Many-Body Surface Strain and Surface Reconstructions in fcc Transition Metals

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Bonding in the near-surface region is strongly influenced by the truncation of the lattice at the surface. This many-body effect is examined quantitatively by use of the embedded-atom method on low-index transition-metal surfaces. An unreconstructed metal surface is found to have a tensile strain of several percent. This many-body surface strain is an important factor in the energetics of surface structure, serving as a parameter combining surface stress and nonlinear elastic effects. In particular, it is demonstrated that the surface strain drives surface reconstruction, and also produces asymmetry in the stability properties of thin mismatched epitaxial overlayers.

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It is difficult to isolate quantities which provide a clear description of the change in structural energetics which occurs upon formation of a free surface. However, based on the bond-order–bond-length correlations first noted by Pauling,[1] it seems clear that surface atoms, for which the effective coordination number is smaller than in the bulk, will "want" to have a smaller interatomic distance than that of the bulk. This reduction of bond length suggests that an unreconstructed free surface of a bulk material is usually, in some sense, in tension. Recent studies of this effect include a calculation by Needs[2] of the surface stress at Al(110) and Al(111) surfaces, in which he finds substantial ($\simeq$10 GPa) tensile stresses. [Vanderbilt[3] has performed a similar calculation of stress on the Si(111) surface, in which a weak ($\simeq$1 GPa) compressive stress was found. In this case the extra angular freedom provided by the covalent structure seems to allow the reduction in lattice parameter at the surface to be accommodated primarily through a small inward relaxation of the surface layer.]

The calculation of surface stress alone can be insufficient to address problems concerned with surface structure. Not only does bonding environment which characterizes the surface result in significant stress at the surface, but the elastic behavior of the near-surface region may also differ considerably from that of the bulk material. As a result, for example, knowledge of the surface stress alone does not allow prediction of surface reconstruction. It is therefore desirable to obtain surface-related quantities which are physically more relevant in the determination of surface structure. In this Letter, the magnitudes of the many-body surface strain and the surface elastic constants are determined for low-index transition-metal surfaces, with use of the embedded-atom method.[4] Surface strain is particularly useful in the determination of surface structure since it combines relevant information about both the surface stress and the near-surface elastic response. The role of surface strain in the structural energetics of surfaces is then illustrated by prediction of reconstructions of low-index transition-metal surfaces and the asymmetric stability properties of strained metal overlayers.

The embedded-atom method provides an accurate description of structural energetics in many nonideal geometries, including layered systems and surface reconstruction.[5,6] The total energy is expressed as the sum of a pairwise potential and an embedding energy, which is the energy produced by the embedding of each atom in the local electron density ρ provided by the other atoms in the structure. This electron density is always well defined, and so treatment of surfaces, interfaces, and defects is unambiguous. The resulting model has proven particularly appropriate for intermetallic structures, since the embedding energy is independent of the source of the electron density.

The surface strain is obtained by determination of the equilibrium structure of a series of free-standing metal slabs of varying thickness. The effective lattice constant of the surface $a_{\parallel}$(surf) is determined by extrapolation to the case where there is no bulk material (2 monolayers). The surface strain is then simply $\epsilon=[a_{\parallel}(\text{surf})-a]/a$, where a is the bulk lattice constant. This extrapolation procedure, however, must be approached with caution. The surface of a metal always exists in the environment provided by the bulk of the metal. This means that, for example, the properties of a free-standing monolayer are irrelevant for the present study. In the embedded-atom method, both the local electron density and the pairwise potential fall off roughly exponentially with the interatomic distance, and their influence is cut off near 5 Å. The thinnest slab which may be modeled in terms of isolated surfaces in contact with a bulk material is thus 4 monolayers thick. Consideration of thinner slabs introduces direct surface-surface interactions, complicating the calculation beyond redemption.

The sample structures have a thickness t of 4, 6, or 10 monolayers, and infinite extent in both directions parallel to the surface simulated by use of periodic boundary conditions. For each slab thickness, the dependence of the structural energy on the lattice constant parallel to

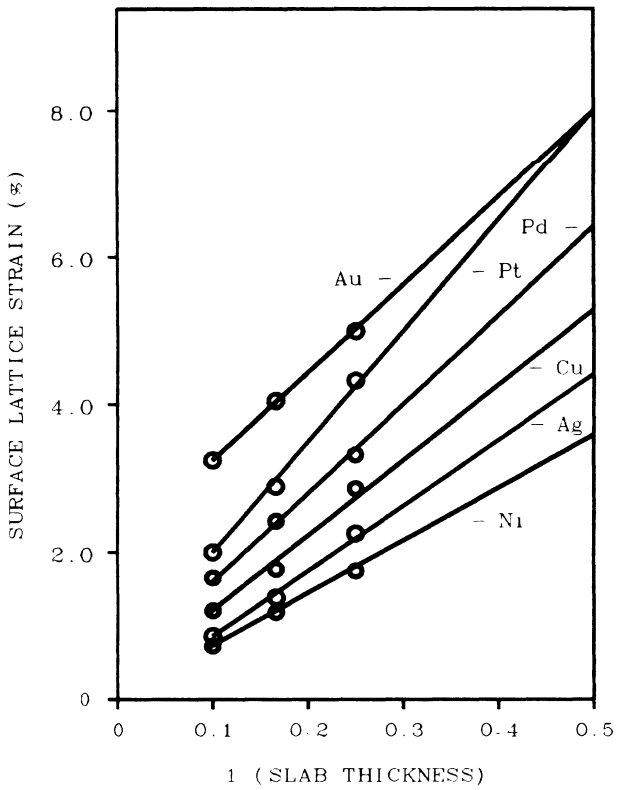

FIG. 1. Surface lattice parameter for free-standing transition-metal slabs as a function of slab thickness. The slabs have [100] free surfaces. The lines, labeled by the slab material, represent linear fits to the simulations, which are used later to determine the effective strain for a [100] free surface on a bulk substrate.

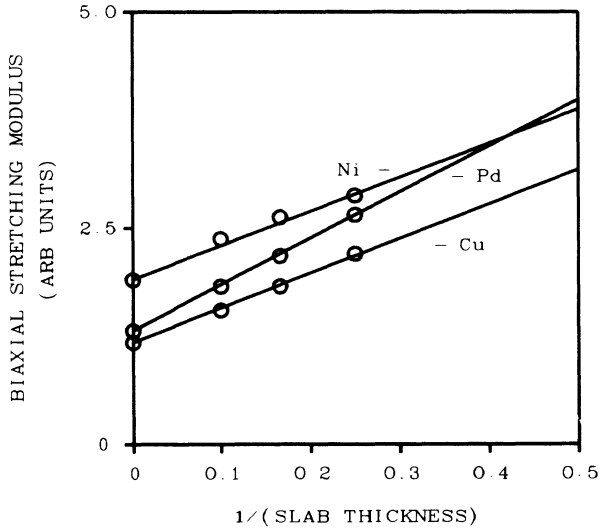

FIG. 2. Biaxial stretching modulus for free-standing transition-metal slabs as a function of slab thickness. The slabs are composed of Cu, Ni, or Pd, and have [100] free surfaces. The influence of the free surface is to increase the stretching modulus considerably. The quality of the linear fit again agrees with the model of the slabs as nearly bulklike material in contact with monolayer surfaces.

the surface was calculated by my fixing the lattice constants in the planes parallel to the surface, and then allowing the lattice to relax to a local minimum in energy under that constraint. The parallel lattice constant is then varied until a global minimum in energy is found. The curvature of the energy at this global minimum, $\partial^2 E/\partial a_{\parallel}^2(t)$ (which is proportional to the biaxial stretching modulus Y[100]), is also determined. The dependence of the equilibrium lattice constant on the film thickness for Ag, Au, Cu, Ni, Pd, and Pt slabs appears in Fig. 1, and the corresponding curvature values for Cu, Ni, and Pd slabs appear in Fig. 2.

Since the effect of the free surface on the near-surface properties scales approximately inversely with the slab thickness, a model wherein the surface monolayers, having a set of characteristic properties, interact with the subsurface material, which has bulk properties, seems justified. In such a model, the lattice constant of the slab parallel to the free surface will vary with slab thickness as

$$a_{\parallel}(t) = a + (2/t)[a_{\parallel}(\text{surf}) - a], \quad (1)$$

which allows determination of $a_{\parallel}(\text{surf})$. This procedure was used to evaluate the surface strain on the (100) surfaces of the fcc transition metals Ag, Au, Cu, Ni, Pd, and Pt (see Table I). The magnitude of the surface strains is quite significant, ranging from 3.5% to 8.0% in tension. These strains are accompanied by increases of the biaxial stretching modulus Y[100] by factors of 2 to 4.

How do these results impact on the properties of real systems? Two areas will be discussed in which these many-body surface effects provide insight into the mechanisms behind the observed behavior. The first area is that of (100) surface reconstruction in the fcc transition metals. These transitions take place by formation of a dense surface layer through introduction of an interfacial misfit dislocation structure at the (100) surface.[7] This (100) surface reconstruction is only observed in Au and Pt, among the metals under consideration here. High-resolution electron microscopy of the reconstructed Au(100) surface directly reveals the presence of a net-

TABLE I. (100) surface strain for various transition metals.

Metal	(100) surface strain (%)	(100) Reconstruction
Ni	3.6	No
Ag	4.4	No
Cu	5.6	No
Pd	6.4	No
Au	8.0	Yes
Pt	8.0	Yes

work of surface Shockley partial dislocations which generate the reconstruction.[8] The resulting structure is similar to that which occurs in lattice-mismatched overlayers when the mismatch is large enough that coherence with the substrate becomes unstable, and misfit dislocations appear in the interface to partially accommodate the mismatch.

An analysis of the stability limits for coherence of a mismatched monolayer on a substrate was worked out several decades ago by Frank and van der Merwe.[9] This model (as well as more recent refinements) predicts a critical mismatch of about 7%. Monolayers having larger mismatch form misfit dislocations between the monolayer and the substrate. In the case of pure metal surfaces, the effective mismatch is simply the surface strain characteristic of the particular metal surface, as described above. Recall that the unreconstructed metal surface is stained into coherence with the bulk structure. However, if the surface strain exceeds roughly 7%, the surface strain should be partially accommodated by interfacial misfit dislocations, which will result in the form of reconstruction observed on the Au(100) and Pt(100) surfaces. The present calculations (Table I) show that only the Au(100) and Pt(100) surfaces have surface strain greater than 7%, which agrees with the observed reconstruction behavior.

An interesting question is why the Au and Pt surfaces have larger surface strain than the other materials. The reason cannot be determined within the embedded-atom method, since the forms of the embedding and pairwise terms are empirical. However, one can form an argument that the trend is correct. There is a strong correlation between the free energy of a defect in a solid and the product of the bulk modulus B and the atomic volume Ω.[10] If, for discussion, the surface of a solid is considered to be a massive defect, one would expect that the extent of relaxation would increase with increasing $B\Omega$. Au and Pt have considerably larger values of $B\Omega$ than do the other metals considered in this study. They would therefore be expected to have the largest surface strain, in agreement with the present calculations.

On extension of these surface strain calculations to (111) surfaces, the (111) Au and Pt surfaces again have the largest strain, but on this surface the magnitude is only about 4.3% for the Au(111) surface, and 3.8% for the Pt(111) surface. One would therefore think that these (111) surfaces should not reconstruct in the manner described above; in fact, the Au(111) surface is observed to reconstruct. However, the nature of this reconstruction does differ somewhat from that occurring on the (100) surfaces. The $\sqrt{3}\times 22$ reconstruction of the Au(111) surface appears to be caused by a much smaller density of misfit dislocations at the surface than is required for the (100) reconstruction. In addition, the type of misfit dislocation appearing in this reconstruction has smaller strain energy per unit length than do those relieving strain on the (100) surface.[11] Accordingly, the amount of strain required to produce reconstruction of the (111) surface should be smaller than that required for reconstruction of the (100) surface, because less energy is required to introduce the dislocations at the (111) surface. This is in accordance with the present calculations.

The second area addresses the destabilization of thin coherent pseudomorphic overlayers in tension relative to those in compression.[12] The critical condition for coherence is based on an energy-balance criterion, where the strain energy of the coherent structure is compared with that of the competing incoherent structure. The many-body surface strain has two clear effects on this energy balance. First, the strain of the surface monolayer increases the effective mismatch of a system predicted by bulk parameters to be in tension, but decreases the effective mismatch of a system in compression. This effect alone would destabilize overlayers in tension, but stabilize overlayers in compression, relative to models based solely on bulk elastic parameters. The increase in biaxial stretching modulus Y[100], however, which results in a corresponding increase in the strain energy, must also be considered. For an overlayer in compression, the reduction in strain energy expected from the decrease in effective mismatch is largely offset by the increase in the elastic modulus. However, in overlayers in tension both the biaxial modulus and the effective mismatch increase. As a result, the strain energy of the coherent structure shows a marked asymmetry between overlayers in compression and in tension, with those in tension being strongly destabilized relative to expectations based on the bulk parameters.

In contrast, the strain energy of the incoherent structure is composed of two terms, one from the misfit dislocations and the other from the residual homogeneous strain. The strain energy of the residual homogeneous strain exhibits the same asymmetry as does that of the pseudomorphic structure. However, the dislocation energy is found to have a weaker dependence on the surface strain, since the dislocation strain is localized near the interface. Accordingly, the strain energy of the incoherent structure exhibits less asymmetry than does that of the coherent structure. As a result, overlayers in compression are slightly more stable than predicted with the bulk parameters, whereas overlayers in tension are strongly destabilized, in agreement with direct calculations of stability of strained metallic overlayers.[12]

Quantitative development of the concept of many-body surface strain at transition-metal surfaces has been carried out in this paper. The utility of this new approach for the understanding of surface phenomena has been demonstrated by analysis of reconstruction of fcc transition-metal surfaces and the stability properties of thin metal overlayers. This concept should prove to have broad application to structural phenomena associated

with surfaces.

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[1]L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, NY, 1960).

[2]R. J. Needs, Phys. Rev. Lett. **58**, 53 (1987).

[3]D. Vanderbilt, Phys. Rev. Lett. **59**, 1456 (1987).

[4]M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).

[5]See, for example, S. M. Foiles, Phys. Rev. B **32**, 7685 (1985); M. S. Daw and S. M. Foiles, J. Vac. Sci. Technol. A **4**, 1412 (1986); M. S. Daw, Surf. Sci. Lett. **166**, L161 (1986); B. W. Dodson, Phys. Rev. B **35**, 880 (1987), and Surf. Sci. **184**, 1 (1987).

[6]S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[7]P. J. Estrup, in *Chemistry and Physics of Solid Surfaces V*, edited by R. Vanselow and R. Howe (Springer-Verlag, New York, 1984).

[8]L. D. Marks and D. J. Smith, Surf. Sci. **157**, L367 (1985).

[9]F. C. Frank and J. H. van der Merwe, Proc. Roy. Soc. (London) A **198**, 216 (1949).

[10]P. A. Varotsos and K. D. Alexopoulos, *Thermodynamics of Point Defects and Their Relation with Bulk Properties* (North-Holland, New York, 1986).

[11]M. El-Batanouny, S. Burdick, K. M. Martini, and P. Stancioff, Phys. Rev. Lett. **58**, 2762 (1987).

[12]B. W. Dodson, Surf. Sci. **184**, 1 (1987).