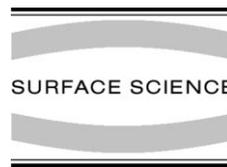




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A first principles study of Rh on Mo(1 1 1) and W(1 1 1) surfaces

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Abstract

Using local density functional calculations, we studied the morphological changes of Mo(1 1 1) and W(1 1 1) upon the adsorption of an ultrathin film of Rh. The unusual relaxations induced by Rh on Mo(1 1 1) and W(1 1 1) surfaces should be caused by competing several factors such as Smoluchowski smoothing effect, change of atomic interactions, and charge transfer between overlayer and substrate. It was found that both Rh/Mo(1 1 1) and Rh/W(1 1 1) can facet to {2 1 1} when the Rh coverage reaches one physical monolayer. The {2 1 1} facets should coexist with the (1 1 1) planar surfaces, which is substantially due to thermodynamic effects, and the onset annealing temperature for inducing facets of Rh/Mo(1 1 1) and Rh/W(1 1 1) should be higher than that for some other metal overlayers such as Pd. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Faceting; Density functional calculations; Growth; Metallic films; Surface thermodynamics (including phase transitions)

1. Introduction

Recently, faceting phenomena induced by ultrathin metal films on metal substrates have attracted much attention due to their novel physical and chemical properties [1–10]. For a better understanding of these bimetallic systems, and for exploring new materials for various applications, experiments have been carried out to study the interaction of ultrathin metal overlayers on

bcc(1 1 1) metal surfaces [1–10]. It was observed [1,2] that atomically rough Mo(1 1 1) and W(1 1 1) surfaces undergo massive 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 a thickness greater than one *physical monolayer* (defined as the number of geometrical monolayers needed to shadow all the substrate atoms). The faceted morphology comprises three-sided pyramids having {2 1 1} facets. It was found by experiments that only some metals can facet bcc(1 1 1), and there exists a rather universal critical coverage of approximately one physical monolayer for faceting induced by these metal overlayers to occur.

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These rather interesting phenomena have been addressed by several theoretical works [11–14]. Chen [11] has used the embedded atom method to study the faceting of the W(111) surface induced by Pd, Pt, Au and Mo. It was found that the surface energy anisotropy of (211) and (111) surfaces of bcc W increased as one or a few monolayers of Pd, Pt, Au and Mo films were deposited and the faceting of W(111) was attributed to the surface energy anisotropy enhanced by metal overlayers. Recently, the behaviors of Au, Ag, Cu, Pt and Pd on substrate Mo(111) have been examined by Che and coworkers [12,13] using first principles calculations. It was found that the surface energy anisotropy was a necessary but not a sufficient condition for faceting, the kinetic factor was also important. It was suggested that there exists an activation barrier to the nucleation and growth of pyramidal facets, which is related to both the surface energy anisotropy and the surface formation energy. Their results can explain the salient features of the experimental observations rather well.

In present work, we extend our systematic studies to Rh/Mo(111) and Rh/W(111) surfaces. Experiments [1,2] show that Rh is also active in inducing Mo(111) and W(111) to facet to {211}. Faceting induced by Rh on Mo(111) and on W(111) have the general features as mentioned above. However, comparing with Au, Pt, Pd overlayers, which result in a completely faceted surface, Rh induces {211} facets which coexist with the (111) planar surface both on Mo(111) and on W(111) [1,2,15]. Whether these anomalous features are primarily kinetic or thermodynamic effects remains still unclear [1,2]. In addition, the onset annealing temperature for Rh to induce faceting on Mo(111) and on W(111) is also higher than for other metals such as Pd [15]. Only annealing to 700 K the substrate surfaces show an obviously faceted LEED patterns for the overlayer Pd, whereas, the annealing temperature needed to induce faceting for overlayer Rh at one physical monolayer coverage is about 900 K [15]. We show in the following the coexistence of the faceting phase and the planar phase for Rh on Mo(111) is substantially due to thermodynamic effects and explain why the higher annealing tem-

perature to induce faceting of Rh/Mo(111) is needed.

2. Methods

The present work was done using total energy calculations within the framework of the local density functional formalism [16,17] together with the norm conserving pseudopotentials [18]. The wave functions were expanded in a mixed-basis set of plane waves with kinetic energy up to 11.5 Ry and Bloch sums of numerical orbitals which are centered at the atomic sites [19,20] and whose shape are chosen to optimize the total energy. This approach has been successfully applied to study many transition metal surfaces [21] and the overlayer induced faceting of Mo(111) and W(111) surfaces [12–14]. It has given good descriptions for the bulk (lattice constants and bulk module) and clean surface properties of molybdenum as well as tungsten. It gives the lattice constant of 3.14, 3.14 and 3.79 Å and the bulk modular of 2.7, 3.2 and 2.9 Mbar for molybdenum, tungsten and rhodium, respectively. The corresponding experimental values read 3.15, 3.16, 3.80 Å, and 2.73, 3.23, 2.704 Mbar.

A standard slab model consisting of 11 layers of the bcc substrate (Mo or W) and additional pseudomorphic overlayers of adatoms on both sides of the slab is adopted. The separating vacuum is about 10 Å. In our calculations the \mathbf{k} points are sampled on a uniform grid of 64 points in the surface Brillouin zones (SBZ) for different orientations considered in this work. To test its convergence, we calculated the surface energy (for its definition see Section 3.2) and the structure of one monolayer of Rh on the Mo(111) and Mo(211) substrate using 100 \mathbf{k} -points in SBZ. The results show that the change of the surface energy is smaller than 0.002 and 0.03 eV for the (111) and (211) orientation, respectively. The difference of layer relaxations given in the percentage change of unrelaxed interlayer spacing is smaller than 0.5% for the (211) orientation, while it is unchanged for the (111) orientation. We changed the energy cut off to 13.5 Ry for the adsorption of one ML Rh on Mo(111) with the equilibrium structure which was

obtained by 11.5 eV energy cutoff. The changes of the surface energy and the forces on atoms are smaller than 0.003 eV and 0.002 eV/Å. To test the effects of the thickness of slabs, we calculated the surface energy of the slab with 13 layers of the substrate and with and without two additional Rh overlayers on each side of the slab for the (1 1 1) and (2 1 1) orientation. For the clean Mo(1 1 1) and Mo(2 1 1) surface, the results show that the slab with 11 layers were found to be adequate to give surface energy and forces on atoms that converged to within 0.02 eV and 0.03 eV/Å. For one monolayer of Rh on Mo in the (1 1 1) and (2 1 1) orientation with 13 layers as the substrate, we found that the change of surface energy is 0.02 eV for both orientations. The maximum difference of the percentage change of the unrelaxed interlayer spacing is 1% and 0.5% for the (1 1 1) and (2 1 1) orientation, respectively. Therefore, we conclude that the slab thickness with 11 layers as substrate and 64 **k**-points in BZ is acceptable within 0.03 eV for surface energy, and gives the layer relaxations expressed in the percentage change of the unrelaxed interlayer spacing that converged to within 1% and 0.5% for the (1 1 1) and (2 1 1) orientation, respectively.

In our calculations the atomic coordinates are fully relaxed within a (1 × 1) surface unit cell by computing the Hellmann–Feynman forces. The 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 model based on the superposition of atomic charge density [22].

3. Results and discussion

3.1. Atomic structures

The top views of the (1 1 1) and the (2 1 1) surfaces of a bcc crystal are shown in Fig. 1. It is clear that one physical monolayer is three geometrical monolayers for bcc(1 1 1) and two geometrical monolayers for bcc(2 1 1). The calculated atomic structures of the clean Mo and W surface as well as of the adsorption of Rh atoms on Mo and W

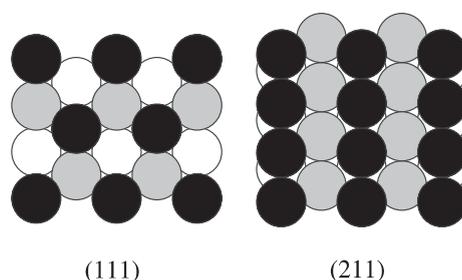


Fig. 1. The top view for bcc(1 1 1) and bcc(2 1 1) surfaces. Atoms in the first, second, and third layers are represented by black, gray, and white circles, respectively.

substrate in the percentage change of interlayer spacing, Δ_{ij} , are listed in Table 1 where Rh₁/Mo(1 1 1), Rh₂/Mo(1 1 1), ..., Rh₂/W(2 1 1) represent one, two ML Rh on Mo(1 1 1), ..., two ML Rh on W(2 1 1). For the adsorbate systems, the rhodium adlayers are placed at the extended structure of the substrates. All atoms are fully relaxed in the 1 × 1 unit cell along the calculated forces until the remaining forces are all smaller than 0.03 eV/Å. Due to the symmetric constraint of the considered 1 × 1 unit cell, the atoms on the (1 1 1) surfaces have relaxations only along the surface normal (*z* direction), and the atoms on the (2 1 1) surfaces have an additional degree of freedom to relax along the $[\bar{1} 1 1]$ direction.

The relaxation pattern of the clean and adsorbate-covered W surfaces is very similar to that of the Mo surfaces, which is expected since tungsten is isoelectronic with molybdenum. Therefore, we focus here on the clean and adsorbate-covered Mo surfaces. The relaxation of the clean and adsorbate-covered Mo surfaces in the (2 1 1) orientation has the generic features, that is, the first interlayer spacing of the Mo(2 1 1) clean surface shows dominant contraction, which can be explained using a Smoluchowski smoothing picture [23,24], while the relaxation of the deeper layer is rather small. Upon adsorption of Rh atoms de-relaxation is expected.

In contrast to that in the (2 1 1) orientation, the clean and adsorbate-covered Mo surfaces in the (1 1 1) orientation show complicated relaxations. The clean Mo(1 1 1) surface exhibits substantial relaxation up to the third layer. The rather complex multilayer relaxations of Mo(1 1 1) upon Rh atoms

Table 1

Layer relaxation (Δ_{ij}) expressed as the percentage change of the interlayer spacing between the i th and j th layers relative to the unrelaxed interlayer spacing where “-” represents contraction and “+” represents expansion of interlayer spacing

System	Δ_{12}	Δ_{23}	Δ_{34}	Δ_{45}	Δ_{56}	Δ_{67}	Δ_{78}	Δ_{89}
Mo(111)	-22	-22	12	-1	3			
Rh ₁ /Mo(111)	-26	-9	9	-14	8	1		
Rh ₂ /Mo(111)	14	-71	38	7	-11	5	-0.3	
Rh ₃ /Mo(111)	-57	20	-4	-20	16	-4	4	-4
W(111)	-23	-24	17	-5	4			
Rh ₁ /W(111)	-25	-8	4	-8	5	1		
Rh ₂ /W(111)	13	-64	29	5	-9	5	0	
Rh ₃ /W(111)	-36	18	-25	-1	10	-5	3	-1
Mo(211)	-19.5	3.0	-0.7	3.7	-2.0			
Rh ₁ /Mo(211)	-20.8	10.0	-7.9	7.2	-2.0	0.2		
Rh ₂ /Mo(211)	-11.8	-4.3	3.1	0.8	-0.1	-0.1	0.2	
W(211)	-15.9	2.0	-0.3	2.3	-1.1			
Rh ₁ /W(211)	-21.3	7.4	-4.8	5.0	-1.1	0.1		
Rh ₂ /W(211)	-5.3	-13.0	6.7	-0.8	1.6	-0.3	0.1	

adsorption have been also found. These complicated relaxations on the clean and adsorbate-covered Mo(111) surfaces might be substantially resulted by competition of the following factors.

When a surface is created by cutting a perfect crystal, the electronic density will relax to search its ground state. In order to reduce its kinetic energy, electronic density becomes smoother. The difference between the unrelaxed and relaxed densities causes an additional potential to give an inward force on surface nuclei. It is the so-called Smoluchowski smoothing effect [23,24]. Obviously this smoothing effect will be much pronounced for an open surface such as the bcc(111) surface, because the layer distance of an open surface is small compared to that of a close-packed surface, so that this effect cannot be completely screened within the top layer. On the other hand, the surface relaxation is dominated also by d electrons due to the short-range screening effects of localized the d electrons. Pettifor pointed out that a perfect crystal of a transition metal is balanced by the attractive force of d bonds against the repulsive force of the sp electrons [25]. Thus, at the surface the sp electrons can escape into vacuum so that the d electrons exert an inward force on the surface atoms. The largest inward force has been found for a half full d band, and the smallest for the empty or completely full d band, which is well known as the parabolic be-

havior. Hence if the surface Mo atom ($5s^14d^5$) is replaced by the Rh atom ($5s^14d^8$), this effect will be more complicated due to the difference in filling d bands. Furthermore, we take the neighbor distribution of surface atoms into account. The bcc(111) surface is the roughest surface among low-index surfaces of a bcc crystal. The surface atom has three nearest neighbors (NN) in the second layer, one NN in the fourth layer, and three next-nearest neighbors (NNN) in the third layer. It is worth noting that an atom in a bcc crystal has eight NN at a distance of $(\sqrt{3}/2)a$ and six NNN at a distance of a , where a is the lattice constant. This fact make it difficult to analyze the effects of d bonds on the relaxation. In addition, rhodium atoms energetically favor an fcc structure. We have found that the difference of energy between the equilibrium fcc structure and the bcc structure is about 0.35 eV/atom, and the equilibrium volume of rhodium in the bcc structure is about 10% smaller than that of bcc molybdenum. Rhodium atoms are thus imposed to an artificial bcc structure with the lattice constant of molybdenum. Moreover, the electrons transfer between the overlayer and the substrate will lead to an additional surface (interface) dipole and thus to an additional forces on surface atoms. These factors contribute together to the anomalous relaxation for Rh adsorbate on the Mo(111) substrate.

Now we consider these effects on the case of one ML Rh on Mo(111), which shows the unusual relaxations in both known and unexpected ways. In this case we deal with the adsorbate Rh layer as the substitute for the surface Mo layer, in order to compare with the relaxations of the clean Mo(111) surface. It can be found in Table 1 that the changes of the second and third interlayer spacing reduce. It means when the surface Mo atom is substituted by the Rh atom, the Smoluchowski smoothing effect and the short-range screening effects of the d electrons weaken as expected due to different filling in the d bonds. The contraction of the first interlayer spacing increases as expected, which can be understood as the results of the additional surface dipole due to the charge transfer induced by substituting Rh for Mo. It is unexpected that the contraction of the fourth interlayer spacing increases from -1% of Mo(111) to -14% of Rh₁/Mo(111). To illustrate this unusual contraction, we give the layer displacements of the top five layers of Rh₁/Mo(111), -0.29 , -0.06 , 0.03 , -0.06 and 0.07 Å, compared with the corresponding values of Mo(111), -0.26 , -0.07 , 0.13 , 0.03 and 0.03 Å. Comparing with Mo(111), both the third and fourth layers as a whole move about 0.1 Å inward and the fifth layer about 0.04 Å outward after adsorption of one ML Rh on Mo(111). It should be contributed by the change of the interactions between the two layers and other layers, (keep in mind that the top surface atom has the nearest neighbor even in the fourth layer for the bcc(111) surface), and it leads thus to charge transfer between these layers. We found that both the fourth and fifth layers gain about 0.1 electron. This kind of fluctuation of charge density imposes the ions moving to minimize the electron–ion interaction energy. The competing and delicate balancing the above mentioned factors may result the much more complicated multilayer relaxations found for two and three ML Rh on the Mo(111) substrate.

3.2. Surface energies

It was experimentally found that some metals on Mo(111) and W(111) can induce faceting to the {211} orientation. Since the (211) direction

makes a small angle of 19.47° with (111), it is natural for the (111) surface to facet to pyramids exposing three equivalent facets of {211} surfaces. The necessary condition is that {211} has a lower surface energy when the pyramids are formed. In addition, the surface energy anisotropy must be big enough to compensate for the increase of surface areas. Thus, faceting from (111) to (211) is thermodynamically favorable when the condition

$$\Delta\sigma = \frac{3}{2}\sigma_{211} - \sigma_{111} < 0 \quad (1)$$

is satisfied [26,27]. 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 number of 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

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

where $E_{A \text{ on } B}$ is the total energy of the slab with A adsorbed on B, and $n_A E_A$ is the total energy of the corresponding number of overlayer A in the bulk environment. σ and $\sigma_{A/B}$ are both orientation dependent and $\sigma_{A/B}$ also depends on the coverage of overlayer. Since one physical monolayer carries *exactly* the same number of adsorbate atoms on a flat (111) and faceted (211) surface, $\Delta\sigma$ does not depend on the reference energy of the overlayer A.

We calculated the surface formation energies of both Mo and W before and after adsorption of Rh films in the (111) and (211) orientations. σ_{111} (squares) and $\frac{3}{2}\sigma_{211}$ (circles) as a function of coverage for Rh/Mo and Rh/W are plotted in Fig. 2. For convenience, the coverage is described in the number of physical monolayers. Zero coverage stands for the clean substrate surface. The marked points are the calculated values.

It was found that for clean Mo the surface energies σ_{211} and σ_{111} are 2.34 and 3.43 eV, respectively. Thus $\frac{3}{2}\sigma_{211}$ is greater than σ_{111} , as shown in Fig. 2(a). The faceting condition, Eq. (1), is not satisfied, the clean substrate is therefore stable as observed experimentally.

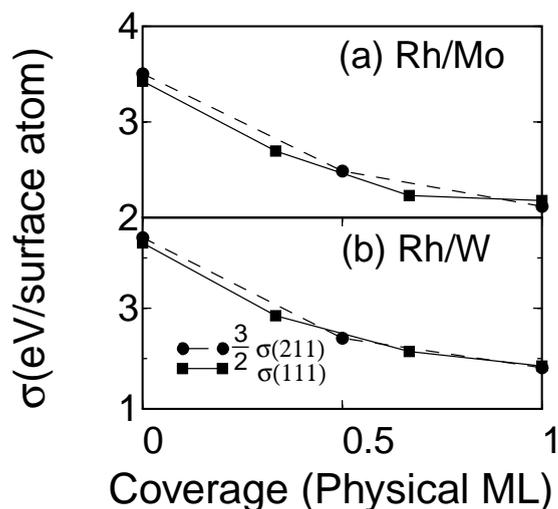


Fig. 2. Surface formation energies per substrate surface atom for Rh on (111) surface and (211) surface of Mo and W. The surface formation energies for the [211] orientation are scaled by a factor of 3/2.

After the adsorption of Rh it can be seen from Fig. 2(a) that the surface formation energy is lowered for both (111) and (211) orientations upon Rh adsorption. At one physical monolayer coverage of Rh on Mo(211) and Mo(111), we got the surface energy of 1.41 and 2.18 eV, respectively. More importantly, $\frac{3}{2}\sigma_{211}$ is now lower in energy than σ_{111} . After scaling by a factor of 3/2 (to take into account of surface area difference between (211) and (111)), the scaled surface energy difference between the {211}-faceted phase and (111) planar phase, see Eq. (1), is only -0.07 eV. This means that the system can gain energy by faceting from (111) to {211} even after taking the area increase due to faceting into account. That is, the faceting transformation from (111) to {211} orientations is energetically possible after the adsorption of one physical monolayer of Rh. However, comparing with the completely faceted case [12], e.g. the scaled surface energy difference for Pd/Mo is -0.19 eV, this difference for Rh/Mo is very small and almost degenerate. Therefore, for Rh/Mo(111), though faceting from (111) to {211} is energetically possible, the {211} facets may coexist with (111) planar surface. Furthermore, this means that this coexistence is mainly a thermodynamics effect.

The coexistence phenomena of two different surface structure phases have also been observed in other systems [28,29]. It was observed [28] that heating a completely {211}-faceted sample of Pd/Mo(111) to a temperature above 840 K caused a reversible faceted/planar phase transition. During the reversible faceted/planar phase transition, there always exists a temperature region at which the {211}-faceted phase coexists with the (111) plane phase no matter whether the phase transition is from the faceted phase to the planar phase upon heating or from the plane phase to the faceted phase by cooling. The reversible faceted/planar phase transition and the coexistence of the {211}-faceted phase with the (111) planar phase of Pd/Mo(111) may be attributed to the surface energy anisotropy change of the two phases with temperature. As the temperature increases, it is generally expected [30] that the surface energy anisotropy will be reduced. If this anisotropy is reduced sufficiently, the free energy balance will turn the other way round to favor the planar form and a faceted/planar phase transition occurs. On the other hand, as the temperature returns to a lower temperature, the surface energy anisotropy will increase again and the planar/faceted phase transition can occur. The facet formation speed is apparently very high. Experiment [28] shows that in the reversible faceted/planar phase transition thermal cycle of Pd/Mo(111), the high temperature planar phase of the sample has never been frozen even with very high cooling rate. Once the sample temperature dropped below 700 K, the surface always became completely faceted. The coexistence of {211}-faceted phase with (111) planar phase on Pd/Mo(111) should be also attributed to the smaller surface free energy anisotropy of the (211) and the (111) orientations at a higher temperature. It means that this phenomenon is also a kind of thermodynamic equilibrium.

The surface energy calculations can only tell whether a faceting transformation is thermodynamically favorable or not. The onset and the limit of such transformations should be governed by kinetics. As discussed previously [12], there must be an activation barrier to the nucleation and growth of pyramidal facets: which depends on the surface energy anisotropy (per unit area), $\Delta\gamma$, the

energy of edges (per unit length), η , and the energy of apexes of the pyramids, C . We have

$$B = -\frac{b^2}{4a} \frac{\eta^2}{\Delta\gamma} + C, \quad (3)$$

where a and b are dimensionless geometrical constants. If the capping of the substrate by an overlayer lowers the surface formation energy, it should also lower the edge and the apex energy in a similar manner. Thus, the smaller the surface energy anisotropy and the bigger the surface formation energy, the higher will be the activation barrier [12]. Comparing with completely faceted systems [12] such as Pd/Mo(1 1 1), the lowering of the surface formation energy for Rh/Mo is also substantial, but the surface anisotropy is much smaller. Therefore, it is expected that the activation barrier to the nucleation and growth of {2 1 1} pyramidal facets is higher for Rh/Mo(1 1 1) than that for Pd/Mo(1 1 1) [12]. The purpose of annealing is to increase the mobility of surface atoms so that the surface phase transition can be kinetically promoted and accomplished. It is not surprising that in order to overcome the higher activation barrier the onset annealing temperature of faceting induced by Rh on Mo(1 1 1) should be higher than that by Pd. The faceting of Pd/W(1 1 1) to {110} can also be explained in a similar way [14]. The surface energy difference between the {110}-faceted phase and the (1 1 1) planar phase is much smaller than that between the {2 1 1}-faceted phase and the (1 1 1) planar phase for Pd/W, and the annealing temperature to initiate faceting is found to be higher for {110} facets than for {2 1 1} facets.

For the clean W surfaces, σ_{211} and σ_{111} are 2.94 and 4.30 eV, respectively. Similar to the case of Mo(1 1 1), $\frac{3}{2}\sigma_{211}$ is also greater than σ_{111} for the clean W surface, so the clean substrate W(1 1 1) is stable.

From Fig. 2(b), it can be seen that the behavior of Rh on the W(1 1 1) substrate is quite similar to the case of Mo(1 1 1). At the coverage of one physical monolayer of Rh on W(2 1 1) and W(1 1 1), σ_{211} and σ_{111} are 1.21 and 1.85 eV, respectively. $\frac{3}{2}\sigma_{211}$ is also lower than σ_{111} , but the surface energy difference is only -0.04 eV. The faceted and unfaceted phases are thus nearly de-

generate in energy within the accuracy of our calculations. Just as the case of Rh/Mo(1 1 1), it is expected that the {2 1 1} facets should coexist with the (1 1 1) planar surface for the Rh/W(1 1 1), and the annealing temperature should be also high.

In summary, using local density functional calculations we studied in this work the faceting induced by Rh on Mo(1 1 1) and W(1 1 1) surfaces. It was found that the complicated multi-layer relaxation induced by Rh on Mo(1 1 1) and W(1 1 1) surfaces should be caused by competing and delicate balancing several factors such as the Smoluchowski smoothing effect, change of atomic interactions, and charge transfer between overlayer and substrate. It is found from the present work that the surface formation energies of both Mo and W in (1 1 1) and (2 1 1) orientations are lowered upon the adsorption of Rh, and the {2 1 1} surface energies are lower than (or almost equal to) that of the (1 1 1) surface at one physical monolayer coverage. The scaling surface energy difference of the two orientations is very small, which might be the reason why the {2 1 1} facets induced by Rh on Mo(1 1 1) and on W(1 1 1) can be found to coexist with (1 1 1) planar surfaces. Moreover it means also that the coexistence of the faceting phase and the planar phase for Rh on Mo(1 1 1) is substantially thermodynamic effects. The onset annealing temperatures are also found to be higher than other adsorbed systems. The effect of Rh on the structure of W(1 1 1) is almost the same as that of Rh on Mo(1 1 1), since both Mo and W have the similar geometric and electronic structure. From LEED experiments [31], it is suggested that the Rh covered W(2 1 1) surface undergoes some kind of reconstruction upon annealing, although the detailed atomic structure have not been characterized. However, these reconstructions cannot be considered in the present calculation due to the large unit cell involved. Whether the reconstructions of Rh/W(2 1 1) may change the picture is a topic for future investigation.

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