

Spontaneous Formation of Stress Domains on Crystal Surfaces

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It is proposed that surfaces of crystals which reconstruct with broken orientational symmetry and exhibit an anisotropic intrinsic stress tensor are unstable to the formation of elastic-stress domains. Thus the ground state of such a surface is not uniform, contrary to previous expectations. Evidence of this for the Si(001) surface is discussed.

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It has always been assumed that the intrinsic ground state of a faceted surface of a crystal, which in general includes a reconstruction, is otherwise atomically smooth and uniform. In this Letter we propose that there exists a class of surfaces where this idealized ground state is not obtained. Specifically, we demonstrate that an anisotropy in the intrinsic surface stress and a degeneracy in reconstructed phases lead to the spontaneous formation of elastic-stress domains on the surface of a solid. The importance of surface stress in driving surface reconstructions and creating misfit dislocations has been recognized in previous work.¹⁻⁴ The idea introduced here, however, is fundamentally different, and more analogous to the domain structure in magnetic systems which arises from the energy of long-range dipolar interactions.

Our analysis will proceed as follows. We shall first use continuum elastic theory to derive general equations for the formation of domains on a surface. Then we use microscopic tight-binding calculations to obtain the stress tensor for a specific system: the (001) surface of silicon. Our choice is motivated by the startling and as yet unexplained results of a recent experiment by Men, Packard, and Webb⁵ on the effects of applied strain on Si(001). Indeed, this experiment provided inspiration for this work and we believe may provide evidence for some of our conclusions.

The two-dimensional intrinsic stress tensor of a sur-

face is defined by⁶

$$\sigma_{ij} = \frac{1}{A} \frac{dE_{\text{surf}}}{d\epsilon_{ij}}, \quad (1)$$

where E_{surf} is the surface energy per unit cell, ϵ_{ij} is the two-dimensional surface strain tensor, and A is the surface cell area. The indices i and j label directions in the plane of the surface. Consider now a surface reconstruction involving broken rotational symmetry, thus allowing for two or more reconstructed phases having the same E_{surf} but for different orientations and therefore different⁷ intrinsic stress tensors σ_{ij} . If the surface has domains of the different reconstructed phases, the system may lower its energy by elastic relaxation. As we shall see, the domain sizes are very large compared to atomic dimensions, so that continuum elastic theory⁸ is appropriate. Prior to relaxation, the intrinsic stresses at the surface generate a force density given by

$$f_i(\rho) = \partial_j \sigma_{ij}(\rho).$$

Here $\rho = (x, y)$ is the position vector on the surface. The displacement $\mathbf{u}(\mathbf{r})$ of the medium at $\mathbf{r} = (\rho, z)$ in response to $f_i(\rho)$ can be written in terms of an elastic Green's function $\chi_{\alpha j}(\rho, z)$:

$$u_\alpha(\mathbf{r}) = \int d^2\rho' \chi_{\alpha j}(\rho - \rho', z) f_j(\rho'), \quad (2)$$

where α runs over (x, y, z) . χ depends only on the bulk elastic properties. The elastic relaxation energy E_{el} per unit area is then the integral of the force density times the displacement of the medium:

$$E_{\text{el}} = - \frac{1}{2L^2} \int d^2\rho f_i(\rho) u_i(\rho) = - \frac{1}{2L^2} \iint d^2\rho d^2\rho' \chi_{ij}(\rho - \rho', 0) f_i(\rho) f_j(\rho'), \quad (3)$$

where L is the system size. Thus the problem of calculating E_{el} reduces to a two-dimensional surface problem where the bulk properties enter only through the 2×2 surface Green's function $\chi_{ij}(\rho) = \chi_{ij}(\rho, z=0)$.

For definiteness, consider a domain structure consisting of two domains, A and B , with

$$\sigma_{ij}^A = \begin{pmatrix} \sigma_{\parallel} & 0 \\ 0 & \sigma_{\perp} \end{pmatrix}, \quad \sigma_{ij}^B = \begin{pmatrix} \sigma_{\perp} & 0 \\ 0 & \sigma_{\parallel} \end{pmatrix}. \quad (4)$$

If the domains alternate along the x direction with spac-

ing l , as illustrated in Fig. 1, then each boundary has a force density of the form

$$f_i(\rho) = \pm F_0 \delta_{ix} \delta(x - x_0), \quad (5)$$

where x_0 is the location of the boundary and $F_0 = \sigma_{\parallel} - \sigma_{\perp}$. The calculation of E_{el} from Eq. (3) is most easily carried out in reciprocal space:

$$E_{\text{el}} = - \frac{1}{2} \sum_{G_x} |f_x(G_x)|^2 \chi_{xx}(G_x). \quad (6)$$

In order to simplify this calculation we assume that the elastic medium is isotropic; then the elastic Green's function takes the form

$$\chi_{xx}(G_x) = \frac{1-\nu}{\mu} \frac{1}{|G_x|}, \tag{7}$$

where μ and ν are the bulk modulus and Poisson's ratio of the medium, respectively. Using Eqs. (5) and (7) to evaluate E_{el} , we obtain

$$E_{el} = -\frac{1}{2l^2} F_0^2 \left(\frac{1-\nu}{\mu} \right) \sum_{G_x} \sin^2 \left(\frac{G_x l}{2} \right) \frac{1}{|G_x|} e^{-2a|G_x|} = -\frac{C_2}{l} \ln \left(\frac{l}{\pi a} \right), \tag{8}$$

where

$$C_2 = \frac{F_0^2}{2\pi} \frac{1-\nu}{\mu}. \tag{9}$$

a is a microscopic cutoff length, introduced via Lorentzian broadening of the force density of Eq. (5). This cutoff should be on the order of a lattice constant. The elastic relaxation energy can be interpreted as reducing the energy per unit length of a domain wall by an amount $C_2 \ln(l/\pi a)$. If we let C_1 denote the "creation energy" per unit length of a domain wall due to dangling bonds, local deformations, and other such factors, then the net domain-wall energy per unit length becomes

$$E_{wall} = C_1 - C_2 \ln(l/\pi a). \tag{10}$$

Notice that for sufficiently large values of l , E_{wall} becomes negative, and it has its minimum value at

$$l_0 = \pi a e^{C_1/C_2+1}. \tag{11}$$

Thus the surface is always unstable to the formation of domains. The exponential form of Eq. (11) makes it natural to obtain equilibrium domain sizes that are orders of magnitude larger than the lattice constant a . This justifies the use of continuum elastic theory. Also, we can safely neglect higher-order corrections in $1/l$ [e.g., $1/l^2$ contributions to Eq. (10) from elastic interactions specific to the domain walls⁹].

We emphasize that the results we have just obtained

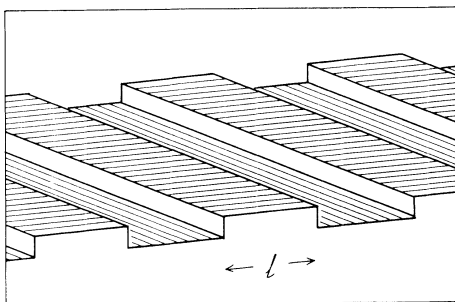


FIG. 1. Schematic representation of a surface with two degenerate reconstructed phases arranged in strips of width l . The domains are shown separated by steps for definiteness. In general, the domain walls need not be steps and the theory applies for any type of domain wall.

are general. The form of Eq. (10) follows directly from Eq. (3) and the scaling relation $\chi_{ij}(\xi, \rho) = |\xi|^{-1} \chi_{ij}(\rho)$, which is valid for general (anisotropic) bulk elastic constants. The specific value of C_2 will depend on the particular mosaic pattern of the stress domains (e.g., striped, checkerboard, hexagonal, etc.), the magnitude of anisotropy in σ_{ij} , and the specific bulk elastic constants. However, the general form of Eq. (10) will remain unchanged. We also note that if the wall creation energy C_1 is very large, then in practice the domain sizes may be determined by kinematics or by local miscuts (which

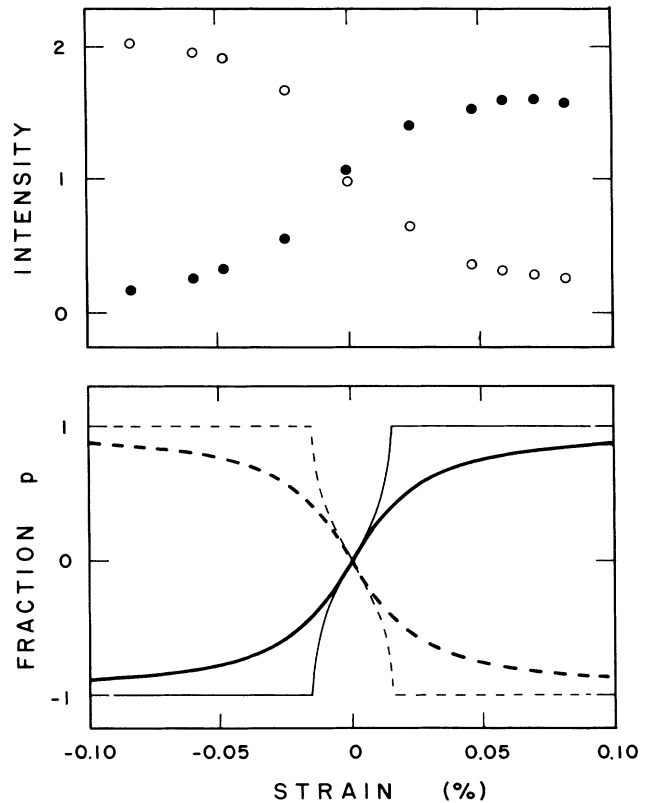


FIG. 2. Top: Experimental intensity of (1×2) (open circles) and (2×1) (filled circles) domains on the Si (001) surface as a function of applied external strain. Bottom: Theory for $\epsilon_0 = 0.03\%$. The thick (thin) lines correspond to quasi-global equilibrium.

impose a maximum average terrace size), rather than by energetic considerations.

We consider now the case when an anisotropic external strain ϵ^{ext} is applied to the surface. This breaks the orientational degeneracy of the surface energy E_{surf} , and the favored domains will grow while the others shrink.¹⁰ Returning to our model example of striped domains, we can readily generalize to the case of alternating A and B domains of unequal widths $(1+p)l$ and $(1-p)l$, respectively. Then Eq. (10) generalizes to

$$E_{\text{el}} = \frac{1}{2} \epsilon^{\text{ext}} p F_0 + \frac{C_1}{l} - \frac{C_2}{l} \ln \left(\frac{l}{\pi a} \cos \frac{\pi p}{2} \right). \quad (12)$$

If l is being held fixed and E_{el} is minimized with respect to the fraction p , we obtain

$$p = \frac{2}{\pi} \tan^{-1} \left(\frac{\pi \epsilon^{\text{ext}}}{2\epsilon} \right), \quad (13)$$

where

$$\epsilon(l) = - \frac{\pi F_0 (1-p)}{4l\mu}. \quad (14)$$

Equation (13) gives the relative abundance of the two domains on the surface as a function of external strain for a situation of quasiequilibrium, where l is being held fixed by surface miscut or by other kinematical constraints. In the case of global equilibrium, where both p and l may vary, E_{el} is minimized by

$$l = l_0 \sec(\pi p/2) \quad (15a)$$

and

$$p = \frac{2}{\pi} \sin^{-1} \left(\frac{\pi \epsilon^{\text{ext}}}{2\epsilon(l_0)} \right). \quad (15b)$$

The dependence of p on ϵ^{ext} is shown in the bottom panel of Fig. 2, for both quasiequilibrium and global equilibrium. In the region where the applied strain is small, both curves coincide, with slope at $\epsilon^{\text{ext}}=0$ given by $\epsilon_0 \equiv \epsilon(l_0)$. However, for large external strain, the behavior is different. When l is fixed, the minority domains shrink with a width inversely proportional to the applied strain. But if l is allowed to vary, the majority domain width diverges, while the minority domain width approaches a constant value $2l_0/\pi$, as ϵ^{ext} approaches $\epsilon_{\text{crit}} = 2\epsilon_0/\pi$. Above ϵ_{crit} a uniform phase, i.e., one domain, is preferred.

We now apply these results for the specific case of the (001) surface of silicon. This surface has a twofold degeneracy in its reconstruction. It can form domains of (2×1) or (1×2) symmetry depending on whether atoms on the surface form dimers in the x or y directions, respectively. The lowest-energy domain walls consist of single-layer steps¹¹ as shown schematically in Fig. 1. The intrinsic stress tensor of each of the surface domains has the form given by Eq. (4). Here σ_{\parallel} and σ_{\perp} are the components parallel and perpendicular to the direction of the dimers, respectively. To calculate the surface stresses we use a semiempirical tight-binding theory for structural energies.¹² In this theory, the total energy E is expressed in terms of the band-structure energy, which is calculated within a realistic tight-binding Hamiltonian H , a sum of pairwise ionic interactions, and an on-site Coulomb repulsion term.¹³ The stress tensor then takes the form

$$\sigma_{ij} = \frac{1}{A} \sum_{\langle \alpha\beta \rangle} \left[\sum_n \left\langle n \left| \frac{\partial H_{\alpha\beta}}{\partial r_{\alpha i}} r_{\beta j} + \frac{\partial H_{\alpha\beta}}{\partial r_{\beta i}} r_{\alpha j} \right| n \right\rangle + \frac{\partial V_{\alpha\beta}}{\partial d_{\alpha\beta}} \frac{(r_{\alpha i} - r_{\beta i})(r_{\alpha j} - r_{\beta j})}{d_{\alpha\beta}} \right], \quad (16)$$

where the sum is over all occupied states n , α and β denote atomic sites, $d_{\alpha\beta}$ is their separation, and $V_{\alpha\beta}$ is the interionic potential. We obtain $\sigma_{\parallel} = 0.035 \text{ eV/\AA}^2$ and $\sigma_{\perp} = -0.035 \text{ eV/\AA}^2$.¹⁴ Note, this predicts that the surface is under tensile stress along the dimer direction and under compressive stress normal to the dimers. Thus the Si(001) surface satisfies the two conditions stated in the first paragraph: It has two degenerate phases, (2×1) and (1×2) , and its surface stress tensor is anisotropic, with $F_0 = \sigma_{\parallel} - \sigma_{\perp} = 0.07 \text{ eV/\AA}^2$.

We are now in a position to analyze and explain quantitatively the experiment of Men, Packard, and Webb. Their results are shown in the top panel of Fig. 2. They observe that upon annealing, the fraction of one type of domain grows at the expense of the other when an external strain is applied to the surface. The domains for which the applied compression is along the dimers are the ones that grow, in agreement with our calculated sur-

face stress tensor. *When the external strain is released, however, the surface returns to its "initial" configuration of equal domain populations.* This surprising result is consistent with our idea of spontaneous formation of stress domains, where the ground state of the surface corresponds to a domain configuration. Comparison of the experimental intensities of domain populations with the theoretical curves (top and lower panels in Fig. 2, respectively) suggests that the experimental surface is only in quasiequilibrium [see Eq. (13)]. This is presumably because of local surface miscuts or kinematic considerations which allow for only local equilibration. Indeed, the difference in the data between positive and negative applied strains is indicative of kinematic constraints.

With our calculated value of the stress anisotropy F_0 , and our fitting the experimental data to determine $\epsilon_0 = 0.03\%$, we can predict the characteristic size of the

domains using Eq. (14). We obtain a value for l between 300 and 1000 Å. The uncertainty comes from the fit of ϵ_0 , from the choice of bulk elastic constants, and from the uncertainty in F_0 . This length scale is consistent with the experiment of Men, Packard, and Webb, which puts a lower bound for l of approximately 500 Å. From Eqs. (9) and (11) we also obtain $C_1 \sim 0.01$ eV/Å and $C_2 \sim 0.003$ eV/Å. A previous calculation of step energies by Chadi,¹¹ using a similar tight-binding model, gives 0.003 and 0.039 eV/Å for the two types of single-layer steps on Si(001); these numbers, however, represent the energy of creating a step *minus* the elastic energy of relaxation of Eq. (10).

Finally, we have assumed that the stress domains on the Si(001) surface have the form of strips, as shown in Fig. 1. In principle, however, one should test all possible patterns to find one which minimizes the energy of the system. In the case of Si(001), domain walls are steps which come in two types, one of which is much lower in energy than the other.¹¹ The fact that a striped pattern can be formed from one type of step alone, while a checkerboard pattern requires both, argues in favor of a striped domain structure. We note that striped domains also occur if a local surface miscut is controlling the domain size. In any event, our general conclusions are still valid regardless of the particular form of the domain structure. Specifically, any surface which reconstructs with degenerate phases that have anisotropic intrinsic surface stress tensors will be unstable to the formation of elastic-stress domains and will exhibit the behavior predicted here.

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¹⁴These values are for a surface with asymmetric dimers. If the dimers are constrained to be symmetric, then $\sigma_{\parallel} = 0.036$ eV/Å² and $\sigma_{\perp} = -0.080$ eV/Å². N. Roberts and R. J. Needs (to be published), have performed a local-density-functional calculation of the stress tensor for a symmetric-dimer surface, and obtained $\sigma_{\parallel} = 0.05$ eV/Å² and $\sigma_{\perp} = -0.13$ eV/Å².