

Anisotropic surface stress on W(110)

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Abstract. – Anisotropic adsorbate-induced biaxial surface stress is measured for the adsorption of sub-monolayers of Fe and O on W(110). Half a monolayer of Fe induces compressive stress of -2 N/m along W[001] and tensile stress of $+1$ N/m along W $[\bar{1}10]$, whereas a (2×1) -O structure induces compressive stress of -1.1 N/m along W $[\bar{1}10]$, and causes only a minute stress of -0.1 N/m along W[001]. The O-induced surface stress is ascribed to a release of the anisotropic surface stress of the clean W crystal, whereas for Fe coverages, the surface stress of the Fe-W composite determines the measured stress.

Numerous investigations have confirmed that surface stress is of key importance in the discussion of fundamental effects like forces acting in a surface layer of a metal [1, 2], surface morphology [3, 4], surface reconstruction [5-7], surface diffusion [8, 9], and adsorbate-induced changes of forces between surface atoms [10-16]. Although the driving force for all these phenomena is clearly the modified electronic structure near the surface region of a metal, a generally applicable model that predicts the amount of surface stress or its change due to adsorption, without having to perform *ab initio* calculations, is still lacking [15]. To our knowledge there are no experiments that measure stress of single crystal surfaces *directly*. Therefore, experiments on adsorbate-induced *changes* of surface stress give important insight into the relevant processes that govern surface stress and are presented in this letter.

We report on the first measurements of *anisotropic* surface stress induced by the adsorption of Fe and O on W(110). We find that the magnitude of adsorbate-induced surface stress is different along the [001] and $[\bar{1}10]$ in-plane directions of the W(110) surface. Sign and magnitude of the adsorbate-induced surface stress depend strongly on the adsorbate. Sub-monolayer (ML) coverages of Fe induce stress of opposite sign along [001] and $[\bar{1}10]$. Whereas 0.5 ML Fe induce *compressive* stress of order -2 N/m along [001] and *tensile* stress of order 1 N/m along $[\bar{1}10]$, the adsorption of the same amount of O induces compressive stress of order -1.1 N/m along $[\bar{1}10]$. Along [001], O induces only a minute stress of order -0.1 N/m. We find that the anisotropy of the adsorbate-induced surface stress depends on the nature of the adsorbate and on the local atomic arrangement of the adsorbate-substrate composite. The O-induced stress is determined by the relief of anisotropic tensile surface stress of the clean W(110) surface. Although anisotropic surface and adsorbate-induced stress might have

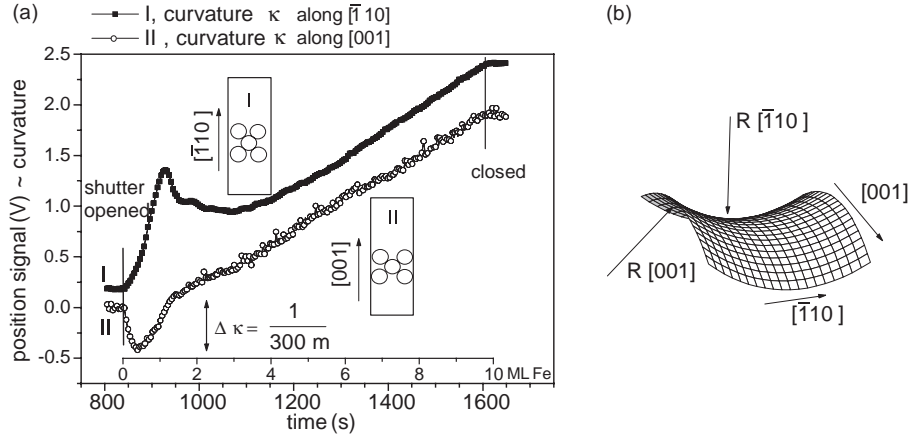


Fig. 1. – Fe-induced biaxial curvature of W(110). (a) Curvature of the W crystal along $[\bar{1}10]$, upper curve I, and curvature along $[001]$, lower curve II, measured on two crystals during the deposition of 10 ML Fe at 300 K. The sketches illustrate the respective crystal orientations. Note the opposite curvature along the two directions in the sub-monolayer range. (b) Anticlastic curvature of the W crystal in the sub-monolayer range. The curvatures are strongly exaggerated. At 0.5 ML Fe they are of order 300 m, the crystal length is 13 mm.

been anticipated from the twofold symmetry of the bcc(110)-surface, the opposite sign of the Fe-induced stress along two orthogonal surface directions remains to be a challenge for future theoretical calculations.

We employ the cantilever bending beam method [17] to measure adsorbate-induced surface stress with sub-monolayer sensitivity. The adsorbate-induced curvature $\kappa = 1/R$ (R : radius of curvature) of a $120\ \mu\text{m}$ thin, 13 mm long and 3 mm wide W(110) single crystal, that is clamped along its width to a sample manipulator, is detected by reflecting a laser beam from the bottom end of the crystal onto a position-sensitive detector [18]. Our set-up yields a position signal proportional to the crystal curvature. Before each stress measurement, the W crystal was repeatedly heated to 1500 K at an O_2 pressure of 10^{-7} mbar, and finally flashed to 2500 K under UHV conditions. This procedure removes C and O contaminants to a surface concentration below 1%, as checked by Auger electron spectroscopy. The flexural rigidity of the W crystals was calculated and experimentally checked by measuring the frequencies of the flexural vibrations of the cantilevered samples *in situ*.

We perform a biaxial stress analysis by measuring the curvature along the length of two differently cut crystals during the deposition of Fe at a rate of ~ 0.8 ML/min [19] onto the front surface of the crystal. The Fe-induced curvature κ along $[\bar{1}10]$ is measured on a W crystal with its long side along $[\bar{1}10]$, as shown in curve I of fig. 1(a), the curvature along $[001]$ is measured on a second crystal with its length along $[001]$, as shown in curve II of fig. 1(a). The positive slope of the position signal of curve I indicates a contraction of the W surface along $[\bar{1}10]$, whereas the initial negative slope of curve II is caused by an expansion of the W surface along $[001]$. One of the main results of our investigation is that the radius of curvature is of opposite sign along the two directions for sub-monolayer coverages. An anticlastic curvature of the W crystal results, that is schematically indicated in fig. 1(b). The expansion of the W surface along $[001]$ is at variance with the curvature expected from the tensile misfit strain of 10% between Fe and W and indicates the diminished importance of strain arguments for sub-monolayer coverages [21, 23].

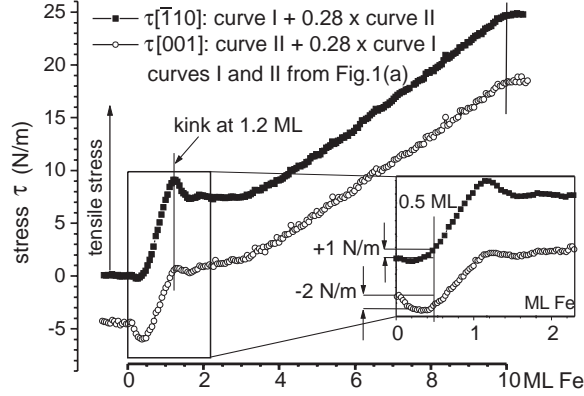


Fig. 2. – Biaxial Fe-induced stress. Curvature data from fig. 1(a), see eq. (1). Upper curve: stress along $[\bar{1}10]$, lower curve: stress along $[001]$. The inset shows an enlarged section of the 0–2 ML range. Note that the sub-monolayer stress is of opposite sign along the two directions up to 0.7 ML. The kink at 1.2 ML is ascribed to the formation of misfit distortions in the Fe film.

To convert the curvature data of fig. 1 to biaxial surface stress with components $\tau[001]$ along $[001]$ and $\tau[\bar{1}10]$ along $[\bar{1}10]$, as presented in fig. 2, the Poisson-type contribution of the second in-plane stress component to the first stress component, mediated via the Poisson effect of the W crystal, has to be taken into account. In general, quite involved relations between the curvatures and the stress components result due to the anisotropy of Young's modulus [16]. For W however, Young's modulus is isotropic and a fairly simple expression follows:

$$\tau_i = \sigma_F t_F = \frac{Y}{(1-\nu^2)} \frac{t^2}{6} \left(\frac{1}{R_i} + \nu \frac{1}{R_j} \right) \quad \text{for } i, j = [001], [\bar{1}10]. \quad (1)$$

Y and ν are Young's modulus ($Y(\text{W}) = 402 \text{ GPa}$) and Poisson's ratio ($\nu(\text{W}) = 0.28$) of the W crystal, and the sample thickness is given by $t = 120 \mu\text{m}$. We follow the usual convention [16], that the surface stress τ is given by the product of a macroscopic stress σ_F with a thickness t_F , so that our results are discussed in units N/m [20]. Note, that the large length-to-width-ratio of our sample of four justifies the assumption of free 2-dimensional bending, that is the basis of eq. (1). In view of the rather large uncertainties in the experimental determination of geometrical dimensions of the set-up, that lead to an upper limit for the error of the absolute value of the quoted stress of $\pm 15\%$, we neglect possible corrections due to the issue of 2-dimensional bending that are expected to be of order less than 1% [16].

The curvature data of fig. 1(a) are transformed with eq. (1) to give the two components of surface stress: curve II of fig. 1(a) is multiplied by $\nu = 0.28$ and added to curve I to give $\tau[\bar{1}10]$, the analogous procedure gives $\tau[001]$, and the results are presented in fig. 2. Half a monolayer of Fe induces compressive surface stress of -2 N/m along $\text{W}[001]$ and tensile surface stress of $+1 \text{ N/m}$ along $\text{W}[\bar{1}10]$. This result is the first direct experimental proof for anisotropic adsorbate-induced surface stress. Before we discuss its origin, we note in passing that the biaxial stress analysis modifies the previously published stress measurements [21]: the tensile contribution of the curvature along $[\bar{1}10]$ to the stress along $[001]$ shifts the maximal compressive stress from -5 N/m to -2 N/m , the kink of the stress curve is shifted from 1.5 ML Fe coverage to 1.2 ML. The almost horizontal section of the stress curves in fig. 2 for coverages between 1.2 ML and 3 ML reveals that the formation of misfit distortions [21, 22] allows a practically stress-free growth of the second and third layer of Fe and may express itself in the

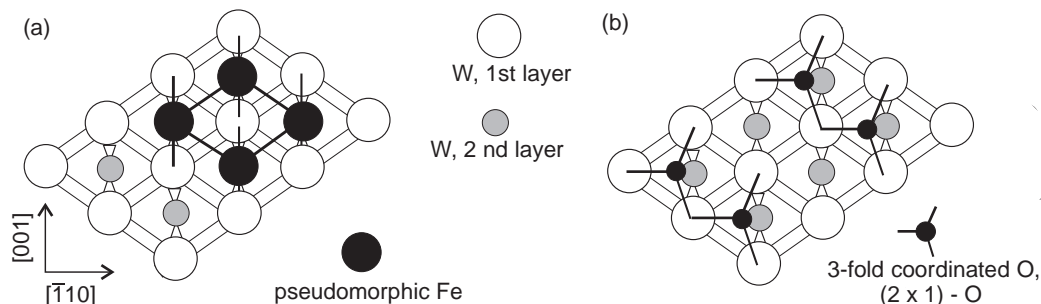


Fig. 3. – Sketch of the adsorption geometry on W(110). (a) Fe atoms are bonded in pseudomorphic sites, that resemble the continuation of the W bulk structure. (b) 2×1 -O structure. O sits in threefold coordinated sites above the W surface.

high coercivity of 1.5 ML Fe [21]. The constant slope of the stress curve in fig. 2 for coverages between 4 ML and 10 ML indicates an isotropic residual stress of order 12 GPa.

The most intriguing result of our work is that Fe induces compressive stress along [001], and tensile stress along $[\bar{1}10]$ for sub-monolayer coverages. This novel result is of considerable importance as it presents a further example for the diminished significance of strain arguments for the discussion of stress at sub-monolayer coverages, as we discussed earlier [23]. Therefore, we neglect potential anisotropic adsorbate-adsorbate interactions in the following. Rather, we ascribe the sub-monolayer stress to an anisotropic surface stress of the Fe-W composite and discuss its origin in view of the atomic structure of Fe on W(110).

LEED studies suggest that Fe grows pseudomorphically in the first layer [22]. We adopt the exact positions of the Fe atoms from a recent photo-electron diffraction study on the structure of an Fe monolayer on W(110) [24] that proposed that the Fe atoms are bonded pseudomorphically in a continuation of the W-bulk structure, as indicated in fig. 3(a). This adsorption site lifts the coordination deficiency of the nearest W surface atoms, as they gain a bulk-like 8-fold coordination. Therefore, the main driving force for surface stress, *i.e.* the lack of bond partners above the surface, is lifted and one might speculate that a relief of the surface stress of W(110) should result.

The amount of stress relief can be estimated from calculations by Ackland and Finnis, who calculated an anisotropic tensile surface stress for W(110) of +0.3 N/m along [001], and of +2.4 N/m along $[\bar{1}10]$ [25]. Along a given direction, the relief of the surface stress of W along that direction plus the Poisson contribution from the second component could be expected as Fe-induced compressive stress. This stress relief model gives a compressive stress of -0.97 N/m (-0.3 N/m $- 0.28 \times 2.4$ N/m) along [001], and of -2.48 N/m along $[\bar{1}10]$. For the Fe coverage of 0.5 ML, the values have to be multiplied by 0.5 and the calculated stress relief along [001] is a factor of four smaller than the experimental value. Along $[\bar{1}10]$, compressive stress is proposed by the model, but tensile stress is measured. In summary, a simple surface stress relief mechanism is not capable of describing the experimental data even qualitatively. We suggest that the main reason for the failure of the stress relief mechanism is that the lack of coordination of surface atoms is simply shifted to the new Fe surface atoms, and that the surface stress of the Fe-W composite has to enter the surface stress balance. Our data indicate that the Fe-W composite at a coverage of 0.5 ML is under larger tensile stress along $[\bar{1}10]$, and under larger compressive stress along [001], than the clean W(110) surface. However, the following discussion of O-induced surface stress demonstrates that the model of stress relief due to adsorption is at least qualitatively applicable in the case of O on W(110).

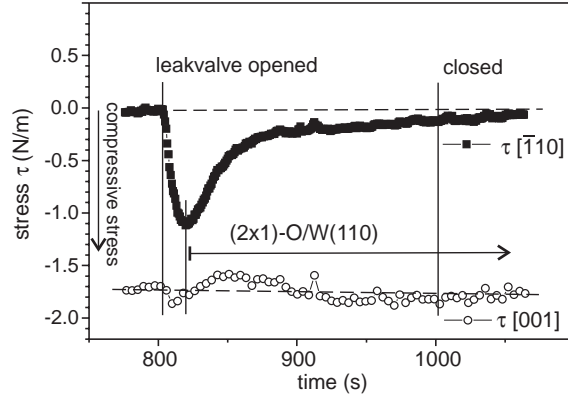


Fig. 4. – Anisotropic O-induced stress on W(110) at 300 K. Note, that along $[\bar{1}10]$ a maximal compressive stress of -1.1 N/m is observed, whereas along $[001]$, the magnitude of the O-induced stress is a factor 10 smaller. After the O-uptake of the frontside of the crystal, the slower O-uptake of the backside brings the total stress back to the broken thermal drift line. LEED reveals a 2×1 structure at the maximal compressive stress.

We measured O-induced changes of the surface stress by exposing the front surface of the crystal to a collimated beam of O_2 that was directed to the sample by a doser. The dosing was performed at an O_2 background pressure of 1×10^{-8} mbar for 200 s at 300 K. The O_2 partial pressure is roughly a factor 5 larger on the frontside than on the backside of the crystal. As the sticking coefficient of O decreases considerably after an O-coverage of 0.5 ML is reached [26], we ascribe the initial compressive stress indicated in fig. 4 to an O-uptake of the frontside before the bending of the crystal is reversed to its initial state by the delayed oxygen uptake of the backside. The exposure of the W(110) surface to O_2 induces a maximal compressive stress of -1.1 N/m along $[\bar{1}10]$, and only a minute compressive stress of -0.1 N/m along $[001]$. After termination of the O-exposure, the surface is covered by a 2×1 -O phase, as we conclude from the observation of a 2×1 -LEED image [26, 27], therefore we assign the maximum of the stress curve along $[\bar{1}10]$ to an O-coverage of 0.5 ML.

The O-induced compressive stress along $[\bar{1}10]$ can be understood qualitatively by analyzing the geometry of the O-adsorption site. A quantitative LEED analysis of the 2×1 -O structure suggests that O is adsorbed in a threefold coordinated site above the W(110) surface [27]. Figure 3(b) shows a sketch of the O-adsorption geometry. This bond site affects the intraplanar W-W bonds of the surface layer much more than the interplanar W-W bonds between atoms of the first and the second layer of W. Ascribing the calculated tensile surface stress of W(110) along $[\bar{1}10]$ [25] to the reduced coordination of the W surface atoms and surface bonds, we propose that the adsorption of O on the threefold-coordinated site resembles an increase of the coordination of the two adjacent W-W intraplanar bonds. Thus, in the vicinity of the O-adsorbate, the tensile surface stress is partially released. As only half of the intraplanar W-W bonds are affected by the 2×1 -O structure, only half of the theoretically predicted tensile surface stress of $+2.4$ N/m [25] should be released. In qualitative agreement with this model, compressive stress of -1.1 N/m is measured along $[\bar{1}10]$. The W-W bonds with projections along $[001]$ are interplanar bonds between the surface layer and the second layer and are not significantly affected by the adsorption of O above the surface. This simplified view is supported by our measurement of an order of magnitude smaller O-induced stress along $[001]$. In conclusion, the discussion of adsorbate-induced surface stress in view of both the local

geometry and coordination arguments seems to be applicable for the adsorbate oxygen.

In the discussion of adsorbate-induced surface stress, the inclusion of the bond angles, and atomic distances between adsorbate and substrate does not seem to be relevant for adsorbates that reside above the substrate surface. This view is supported by the experimentally confirmed bond lengths of Fe-W ($d = 2.604 \text{ \AA}$ [24]) and O-W ($d = 2.08 \text{ \AA}$ [27]). These bond lengths deviate by less than 0.3% from the sum of the covalent radii of W ($r = 1.368 \text{ \AA}$) and Fe ($r = 1.243 \text{ \AA}$). The O-W bond length of 2.08 \AA falls exactly in the bond length range of 1.9 \AA – 2.1 \AA observed in various W_3O compounds [28]. Therefore, we do not expect that the adsorption induces any significant forces due to bond length mismatch in the surface layer. This is in contrast to the O-induced surface stress on Si [29], where the incorporation of O into Si-Si bond induces surface stress that was modelled satisfactorily by a valence force field that took the strained bonds of the Si-O-Si complex explicitly into account.

In conclusion, we suggest a contribution from the surface stress of the Fe-W composite to the Fe-induced anisotropic surface stress, whereas for O the release of the surface stress of the clean substrate should be dominant. We propose that coordination arguments are applicable and predict compressive adsorbate-induced surface stress, due to the relief of intrinsic tensile surface stress of the clean metal, for those adsorbate-substrate coordinations that resemble a bond coordination that is found in other adsorbate-substrate components. This is the case for oxygen bonded in the 3-fold coordination on W(110), as evidenced by numerous inorganic compounds that exhibit the W_3O coordination [28]. Feibelman's recent *ab initio* calculations [15] have proven that adsorbate-induced stress relief can be expected, but more theoretical and experimental work is clearly called for to understand the atomic origin of surface stress.

We thank one of the Referees for suggesting a physical appealing model for Fe-induced tensile sub-monolayer stress along $[\bar{1}10]$: In contrast to the Fe-W bond length along $[001]$ of 2.6 \AA , that is not expected to induce any stress for the reason mentioned above, the larger Fe-W bond length along $[\bar{1}10]$ of 3.04 \AA makes it conceivable that bond energy could be gained for a shrinkage of this Fe-W bond. The symmetry of the surface does not allow for this strain, and a *tensile* stress could be expected along $[\bar{1}10]$, as measured in our experiments.

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