Surface stress of W(001) and the effect of an Fe overlayer from first principles

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Abstract
Surface stress was determined using a composite elastic model for the relaxed seven-monolayer W(001) slab. The W(001) surface was found to be under a strong tensile stress of 4.46 mRyd/bohr^2 (3.47 N m^{-1}). The composite elastic model was further extended to determine the surface stress where there is an Fe overlayer on the W substrate. It was found that the surface tensile stress increases to 6.71 mRyd/bohr^2 (5.22 N m^{-1}) after deposition of one monolayer of Fe. This is an increase of almost 50%. The effect of adsorbates on the surface stress is discussed in terms of anisotropic bonding of the d orbitals. By comparing spin-polarized and non-spin-polarized calculations, it was found that magnetization of the Fe overlayer is favoured in terms of minimizing the total energy and reducing surface stress.

1. Introduction

Surface stress plays an important role in surface reconstruction and self-assembly [1, 2]. It is also an important quantity in nanomaterial fabrication [3]. Studying surface stress is crucial to understanding magnetostriction and magnetoelastic coupling [4–7] in magnetic thin films. Magnetostriction relates magnetism to the change of elastic properties in materials. Surface stress is an important measure of the elastic properties of thin films. To date, changes in surface stress have only been determined experimentally. Therefore a theoretical study of surface stress is very valuable for pure substrate films and for understanding many interesting surface phenomena that have been observed.

There are also a number of puzzling questions that require theoretical elucidation. One of them is the fact that a compressive stress is measured for Fe, Ni, and Co adsorbates on bcc W(001) and W(110) substrates when the coverage is less than one monolayer, at which tensile stress is expected for these systems [5–8]. Tensile stress is restored for these surfaces only beyond monolayer coverage. Some investigators ascribe this phenomenon to an electronic effect without providing a detailed explanation except that the tensile stress of the W surface is relieved by the adsorbates.

Surface stress for Fe/W(110) in the sub-monolayer range reveals some very interesting and surprising results [6]. Using the conventional strain argument for Fe/W(110), tensile stresses are expected for both the in-plane [001] and [1$\bar{1}$0] directions since bcc Fe has a much smaller lattice parameter compared to W, a mismatch of ~9.4%. However, compressive stress is measured when the Fe coverage is in the sub-monolayer range (<1.2 ML) along [001], while tensile stress is measured along [1$\bar{1}$0].

So far there are only a few theoretical studies on thin film surface stress available in the literature [9–21]. The problem is compounded by the fact that most surface stress calculations rely on the value of surface energy by subtracting the bulk energy from the total energy of the system. In modern computational methods, accurate small energy differences can only be obtained for very similar systems in terms of their atomic structures. Since the atomic structures of the bulk and thin film are very different due to the presence of surfaces and/or interfaces in the thin films, the calculated surface energy is not as accurate as one would hope to obtain. Even though Feibelman [13] found a way to minimize this effect, there are still some uncertainties concerning surface stresses determined theoretically.

We have developed a composite elastic model [17] to evaluate the surface stress of a film avoiding using the surface energy explicitly. In this composite elastic model, a thin film slab is divided into two regions, the symmetric surface regions on each side and the bulk region in the middle. The surface and bulk regions have different lattice and elastic constants. The thin film is held in equilibrium by the general tensile stress in the surface region and the compressive stress in the bulk region. In reality, the slab will only adopt one lattice constant a_Q. The increase in strain energy in the bulk region is compensated for by the reduction in surface energy at the slab equilibrium. The total energy of the slab is calculated along its epitaxial Bain path (EBP) [22], where the vertical lattice spacings are completely relaxed. The EBP is a Bain path along which there is isotropic stress or strain in the (001) plane of a tetragonal phase, whereas the stress perpendicular to the plane is zero. In our earlier studies, this composite elastic model was applied to determine the surface stress on a bare substrate with a square symmetry only. The derived slope and curvature methods were found to yield the same stress results under the linear elastic approximation. The linear elastic approximation was found to be valid for small strains (<2%). Surface stress thus determined is likely to be more quantitative compared to the earlier theoretical results. Further, quantum well states were found to play a role in surface stress [23]. An oscillation of surface stress is found for the Mo(001) slab as a function of thickness. This oscillation is demonstrated to arise from quantum well states in Mo thin films. Here we extend this model to determine the surface stress when there are adsorbates present if the square symmetry of the substrate remains unchanged. The details of the adsorbate–substrate interaction will not affect the validity of the model so long as the symmetry remains the same.

2. Composite elastic model for adsorbate systems

In the composite elastic model developed earlier for a bare substrate with a square symmetry [17], the surface and the bulk regions have lattice and elastic constants a_{s0} and Y_{s0}, a_{b0} and Y_{b0} respectively. The surface and bulk regions have thicknesses t_s and t_b respectively. The surface stress can be determined by evaluating the slope and curvature of the total energy curve along its EBP as shown below in equations (1) and (2). The details of the treatment can be found in our earlier publications [17–19].

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

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

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^{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 thus calculated is actually independent of the assumptions we have used in the model, and is also independent of the surface region parameters as can be seen from the expressions in equations (1) and (2). It can be further proven that the slope and curvature methods are equivalent to each other when linear elastic theory is valid. Here we will focus on the slope method alone in the adsorbate systems since its physical meaning is more transparent.

The surface stress determined from the slope method can be interpreted as the derivative of total energy along the EBP at the bulk lattice constant a_{b0}, where there is no strain in the bulk region. Physically, it is the change of the surface energy under unit strain which is the definition of surface stress. Since surface stress only relies on the total energy of the slab along its EBP, it eliminates the uncertainties in calculating the actual surface energy. The formula only applies to systems with a square lattice where there is only one value for the isotropic surface stress.

In adsorbate systems where there is no surface reconstruction and for complete monolayer epitaxial coverage, the symmetry of the substrate is maintained. If we take both the adsorbate and the neighbouring layers as the surface region, then it is still valid to use the slope method to determine surface stress. At the bulk equilibrium constant a_{b0} the change in total energy along the EBP for the slab is equivalent to the change of surface energy since there is no strain energy in the bulk region. As a result of the adsorbate, the change in surface energy under strain will have a different value compared to that of the bare substrate due to the adsorbate–substrate and adsorbate–adsorbate interactions. Further, a different equilibrium lattice constant a_Q for the slab is expected. Actually, even for the bare substrate case, due to different relaxations of the vertical lattice spacings for the surface and inner layers, the surface region is no longer homogeneous. Thus the surface layer can also be considered as an adsorbate layer even for the bare substrate case.

3. Results and discussion

Our calculations are based on the full-potential linearized augmented plane-wave method (FP-LAPW). The WIEN97 code [24] was used in the calculations. The details of our numerical procedure have been published earlier [17]. The total energies of a 7 ML W(001) slab are calculated at three different in-plane lattice parameters at 5.902, 5.981 and 6.0563 au. The vertical lattice spacings are relaxed to yield zero vertical stress. The relaxed vertical lattice spacings at three different in-plane lattice parameters and their corresponding total energies are shown in table 1. The total energies of the system with 1 ML Fe coverage on both 5 ML W(001) substrate surfaces with and without spin-polarization were also calculated at the same lattice parameters as the 7 ML W(001) substrate. The relaxed vertical lattice spacings are also shown in tables 2 and 3 respectively. The calculated data points are fitted with a quadratic function, which was later used to determine the surface stress for each system.

From tables 1–3, it can be seen that there are significant first interlayer relaxations as observed in other studies [18]. The contractions for the first interlayer distances are ~13% in the 7 ML W(001) and ~20% and ~30% in the spin-polarized and non spin-polarized 1Fe/5W/1Fe(001) systems respectively. The contractions are determined with respect to their inner W–W interlayer distances. There are only very slight variations for the second and third interlayer distances. Significant relaxations only occur for the surface layer as observed in other Fe/W systems with monolayer coverage [25, 26]. This confirms our earlier conclusion

Table 1. The out-of-plane lattice spacings (d_{12}, d_{23}, d_{34}) for the 7 ML W(001) relaxed structures at three different in-plane lattice parameters a. The total energies at each in-plane lattice parameter are also tabulated.

a (au)	d_{12} (au)	d_{23} (au)	d_{34} (au)	$E_{tot} + 226\,347$ (Ryd)
6.0563	2.6712	3.0787	2.9786	$-0.915\,603$
5.981	2.7302	3.0988	3.0053	$-0.919\,192$
5.902	2.7994	3.1235	3.0565	$-0.914\,096$

Table 2. The out-of-plane lattice spacings (d_{12}, d_{23}, d_{34}) for the 1Fe/5W/1Fe spin-polarized relaxed structure at three different in-plane lattice parameters a. The total energies at each in-plane lattice parameter are also tabulated.

a (au)	d_{12} (au)	d_{23} (au)	d_{34} (au)	$E_{tot} + 166\,769$ (Ryd)
6.0563	2.3644	3.0479	3.0140	$-0.632\,496$
5.981	2.4189	3.0947	3.0443	$-0.641\,020$
5.902	2.4474	3.1334	3.0745	$-0.642\,563$

Table 3. The out-of-plane lattice spacings (d_{12}, d_{23}, d_{34}) for the 1Fe/5W/1Fe non-spin-polarized relaxed structures at three different in-plane lattice parameters a. The total energies at each in-plane lattice parameter are also tabulated.

a (au)	d_{12} (au)	d_{23} (au)	d_{34} (au)	$E_{tot} + 166\,769$ (Ryd)
6.0563	2.0576	3.0779	3.0101	$-0.602\,956$
5.981	2.1143	3.1107	3.0426	$-0.612\,119$
5.902	2.1703	3.1467	3.0856	$-0.614\,091$

that the surface region is only two to three layers thick for both Mo(001) and W(001) films. In addition, the effect of magnetism on the 1Fe/5W/1Fe(001) system can also be observed. The first interlayer distance is much larger in the spin-polarized case ($\sim$2.4 au) than that of the non spin-polarized system ($\sim$2.1 au) due to the magnetovolume effect. The second and third W–W interlayer distances are only slightly affected by magnetism. The slab in-plane equilibrium lattice constants a_Q are 5.9254 and 5.9216 au with and without spin polarization respectively. The in-plane lattice constant is slightly larger for the magnetic Fe/W/Fe(001) system than for the non-magnetic system due primarily to the magnetovolume effect. As expected, the total energy of the spin-polarized Fe/W(001) thin film is slightly lower than that of the non-spin-polarized case since the ground state is magnetic [26]. The in-plane equilibrium lattice constant a_Q for the 7 ML W(001) slab is 5.9882 au, about 1% larger than the 1Fe/5W/1Fe(001) slab. The reason is perhaps that the Fe covered surface region is softer than the bare W surface and that the Fe covered system has a higher tensile surface stress (see later).

Both the slope and curvature methods yield the same tensile stress values for these systems. These results together with the stress value of 7 ML Mo(001) are shown in table 4. The tensile stress on the 7 ML W(001) surface is 4.46 mRyd/bohr^2, larger than the stress value of 2.98 mRyd/bohr^2 on the 7 ML Mo(001) surface. The fact that 5d transition metals have a higher surface tensile stress than their 4d counterpart agrees with earlier calculations [12]. One monolayer of Fe on W(001) substrate increases this tensile stress to 6.71 and 7.13 mRyd/bohr^2 for the spin-polarized and non-spin-polarized systems respectively.

Previously Feibelman [15] raised a number of questions concerning various stress models and the nature of surface stress. The models discussed include (1) the bond order model [15], (2) the effective medium model [11], (3) the relief of kinetic pressure model [9], and (4) the

Table 4. Theoretical surface stresses for 1Fe/5W/1Fe(001) non-spin-polarized, 1Fe/5W/1Fe(001) spin-polarized, 7 ML W(001), and 7 ML Mo(001) systems.

System	1Fe/5W/1Fe(001) non-spin-polarized	1Fe/5W/1Fe(001) spin polarized	7 ML W(001)	7 ML Mo(001)
Surface stress (mRyd/bohr^2)	7.13	6.71	4.46	2.98

backbond model [27]. The major problem in the first two and the last models according to Feibelman is that these models cannot reconcile the surface tensile stress and the expansion of the first interlayer distance exhibited by Pt(111) and Al(111) surfaces. The problem with the third and fourth models is that they cannot explain surface stress results for H and O adsorption on Pt(111) [15]. In both cases, compressive stresses were found even though H is an electron donating element and O is an electron withdrawing element. Later on Ibach and co-workers [20] revised their backbond model to explain the surface stress results of Li/W(110) in submonolayer coverage using a bond enhancing or weakening mechanism.

In all these models, the authors did not taken into account the anisotropies of the p and d orbitals. The fact that bcc and fcc (100), (110) and (111) surfaces have different degrees of relaxation is due to their different numbers of nearest neighbours missing on each surface atom as pointed out by Feibelman [15]. In order to reconcile the tensile surface stress with the outward expansion of the Pt(111) surface layer, the anisotropy of the d orbitals has to be considered. As a result of the missing bonds and the lowering of the symmetry at the (111) surfaces, the energy levels of the 5d ($d_{x^2y^2}$, d_{xy}, d_{xz}, d_{yz}, and d_{z^2}) orbitals are rearranged due to the crystal-field effect [26]. Hence the strength of the nearest bonds on the surfaces and those below the surfaces are no longer the same. It is likely that the d orbitals perpendicular to the surface plane become more antibonding, while those in plane become more bonding. It is therefore possible that the nearest bonds in the surface plane prefer a shorter distance while the ones between the layers prefer a longer distance. Thus a surface tensile stress does not necessarily correlate with a contraction in the first interlayer distance. This is most likely what happens in Pt(111); an expansion of the first interlayer distance was observed while a tensile surface stress was calculated. These models are all correct to a certain extent. The limitation is that they cannot explain all the surface stress phenomena. The revised backbond model correlating stress change with the change of inter-atomic bond strength is perhaps most appropriate, even though it is still too simplistic without considering the anisotropy of the valence d-orbitals.

The compressive stresses measured for Fe, Ni, and Co adsorbates on W(100) substrates below one monolayer coverage are indeed due to an electronic effect. Surface stress by definition is the change of surface energy under unit strain. Since there is a large lattice mismatch (~9%) between the Fe, Ni, and Co and the W substrate, and the Fe, Ni, and Co atomic radii are much smaller than that of W, the electronic interactions between Fe, Ni, and Co adsorbates at very low coverage (typically <1 ML) are very weak and most likely through the W substrate. For the epitaxially grown adsorbates (Fe, Ni, and Co) below a certain sub-monolayer coverage, the overlap of valence orbitals is negligible since these atoms are far apart due to the larger W substrate lattice parameter. Since surface energy is determined by the bonding of the surface atoms with their neighbouring atoms, surface energy change under strain has to come mainly from the change of energy due to the change of W–W interaction for very low adsorbate coverage (<1 ML).

As can be seen from the above theoretical results, the bare W surface is under a strong tensile stress. When adsorbates are deposited on the surface pseudomorphically at very low

coverage, their primary interactions are with their immediate four neighbouring W atoms. Since Fe, Co and Ni atoms have almost the same electronegativity as that of the substrate W atoms, substantial charge transfer is not likely to occur as shown in our earlier results [28]. However, the W–W bond weakens due to the formation of the adsorbate–W bond with an Fe–W binding energy of 4.1 eV/atom, which is rather high. The surface stress switches from tensile to compressive due to this weaker W–W bonds in agreement with the backbond model [20].

As the adsorbate coverage increases to a certain coverage θ, the valence orbitals of the adsorbate atoms start to overlap with each other, i.e. *bonding between the adsorbate atoms occurs*. As a result, surface energy will be increasingly dominated by the adsorbate–adsorbate interactions. Strain will change their bonding energy due to these interactions. Since the pure Fe, Co and Ni surfaces are also under tensile stress, the increase of the adsorbate coverage will decrease the compressive stress as observed in experimental studies [5–8]. After the coverage reaches 1 ML, the adsorbate–adsorbate interaction and adsorbate–substrate interaction become the dominant contributions to the surface energy. Thus a tensile stress is again expected. Experimentally, compressive stress was measured at 1 ML coverage. Tensile stress was restored only beyond 1 ML [5–8]. This discrepancy with our current theoretical results at 1 ML coverage is perhaps due to the fact that experimentally the possibility of formation of local double layers of Fe on the W(001) substrate exists even though the total coverage is less than 1 ML. Our theoretical treatment is for ideal 1 ML coverage only.

For a monolayer Fe on W(001) substrate, a higher surface tensile stress than that of the bare W(001) substrate is found. This enhanced surface stress is perhaps due to the large lattice mismatch between the bcc Fe and bcc W. Actually, all surface phenomena are due to an electronic effect since each atomic structure uniquely determines an electronic structure. Any modification in the atomic structure will change the electronic structure of the system. Surface stress ultimately has to be linked with the electronic structure of the system.

The reason that the 5d transition metals generally have a higher tensile stress than *their* 4d counterparts [12] is also due mainly to their different valence d-orbital overlaps. The 4d and 5d transition metals have almost the same lattice constants as a consequence of the relativistic effect. The bonds in the 5d transition metals are stronger than those in the 4ds since 5d valence orbitals overlap more than the 4d orbitals. As a result, surface relaxations are small for the 5d transition metals compared to those of the 4d metals. Surface energy is larger for the 5d transition metals due to the stronger overlap between the 5d valence orbitals. Change of surface energy per unit strain will also be larger in the 5d metals compared to their 4d counterparts, thereby a larger surface tensile stress for the 5d metals is expected. This is demonstrated by our 4d Mo(001) and 5d W(001) surface stress results shown in table 4.

It is also easier to explain why there are different stress signs for the sub-monolayer Fe coverage on W(110) substrate. Since the bonding in the [001] direction is the strongest, the effect of the adsorbate on its stress will be most significant. The W–W bonds in the [001] direction are weakened most due to the adsorbate–substrate interaction. The W–W bonds in the [1$\bar{1}$0] direction are much weaker and not strongly affected by the adsorbate. Therefore, a compressive stress was measured in the [001] direction, and a tensile stress remains in the [1$\bar{1}$0] direction.

4. Conclusions

Surface stress was determined for the three different slabs using a revised composite elastic model for the monolayer adsorbate systems when the tetragonal symmetry is not affected by the adsorbates. Surface stress in W(001) is tensile and larger than that of the corresponding Mo(001) surface. The Fe overlayer on the W(001) surface increases the surface tensile stress.

The appearance of magnetism reduces both the surface stress and total energy. The compressive surface stress observed below monolayer coverage for Fe, Ni, and Co on W(001) and W(110) substrates is due to the weakened W–W bond resulting from the formation of the W–adsorbate bond. The anisotropic surface stress observed in the Fe/W(110) system is due to the anisotropic atomic structure of the system.

Acknowledgment

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