Energetics of Surface Multilayer Relaxation on W(001): Evidence for Short-Range Screening

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Multilayer relaxation of the W(001) surface is explored by the all-electron local-density-functional total-energy approach. In agreement with recent experiments, we find a contraction of the topmost interlayer spacing by 5.7%. Surprisingly, the amount of this contraction is independent of the relaxation of the inner layers, which are predicted to be expanded by 2.4% and 1.2% for the second and third interlayer spacings, respectively. Thus, the driving mechanism for the relaxation process appears to be of a local nature because of short-range screening effects at the transition-metal surface.

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Relaxation and reconstruction play a fundamental role in the physics and chemistry of surfaces and thus have been the object of intense experimental efforts. Their observation in such diverse systems as semiconductors and clean and adsorbate-covered metal surfaces indicates that these structural changes can be considered to be the rule rather than the exception. In some cases such as the Al(110),[1] the Cu(110),[2] or the V(100)[3] and Re(0101)[4] surfaces, it has been possible recently to present experimental evidence for multilayer relaxation effects. Earlier theoretical attempts to calculate surface relaxation effects have been limited to semiempirical tight-binding calculations[5-7] or to simplified model Hamiltonians.[8] The accurate experimental determination of multilayer relaxation effects have called attention to the need for precise theoretical determinations of the energetics and detailed information on the driving mechanism behind the observations. First-principles self-consistent calculations have confirmed a damped oscillatory multilayer relaxation for the Al(110) surface.[9] On the other hand, for the important class of transition-metal surfaces, no *ab initio* study of any surface multilayer relaxation has been reported and little is known about the energetics of such a process. For well-studied surfaces such as W(001) no multilayer relaxation has been observed and even the extent of the relaxation of just the first layer has been a matter of controversy: The values of the low-energy electron-diffraction (LEED) analyses for this contraction vary between[10-15] $(4.4 \pm 3)\%$ and $(11 \pm 2)\%$. Backscattering-channeling experiments[16] using megaelectronvolt ions lead to the conclusion that the value for the contraction does not exceed 6%. A recent spin-polarized LEED study[17] suggests a value of $(7.0 \pm 1.5)\%$.

In this Letter, we present the results of the first all-electron local-density functional[18] (LDF) study of the energetics of the multilayer relaxation process on the W(001) surface employing the full-potential, linearized, augmented plane-wave[19] (FLAPW) total-energy[20] approach. We predict a contraction of the topmost layer by 5.7% accompanied by an outward relaxation of the second and third layers leading to an increase of the second and third interlayer spacings by 2.4% and 1.2%, respectively. Surprisingly, we find that the relaxation of the second and third interlayer spacings does *not* influence the equilibrium spacing between the two topmost layers, i.e., keeping the inner layers unrelaxed leads to practically the same equilibrium distance between the first and second layer as is found for the fully relaxed system. Thus, the equilibrium between the adjacent layers appears to be governed by highly screened local interactions. This decoupling of the relaxation for the topmost and the inner layers is the more remarkable since 25% of the total relaxation energy of 0.06 eV originates from the relaxation of the inner layers.

In this investigation the W(001) surface is described by the single-slab approach using five- and seven-layer films—thicknesses which have been demonstrated sufficient to describe accurately the electronic structure of this system.[21] Here we focus on relaxation effects only, i.e., we do not consider possible additional reconstruction effects as has been observed[22,23] for the low-temperature phase of the W(001) surface. Although additional reconstruction effects could modify somewhat the interlayer spacing between the surface and subsurface layers, they are very unlikely to change the overall mechanism and results of multilayer relaxation discussed here.

The Kohn-Sham LDF equations incorporating the Wigner exchange-correlation potential[24] are solved self-consistently by use of the all-electron FLAPW method.[19] As a reference system we use

the unrelaxed surface geometry corresponding to the experimental bulk lattice constant of 5.973 a.u. (From independent total-energy FLAPW calculations for bulk bcc tungsten[25] it is known that this experimental value is reproduced by all-electron LDF theory to within 0.5%.) A total of 360 and 480 LAPW basis functions are used for the five- and seven-layer films, respectively. In all calculations the muffin-tin radius of the W sphere is set to 2.487 a.u. Inside the muffin-tin spheres, charge densities and potentials are expanded in lattice harmonics with angular momentum up to $l=8$. The core electrons, including the W $5p$ states, are treated fully relativistically within a central field and are recalculated in each iteration. The valence electrons, derived from the atomic $6p$ and $5d$ orbitals, are treated semirelativistically,[26] i.e., dropping the spin-orbit term, but retaining the other relativistic terms in the Hamiltonian. Within the irreducible wedge of the two-dimensional Brillouin zone, eigenvalues and eigenvectors are evaluated by use of 28 k points in the self-consistency procedure; a Gaussian interpolation scheme[27] is used to perform the integrations over the first Brillouin zone. Self-consistency is assumed when the input and output charge densities differ on the average by less than 3×10^{-4} electron/(a.u.)^3. By then, the total energies are stable to better than 0.1 mRy.

In order to explore the energy hypersurface which determines the multilayer relaxation process in the case of the five-layer film, the interlayer spacings between first and second (d_{12}) and second and third layers (d_{23}) are varied independently. For the seven-layer film three interlayer spacings, d_{12}, d_{23}, and d_{34}, are treated as independent quantities. The energy hypersurface is scanned by varying d with a step width of 1.5% of the bulk lattice constant. Near the equilibrium geometry, these discrete points of the energy hypersurface are parabolically fitted as shown in Fig. 1. The root mean square (rms) value of this parabolic fit is less than 0.2 mRy showing that, as expected, the system behaves harmonically around its equilibrium positions. Furthermore, this small rms value demonstrates the high numerical precision and stability of our approach.

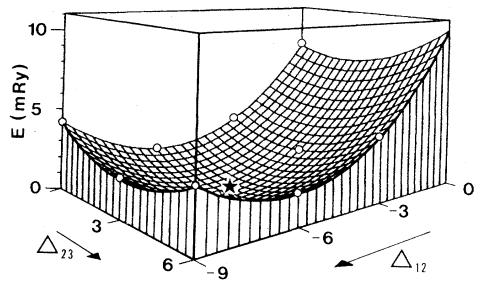

FIG. 1. Energy hypersurface for a seven-layer W(001) film as a function of the relative changes (in percent) of the first two interlayer spacings. For this plot, the third interlayer spacing is kept at its bulk value. The minimum in the total energy, indicated by the star, is set equal to zero, i.e., subtracting 226 144.0175 Ry. The open circles indicate the geometries where self-consistent calculations have been performed.

The results are summarized in Table I where n_r denotes the number of layers which are allowed to relax and the entries give the relative change of the interlayer spacings, Δ_{12}, Δ_{23}, and Δ_{34} in percent as referred to bulklike interlayer spacings. (A negative sign means contraction and a positive sign an expansion). The last row shows the relaxation energy, E_r, defined as one-half of the total energy difference between the relaxed and the unrelaxed films. As expected, the relaxation energy increases with increasing number of allowed degrees of freedom. The relaxation of d_{12} and d_{23} makes up the largest contribution to E_r; that from the relaxation of d_{34} is rather small. This indicates that underneath the fourth layer a bulklike interlayer spacing can be assumed.

Surprisingly, for all cases listed in Table I we find the same contraction (5.5 ± 0.5)% for the topmost layer, i.e., independent of the assumed relaxation process underneath. This theoretical value is consistent with recent experimental results.[11,13,15–17] For Δ_{23} we predict an expansion of 2.4% and for Δ_{34} an expansion of 1.2%. The positive sign of Δ_{34} is unexpected, since intuitively one might expect an alternation of contractions and expansions upon going from the surface into the interior of the system as has been reported[1,9] for the Al(110) surface. It

TABLE I. FLAPW total-energy results for the multilayer relaxation of W(001): n_r denotes the number of relaxed layers and Δ_{ij} is the percentage change of the interlayer spacing between layers i and j as referred to the bulk value. The last row gives the surface relaxation energy, E_r.

	five layers		seven layers		
	$n_r=1$	$n_r=2$	$n_r=1$	$n_r=2$	$n_r=3$
Δ_{12}	−5.4	−5.2	−5.5	−5.8	−5.7
Δ_{23}	· · ·	2.4	· · ·	2.7	2.4
Δ_{34}	· · ·	· · ·	· · ·	· · ·	1.2
E_r (eV)	0.034	0.044	0.048	0.059	0.061

should be noted that the small differences between the results obtained for the five-layer and for the seven-layer slabs originate from residual interactions between the two surfaces of the slab which cause a splitting[21] of the surface states.[28] Around the equilibrium, the total energy changes parabolically so that harmonic behavior to within $\pm 5\%$ around the equilibrium position can be assumed. From the curvature of the total energy as a function of d_{12} (with fixed bulk values for d_{23} and d_{24}) we deduce a frequency of 4.3 THz for the vibration of the top surface layer. This frequency is found to be unchanged by use of the relaxed values of d_{23} and d_{34} (cf. the curvatures in Fig. 1).

The electronic origin of the relaxation on a transition-metal surface such as the W(001) surface may be understood by considering the simultaneous effects of bonding of localized *d* electrons and delocalized *sp* electrons. In the bulk of a transition metal, the bond formation[29] driven by *d* electrons tends to decrease the interatomic distances while the free-electron-like *sp* electrons minimize their contribution to the total energy by expanding the system which decreases their kinetic energy. The balance between these two mechanisms leads to the bulk equilibrium geometry. At the surface, the *d*-*d* bonding between the surface and subsurface atoms is enhanced, i.e., the bond distance can be shortened, since the *sp* electrons can be pushed into the vacuum region above the surface. Thus, the binding energy is increased by enhanced *d*-*d* bonding while the *sp* electrons can maintain their low kinetic energy by extending further out into the vacuum. As a consequence of this increased spillout of electrons into the vacuum, the topmost interlayer spacing is contracted relative to the bulk layer spacing. This balance between these two mechanisms also results in a work function ($\Phi = 4.6$ eV) which shows very little variation (less than 0.1 eV) for all the relaxation processes studied here, i.e., the enhancement of the *d*-*d* bonding enhances Φ, while the rearrangement of the *sp* electrons decreases the surface dipole layer as the surface layer spacing is contracted. Further, the surface relaxation energy, 0.06 eV, amounts to only 2% of the surface energy.[30] Thus, the surface relaxation mechanism does not lead to a significant change in the surface energy.

In summary, the all-electron LDF total-energy approach employing the FLAPW method for thin films predicts a multilayer relaxation of the W(001) surface. From our analysis of five- and seven-layer films we conclude that this multilayer relaxation is essentially confined to the three topmost layers and a bulk spacing can be assumed underneath. The relaxation energy is found to be 0.06 eV with about 25% of this energy being due to the relaxation of d_{23} and d_{34}. These results provide a sensitive demonstration that the all-electron LDF total-energy approach is capable of describing subtle aspects in the energetics of transition-metal surfaces such as multilayer relaxation processes, involving even high-Z atoms such as tungsten. Finally, the results reveal that the equilibrium distance between the two topmost layers of the W(100) surface is unaffected by additional relaxation of the inner layers. This demonstrates that because of the highly effective screening in a transition metal, the basic interaction mechanism which drives the surface relaxation in W(001) is of such a local nature that essentially only interactions between adjacent layers are involved. This finding should be valid for a variety of transition-metal surfaces similar to W(100).

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