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Relaxation of the Mo(112) and W(112) surfaces

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Abstract. Relaxation of the Mo(112) and W(112) surfaces has been simulated within DFT in local density approximation. It has been found that the surface relaxation, which can be described as a 14% contraction of the topmost surface layer with a small (0.1%) shift of surface atomic rows, results in a strong decrease of the surface energy with respect to the bulk truncated crystal surfaces (from 0.2 to 0.17 eV/Å^2 for the Mo(112) and from 0.36 to 0.33 eV/Å^2 for the W(112)). The surface relaxation is accompanied by the redistribution of the surface density of states, associated with the transformations of surface states.

PACS. 68.35.Bs Structure of clean surfaces (reconstruction) – 71.15.-m Methods of electronic structure calculations

1 Introduction

Furrowed transition metal surfaces, such as W(112) and Mo(112) (Fig. 1), have very similar structures, which can be described as built from close-packed ($a_1 = 2.73 - 2.74$ Å) atomic rows with rather large spacing between them ($a_2 = 4.45 - 4.47$ Å). In spite of a large surface corrugation, the Mo(112) and W(112) surfaces exhibit surprising stability [1–5], making these surfaces suitable as templates for growing unusual "one dimensional" surface structures [5–8]. It should be mentioned also that W and Mo stepped surfaces are characterized by different decorated structures: Au nanowires grow regularly on Mo vicinal surfaces, whereas rough structures appear on W surfaces, which can be attributed to difference of surface electronic structures of the W and Mo surfaces [9]. Adsorption of alkalis or alkaline earths [10–12] does not induce reconstructions of the Mo(112) surface, as do carbon, oxygen, and rare earth adsorbates at elevated temperatures [3,5,13,14]. Also, only limited surface relaxation has been suggested in recent first-principle simulations for the Mo(112) surface [4] and for the Li/Mo(112) and Sr/Mo(112) adsorption systems [15].

The aim of the present work is to compare the surface relaxation of W(112) and Mo(112) surfaces using the same simulation methods for both surfaces. This approach allows for a detailed comparison of results of the modeling with experiment for the Mo(112) surface and, on the other hand, provides novel results for relaxation of the W(112) surface [16]. Obviously, the electronic structure of a surface depends on the atomic structure, and therefore estimated densities of states (DOS) for the W(112) and Mo(112) surfaces are compared with results of recent detailed studies (both experimental and theoretical) of the electronic structure of these surfaces [1–4,17–21].

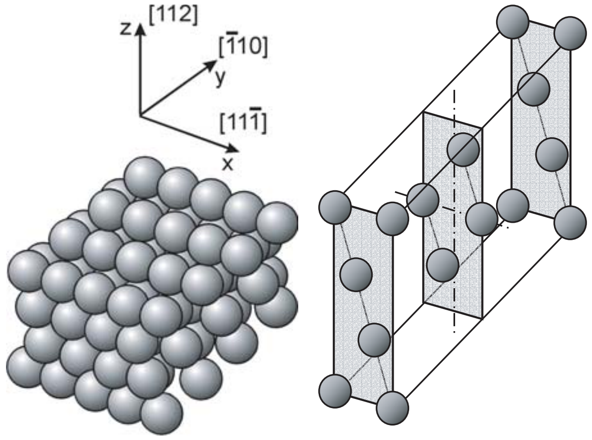

Fig. 1. The Mo(112) surface and the unit cell for the 7-layer slab.

2 Method of calculations

The DFT semirelativistic calculations within the local density approximation were carried out with FHI98md code [22], using norm-conserving Troullier-Martins pseudopotentials in Kleinman-Bylander form [23] and PW-92 [24] exchange-correlation potential. Quality and transferability of the pseudopotentials was carefully verified with standard tests [23].

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As a refined test of the method and quality of generated pseudopotentials, equilibration of the bulk Mo and W crystals has been performed. For Mo, minimum in the total energy has been found with the lattice constant of 3.16 Å, which is slightly larger than the experimental value 3.15 Å. Agreement with experiment for W appears even better – the equilibrium lattice constant is found to be about 3.16 Å. Thus, despite the well-known tendency for overestimation of lattice constants in LDA calculations, agreement with experimental values both for Mo and W seems very good. It should be mentioned that the plane-waves energy cut-off for the Mo and W, in contrast to simple metals, had to be increased to 30–40 Ryd to provide high-convergence results. Further verification of the potential was obtained through calculations of the band structures and densities of states for the bulk Mo and W, which, again, were in good agreement with published data [17,21,25–27]. In particular, the calculated bandwidths for Mo and W, in agreement with UPES data [18,21] and LAPW calculations [17,21], were of 6.8 eV and 9.75 eV, respectively.

To restore periodicity in the direction normal to the surface, a repeat-slab model was adopted. The thickness of the model slab was adjusted with due regard to the "convergence" of surface properties such as values of obtained shifts of surface atoms and surface DOS. A 7-layer Mo(112) slab (Fig. 1) with the vacuum gaps of approximately half a thickness of the slab was found to be sufficient for these purposes. For the W(112), the 9-layer slab better reproduced the "bulk" DOS, while the surface relaxation, surface energy and surface-induced peaks in calculated DOS were almost the same as those for the 7-layer slab. In the course of optimization, structure of the central 3 layers of the films was kept fixed while atoms in the other layers were allowed to relax, in other words, for the 7-layer slab calculations, atoms of the outmost surface and next to surface planes were not frozen. In the 9-layer films, the third subsurface layer was also allowed to relax.

Special attention was paid to accuracy of convergence toward equilibration with respect to the energy cut-off. This required high accuracy of the self-consistent procedure at each iteration step, and a sufficient number of k points. In the present work, the energy cut-off in slab calculations was of 40 Ryd. Various sets of k-points (including Monkhorst-Pack [28] and Chadi-Cohen [29] sets of special points) were tested with respect of convergence of results. It was concluded that the $8 \times 8 \times 8$ Monkhorst-Pack set in bulk and $8 \times 8 \times 1$ in surface simulations were sufficient to obtain the required accuracy. For DOS calculations, the tetrahedral method of integration over the BZ and its two-dimensional analog [30] (triangular method) was used for the bulk and surface DOS, respectively. Thus, for the surface DOS calculations, a moderate number of specially chosen k-points (in the current program, 4 points in the corners, 4 points in the middles of the borders, 4 special Chadi-Cohen points, and 1 point in the center of the $^1/_4$ irreducible part of the rectangular BZ) was found to give well-converged results.

3 Results and discussion

The Mo(112) surface relaxation is generally described by both surface layer translation in the plane of the surface and a surface contraction. Due to absence of neighbors from the vacuum side, the topmost atomic rows tend to shift along the $\langle 11\bar{1} \rangle$ direction (denoted as x, see Fig. 1) towards higher coordination position at the surface. Though this shift is rather small (approximately 0.1% of the surface lattice period $a_x = 2.73$ Å), this allows surface Mo atoms to come closer to subsurface atoms, thus decreasing interlayer spacing, as detailed in Table 1. Subsurface Mo atoms are also got involved into the surface relaxation, though their shifts from the bulk positions are less pronounced (cf. Tab. 1).

It should be noted that there is agreement of present calculations with what is known of the structure from low energy electron diffraction intensity versus voltage (LEED *IV*) data [3] as well as with earlier calculations by Che et al. [4]. Indeed, the differences in the estimated shifts of the surface atoms and those found in experiment does not exceed error bars while the qualitative picture of the Mo(112) surface relaxation is generally the same. Some disagreement exists only in direction of the shift of the subsurface atoms along the $\langle 11\bar{1} \rangle$ direction. Both present and other calculations give this shift in the same direction as for the topmost surface atoms, while the best R-factor in the LEED *IV* analysis [1] was obtained for a tiny shift in opposite direction. The origin of this contradiction is not quite clear, because, on the one hand, the value of this shift is within the error bars [1], while, on the other hand, it provides a quite small gain in total energies and local forces in slab calculations and therefore hardly can be very reliable.

The surface relaxation results in substantial decrease of the total energy of the slab. Obviously, this effect originates from decrease of the surface energy E_s which can be estimated [4] as

$$E_\mathrm{s} = {}^1/_2 [E_\mathrm{slab} - 7 \times E_\mathrm{bulk}]/A, \qquad (1)$$

(that is, as the difference of total energies for the unit cell of the slab E_slab and related bulk cell ($7 \times E_\mathrm{bulk}$), divided by the area A of the surface unit cell). Thus estimated values of the surface energies for the Mo(112) and W(112) are given in the last column of Table 1 together with data from references [4,16].

The driving force of the surface relaxation is the gain in the surface energy, which should be accompanied by redistribution of surface states [31]. This is just what can be seen in Figure 2, where densities of states, calculated for the "ideal" and relaxed films are presented. Thus, in the DOS plot for the ideal (bulk terminated) surface, (shown by a dashed line in Fig. 2), there are pronounced peaks in vicinity of the Fermi level, while the surface relaxation results in the shift of these peaks downwards in energy. It is worth noting, however, that the decrease of the DOS in vicinity of Fermi level due to Mo(112) surface relaxation is rather small in comparison with dramatic changes in DOS reported for relaxation of dielectric surfaces [31],

Table 1. Relaxation of the surfaces of Mo(112) and W(112). Shifts of the topmost surface atoms along the normal to the surface are denoted as z_1 and the shifts of the atoms in the next layer are z_2. Relative shifts are given with respect to the interlayer spacing, h ($h = 1.29$ Å and $h = 1.30$ Å for the Mo(112) and W(112), respectively).

Surface	Source	z_1 (Å)	z_1/h	z_2 (Å)	z_2/h	E_s (eV/Å^2)
Mo(112)	*IV* LEED [1]	−0.20	−15.4%	+0.02	$+2 \pm 3$%	
	DFT [4]	−0.21	−16.2%	+0.04	2.9%	0.19
	Present	−0.18	−14%	−0.01	−0.4%	0.17
W(112)	Theory [16]	−0.1	−8%	−0.02	−2%	
	Present	−0.17	−13.2%	+0.01	0.3%	0.33

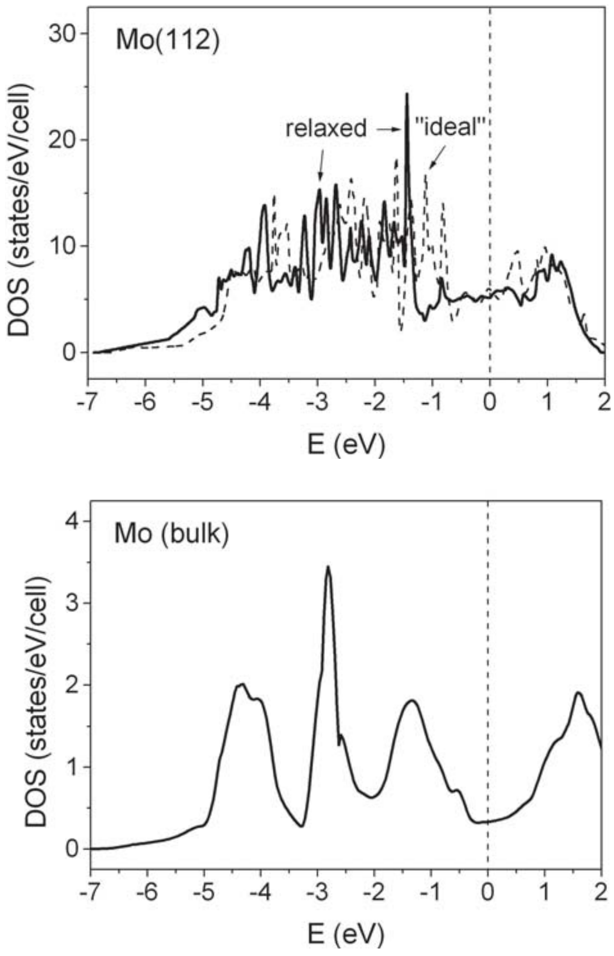

Fig. 2. Density of states (DOS), calculated for the "ideal" (bulk truncated) (dashed line) and relaxed Mo(112) surface (solid line) of the 7-layer slab. DOS of the bulk Mo (at bottom) is shown for comparison.

and therefore it is not surprising that the DOS for the relaxed surface is still in good agreement with results of earlier calculations performed for the unrelaxed Mo(112) surface [17,19–21].

For W(112), the surface relaxation is similar. As with Mo(112), the topmost atomic rows are shifted slightly towards a higher coordination position on the surface and inwards the slab (cf. Tab. 1). Subsurface W atoms are also involved into the surface relaxation, while their shifts are less pronounced. This similarity in the surface relaxation of the W(112) and Mo(112), probably, can be attributed to similarity of electronic configurations of Mo and W atoms, which results also in very similar bulk band structures of these metals.

The surface energy of the W(112) appears to be higher than for Mo(112) (see Tab. 1). This feature probably results from substantially higher surface DOS in close proximity to the Fermi level for the W(112) (Fig. 3a) than for the Mo(112) surface (cf. Fig. 2) (surface origin of the peaks in DOS immediately follows from comparison with bulk densities of states, also shown at bottom of Fig. 2 and in Fig. 3c). Detailed comparison of available UPS data with W(112) surface electronic structure, calculated by the film-LAPW method for the 7-layer slab with a bulk-terminated surface structure [21] has shown a rather good agreement between the theory and experiment, as was also reported for the Mo(112) surface [17–20]. It follows from present calculations, a moderate surface relaxation does not lead to substantial changes in surface electronic structure for either the Mo(112), or W(112) surfaces.

The surface relaxation performed for a 9-layer W(112) has not revealed any substantial difference with results obtained for the 7-layer slab. Shift of the atoms of the third layer is found to be quite small and does not allow for its unambiguous determination. When increasing the thickness of the slab in model calculations, one may expect a possible better account for bulk-induced features in total DOS. Indeed, the DOS, calculated for a 9-layer W(112) slab with relaxed surface (Fig. 3b), apart from a general similarity with the DOS for the 7-layer slab, differs nonetheless from the latter by small shifts of certain peaks towards characteristic positions pertinent to bulk DOS peaks (cf. Fig. 3c). This observation is consistent with results of recent study of the W(112) surface [21], which has revealed a combined nature of the UPS peaks, that is, these peaks contain contributions both from surface and from bulk photoemission.

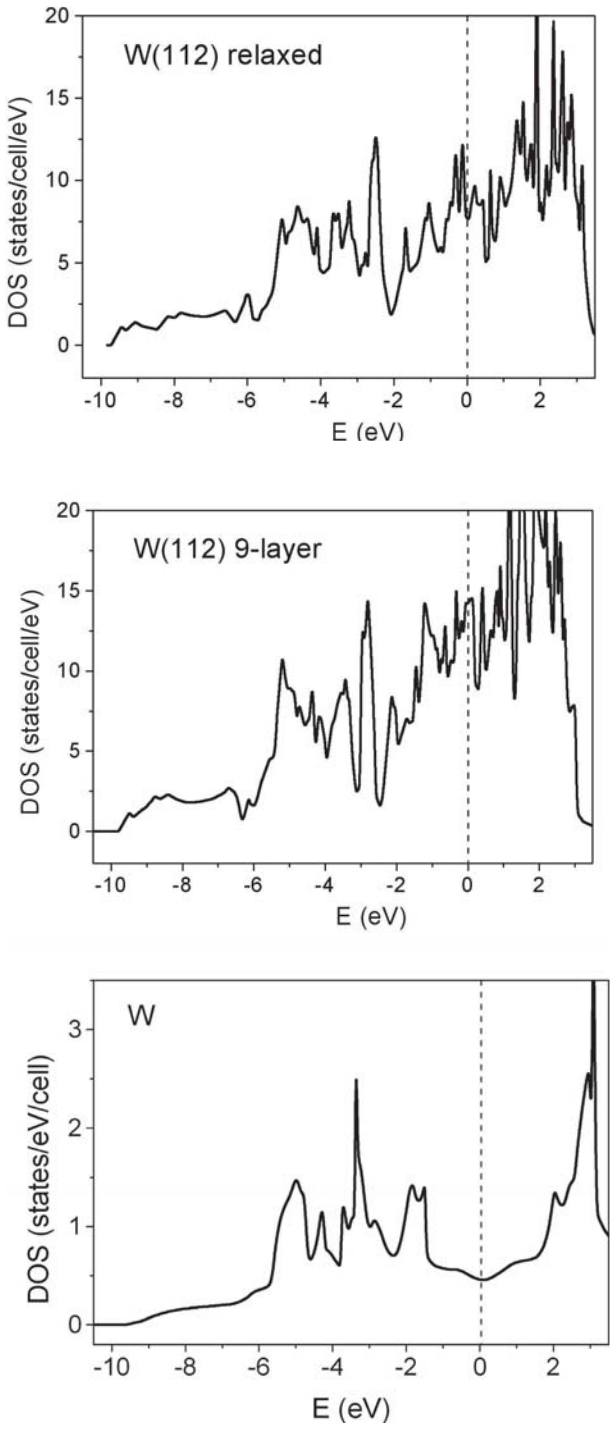

Fig. 3. Densities of states, calculated for relaxed surfaces of the 7-layer (a) and 9-layer (b) W(112) films. (c): DOS of the bulk W.

4 Conclusion

Very recent experimental studies have revealed a substantial reconstruction of the Mo(112) surface caused by oxygen and some rare earth adsorbates at elevated temperatures [3,5,13,14]. In contrast, the W(112) surface demonstrates surprising stability under such conditions [5,7,21]. This different behavior of the surfaces, which are expected to be quite similar in their properties due to similar electronic configurations of W and Mo atoms and similar band structures of the metals, deserves further experimental and theoretical efforts. In particular, much here can be clarified through the first-principle modeling, and, hopefully, the results of the present simulations of the W(112) and Mo(112) surface relaxation will be able to serve as a background for future studies.

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