Faceting Induced by Ultrathin Metal Films: A First Principles Study

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Using first principles calculations, we studied the overlayer growth mode and the substrate stability when ultrathin layers of various metals are grown on a Mo(111) substrate. We found that the growth mode is Stranski-Krastanov, and the overlayer can induce the substrate to facet, in accordance with recent experimental observations. The growth-induced instability of the substrate towards faceting is driven by the enhancement of the surface energy anisotropy. However, faceting can be forbidden in some cases if the overlayer adsorption does not lower the surface formation energy significantly. [S0031-9007(97)04532-8]

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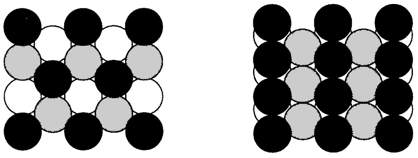
Ultrathin metal films supported on metal substrates can have novel physical and chemical properties that render them useful in applications such as magnetic technology, catalysis, and material science. These novel properties depend on factors such as the overlayer-substrate interaction, the overlayer growth mode, and the substrate morphological change. Recently, some metal overlayers are observed to induce the substrate to facet [1]. Such a flat to hill-and-valley surface reconstruction involves morphological changes in a macroscopic scale, and is quite different from the more familiar atomic scale adatom-induced surface reconstruction [2]. The main objective of this paper is to use first principles calculations to study the overlayer growth and the induced substrate faceting. We focus on various metallic overlayers on bcc (111) substrates, where there exist comprehensive experimental data [1,3,4]. These systems are particularly worth studying since they involve simultaneously the physics of the surfaces, thin films, bimetallic interfaces, and reconstructions in macroscopic length scales. Each of these aspects is interesting in its own right and when combined together, they present a complex and challenging problem that mandates the use of *ab initio* calculations for an accurate description at the atomic level. This is to our knowledge the first attempt using first principles calculations to address directly the problem of overlayer-induced faceting.

When thin metal layers are grown on the (111) surface of bcc metals like Mo and W, the following generic features are observed [1,3,4]: (1) The clean surfaces are stable. (2) Annealing is needed to observe the overlayer-induced faceting. (3) The (111) surfaces 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. The observed faceting is thus a macroscopic morphological change of the substrate induced by the overlayer. (4) Excess overlayer atoms form 3D islands after the completion of one wetting “physical monolayer” (PML), which is defined as the number of geometrical monolayers needed to shadow all the substrate atoms. One PML is two geometrical monolayers for bcc(112) and three geometrical monolayers for bcc(111). (5) Only some metals like Au, Rh, Pt, Ir, and Pd (with Pauling electronegativity >2) cause faceting. Others do not. (6) A critical coverage of approximately one PML is needed to induce the facet formation.

The general phenomenon of faceting has attracted much attention for almost a century [5,6], and the thermodynamic driving force is attributed to the surface energy anisotropy [5–8]. Low index clean metal surfaces seldom facet since the anisotropy is usually small, but stable metal surfaces can facet upon adsorption of O and Cl [9]. Embedded-atom [10] and earlier local-density approximation (LDA) results [11] indicate that metal overlayers can also enhance surface energy anisotropy significantly, although these phenomena are actually rather subtle since isoelectronic metals like Cu, Ag, and Au can behave differently [1].

We seek to understand these observations by first principles calculations. We choose Mo as the substrate, and we consider the energetics of the adsorption and growth of pseudomorphic layers of different fcc metals (Cu, Ag, Au, Pd, Pt) on different orientations of the Mo substrate. The calculations are done using the local density formalism [12] and norm conserving scalar-relativistic pseudopotentials [13]. We employ a mixed basis set [14], which consists of both numerical orbitals centered on the atomic sites, and plane waves with a kinetic energy up to 11.5 Ry. The **k** points are sampled on a uniform grid of not less than 64 points in the surface Brillouin zones. The substrate is represented by a slab of 11 layers of Mo, and the overlayers are added as additional pseudomorphic layers on either side of the slab. The slabs are separated by a distance of 9.5 Å. All atomic positions are fully relaxed.

A schematic top view of bcc(111) and (112) is given in Fig. 1. Since the [112] direction makes the smallest angle with [111], it is natural for the (111) surface to facet to pyramids exposing three equivalent facets of {112} surfaces, provided that {112} has a lower surface energy and that the surface energy anisotropy is big enough to



(111) (112)

FIG. 1. The top view for bcc(111) and bcc(112). Black, grey, and white balls are on the top, second, and third layers, respectively. Physical monolayer (PML) refers to three geometrical layers for (111) and two for (112), respectively.

compensate for the increase in surface area. Faceting from (111) to (112) is thermodynamically favorable when [5]

$$\gamma_{112}/\cos(\theta) - \gamma_{111} < 0\,, \tag{1}$$

where $\theta = 19.47°$ is the angle between the two orientations, and γ is the surface formation energy per unit area. In terms of the surface formation energy per surface atom (σ), the faceting condition is $\Delta\sigma = \frac{3}{2}\sigma_{112} - \sigma_{111} < 0$. The factor of $3/2$ in the above expression takes care of *both* the difference in area per surface atom *and* the increase in total surface area due to faceting. We define a surface formation energy of a substrate B covered by ultrathin layers of A as

$$\sigma_{A/B} = \sigma_B + H\,, \tag{2}$$

where H is the heat of formation of overlayers of A on substrate B (using bulk cohesive energies as references). It is orientation and coverage dependent. Since one physical monolayer carries *exactly* the same number of adsorbate atoms on a flat (111) and a *faceted* (112) surface, $\Delta\sigma$ does not depend on the reference energy of the overlayer A.

We found that for clean Mo, σ_{112} and σ_{111} are 2.36 and 3.51 eV, respectively [15]. Thus, $\frac{3}{2}\sigma_{112}$ is greater than σ_{111}, and the clean substrate is stable as observed experimentally.

We now consider the change when overlayers are added. In Fig. 2, we plot $\frac{3}{2}\sigma_{112}$ and σ_{111} vs coverage for a number of metal overlayers. If $\frac{3}{2}\sigma_{112} < \sigma_{111}$, it is energetically favorable for the surface to facet. The marked points are the calculated values. The surface energy at intermediate coverages will follow the straight lines connecting the calculated points if large and compact (not dendritic) islands are formed. 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.

We will first focus on Au [Fig. 2(a)]. We see that the surface formation energy (SFE) is lowered upon Au adsorption, implying that Au *wets* Mo(111) and Mo(112). The SFE decreases monotonically up to one PML for both orientations after which the SFE increases. When an additional geometrical monolayer is added, the SFE per surface atom increases by 0.2 eV for (111) and 0.05 eV for (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 [Figs. 2(b) and 2(c)], the other faceting agents, show similar behavior. For these elements, the lowering of SFE is substantial, and surface energy anisotropy is much larger than for the clean surface, and most importantly, (112) is now lower in energy than (111) even after taking into account of the area increase due to faceting, so that these systems should facet [16].

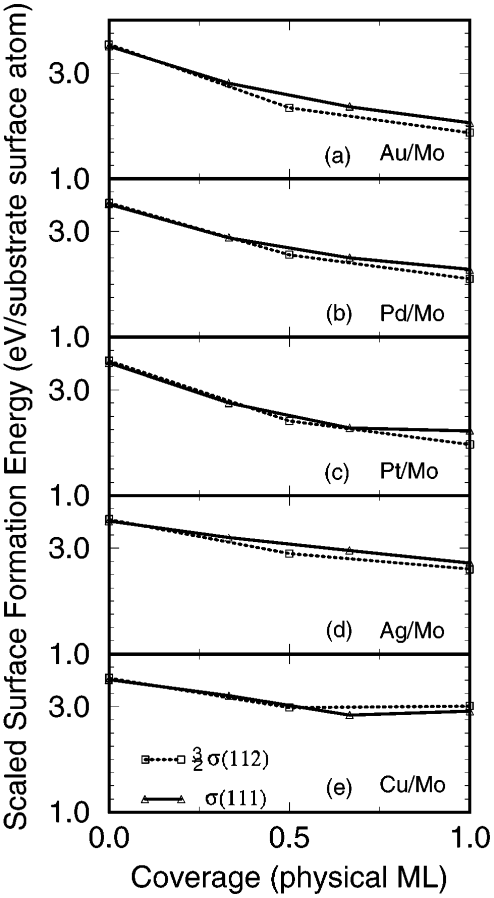


FIG. 2. Surface formation energies per *substrate* surface atom for Au, Pd, Pt, Ag, and Cu on Mo(111) (triangles) and Mo(112) (squares) as a function of the overlayer coverage given in the number of physical monolayers. The surface formation energies for the [112] orientation are scaled by a factor of 3/2.

For nonfaceting agents like Ag and Cu, we found that the energetics are different [Figs. 2(d) and 2(e)]. First, the surface formation energies decrease only slightly initially, and for Cu, it increases again before the completion of the physical monolayer. It means that Ag and Cu also wet Mo, but for Cu, 3D islands may form at a coverage less than one PML for both (111) and (112). This signals weaker overlayer-substrate interaction compared with the faceting agents (if we use the cohesive energy of the overlayer element as reference). Adsorption of Ag and Cu only lowers the surface formation energy of the Mo substrate slightly. For the case of Cu, although the Herring condition [Eq. (1)] is marginally satisfied at half PML, σ_{111} at a coverage of 2/3 PML is lower than $\frac{3}{2}\sigma_{112}$ at any coverage of Cu. There is thus no thermodynamics reason for Cu/Mo(111) to facet. However, for the case of Ag, $\frac{3}{2}\sigma_{112}$ is clearly lower than σ_{111} at half physical monolayer coverage. There is a thermodynamical driving force for Ag/Mo(111) to facet, although the surface energy anisotropy is smaller than the typical faceting agents.

We found that metals that cause faceting have a larger heat of overlayer formation relative to their bulk cohesive energies than those that do not. For example, the calculated heats of formation for the first geometric monolayer (1/3 PML) on Mo(111) for Au, Pd, and Pt are found to be -0.71, -0.63, and -0.76 eV/atom, respectively, and are higher than the -0.31 and -0.30 eV we found for Ag and Cu [17].

These fcc metals wet the Mo surface because Mo has relatively high surface energy, and the exposed Mo surface atoms with half-filled d shells can gain a lot of energy by being covered with overlayers of fcc elements (with typically much lower surface energy). The first geometrical monolayer, which has the maximum number of Mo substrate atoms as neighbors, has the most negative (favorable) heat of formation; while the energy of second and third geometrical layers becomes progressively less favorable as they are increasingly shielded from the substrate by other adatoms. Upon the completion of the PML, which is three geometrical monolayers for (111), additional overlayer atoms will not have any Mo atoms either as nearest or next nearest neighbors. It is then more favorable for these additional atoms to form 3D islands than to form overlayers at a wrong structure and at an unfavorable lattice constant. The d states of Ag and Cu are more corelike than those of Pt, Pd, and Au, and as a consequence, they tend to bond weaker with Mo and their adsorption causes a smaller drop in SFE than the faceting agents. Cu switches to 3D-island formation before the completion of the PML because of the weaker adatom-substrate interaction, and large overlayer strain (atomic volume of Cu is 25% smaller than Mo).

The (112) surface is more compact and has less broken surface bonds than (111), so that γ_{112} is generally lower than γ_{111}. However, clean Mo(111) is stable as the anisotropy is too small for the clean surface to compensate for the increase in area upon faceting. Upon overlayer adsorption, the heat of formation includes both adatom-substrate and adatom-adatom interaction, and the interaction is more favorable for overlayer atoms on (112) than on (111) again because (112) is more compact. The more negative heat of formation of the adsorbed overlayers on (112) lowers the SFE of (112) further relative to (111), increasing the surface energy anisotropy to the extent that the Herring condition may be satisfied, and this provides the thermodynamic driving force for faceting. The elements that have larger heats of formation are quite naturally stronger faceting agents.

The results agree well with the salient features observed in experiments. The questions remaining are: (i) Why should Ag/Mo(111) be stable, although it also satisfies the Herring faceting condition? (ii) Why should faceting be strongly correlated with low surface formation energy although thermodynamics states that it is only the anisotropy that matters?

These can be understood intuitively with the following considerations. The thermodynamic (Herring) condition for faceting [Eq. (1)] assumes macroscopically big facets so that boundary effects can be ignored. When the pyramidal facets are small, faceting causes an energy change: $\Delta E = a(\Delta\gamma)l^2 + b\eta l + C$, where $\Delta\gamma = \gamma_{112}/\cos(\theta) - \gamma_{111}$ is the surface energy anisotropy (per unit area), η and C are, respectively, the energy of the "edges" (per unit length) and "apexes" of the pyramids, l is the length of the base of pyramids, and a, 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 $l_c = \frac{-b\eta}{2a(\Delta\gamma)}$ less than which the energy change is positive (unfavorable) with an energy barrier of $B = \frac{b^2}{4a}\frac{\eta^2}{(-\Delta\gamma)} + C$. In order to overcome the formation barrier at a reasonable temperature, B must be small, which means that (i) $\Delta\gamma$ must be big (and negative), and (ii) η and C must be small. While it is impractical to calculate η and C by first principles calculations, we expect that a lower surface formation energy should imply lower edge and apex energies. The surface formation energies, the edge, and the apex energies may all be viewed as defect formation energies due to the truncation of the bulk in different manners. 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 nonfaceting agents Ag and Cu have smaller $\Delta\gamma$ and larger values of γ [18]. 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 is at its minimum on the completion of the PML, so that the thermodynamic driving force is at its maximum and the barrier is at its minimum at one PML. This behavior underlies the experimental observation of an universal threshold coverage of approximately one physical monolayer.

One may argue that these bigger barriers can be overcome by just annealing to higher temperatures. This is not viable for two reasons. First, these overlayers desorb at higher temperatures [1,3,4]. Second, the surface energy anisotropy, which is the thermodynamic driving force, generally decreases with increasing temperature [19]. Although $\Delta\gamma = \gamma_{112}/\cos(\theta) - \gamma_{111} < 0$ at $T = 0$, it can become positive as γ_{112} approaches γ_{111} as temperature rises. In that case, even a faceted surface can "defacet" and becomes flat again below the onset temperature for desorption. Such phenomena have been observed recently by Song *et al.* [3].

In summary, we found that faceting agents wet the substrate with one physical monolayer, while for nonfaceting agents, 3D islands may form before the completion of the PML. Our results highlight the significant qualitative difference in adsorption energetics between faceting agents and nonfaceting agents. It is customary to focus all the attention on the surface energy anisotropy. Faceting agents like Pt, Pd, and Au do induce significant anisotropy in the surface energy. Experimentally, elements like Ag and Cu do not facet bcc(111) substrates. It does not necessarily mean that the thermodynamics condition is not satisfied, but rather that the surface formation energy is not low enough and faceting is probably forbidden by kinetics. This shows 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.

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[15] $\sigma = \frac{1}{2}(E_{\mathrm{slab}} - nE_{\mathrm{bulk}})$, where E_{slab} is the total energy of the slab and nE_{bulk} is the total energy of the corresponding number of atoms in the bulk. With 64 k points and 11-layer slabs σ_{112} and σ_{112} are 2.363 and 3.512 eV, respectively. Changing to 100 k points and 13-layer slabs, the numbers become 2.377 and 3.517 eV. Our main conclusions actually do not demand very high accuracy on surface energy calculations, since adsorption generally carries fairly large heat of formation and also enhances surface energy anisotropy. Thus our Fig. 2 can be presented in a large energy scale.

[16] For the case of Au, there is some controversy. References [1,4] found that it facets Mo(111), while Ref. [3] found that Au facets vicinal Mo(111) surface.

[17] If we want to compare with experimentally measured heats of adsorption, one should use the atomic energies of the overlayer atoms as reference.

[18] The γ here is defined in the same way as in Eq. (2), except that it refers to surface formation energy per unit area.

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