Comment on "Should All Surfaces Be Reconstructed?"

In a recent Letter, Wolf [1] reported a theoretical study of the stability of solid surfaces against reconstructions involving changing the density of surface atoms. Wolf developed a criterion for whether the unreconstructed surface has a tendency to increase or decrease its density of atoms, which was then applied to the Au(110) surface. The main purpose of this Comment is to show that this criterion is not applicable to the reconstructions of the Au(110) surface considered in [1]. This criterion is, however, relevant for reconstructions which involve a small straining of the surface atomic layer, and I discuss the physical reasons why many surfaces are in fact stable against such reconstructions.

In [1] Wolf obtained the result that the driving force for a surface reconstruction involving changing the density of surface atoms is the difference between the surface stress and the surface energy, i.e., the strain derivative of the surface energy. Consequently a surface tends to reconstruct towards a state in which the surface stress is equal to the surface energy. When the strain derivative of the surface energy is positive there is a tendency for the density of surface atoms to increase, and vice versa for a negative value. This criterion was derived within linear elasticity theory and, strictly speaking, applies only for *small* uniform strains when the surface layer and bulk are strained *together*. Wolf then applied this criterion to the case of the Au(110) surface which undergoes a missing row reconstruction in which alternate [1̄10] rows of atoms are removed from the surface. This application is not correct because the removal of one-half of the surface layer of atoms cannot plausibly be described within linear elasticity theory. The reconstruction leading to the missing [1̄10] row surface (and the missing [001] row surface which was also considered by Wolf) involves very large changes in the local environments of some atoms, which cannot be described within this framework.

Although the above argument is sufficient to demonstrate the inapplicability of surface stress-strain arguments to the formation of missing row surfaces, another powerful objection can be raised. If the criterion suggested by Wolf were correct then it should apply to the reconstructed surfaces as well as the unreconstructed surface. For the sake of clarity consider the case of the missing [001] row model, which is very high in energy. If [001] rows are added to *or* removed from this surface we expect the surface energy to decrease because the resulting surface structure is closer to the much lower energy unreconstructed surface. However, according to Wolf's calculations, the criterion based on the strain derivative of the surface energy predicts that the missing [001] row surface would like only to remove more [001] rows. A similar objection can be raised in the case of the missing [1̄10] row surface, in which adding or subtracting rows are both expected to increase the surface energy. Finally, according to Wolf's calculations, the components of the strain derivative of the surface energy have smaller magnitudes for the high energy missing [001] row surface than for the unreconstructed or missing [1̄10] row surfaces, which conflicts with the basic criterion for reconstruction that the surface tends to reconstruct towards a state in which the surface stress is isotropic and equal in magnitude to the surface energy. In conclusion it cannot be true that a reduction in the magnitudes of the components of the strain derivative of the surface energy is the driving force for these reconstructions.

The strain derivative of the surface energy *is* connected with the propensity for a surface to change its atomic density, but one must be careful to consider only reconstructions which involve small strains of the surface layer. Indeed, the result that the strain derivative of the surface energy is the driving force for changing the density of surface atoms by small strains of the surface layer was obtained previously by Mansfield and Needs [2]. The question raised by Wolf, "Should all surfaces be reconstructed?", given that the driving force for reconstruction (the strain derivative of the surface energy) is unlikely ever to be zero, is simply answered in the context of such reconstructions. As mentioned above, the surface stress determines the change in the surface energy when the surface and bulk are strained *together*, and contains no information about changes in the surface-substrate bonding caused by straining the surface layer of atoms on its own. A reconstruction involving straining the surface layer alone necessarily changes the surface-substrate bonding, which generally costs energy. It is precisely this effect which stabilizes many unreconstructed surfaces. In [2] and [3] we used the Frenkel-Kontorova model to describe the surface-substrate interaction and showed that, even when the strain derivative of the surface energy is nonzero, the unreconstructed surface is stable, provided the surface-substrate interaction is strong enough. Finally, although Wolf is correct to criticize the work of Ref. [4] because it considered the surface stress and not the strain derivative of the surface energy as the driving force for reconstruction, Cammarata subsequently published a paper [5] which built on the work of Refs. [2] and [3], and fully rectified this error.

R. J. Needs
Cavendish Laboratory
Madingley Road
Cambridge CB3 0HE, United Kingdom

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