



# Changes in surface stress caused by the adsorption of an epitaxial metal monolayer

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## Abstract

The adsorption of a metal monolayer on a foreign substrate generates a change in the surface stress. We calculate this change for a number of substrate/adsorbate systems using the embedded-atom method. The results are compared with those obtained from a continuum model. A cycle, in which the stretching of a substrate/adsorbate system is decomposed into several steps, helps in understanding the numerical results. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The advent of the scanning tunneling and atomic force microscopes has made it possible to measure surface-induced deformations of solids with greater precision than before. This has spurred renewed interest in the thermodynamics of solid surfaces and induced researchers to investigate the surface stress for a variety of systems both in vacuum and in electrochemical cells. These recent developments have been well reviewed by Ibach [1].

The surface stress is modified by the formation of adsorbate layers. This effect is particularly large when a monolayer of a foreign metal is adsorbed on the surface of another metal, a process which is known as *underpotential deposition* in electrochemistry. An understanding of this effect is clearly desirable, particularly since the formation of a monolayer often precedes the bulk deposition of metals, a process of great technological importance. We have therefore performed model calculations for the changes in surface stress induced by the formation of epitaxial metal films. Adsorption on the (111)-surface

of face-centered cubic (fcc) metals has been chosen as an example to explore the principles involved in these stress changes. We shall show that our results can be interpreted in terms of a cycle, in which the substrate and the layer are first separated, then stretched individually, and finally recombined.

## 2. A model for calculating the surface stress

We consider a metal surface in the vacuum at a temperature  $T = 0$  so that entropy effects are excluded. The surface-stress tensor  $g_{nm}$  is then defined by the change of the internal surface energy  $U_s$  under an elastic deformation:

$$dU_s = A \sum_{n,m} g_{n,m} d\epsilon_{nm} \quad (1)$$

where  $A$  is the surface area, and  $\epsilon_{nm}$  the strain causing the deformation. All other variables, in particular the surface composition, are kept constant. In the following we will present model calculations for

epitaxial films on (111)-surfaces of metals with fcc symmetry, so that the stress tensor is diagonal, and its tensor character can hence be neglected.

We are interested in the change  $\Delta g$  that an adsorbed film induces in the surface stress. This change can be calculated as the difference between the surface stress of the substrate with and without the film:

$$\Delta g = \frac{dU_{S/M}}{dA} - \frac{dU_S}{dA}. \quad (2)$$

$U_{S/M}$  is the internal energy for the film-covered surface, and  $U_S$  that of the bare surface.

We have calculated the internal energies by the embedded-atom method. This is a simple approach to metallic bonding that takes into account the many-body interactions [2,3] between the electrons. Within this method, the total energy of the system  $E_{\text{tot}}$  is expressed as the sum of two contributions:

$$E_{\text{tot}} = \sum_{i=1}^N F_i(\rho_{h,i}) + \frac{1}{2} \sum_i \sum_{j \neq i} \phi_{ij}(r_{ij}). \quad (3)$$

$\rho_{h,i}$  is the host electron density at atom  $i$  due to the other atoms of the system; it is calculated as the superposition of the electronic densities:

$$\rho_{h,i} = \sum_{j \neq i} \rho_j(r_{ij}) \quad (4)$$

where  $\rho_j(R)$  is the contribution of atom  $j$  to the electronic density.  $F_i(\rho)$  is an attractive term and corresponds to the energy to embed atom  $i$  into the background electron density  $\rho$ .  $\phi_{ij}(R_{ij})$  represents a core–core pair repulsion between atom  $i$  and  $j$  separated by the distance  $R_{ij}$ :

$$\phi_{ij}(r_{ij}) = z_i z_j / R_{ij} \quad (5)$$

where  $z_i$  is the effective charge on atom  $i$ . For the embedding potential  $F(\rho)$  and for the effective charges we have used the parameterization proposed by Foiles et al. [3]. A study of the surface reconstruction of transition metals by Dodson [4] shows that the embedded-atom method is well suited to the study of stress phenomena. The same method has also been employed in a recent molecular-dynamics simulation for the stress in thin films [5].

In electrochemical systems the film is in contact with the solution; in some cases it is also covered by weakly adsorbed anions. The contributions of both

the solvent and anionic layers to the surface stress are small [1,6]. Therefore our calculations should also be relevant for metallic monolayers formed by underpotential deposition in electrochemical cells, with one caveat: our calculations have been performed for uncharged surfaces, so any variation in surface stress caused by a change in the surface-charge density during film formation is disregarded. But again, changes of the surface stress with the charge density are typically much smaller than those caused by the formation of metal films, and can therefore be neglected to a first approximation.

The change of surface stress  $\Delta g$  caused by the adsorption of an epitaxial monolayer can also be estimated from a simple continuum model [1,5]. If we assume that the change in the surface stress is caused by adjusting the lattice constant  $a_M$  of the adsorbed metal to the lattice constant  $a_S$  of the substrate, then the strain induced by the misfit is:  $\epsilon_{\text{mf}} = (a_S - a_M)/a_M$ , and for a (111)-surface we have [1]:

$$\Delta g = \frac{Y_{111}}{1 - \nu_{111}} \epsilon_{\text{mf}} d_{111} \quad (6)$$

where  $d_{111}$  is the thickness of the adsorbed monolayer and  $Y_{111}$  and  $\nu_{111}$  are Young's modulus and Poisson's ratio for the (111)-surface. These can be calculated from the corresponding compliances  $\sigma_{ij}$  according to

$$Y_{111} = \frac{4}{2\sigma_{11} + 2\sigma_{12} + \sigma_{44}}$$

$$\nu_{111} = -\frac{Y_{111}}{12}(2\sigma_{11} + 10\sigma_{12} - \sigma_{44})$$

The compliances  $\sigma_{ij}$  have been obtained from the experimental elastic constants [7].

### 3. Results and discussion

We have calculated the changes in the surface stress caused by the adsorption of a metallic monolayer on a (111)-surface of a foreign substrate for a number of systems. In Table 1 we give the equilibrium lattice constants of the bulk metals and the corresponding values for monolayers isolated in vacuum, in Table 2 our results from the embedded-atom

Table 1

Equilibrium lattice parameters  $a_S^0$  for the bulk metals and  $a_{\text{mon}}$  for the isolated monolayers in vacuum; all values are given in Ångstroms

Metal	Ag	Au	Pt	Pd	Cu
$a_S^0$	4.09	4.08	3.92	3.89	3.62
$a_{\text{mon}}$	3.96	3.78	3.59	3.64	3.48

method. In all cases we have assumed a  $(1 \times 1)$  structure, even though in some systems the stress is so large that such a structure would not be stable.

Whenever the atoms of the adsorbate are larger than those of the substrate – these are the systems below the diagonal in Table 2 – the calculated stress is compressive, as expected. The change in stress correlates roughly with the difference in the lattice constants, but there are a few exceptions to this rule. In the opposite case, when the adsorbate atoms are smaller, the change in stress can be either compressive or tensile.

Before we analyze our results in detail, it is interesting to compare them with those of the continuum model, which are given in Table 3. In the latter model the sign of the stress change is determined by the difference of the atomic sizes, with  $\Delta g$  usually increasing when moving upwards along a column or to the left along a row. This order is strict in the case of the columns, because of Eq. (6), where the role of the substrate is exclusively linked to the misfit  $\epsilon_{\text{mf}}$  for given elastic constants of the adsorbate. Along a row, the increasing of  $\Delta g$  is also reasonable because of the increasing misfit, but this trend is modulated by the different elastic constants of  $M$  for a given  $S$ . On the other hand, the results of

Table 2

Change of surface stress produced by the adsorption of a monolayer of a metal  $M$  on a (111) single crystal surface of a substrate  $S$  according to the embedded atom method. All the values are given in  $\text{J}/\text{m}^2$ , and the metals are ordered along the rows and columns by decreasing lattice constants

$S \backslash M$	Ag	Au	Pt	Pd	Cu
Ag	–	0.68	3.35	1.81	2.45
Au	–2.81	–	1.02	–0.10	–0.28
Pt	–7.76	–5.92	–	–3.15	–2.84
Pd	–5.13	–4.34	–0.36	–	–0.53
Cu	–15.19	–12.92	–8.28	–7.21	–

Table 3

Change of surface stress produced by the adsorption of a monolayer of a metal  $M$  on a substrate  $S$  according to the continuum model (Eq. (6)). All values are given in  $\text{J}/\text{m}^2$

$S \backslash M$	Ag	Au	Pt	Pd	Cu
Ag	–	0.11	3.31	3.32	7.18
Au	–0.10	–	3.11	3.16	7.03
Pt	–1.71	–1.76	–	0.50	4.61
Pd	–2.00	–2.09	–0.58	–	4.16
Cu	–4.76	–5.11	–5.94	–4.57	–

Table 2 are not so straightforward to interpret, because besides elastic considerations some chemistry is involved. Though the stress changes predicted by the continuum model are of the same order of magnitude as those calculated from the embedded-atom method, the quantitative differences are substantial, and in a few cases the two methods even predict different signs.

In order to understand the various contributions that determine the change in surface stress we consider the cycle shown in Fig. 1. As the initial state ‘i’ we take our model system, a monolayer of  $M$  ad-

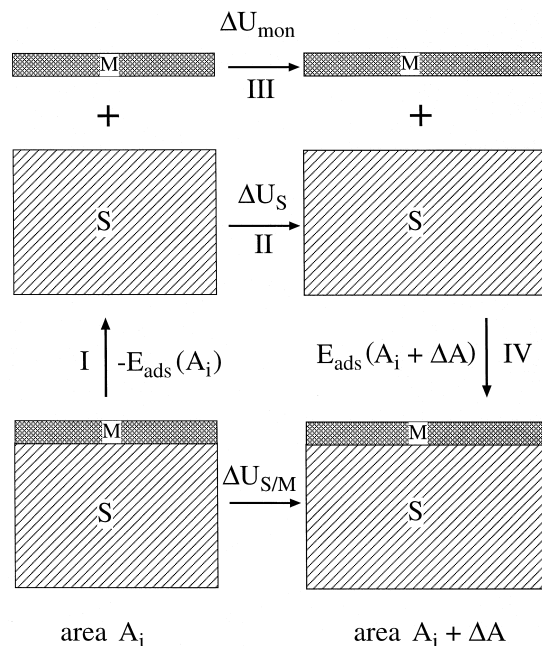


Fig. 1. A cycle for decomposing the the change in the surface stress caused by an adsorbed metal monolayer.

sorbed on the substrate S; the lattice constants for adsorbate and substrate are given by the equilibrium constant  $a_s^0$  of the substrate. By  $A_i$  we denote the surface area, and by  $U_{S/M}^i$  the surface energy. We then stretch the system isotropically to a final state 'f' with surface area  $A_f = A_i + \Delta A$ . The corresponding energy change is:

$$\Delta U_{S/M} = U_{S/M}^f(A_i + \Delta A) - U_{S/M}^i(A_i) \quad (7)$$

The ratio  $\Delta U_{S/M}/\Delta A$  gives us the first term of Eq. (2) in the limit  $\Delta A \rightarrow 0$ .

Let us now obtain  $\Delta U_{S/M}$  by the cycle shown in Fig. 1. In step I we desorb the monolayer of M into the vacuum; the corresponding energy change is the negative of the adsorption energy for the given area:  $-E_{\text{ads}}(A_i)$ . In step II we expand the bare substrate surface from the area  $A_i$  to the area  $A_i + \Delta A$ , which requires an energy  $\Delta U_S$ . Next we stretch the isolated layer of M, which entails an energy change  $\Delta U_{\text{mon}}$ , and in step IV we adsorb the expanded monolayer of M onto the expanded surface of S, with energy change  $E_{\text{ads}}(A_i + \Delta A)$ . Taking the limit  $\Delta A \rightarrow 0$  gives:

$$\frac{dU_{S/M}}{dA} = \frac{dE_{\text{ads}}}{dA} + \frac{dU_S}{dA} + \frac{dU_{\text{mon}}}{dA}. \quad (8)$$

Substituting into Eq. (2) gives:

$$\Delta g = \frac{dE_{\text{ads}}}{dA} + \frac{dU_{\text{mon}}}{dA}. \quad (9)$$

This equation allows us to reinterpret the change of the surface stress upon adsorption of a monolayer of M on a substrate S in terms of two different contributions. The first contribution corresponds to the change of the adsorption energy of the monolayer of M with an elastic change of the substrate surface, and the second contribution corresponds to

Table 4

Contribution to the change of surface stress by the change of the adsorption energy of the monolayer of M with an elastic change of the substrate surface,  $\frac{dE_{\text{ads}}}{dA}$ . All values are given in J/m<sup>2</sup>

S\M	Ag	Au	Pt	Pd	Cu
Ag	–	–5.30	–7.67	–5.23	–3.65
Au	–4.99	–	–9.98	–7.15	–6.38
Pt	–6.84	–9.50	–	–9.21	–8.83
Pd	–3.43	–7.33	–9.70	–	–6.44
Cu	–1.79	–6.36	–9.52	–6.35	–

Table 5

Contribution to the change of surface stress by the expansion of the monolayer in vacuum,  $dU_{\text{exp}}^{\text{mon}}/dA$ . All values are given in J/m<sup>2</sup>

S\M	Ag	Au	Pt	Pd	Cu
Ag	–	5.98	11.02	7.04	6.10
Au	2.18	–	11.00	7.05	6.10
Pt	–0.92	3.58	–	6.06	5.99
Pd	–1.70	2.99	9.34	–	5.91
Cu	–13.40	–6.56	1.24	–0.86	–

the energy change due to the expansion of the isolated monolayer.

Chemical intuition suggests that the first term in Eq. (9) should be negative. It corresponds to the formation of metallic bonds at constant interatomic spacing, which should become more favorable when the area is increased. This expectation is borne out by our model calculations (see Table 4). The second term, which is listed in Table 5, is of the same order of magnitude, but can have a positive or a negative sign. Though it is a property of the isolated monolayer, it depends indirectly on the equilibrium lattice constant  $a_s^0$  of the substrate, since the derivative  $dU_{\text{mon}}/dA$  is to be taken at a surface area corresponding to the lattice constant  $a_s^0$ . The trends in this term can be understood by comparing the equilibrium lattice constants for the monolayer, which are also given in Table 1, with the lattice constants of the substrate. Let us take the adsorption of a monolayer of Ag on various substrates as an example. The lattice constant of the isolated Ag monolayer is smaller than the lattice constant of bulk gold, but larger than those of bulk Pt, Pd and Cu. Thus, in order to fit onto the substrate, the monolayer is expanded in the former case but compressed in all others. A similar analysis can be performed for the other cases. It should also be noted that both in each row (i.e. for a given substrate) and in each column (for a given adsorbate) the values of  $dU_{\text{mon}}/dA$  follow the same trends as the cohesive energies of the pure metals (see Table 6), viz.  $E_{\text{coh}}^{\text{Pt}} < E_{\text{coh}}^{\text{Au}} < E_{\text{coh}}^{\text{Pd}} < E_{\text{coh}}^{\text{Cu}} < E_{\text{coh}}^{\text{Ag}}$ .

Table 6

Cohesive energies of bulk metals

Metal	Ag	Au	Pt	Pd	Cu
$E_{\text{coh}}/\text{eV}$	–2.85	–3.93	–5.77	–3.91	–3.54

There are few quantitative experimental data with which we can compare our results, but the measurements of Grossman et al. on the surface stress generated by the deposition of Ag on Pt(111) [8] are worth mentioning. These authors report a value of  $\Delta g = -8.8$  N/m per monolayer for the growth of two monolayers. This agrees well with our calculated value of  $-7.76$  N/m; in particular our model explains why this value is much larger than estimates based on the lattice mismatch alone: our consideration above show that there is an additional contribution from the change of the adsorption energy with strain. A further analysis of our results supports the idea proposed in Ref. [8] that charge transfer plays a role: according to our calculations the work function of Pt(111) drops by 0.85 eV upon adsorption of a monolayer of silver.

#### 4. Conclusion

Our model calculations illustrate the principles that are involved in the stress changes accompanying the formation of epitaxial films both in the vacuum and in electrochemical systems. The embedded-atom method, which we employed, should be good enough to predict trends and orders of magnitude. Numerically more demanding methods will produce better quantitative results, but should add little to our understanding of the underlying phenomena. Finally we

note that the embedded-atom and similar methods are particularly suited to study the dynamics of surface reconstructions [5,9], a related topic which we have not addressed here.

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