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2005 J. Phys.: Condens. Matter 17 581

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## Surface stress oscillation in Mo(001) thin films

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Received 13 September 2004

Published 14 January 2005

Online at [stacks.iop.org/JPhysCM/17/581](http://stacks.iop.org/JPhysCM/17/581)

### Abstract

The surface stress was evaluated employing a composite elastic model using the first-principles full-potential linearized augmented plane-wave (FP-LAPW) method for 5, 7 and 9 monolayer (ML) Mo(001) thin films. The surface stress calculated from previously derived slope and curvature methods yields a very similar result. The surface stress is found to vary with the number of the Mo thin film layers. This variation is found to be consistent with the existence of quantum well states in these thin films.

### 1. Introduction

Through the study of surface stress, significant information can be gained concerning the bonding and stability of nanostructures and thin films, magnetostriction and magneto-elastic coupling in magnetic films. However, surface stress is very difficult to measure and quantify. So far, it has not been possible to measure stress on a bare substrate directly. Experimentally, only changes in stress, caused by adsorbates or reconstruction, have been determined [1–7].

We have developed a composite elastic model [8–10] to calculate the surface stress and surface elastic properties through *ab initio* methods for various metals and semiconductors directly for surfaces with square symmetries. The composite elastic model gives the surface stress an atomic level description in which the average stress over a specific atomic depth is found and the surface stress is the integrated stress over that depth. The stress in the vertical direction will always be zero since all the vertical lattice spacings are free to relax as in experimental studies. In this composite elastic model for surface stress calculations, a thin film slab is divided into three regions, two symmetrical surface regions on each side and one bulk region in the middle. The surface region and the bulk region will adopt different equilibrium lattice constants,  $a_{s0}$  and  $a_{b0}$  respectively. The surface region will have an epitaxial elastic constant  $Y_s$  which is different from the bulk elastic constant  $Y_b$ . The lattice and elastic constants  $a_{s0}$  and  $Y_s$  in the surface region, and the surface region thickness  $t_s$ , are unknown parameters.

In experiments and in slab calculations, a thin film will adopt only one single equilibrium in-plane lattice constant  $a_0$  for the entire thickness of the region. The vertical lattice spacings will relax to yield zero vertical stress. By finding the equilibrium state total energy  $E_{\text{tot}}$  and

the in-plane lattice constant  $a_Q$  of the thin film through an epitaxial Bain path (EBP) [11], the surface stress can be evaluated according to our model using either a slope method or a curvature method. Details of the treatment can be found in our earlier publications [8–10]. In our earlier work [8–10], the surface stress  $S_s$  of a 7 ML Mo(001) slab was determined. In addition, surface region parameters including surface region lattice constant  $a_{s0}$  and elastic constant  $Y_s$  were also determined. The surface stress derived from our composite elastic model was found to be independent of the assumptions used in the model, such as homogeneity and continuity in both the surface and bulk regions respectively. The surface stress is also found to be independent of the surface region lattice and elastic constants, and the thickness of the surface region.

In this investigation, our composite elastic model is used to determine the surface stress of Mo(001) thin films with 5 and 9 layers respectively. Results are compared with our previous 7 ML Mo(001) slab results. In both experiments and general stress models, the surface stress is considered to be independent of the film thickness for relatively thicker films (>5 ML) when there is no surface reconstruction or phase change since surface relaxation is found generally to be limited to the first 2–3 layers of the film. Here the surface stress is found to be dependent on film thicknesses in these Mo(001) slabs, most likely due to the quantum size effect. This oscillation of surface stress is found to correlate well with the changes of electron charges on the surface and neighbouring atoms at different thicknesses.

## 2. Results and discussions

The calculations are based on the all electron full-potential linearized augmented plane-wave (FP-LAPW) method. The WIEN97 code [12] was used for structural relaxation and total energy calculations. The details of the calculations can be found in our earlier publications [8].

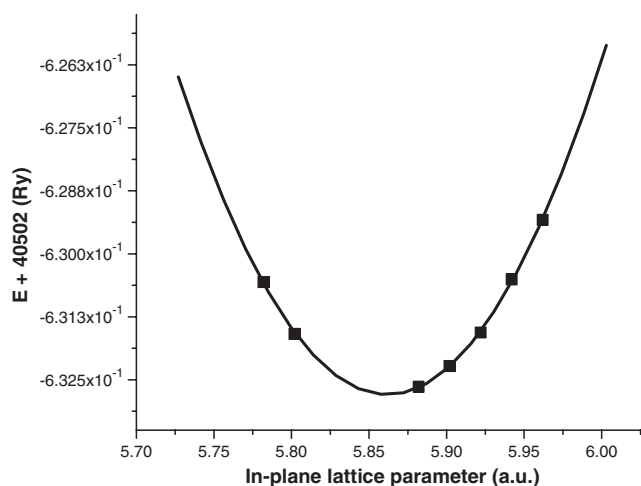
It was shown [9] that both the slope and curvature methods represented by equations (1) and (2) respectively can be used to determine the surface stress  $S_s$  along the EBP for a slab with tetragonal symmetry.

$$S_s \text{ (slope)} \equiv \frac{1}{4A} \left( \frac{dE^{\text{EBP}}(a)}{d\varepsilon_s} \right)_{a=a_{b0}} \approx \frac{1}{4a_Q} \left( \frac{dE^{\text{EBP}}(a)}{da} \right)_{a=a_{b0}} \quad (1)$$

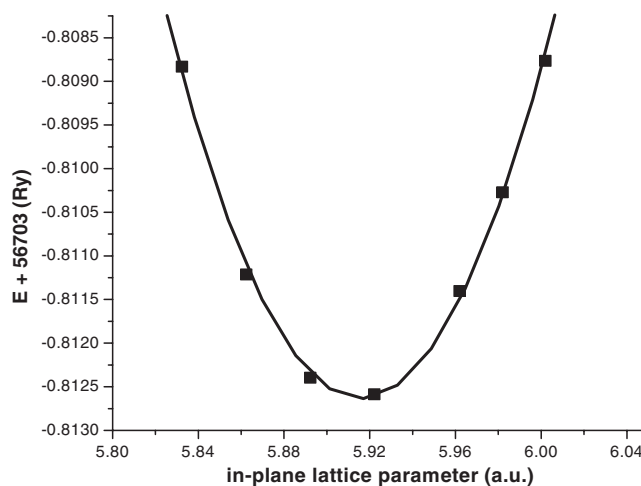
$$S_s \text{ (curvature)} \equiv \frac{(a_{b0} - a_Q)}{4a_Q} \left( \frac{d^2 E^{\text{EBP}}}{da^2} \right)_{a=a_Q}. \quad (2)$$

Here,  $A = a_Q^2$ , is the area of the unit cell at slab equilibrium,  $a_Q$  is the in-plane lattice constant of the slab at equilibrium,  $a_{b0}$  is the theoretical bulk lattice constant,  $E^{\text{EBP}}$  is the total energy of the slab along the EBP, and  $\varepsilon_s = (a_s - a_{s0})/a_{s0}$  is the surface region strain with respect to the theoretical surface region lattice constant  $a_{s0}$ . The surface stress  $S_s$  calculated using the slope method can be interpreted as the change in slab energy with respect to in-plane strain when the in-plane lattice constant equals the theoretical bulk lattice constant, since the bulk region has no strain energy at the theoretical bulk lattice value  $a_{b0}$ . The approximation in equation (1) is valid when high-order terms in strain are discarded. Even though the surface stress derived from the curvature method is based on the composite elastic model, it is independent of the model itself, since it does not depend on the surface region parameters.

In our previous calculations [9], it was shown that both the slope and curvature methods give very similar results for the 7 ML Mo(001) slab. In fact, it can be further proven that the slope and curvature methods are identical to each other when and only when linear elastic theory is valid. Indeed, the calculated surface stresses for 5 and 9 ML Mo(001) slabs using the two methods are almost the same, as shown in table 1.



**Figure 1.** The total energy of the 5 ML Mo(001) slab along its EBP. The squares (■) are the calculated points at different in-plane lattice constants. The solid curve (—) is the quadratic fit to the calculated results.

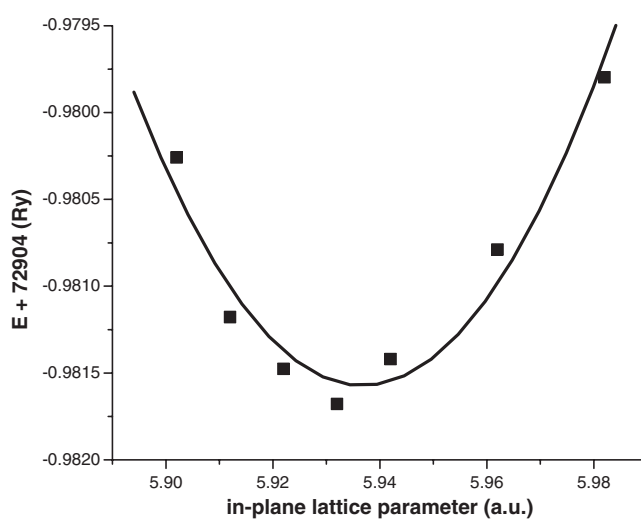


**Figure 2.** The total energy of the 7 ML Mo(001) slab along its EBP. The squares (■) are the calculated points at different in-plane lattice constants. The solid curve (—) is the quadratic fit to the calculated results.

**Table 1.** The equilibrium lattice constants  $a_Q$ , surface energy  $\Delta E_s$  and surface stress  $S_s$  determined from both the slope and curvature methods for 5, 7 and 9 ML Mo(001) slabs.

Mo(001) slab (ML)	$a_Q$ (au)	$\Delta E_s$ (mRyd)	$S_s$ (slope) (mRyd/bohr <sup>2</sup> )	$S_s$ (curvature) (mRyd/bohr <sup>2</sup> )
5	5.8617	147.92	3.58	3.57
7	5.9159	143.72	2.98	2.97
9	5.9368	144.97	3.60	3.60

Figures 1–3 show the total energies of 5, 7 and 9 ML Mo(001) slabs as a function of the in-plane lattice parameter along their respective EBPs. The vertical lattice spacings are fully



**Figure 3.** The total energy of the 9 ML Mo(001) slab along its EBP. The squares (■) are the calculated points at different in-plane lattice constants. The solid curve (—) is the quadratic fit to the calculated results.

relaxed at each point. The numerical data were fitted with a quadratic curve representing the linear elastic approximation. It can be seen that linear elastic theory is valid for both 5 and 7 ML Mo(001) slabs for small strains ( $<2\%$ ), since the quadratic curve fits the data perfectly. The quadratic curve fit for the calculated results from the 9 ML Mo(001) slab is not as good as those of the 5 and 7 ML slabs. One reason is perhaps the larger uncertainty in the atomic structures of the 9 ML slabs. In our calculations, convergence was reached when the force on each atom is less than  $1 \text{ mRyd au}^{-1}$ . Apparently there will be more variation from the exact structure in the 9 ML slab, since there are more interlayer spacings in the 9 ML film compared to the 5 and 7 ML cases. In the 9 ML slab, at each in-plane lattice constant, the errors in the vertical lattice spacings add up. As a result, there are more possibilities to deviate from the exact equilibrium structure. The total energies thus calculated will scatter more for the 9 ML slabs compared to the 5 and 7 ML slabs, as seen from figures 1 to 3. Further, from the curve-fitting error analysis, the error in the quadratic fit increases from 5 and 7 to 9 ML slabs. The equilibrium lattice constants and calculated surface stresses are shown in table 1. The surface energies of the slabs were taken as the difference in slab energies minus the calculated bulk energy with the same number of atoms in the unit cells divided by 2 to account for the two surfaces on each slab.

The surface stress results show a very interesting trend. Both the 5 and 9 ML slabs have very similar surface stress of  $\sim 3.6 \text{ mRyd/bohr}^2$ . However, the 7 ML Mo(001) slab has a considerably lower surface stress of about  $\sim 3.0 \text{ mRyd/bohr}^2$ . The surface energy of the 7 ML Mo(001) slab is also lower than that of the 5 and 9 ML slabs. From our previous determination of surface region parameters [10], the surface region thickness was estimated to be 2–3 layers thick for the Mo(001) slabs. Therefore the surface stress should not change as the film becomes thicker, according to continuum elasticity. If, on the other hand, the surface region extends far deeper than 2–3 layers, then we would expect a monotonic change of surface stress as the film becomes thicker. The oscillation of surface stress could not be explained by the limitation of our model, since the surface stress is independent of the surface region parameters; neither can it be explained by the numerical errors, since all calculations use very similar cut-offs. Even

**Table 2.** The relaxed interlayer spacings of the 5, 7 and 9 ML Mo(001) slabs with an in-plane lattice constant  $a_0$  closest to the equilibrium lattice constant  $a_Q$  for all calculated points.

Mo(001) slabs (ML)	$a_0$ (au)	$d_{12}$ (au)	$d_{23}$ (au)	$d_{34}$ (au)	$d_{45}$ (au)	$t$ (au)
5	5.862	2.751	3.074			11.65
7	5.912	2.712	3.069	3.015		17.59
9	5.932	2.992	3.007	3.077	2.670	23.49

**Table 3.** The electron charges inside the muffin-tin sphere for all the layers in 5, 7 and 9 ML slabs. S represents the surface layer, S-1 represents the layer next to the surface layer and so on. The charge  $Q$  include 4s, 4p, 4d and 5s electrons inside the muffin-tin sphere.

Mo(001) slab	5 ML	7 ML	9 ML
$Q(\text{Mo(S)})$	11.922	11.835	11.934
$Q(\text{Mo(S-1)})$	12.037	11.977	12.024
$Q(\text{Mo(S-2)})$	11.957	11.987	11.949
$Q(\text{Mo(S-3)})$		12.005	11.975
$Q(\text{Mo(S-4)})$			11.960

if numerical error does play a role, a monotonic increase in the error is expected as the film becomes thicker, as discussed earlier. On the other hand, if we consider quantum well states, it is possible to obtain a reasonable explanation for the surface stress oscillation. The quantum well effect means that the thin film property may not vary monotonically as the film thickness changes due to quantum confinement of electronic states.

It is well known that quantum well states exist in ultrathin films [13–18]. The energy levels of these states change as the thickness of the film changes. Since these states can be considered to arise from a one-dimensional quantum well perpendicular to the film plane, the energy levels of these states will be inversely proportional to the square of the film thickness  $E \propto n^2/t^2$ , where  $n$  is the quantum number and  $t$  is the film thickness. In the equilibrium states of the 5, 7 and 9 ML slabs, the thicknesses of the films are 11.65, 17.59 and 23.49 au, respectively, determined from our calculations as shown in table 2. It can be seen that the thickness of the 9 ML slab is about twice that of the 5 ML slab. This means that the 5 and 9 ML slabs should have some quantum well states that are very similar. On the other hand, the 7 ML thickness bears no integer relationship with either the 5 ML or the 9 ML thicknesses, i.e. the 5 and 9 ML Mo(001) slabs are more similar compared to the 7 ML slab in its quantum well electronic states. In order to confirm that the surface stress does depend on quantum well states in the Mo(001) slabs, the electron charges (4s + 4p + 4d + 5s) on the atoms inside their muffin-tin spheres for all the layers in the films are shown in table 3. It can be seen that there is charge oscillation from the surface layer to the central layer in both the 5 and 9 ML slabs. However, the charge numbers increase slightly from the surface layer to the central layer in the 7 ML slab without oscillation. The charges of the surface atoms are 11.922, 11.835 and 11.934 for the 5, 7, and 9 ML slabs, respectively. The charges of the central atoms are 11.957, 12.005 and 11.960 for the 5, 7, and 9 ML slabs, respectively. Once again it is evident that the 5 and 9 ML slabs bear more resemblance to each other but not to the 7 ML slab. Since surface charge is one of the most direct indicators for surface stress [19, 20], it is expected that the 5 and 9 ML slabs would behave more similar to each other.

It is known that valence electrons fill both bonding and antibonding orbitals in metallic Mo and W thin films [21, 22]; lower surface charge means that there are few electrons in the antibonding orbitals since these orbitals are higher in energy and therefore easier to be

depleted. The lower the number of electrons in the antibonding orbitals, the higher the bond order. Consequently, a stronger bonding and lower surface stress for the surface atom is expected. The fact that the surface charge of the 7 ML Mo(001) slab is lower than those of the 5 and 9 ML slabs means that our calculated surface stress results for the 5, 7 and 9 ML Mo(001) slabs are consistent with previous theory relating surface charge to its surface stress [19, 20].

### 3. Conclusions

It can be seen from our surface stress results for the 5, 7 and 9 ML Mo(001) slabs that both the slope and curvature methods developed previously yield almost the same results within the limits of linear elastic theory. Linear elastic theory appears to be valid for these ultrathin films. The surface stress is found to oscillate for the 5, 7 to 9 ML Mo(001) thin films. The 5 and 9 ML Mo(001) slabs have a higher surface stresses while the 7 ML slab has a lower surface stress. The oscillation of the surface stress can be explained by the existence of quantum well states. The change in quantum well states for the 5, 7 and 9 ML Mo(001) slabs is demonstrated through the change in charge number on both the surface and inner layers atoms. The higher surface charge together with a slight charge oscillation inside the 5 and 9 ML slabs corresponds to a higher surface stress, while a lower surface charge together with the monotonic charge increase from the surface to inner layers in the 7 ML slab corresponds to a relatively lower surface stress.

### Acknowledgments

The authors would like to thank W Hübner, P M Marcus, J Kirschner for helpful discussion and support.

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