Calculation of the surface stress anisotropy for the buckled Si(001)(1×2) and $p(2\times2)$ surfaces

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Knowledge of the surface stress anisotropy is a prerequisite for the description of the mesoscopic structure of stepped Si(001) surfaces. However, it is known that results from first-principles calculations for the (1×2) reconstructed surface surpass the experimental value by about a factor of 2. We demonstrate that this discrepancy is primarily not an extrinsic effect due to surface defects but a consequence of the elastic interaction between the dimers on the defect free surface.

The basic concepts useful for the description of step-step interactions on solid surfaces have been described by Marchenko[1] in 1981. However, it was the papers by Alerhand *et al.*[2,3] that, by identifying a transition from single to double atomic height steps on vicinal Si(001)(1×2) surfaces, have attracted a lot of attention and stimulated a variety of experimental as well as theoretical investigations concerning the morphology of stepped Si(001) surfaces.[4–6] As pointed out by Alerhand, these phenomena are due to strain field mediated step-step interaction and can be explained by means of standard elasticity theory. The surface stress tensor is an important quantity entering the elastic theory of step-step interaction. However, it turned out that the experimental value for the surface stress anisotropy measured by Webb and coworkers[7,8] is about a factor of 2 smaller than the theoretical value.[9,10] This indicated a serious deficiency in the understanding of the Si(001) surface.

In this paper we demonstrate that this apparent discrepancy between theory and experiment is a shortcoming of previous calculations. In particular, we show that the small surface stress anisotropy measured in experiment is an intrinsic property of the perfect surface. We show that theory is indeed reconciled with experiment when calculations are carried out for the correct character of the surface reconstruction. Therefore the influence of surface defects, which was called upon by Tersoff[11] to explain the measured stress anisotropy, is of less importance than it has been anticipated.

The atomic structure of the Si(001) surface has been discussed controversially for quite some time, especially with respect to whether the dimer bond is parallel to the surface or not (see Fig. 1). Recently, convincing evidence has been gathered for the existence of buckled dimers.[12–15] In scanning tunneling microscopy pictures Wolkow[13] directly observed the freeze-in of buckled dimers: At low temperatures, the buckled dimers form local $p(2\times2)$ and $c(4\times2)$ patterns. Moreover, buckled dimers are also favored by well converged *ab initio* DFT-LDA (density-functional theory within the local-density approximation) total energy calculations.[12,16] At room temperature the dimers flip between both equilib-

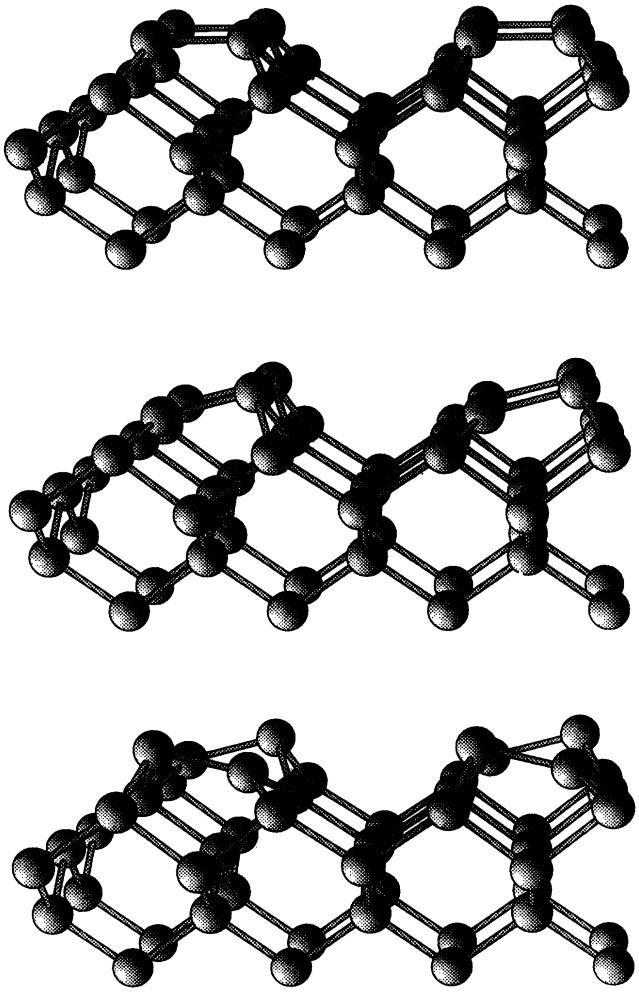

FIG. 1. Perspective side view of different models for the geometric structure of the Si(001) surface. Top: (1×2) structure with symmetric dimers (i.e., the dimer bond is parallel to the surface). Middle: (1×2) structure with buckled dimers (buckling angle $\theta \approx 15°$). Bottom: $p(2\times2)$ structure. The buckling angle alternates between plus and minus 15° along the dimer rows.

rium positions, i.e., the angle between the dimer bond and the surface plane flips between $+15°$ and $-15°$.[12] However, the motion of neighboring dimers is correlated along the dimer rows, therefore a local "antiferromagnetic" ordering (i.e., a preference for alternating buckling) of the asymmetric dimers is still preserved at least at room temperature.[17] The stress anisotropy measured by Webb *et al.* reflects surface properties at the freeze-in temperature,[7,8] which was estimated to be $\approx 500\,°C$. Below this temperature, the position of steps on the vicinal surface is frozen-in, because the surface diffusion slows down rapidly with temperature, and the surface cannot react to an externally applied strain field by changing the ratio of its (1×2) to (2×1) terrace size any more (this ratio is used to measure the stress anisotropy). The measured terrace size ratio depends therefore on the density of temperature-induced antiphase boundaries (with a local "ferromagnetic" orientation of dimers along the dimer string) between domains with alternating buckling direction. If this density were known, a first rough estimate of the importance of the antiphase boundaries with respect to the surface stress anisotropy could be extracted from a comparison of our zero-temperature results for the $p(2\times2)$ ("antiferromagnetic") structure with those for the buckled (1×2) ("ferromagnetic") structure. The measured surface stress anisotropy can be estimated from a weighted average of the surface anisotropies calculated by us for the "antiferromagnetic" and the "ferromagnetic" structure.

By definition, the surface-stress tensor σ_{ij} describes the linear relationship between the surface energy E and the strain field ϵ_{ij}. The change in the surface energy is, up to linear order in ϵ_{ij}, equal to

$$\Delta E = \sum_{i,j=1}^{2} \int_A \sigma_{ij}\epsilon_{ij} dA \quad , \tag{1}$$

where A is the area of the unstrained surface. For strains around the bulk equilibrium conditions, the change in the bulk elastic energy is of second (and higher) order in ϵ_{ij}. Due to the symmetry, the stress tensor becomes diagonal in the coordinate system with axes along [110] and $[\bar{1}10]$; the diagonal components represent the stress parallel ($\sigma_\parallel$) and perpendicular ($\sigma_\perp$) to the dimer bond.

To determine the surface stress, we use a direct approach: We start with a relaxed Si(001) slab, where the lattice constants parallel to the surface are given by the bulk value. Then the slab is strained along one of the principal directions ([110] or $[\bar{1}10]$) and the change in the total energy is evaluated. The calculated total-energy changes contain bulk and surface contributions which are numerically difficult to separate. However, because the [110] and $[\bar{1}10]$ directions are equivalent in the bulk, the bulk contributions cancel when the stress anisotropy is calculated. The same holds for the stress difference between two structures, calculated for any direction. The calculations are further simplified by the fact that it is not necessary to relax the atomic positions after straining the slab, because the corresponding relaxation energy will be of second order in the applied strain (both the strain induced forces and the displacements due to relaxation are of at least first order in ϵ_{ij}).

To compute total energies of strained Si(001) slabs we performed self-consistent *ab initio* density-functional calculations. The exchange-correlation functional was treated within the local-density approximation with Perdew and Zunger's parametrization[18] of Ceperley and Alder's data[19] for the correlation energy. We used a fully separable, norm-conserving pseudopotential.[20,21] To simulate surfaces we used supercells containing 10 layers of atoms and 15 bohr of vacuum; the lattice constant $c = 10.16$ bohr was obtained from bulk calculations. The positions of all atoms within the four topmost layers on both sides of the unstrained slab were relaxed until the residual forces were smaller than 5×10^{-4} hartree/bohr; further relaxation had no numerically significant effects. Carrying out tests for various numbers of relaxed layers in 10, 12, and 14 layer slabs for both the symmetric and the buckled (1×2) surface, we verified that the stress anisotropies are neither affected by the slab thickness nor by the relaxation of the fifth and sixth layer in any important way. The Kohn-Sham equations were solved using the computer code *fhi93cp* (Ref. 22) which employs a Car-Parrinello-[23]like technique. The plane wave basis set was defined by the cutoff energy of 8 Ry and convergence tests were performed for cutoff energies up to 12 Ry. The electron density was calculated from a set of 8 special $\mathbf{k}_\parallel$ points in the irreducible part of the surface Brillouin zone for the 1×2 elementary cell which assures a sufficient convergence in $\mathbf{k}$ space.[12]

Our results are summarized in Table I. From calculations for different strains, together with the convergence tests mentioned above, we estimate the results to be accurate within about ±10 meV/Å^2. The stress anisotropy of the symmetric (metallic) (1×2) surface compares well with the values from the two previous DFT-LDA calculations,[9,10] while all these theoretical numbers are in plain contradiction to experiment. However, there is an empirical tight-binding calculation by Alerhand *et al.*[2] which suggests that for the buckled surface the stress anisotropy might be much smaller than for the symmetric surface. This motivated us to investigate whether and how the surface stress tensor is affected by the buckling of dimers. Calculating the difference between the symmetric (1×2) and the buckled (1×2) surface, we find that the buckled surface is more tensile (by ≈ 30 meV/Å^2) along the dimer bond and less compressive (by ≈ 75 meV/Å^2) perpendicular to the bond. The increase of the tensile stress parallel to the dimer bond can be understood intuitively: An increase of the lattice constant leads to a decrease of the buckling angle and thus to a smaller energy gain due to the buckling. Thereby the slope of the surface energy versus the lattice constant is larger for the buckled surface, which means that the surface stress is more tensile. The stress anisotropy gets smaller by 45 meV/Å^2 for the buckled surface, however it is still larger than the experimental value. Therefore the difference between theory and experiment cannot be explained as being solely due to the dimer buckling in the simple (1×2) structure.

The comparison with experiment is further improved when a realistic surface reconstruction is considered. In

TABLE I. Comparison of surface stress for the symmetric and the buckled Si(001) (1×2) and $p(2\times2)$ surface. Components of the stress tensor parallel and perpendicular to the dimer bond are denoted by $\sigma_{\parallel}$ and $\sigma_{\perp}$. Results for the symmetric and the buckled surfaces are distinguished by superscript s and b, respectively. All values are in meV/Å^2. ETBM denotes values that were calculated by Alerhand *et al.* using an empirical tight-binding method; results quoted from SW are based on the empirical Stillinger Weber potential, which is a classical potential including two- and three-body interactions.

Method, structure	$\sigma_{\parallel}^{s}-\sigma_{\perp}^{s}$	$\sigma_{\parallel}^{b}-\sigma_{\perp}^{b}$	$\sigma_{\parallel}^{b}-\sigma_{\parallel}^{s}$	$\sigma_{\perp}^{b}-\sigma_{\perp}^{s}$
SW (Ref. 4), (1×2)	77	-	-	-
ETBM (Ref. 2), (1×2)	116	70	−1	45
DFT-LDA (Ref. 9), (1×2)	166	-	-	-
DFT-LDA (Ref. 10), (1×2)	179	-	-	-
Present work, (1×2)	150	105	30	75
Present work, $p(2\times2)$	150	55	30	125
Experiment (Ref. 7)	-	60–80	-	-

fact, it turned out that for the $p(2\times2)$ structure our DFT-LDA result of the surface-stress anisotropy (55 meV/Å^2) is within the error bars identical to the experimental value[7] (60–80 meV/Å^2). In particular, the component of the surface stress parallel to the dimer bond ($\sigma_{\parallel}$) is the same as for the the buckled (1×2) structure, i.e., the differences $\sigma_{\parallel}^{b}-\sigma_{\parallel}^{s}$ given in Table I are equal for the $p(2\times2)$ and (1×2) structures. This was to be expected, because the tensile stress $\sigma_{\parallel}$ is due to the tendency of the dimer bond to contract the underlying solid:[9] The dimer atoms are not nearest neighbors in the bulk lattice and have to be displaced towards each other to form the surface dimer bond. The component $\sigma_{\parallel}$ of the stress tensor is a property of an individual dimer, and therefore independent of whether the buckling angle alternates along the dimer rows or not. In contrast, the compressive stress $\sigma_{\perp}$ perpendicular to the dimer bond is drastically lowered for the $p(2\times2)$ structure. This is due to the relaxation of the second layer atoms: The dimer atom closer to the bulk tends to push its neighboring second layer atoms apart perpendicular to the dimer bond. If the buckling angle alternates, the second layer atoms move outwards away from that dimer atom, thereby relaxing the stress $\sigma_{\perp}$.

We do not expect that our results change appreciably when the $c(4\times2)$ reconstructed surface is considered. The $p(2\times2)$ and $c(4\times2)$ structures differ only in the relative alignment of the dimer rows: The $c(4\times2)$ structure can be constructed from the $p(2\times2)$ structure by flipping all dimers in every second dimer row. The interaction between adjacent dimer rows is expected to be small, and the displacements of the second layer atoms with respect to the bulk positions[24] are very similar for both structures. As this relaxation is responsible for the decrease in surface stress anisotropy when going from the buckled (1×2) to the $p(2\times2)$ structure, the stress should be very similar for both structures.

To summarize, we have shown that the surface stress anisotropy $\Delta\sigma$ of the $p(2\times2)$ reconstructed Si(001) surface is drastically smaller than that of a surface with symmetric dimers. The value for the $p(2\times2)$ surface ($\Delta\sigma = 55 \pm 10$ meV/Å^2) is in excellent agreement with experiment[7] ($\Delta\sigma = 70 \pm 10$ meV/Å^2). This solves the contradiction between previously published DFT-LDA calculations and experiment, as those calculations only referred to symmetric dimers. Moreover, we have shown that the "ferromagnetic" orientation of dimers [the (1x2) structure] results a smaller reduction of the stress anisotropy (to $\Delta\sigma = 105 \pm 10$ meV/Å^2) with respect to the symmetric dimers. Because the measured $\Delta\sigma$ reflects the situation where both "antiferromagnetic" and "ferromagnetic" orientations of dimers are present, the increment of $\Delta\sigma$ by the local "ferromagnetic" orientation of dimers at the antiphase boundaries is presumably cancelled by the presence of surface defects.[11] This latter effect is, however, smaller than it has been previously anticipated.

After having derived these results we learned that Garcia and Northrup performed similar calculations for the surface-stress anisotropy of the $c(4\times2)$ and the buckled (1×2) Si(001) surfaces.[25] Similar to our results they found a reduction of the surface stress anisotropy from $\Delta\sigma \simeq 160$ meV/Å^2 for the symmetric dimers to $\Delta\sigma \simeq 120$ meV/Å^2 in the buckled (1×2) structure and to $\Delta\sigma \simeq 55$ meV/Å^2 in the $c(2\times4)$ structure. This provides further confirmation that the buckling of dimers is essential for the step-step elastic interaction on the clean Si(001) surface and that the reduction of the stress anisotropy from the "ferromagnetic" to the "antiferromagnetic" orientation of the buckled dimers is caused by the relaxation of the second layer atoms.

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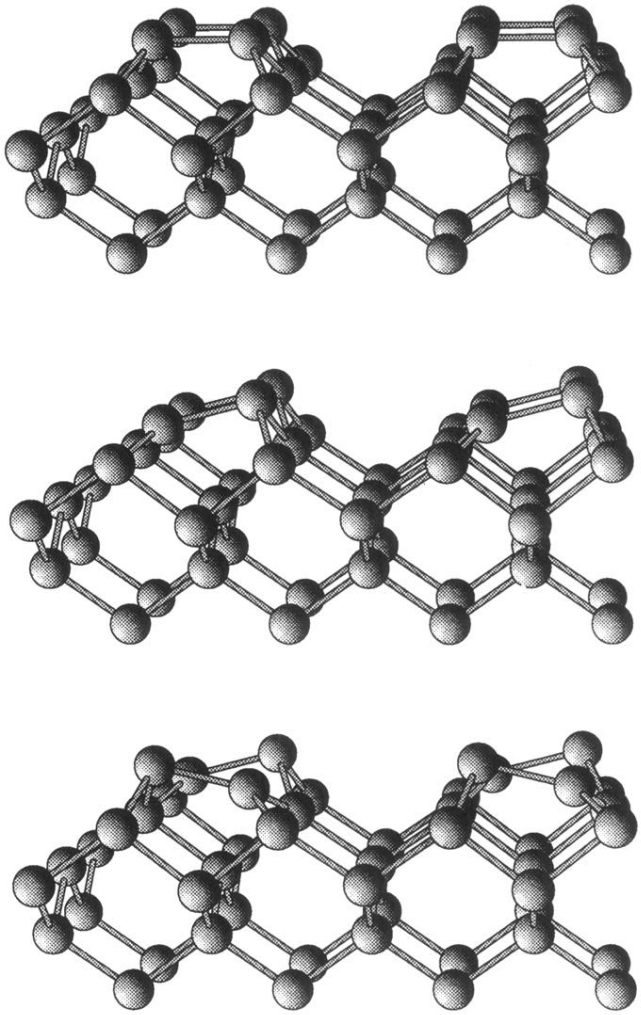

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