Comment on "Should All Surfaces Be Reconstructed?"

In a recent Letter [1], it was suggested that the driving force for surface reconstruction is given by the difference between the surface energy and stress, leading to a "globally relaxed" state characterized by an isotropic and diagonal stress tensor. The diagonal components were claimed to be equal to the surface energy γ_0 of the unstrained surface. In this Comment we remark that the theory is incomplete insofar as it neglects the associated defect formation energies, and that the cited results of Au(110) do not actually support the theory. In addition, we point out an inconsistency in the derivation of the surface stress in the relaxed state.

Following the notation of [1], γ and $\sigma_{\alpha\beta}$ denote the surface free energy per unit area and surface stress, respectively. The surface strain tensor $\hat{\varepsilon}$ (with elements $\varepsilon_{\alpha\beta}$) was used as a parameter to specify a strained configuration with reference to an ideal unstrained slab. γ was then expanded about $\hat{\varepsilon} = 0$ and the "equilibrium" strain $\hat{\varepsilon}^{\min}$ was determined in [1] by finding the global minimum of γ, namely, $\partial\gamma/\partial\varepsilon_{\alpha\beta} = 0$.

The conclusion that the driving force for surface reconstruction is the difference between surface stress and surface energy is similar to the results of some previous studies [2, 3] on surface densification. However, in those studies [2, 3] it was shown that this driving force does *not* result in any reconstruction unless it exceeds some critical strength that reflects the formation energy of misfit dislocations between the surface layer and the underlying lattice. Similarly, formation of point defects, impurity segregation, or reconstruction of the surface will also entail energy costs, not considered in [1], which can easily exceed the elastic energy savings. Thus, we conclude that *not* all surfaces should be reconstructed.

Turning now to the numerical results for Au(110) presented in [1], the driving force for densification along the x direction is found to be 5 times larger in magnitude than that for expansion along the y direction. The theory therefore appears to predict a density *increase* along x, which is not observed experimentally. Moreover, the predicted density decrease along the y direction appears to be only $\varepsilon_{yy}^{\min} = 0.05\%$, which can hardly be said to agree with the observed removal of 50% of the atoms in the missing-row reconstruction. Thus, the theory of [1] does not appear to give a useful description of this reconstruction.

Finally we show that the surface stress for the strained slab at $\hat{\varepsilon}^{\min}$ was not given correctly. Even for a state with $\hat{\varepsilon} \neq 0$, it is still meaningful to consider the work necessary to increase the surface area by unit amount by means of a stretching process. (This work is the excess above and beyond that which may be necessary to deform the volume of the crystal [4–6].) Therefore, for a state characterized by $\hat{\varepsilon}$, surface stress can be defined as usual by the "strain" derivative of the total surface free energy divided by the area:

$$\sigma_{\alpha\beta}(\hat{\varepsilon}) \equiv \left.\frac{1}{A}\frac{\partial(A\gamma)}{\partial\chi_{\alpha\beta}}\right|_{\chi_{\alpha\beta}=0} = \gamma(\hat{\varepsilon})\delta_{\alpha\beta} + \left.\frac{\partial\gamma}{\partial\chi_{\alpha\beta}}\right|_{\chi_{\alpha\beta}=0}. \tag{1}$$

Note that here the strain $\chi_{\alpha\beta}$ is defined with respect to the reference state specified by $\hat{\varepsilon}$, *not* the ideal ($\hat{\varepsilon} = 0$) surface. At $\hat{\varepsilon}^{\min}$ we have $(\partial\gamma/\partial\chi_{\alpha\beta})_{\chi_{\alpha\beta}=0} = 0$, so that $\sigma_{\alpha\beta}(\hat{\varepsilon}^{\min}) = \gamma(\hat{\varepsilon}^{\min})\delta_{\alpha\beta}$. This result is exact, i.e., not dependent on a low-order expansion of γ in $\hat{\varepsilon}$. Thus, the stress is isotropic and diagonal, but not equal to $\gamma_0\delta_{\alpha\beta}$ as claimed in [1]. [For the case of Au(110) in [1], the numerical difference is quite small because $\varepsilon_{\alpha\beta}^{\min}$ is small.] If $\sigma_{\alpha\beta}(\hat{\varepsilon})$ is to be expanded around $\hat{\varepsilon} = 0$, one more linear term, $(\partial\gamma/\partial\varepsilon_{\phi\psi})_0\,\varepsilon_{\phi\psi}\delta_{\alpha\beta}$, should be added to Eq. (7) in [1].

M. Y. Chou and Siqing Wei
    School of Physics
    Georgia Institute of Technology
    Atlanta, Georgia 30332-0430

David Vanderbilt
    Department of Physics and Astronomy
    Rutgers University
    P. O. Box 849
    Piscataway, New Jersey 08855-0849

[1] D. Wolf, Phys. Rev. Lett. **70**, 627 (1993).
[2] M. Mansfield and R. J. Needs, J. Phys. Condens. Matter **2**, 2361 (1990); R. J. Needs, M. J. Godfrey, and M. Mansfield, Surf. Sci. **242**, 215 (1991).
[3] R. C. Cammarata, Surf. Sci. **279**, 341 (1992).
[4] R. Shuttleworth, Proc. Phys. Soc. London Sect. A **63**, 444 (1950).
[5] W. W. Mullins, in *Metal Surfaces: Structure, Energetics, and Kinetics* (American Society for Metals, Metals Park, OH, 1963), p. 17.
[6] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).