, \tag{4}$$

where $\cos(\theta)$ is the angle between the directions $[hkl]$ and $[h'k'l']$.

It is more convenient to recast this equation in terms of the surface energy per surface atom. Equation (4) then becomes

$$\sigma_{hkl} > \sigma_{h'k'l'} \left(\frac{A_{hkl}}{A_{h'k'l'} \cos(\theta)} \right), \tag{5}$$

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

$$\sigma_{\mathbf{b}}\left(\frac{\delta_{\mathbf{a}}}{\delta_{\mathbf{b}}}\frac{\mathbf{a}\cdot\mathbf{a}}{\mathbf{a}\cdot\mathbf{b}}\right) < \sigma_{\mathbf{a}}\,, \tag{6}$$

where $\mathbf{a} = [hkl]$ and $\mathbf{b} = [h'k'l']$, and $\delta = 1$ or 2 depending on whether $h+k+l$ is even or odd. For example, for the faceting transformation bcc(111) → bcc{112}, Eq. (5) becomes

$$\frac{3}{2}\sigma_{112} < \sigma_{111}\,, \tag{7}$$

while the bcc(111) → bcc{110} transformation is favorable when

$$3\sigma_{110} < \sigma_{111}\,. \tag{8}$$

3. Results

In order to understand the stability of Mo(111) before and after the adsorption of various metallic overlayer, it is instructive to look at the Wulff plot [9] (equilibrium crystal shape) for clean Mo. We will assume that only four low index surfaces, namely {100}, {110}, {111}, and {112} will appear on the Wulff plot. The surface energies of these orientations for Mo are calculated and the Wulff plot for clean Mo is shown in Fig. 1. This corresponds to the equilibrium

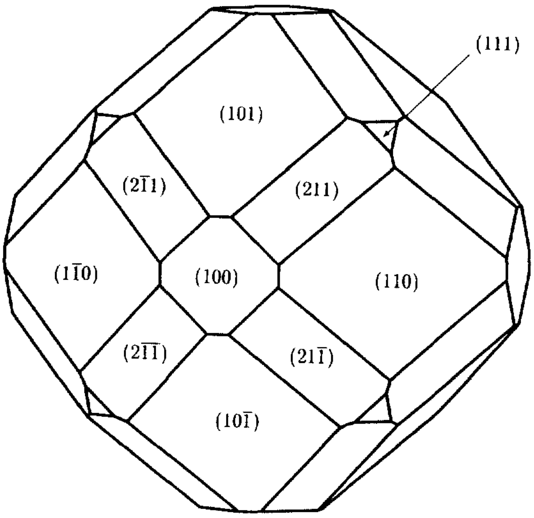

Fig. 1. Wulff plot for Mo.

shape of a Mo crystallite at $T = 0$ under ideal conditions, as determined by a first principles calculation. We note that (111) appears on the Wulff plot, implying that clean (111) should be stable in an ideal environment [13]. However, we can infer from the figure that the area occupied by the {111} facets is small and it is just marginally stable against faceting to {112}. It is then not surprising that the growth of another material on Mo can drive the (111) surface to facet.

We now focus on the faceting transition from (111) to (112). In Fig. 2, we plot $\frac{3}{2}\sigma_{112}$ and σ_{111} vs. coverage for a number of metal overlayers. If the scaled surface formation energy $\frac{3}{2}\sigma_{112}$ is less than σ_{111}, it is energetically favorable for the surface to facet. The adatom coverages are given in the number of physical monolayers, which carry the same density of adatoms on the flat (111) and faceted (112) surfaces.

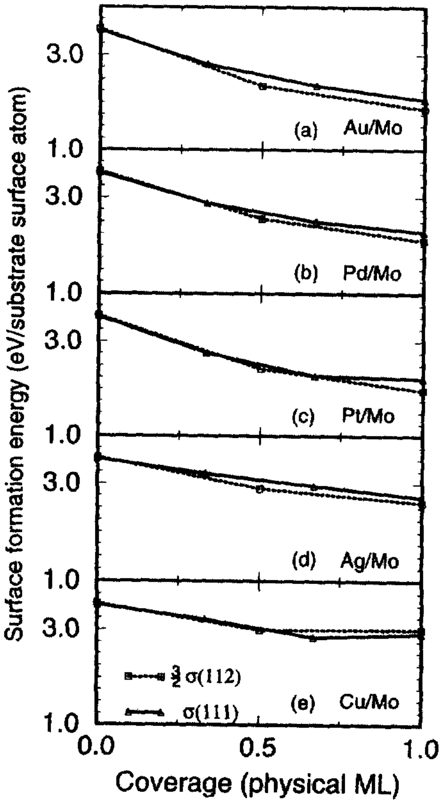

Fig. 2. Scaled surface formation energies per surface atom for Au, Pd, Pt, Ag, and Cu on Mo(111) (triangles) and Mo(112) (squares) as a function of the overlayer coverage given in the number of physical monolayers. The surface formation energies for the [112] orientation are scaled by a factor of 3/2, which takes care of both the difference in the area per surface atom and the increase in total surface area due to faceting.

We will first look at Au (Fig. 2a). We see that the surface formation energy is lowered upon Au adsorption, implying that Au *wets* Mo(111) and Mo(112). The surface formation energy decreases monotonically up to one physical monolayer for both orientations after which the surface formation energy increases. When an additional geometrical monolayer is added, we found that the surface formation energy per surface atom increases for both (111) and (112). This means that the growth mode is Stranski-Krastanov: 3D islands should form after the substrate is covered by one physical monolayer of Au for both (111) and (112), consistent with experimental observations. Pd and Pt (Fig. 2b and c), the other faceting agents, show rather similar behavior. For these elements, the lowering of surface formation energy is substantial, and surface energy anisotropy is much larger than for the clean surface. At one physical monolayer coverage, (112) is clearly lower in energy than (111) even after taking into account of the area increase due to faceting, so that these systems should facet.

Since Mo has relatively high surface energy, it is not surprising that fcc elements (with typically lower surface energy) would wet the surface, although they do not dissolve in the bulk. For orientations like (111) and (112), the interlayer spacing is relatively small, and overlayer atoms that bond strongly with the substrate will try to cover all the exposed substrate atoms, even if they are not on the top layers. After the completion of the physical monolayer, the surface formation energies tend to increase if we force the system to growth in the layer by layer mode. This has a geometrical reason. Take (111) for example: the physical monolayer has three geometrical monolayers, each at a different distance from the surface. Let us label them A, B, and C, where A is closest to the substrate and C is the furthest away. A simple counting exercise shows that A has 4 Mo substrate atoms as nearest neighbors (NN), and 3 Mo atoms as next nearest neighbor (NNN), while B has 1 NN Mo and 3 NNN Mo; and C has 1 NN Mo and no NNN. Any additional ad-atoms are completely shielded from the substrate and will have no Mo atoms as NN or NNN. The overlayer atoms are wetting the Mo substrate to bond with the exposed Mo atoms with high surface energies. The more substrate Mo atoms it sees, the stronger is the cohesion. After the completion of the physical monolayer (i.e., 3 geometrical layers for the (111)), the adsorbing atoms are completely shielded from the substrate and there are no reason for it to form strained layers with a wrong structure.

For non-faceting agents like Ag and Cu, we found that the energetics are different (Fig. 2d and e). Adsorption of Ag and Cu only lowers the surface formation energy of the Mo substrate slightly. This signals weaker overlayer-substrate interaction compared with the faceting agents. For Cu, although the Herring condition is marginally satisfied at half physical monolayer, σ_{111}

at a coverage of 2/3 physical monolayer is lower than $\frac{3}{2}\sigma_{112}$ at any coverage of Cu. There is thus no thermodynamic reason for Cu/Mo(111) to facet when one physical monolayer of Cu is present on the surface, consistent with experimental observation. However, for the case of Ag, $\frac{3}{2}\sigma_{112}$ is slightly lower than σ_{111} at half physical monolayer coverage, although the surface energy anisotropy is smaller than the typical faceting agents. There is a thermodynamic driving force for Ag/Mo(111) to facet. We will explain why Ag does not facet Mo(111) in the following sections.

We found that faceting agents have larger heats of overlayer formation relative to their bulk energies than those that do not. For example, the calculated heats of formation for the first geometric monolayer (1/3 physical monolayer) on Mo(111) for Au, Pd and Pt are found to be −0.71, −0.63 and −0.76 eV per substrate surface atom, respectively, and are higher than the −0.31 and −0.30 eV we found for Ag and Cu. In Fig. 3, we show the local-density-of-state (LDOS) at the fcc metal site for Au, Pd, Pt and Ag on Mo(111) at a coverage of one geometrical

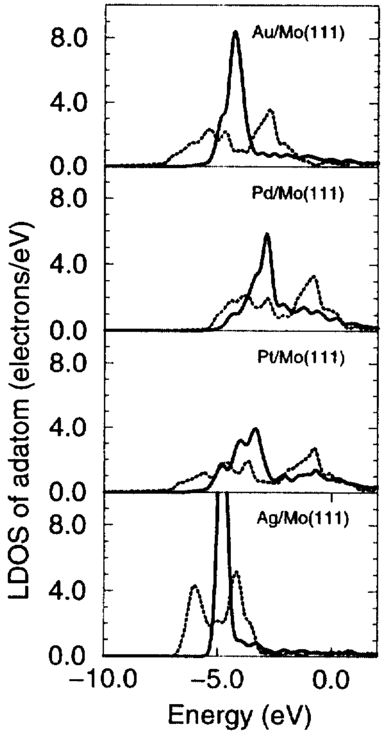

Fig. 3. Local density of states at the fcc overlayer metal site at 1/3 physical monolayer coverage (solid lines). The Fermi energy is at 0 eV. The dotted lines are the bulk DOS for the fcc metals in a bulk bcc environment.

monolayer (1/3 physical monolayer). For comparison, we show in dotted lines the bulk density of states of these overlayer elements in the bcc structure. We see that the non-faceting agent Ag has a relatively small valence band width when it is placed on Mo(111), while the faceting agents like Au, Pd and Pt have wider band widths. Cu (not shown), a non-faceting agent, shows the smallest band width. For the first geometrical monolayer on Mo(111), the ad-atoms are rather far apart so that the ad-atom LDOS basically reflects the interaction between the ad-atom and the Mo substrate. Judging from the heat of formation and from the local density of states, we found that the faceting agents interact stronger with the Mo surface atoms. This causes a more significant lowering in surface formation energy and at the same time enhances the surface energy anisotropy and making the faceting transformation thermodynamically allowed.

The results agree well with the salient features observed in experiments. We will now explain some subtleties such as (i) Why should Ag/Mo(111) be stable although it satisfies the Herring faceting condition? (ii) Why should faceting be strongly correlated with low surface formation energy? (iii) Why should there be a near universal critical coverage of about one physical monolayer in order to induce faceting?

These can be understood intuitively with the following considerations. The thermodynamic (Herring) condition for faceting (4) assumes macroscopically big facets so that boundary effects can be ignored. When the pyramidal facets are small, faceting causes an energy change

$$\Delta E = a(\Delta\gamma)l^2 + b\eta l + C, \tag{9}$$

where

$$\Delta\gamma = \frac{\gamma_{112}}{\cos(\theta)} - \gamma_{111} \tag{10}$$

is the surface energy anisotropy (per unit area), η and C are the energy of the "edges" (per unit length) and "apexes" of the pyramids, l is the length of the base of pyramids, while a and b are dimensionless geometrical constants. The edge and apex energy can be regarded as the extra energies needed to buckle flat {112} facets to form a pyramid and are positive in values. If $\Delta\gamma < 0$, ΔE is necessarily negative for large enough l, but there exists a critical size of the pyramid l_c,

$$l_c = -\frac{b\eta}{2a(\Delta\gamma)}, \tag{11}$$

less than which the energy change is positive (unfavorable) with an energy barrier of

$$B = \frac{b^2}{4a} \frac{\eta^2}{(-\Delta\gamma)} + C. \tag{12}$$

In order to overcome the formation barrier at a reasonable temperature, the barrier B must be small, which means that (i) the surface energy anisotropy $\Delta\gamma$ must be big and negative; and (ii) the line and apex energies η and C must be small. If the capping of the substrate by an overlayer lowers the surface formation energy, it should also lower the edge and the apex energies in a similar manner. Thus, we have a smaller barrier to "nucleate" the pyramidal facets if we have *large* surface energy anisotropy and *low* surface formation energy. We do find large $\Delta\gamma$ and small γ for the faceting agents Au, Pd and Pt, while the non-faceting agents Ag and Cu have smaller $\Delta\gamma$ and large values of γ. We also see from Fig. 2 that $\Delta\gamma$ becomes negative for Au, Pd and Pt *before* the completion of the physical monolayer. However, the value of γ for the faceting agents reaches its minimum on the completion of the physical monolayer, so that the thermodynamic driving force is at its maximum and the barrier is at its minimum at one physical monolayer (γ increases for higher coverages). This behavior provides a plausible explanation for the experimental observation of a nearly universal threshold coverage of approximately one physical monolayer.

For a bcc metal, the (110) surface usually have the lowest surface energy per unit area. Could the (111) surface also facet to {110}? In order to address this issue, we see whether the condition $3\,\sigma_{110} < \sigma_{111}$ is satisfied. The scaled surface energies are compared in Fig. 4 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 σ_{111}. The surface energy per unit area for (110) is quite a bit lower than that of (111), but the (111) → {110} faceting is not energetically favorable because of the large ($\sim 22\%$) increase in total surface area in the faceting transformation. Overlayer adsorption lowers the surface formation energy and increases the surface energy anisotropy. For Pd and Pt, the surface energy anisotropy enhancement caused by the overlayer is large enough that $3\,\sigma_{110} < \sigma_{111}$ is clearly satisfied at the physical monolayer coverage. In other words, Pd/Mo(110) and Pt/Mo(110) has 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 22%. However, even for Pd and Pt, the system gains more energy in faceting from (111) to {112} than to {110} because of the smaller area penalty in the (111) → {112} transformation. Our calculated results for W(111) are qualitatively the same: It is energetically favorable for Pd/W(111) to facet to either {110} or {112}, but {112} gains more energy. This is consistent

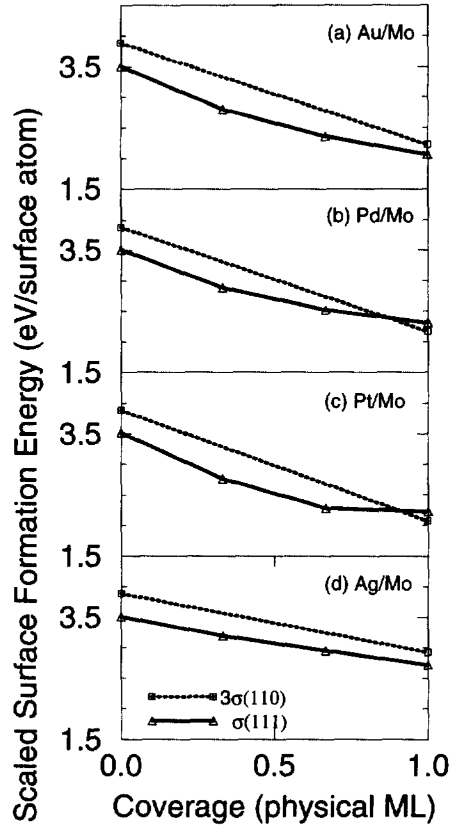

Fig. 4. $3\sigma_{110}$ vs. σ_{111} for various metals on Mo(110) (squares) and Mo(111) (triangles) as a function of the overlayer coverage given in the number of physical monolayers. One physical monolayer corresponds to 3 geometrical layers for (111) and one geometrical layer for (110).

with the observations in recent STM experiments [14] that under certain annealing conditions, triangular-based {110} facets of W covered by a pseudomorphic Pd monolayer are found on Pd/W(111), but these small {110}-faceted pyramids are always co-existing with a majority of much larger pyramids with {112} facets.

When the faceting transformation is concerned, it is customary to focus all the attention on the surface energy anisotropy. Our calculations show that the surface energy anisotropy is a necessary but not sufficient condition for faceting and other factors like low surface formation energy is also as important. This is particularly important here because there is a relatively small temperature range that can be used to drive the transition since the thermodynamic driving force itself disappears at high temperatures.

In summary, we see that the results of a first-principles calculation can give useful information for atomic scale reconstructions as well as large-scale morphological changes such as growth and faceting.

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