Influence of Supersaturation on Surface Structure

J. B. Hannon, J. Tersoff, M. C. Reuter, and R. M. Tromp

IBM Research Division, T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

Using low-energy electron microscopy, we have investigated the influence of an external flux on the structure of the Si(111) surface during growth and etching at elevated temperatures. We find that varying the adatom supersaturation effectively changes the surface free energies of coexisting 7×7 and '1×1' regions of the surface. In response, the boundaries separating the phases adopt a new steady-state configuration. The measured configuration can be used to quantitatively determine the difference in free energy between the phases, $\Delta\gamma$. The change in $\Delta\gamma$ provides a measure of the local supersaturation at the surface, and can be interpreted as a change in the phase-transition temperature.

There is vast literature on the equilibrium structure of surfaces. However, during growth or etching, a surface is necessarily driven away from equilibrium, with a supersaturation or undersaturation of mobile adatoms. Understanding how this influences structure is important in developing a complete picture of the thermodynamics of growth. Yet, at present, little is known about the effect of this supersaturation on the structure. In equilibrium, varying parameters such as temperature, surface stoichiometry [1], or strain [2] can drive a phase transition from one surface structure to another. One intriguing study [3] has shown qualitatively that rapid growth can also drive a structural change.

Here we investigate how a growth flux influences surface structure by changing the free energies of competing surface phases. Specifically, we investigate the effect of supersaturation on the structure of the Si(111) surface near the first-order phase-transition temperature, $T_c = 1135$ K. We show that the difference in free energy (per unit area) between the 7×7 and '1×1' surface phases, $\Delta\gamma$, changes in the presence of a flux, and that the change is proportional to the density difference between phases. An advantage of working close to T_c is that $\Delta\gamma$ is small. Consequently, small changes in the supersaturation can significantly alter the surface structure. Our analysis provides a method for determining the chemical potential locally during growth that does not require knowledge of kinetic parameters (e.g., diffusion constants or attachment rates).

Below T_c, the equilibrium structure of the Si(111) surface is the 7×7 dimer-adatom-stacking fault structure [4], while above T_c the equilibrium '1×1' phase is essentially a disordered lattice gas of ~ 0.2 monolayers (ML) of Si on the bulk terminated surface [5]. Here we show how a measurement of the relative sizes and orientations of coexisting 7×7 and '1×1' domains in a stable configuration can be used to measure local changes in $\Delta\gamma$ during Si homoepitaxy. A quantitative analysis is possible because the relevant elastic and thermodynamic properties of the phases have been measured experimen-

tally, allowing the direct numerical computation of the forces on the phase boundaries. A general thermodynamic argument shows that, during growth (or etching), the change in $\Delta\gamma$ is proportional to the local supersaturation at the surface, for small supersaturations. The values of the chemical potential derived from $\Delta\gamma$ are consistent with estimates based on the known kinetic parameters of the surface.

Within a few degrees of T_c, coexistence of the 7×7 and '1×1' phases is observed, despite the fact that the free energies of the two phases are unequal [6,7]. Coexistence occurs because any two phases will in general have different surface stress, leading to elastic relaxation near the phase boundary. The gain in relaxation energy can offset the energy cost of the unfavorable phase. The equilibrium configuration of the domains reflects a balance between elastic relaxation and $\Delta\gamma$. Using low-energy electron microscopy (LEEM) [8,9], we have measured these equilibrium configurations of coexisting 7×7 and '1×1' domains.

A sequence of images of a large terrace is shown in Fig. 1. In the absence of a flux, a stable configuration of 7×7 and '1×1' domains is observed [Fig. 1(a)]. When the surface is exposed to disilane, a new stable configuration is reached with a smaller area fraction of the 7×7 phase [Fig. 1(b)]. When the flux is removed, the original configuration is largely recovered [10]. Conversely, during etching of the surface with molecular oxygen, which presumably lowers the Si adatom density, the equilibrium configuration has a larger area fraction of the 7×7 phase [Fig. 1(c)] [11]. Again, when the background oxygen pressure is removed, the original configuration of the surface is restored. These results show that a Si flux favors the '1×1' phase relative to the 7×7 phase, while exposure to oxygen has the opposite effect.

Our interpretation is that the supersaturation (or undersaturation) of Si adatoms at the surface changes the free energies of the two phases. The influence of steps, which act as sinks and sources for Si and limit the supersaturation, supports this view. Regions of the
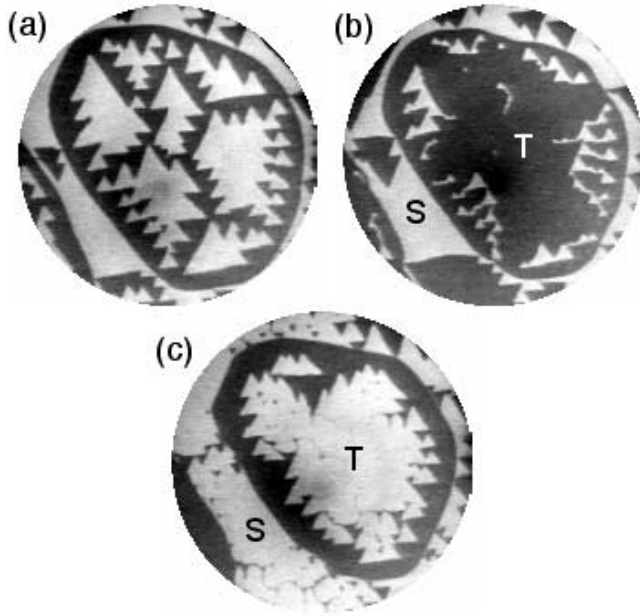
FIG. 1. Bright-field LEEM images (10 eV) of the Si(111) surface at the phase transition temperature. Under these imaging conditions, the 7×7 areas of the surface appear brighter than the '1×1' regions. The images correspond to (a) no flux, (b) 5×10^{-7} Torr disilane, and (c) 7×10^{-8} Torr molecular oxygen. The field of view is 9 μm. "T" marks the center of the terrace and "S" marks the bounding step edge.

surface near steps (labeled "S" in Fig. 1) are less affected by the flux than domains near the center of the terrace ("T"), where the supersaturation is largest. In addition, changes in the area fractions are more pronounced on large terraces, as expected since the maximum concentration is roughly proportional to the terrace area.

We can make these qualitative observations precise by measuring the equilibrium domain configuration during oxygen or disilane exposure, and using changes in configuration as a probe of the forces on the domain boundaries. The force on the ith straight segment of boundary can be written as

$$f_i = \Delta\Gamma \frac{dA}{dx_i} - (\mu_i - \mu_c)\frac{dN}{dx_i} + \beta\frac{dP}{dx_i} + \frac{dU}{dx_i}, \quad (1)$$

where $\Delta\Gamma$ is the free energy difference between the phases in equilibrium, β is the boundary creation energy per unit length (excluding long-range elastic interactions [12]), A is the total 7×7 area of the configuration, P is the total perimeter, U is the elastic relaxation energy of the configuration, and dx_i is the displacement of the ith segment along its normal.

The second term $(\mu_i - \mu_c)dN/dx_i$ requires some discussion. In Eq. (1), we follow the usual convention, defining the surface energy Γ relative to an equal number of bulk atoms [1]. However, the two phases have different atom density, so any motion of the phase boundary re-

quires capturing or ejecting atoms from the crystal into the "reservoir" of mobile atoms on the surface. This contributes an extra change $(\mu_i - \mu_c)dN$ in free energy, where dN is the *net* number of atoms incorporated when the phase boundary moves, μ_i is the chemical potential of the reservoir (i.e., the adatoms) averaged over the ith boundary, and μ_c is the chemical potential of the bulk crystal. The subscript on μ_i simply reflects the fact that the density of mobile atoms is inhomogeneous during growth.

In equilibrium, the chemical potential μ_i of the reservoir is established by capture and release of mobile surface atoms at (distant) steps on the crystal surface, so $\mu_i = \mu_c$. However, during growth there are extra atoms on the surface, relative to equilibrium. This corresponds to a supersaturation $\mu_i > \mu_c$, which favors growth of the higher-density surface phase at the expense of the lower-density phase. [The increase in atom density ρ also changes Γ, but in equilibrium $d\Gamma/d\rho = 0$, so this gives no contribution to f_i to first order in $(\mu_i - \mu_c)$.]

Equivalently, we can incorporate the dN term in Eq. (1) into a generalized surface energy, $\gamma = \Gamma - (\mu - \mu_c)\rho$:

$$f_i = \Delta\gamma_i \frac{dA}{dx_i} + \beta\frac{dP}{dx_i} + \frac{dU}{dx_i}, \quad (2)$$

where $\Delta\gamma_i$ is the difference in γ across boundary segment i (i.e., averaging μ along the boundary), and ρ is the density of "surface atoms." As discussed by Noziéres [13], there is an inherent arbitrariness in defining a density of surface atoms (unless we define it to be zero). But there is no ambiguity in the density *difference* $\Delta\rho = dN/dA$ between different regions of the surface, if we count upward from any bulk crystal plane running parallel to the surface.

In equilibrium, $f_i = 0$ for all segments in the configuration. Each segment gives rise to an expression relating $\Delta\gamma$, β, and U. A practical difficulty in applying Eq. (2) to an arbitrary domain configurations is evaluating U. One way this can be done is to sum the elastic interaction between *pairs* of segments in the configuration [12]. With this approach, U can be expressed as a product of an elastic prefactor with a geometric sum:

$$U = \frac{(1+\nu)\lambda^2}{\pi M}\sum_{i,j}\frac{1}{2}u_{ij}, \quad (3)$$

where ν is Poisson's ratio, M is Young's modulus, and λ is the difference in surface stress between the two phases. The sum includes all pairs of phase boundaries i and j. The quantity u_{ij} is a function of the geometry of the configuration: the relative separation and orientation of the two segments i and j [14]. In our simulations, we compute U by evaluating u_{ij} in Eq. (3) numerically [12]. All the material properties of the surface are contained in the elastic prefactor, $F_0 = (1+\nu)\lambda^2/\pi M$.

Equation (2) expresses $\Delta\gamma_i$ in terms of β and F_0. The relationship can be further simplified because β is fundamentally related to F_0. As explained in Ref. [6], β can be determined by measuring the equilibrium size of isolated triangular 7×7 domains above T_c. Specifically, $\beta = 2.43F_0$ for the value of the cutoff used in these calculations [14]. Thus, the stable configuration of domains is governed only by the ratio $\Delta\gamma_i/F_0$. We can use the value of $F_0 = 3.565$ meV/nm, measured by Twesten and Gibson [15], to determine $\Delta\gamma$—or equivalently, $\Delta\mu = \mu - \mu_c$—from our measurements.

LEEM images of a 2.7 μm diameter "mesa" are shown in Fig. 2. The images show a ring of 7×7 domains (that nucleated at the step edge) surrounding a central triangular domain. The boundaries of the triangular domain are unconstrained (i.e., not attached to the step edge). Each panel shows the equilibrium domain configuration at a
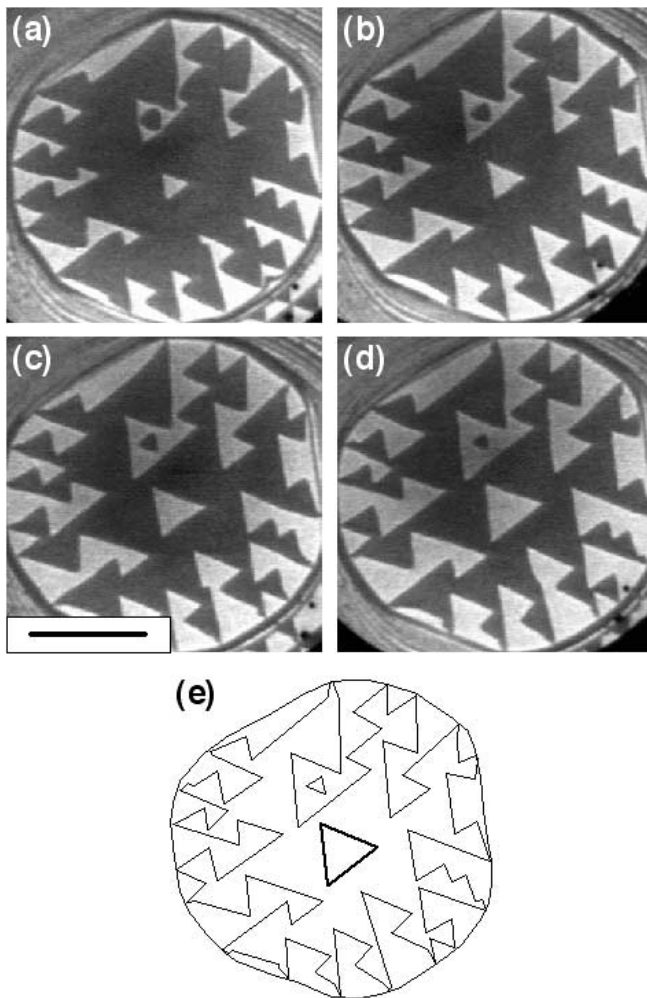
different background pressure of disilane, but at the same sample temperature. At the highest pressure (largest Si flux) the central domain is small. When the flux is reduced, the domain grows in size. The process is reversible, with very little hysteresis. Following the procedure outlined above, we use the measured geometry to determine the value of $\Delta\gamma$ near the central domain at each disilane pressure. To compute the elastic relaxation energy, we include the boundaries of all the domains on top of the mesa. For example, the geometry used to compute U for the configuration in Fig. 2(d) is shown in Fig. 2(e). The three boundaries of the central domain give three values for $\Delta\gamma_i$, which we average to obtain a best value for $\Delta\gamma$ in this region [16]. The dependence of $\Delta\gamma/F_0$ on disilane pressure is shown in Fig. 3. While the absolute change in $\Delta\gamma$ is small—on the order of a few micro-eV per '1×1' cell—the effect on the equilibrium structure of the surface is clearly significant.

We can use the measurements of $\Delta\gamma$ to determine $\Delta\mu$. $\Delta\gamma$ contains a term proportional to $\Delta\mu\Delta\rho$, where $\Delta\rho$ is the density difference between the '1×1' and 7×7 phases. Yang and Williams determined $\Delta\rho$ by quenching the Si(111) surface rapidly from above T_c, and measuring

FIG. 2. LEEM images of a mesa during exposure to disilane at fixed temperature. Scale bar, 1 μm. The disilane pressures (Torr) are (a) 3.6×10^{-7}, (b) 2.2×10^{-7}, (c) 1.4×10^{-7}, and (d) 7.6×10^{-8}. The geometry used to numerically compute the elastic relaxation energy of the center domain in (d) is shown in (e).
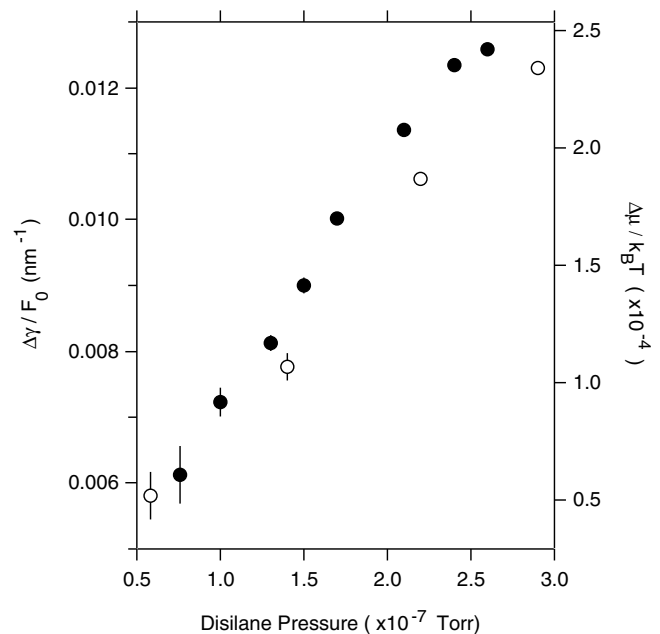

FIG. 3. The dependence of $\Delta\gamma/F_0$ on disilane pressure near the center of the 2 μm-diameter mesa shown in Fig. 2. The data show that $\Delta\gamma$ varies linearly with pressure. Data obtained while the pressure was increased (open circles) and decreased (filled circles) show that hysteresis effects are small, and that the temperature did not drift significantly during the experiment. The right axis indicates the corresponding values of $\Delta\mu/k_BT$ using measured values for F_0 and $\Delta\rho$. All data points have error bars (most are smaller than the symbol), which indicate the standard deviation of the three measurements used to determine $\Delta\gamma/F_0$.

the total coverage of islands that form from the excess Si liberated when '1 × 1' converts to 7 × 7. They found $\Delta\rho = 0.13$ atoms per '1 × 1' cell [5]. Using the measured values of $\Delta\rho$ and F_0, we can determine $\Delta\mu$ from our measurements of $\Delta\gamma$. The results are shown in Fig. 3. The derived values of $\Delta\mu/kT$ are extremely small, corresponding to supersaturations on the order of 10^{-4}.

We can check the consistency of this result by independently estimating $\Delta\mu$ from our knowledge of the flux. If we assume that mass transport is diffusion limited, as was concluded by Hibino *et al.* [17], we can roughly estimate the supersaturation near the center of the terrace by treating the diffusing adatoms as an ideal gas. Specifically,

$$\Delta\mu/k_BT \approx FR^2/4Dc_0, \tag{4}$$

where D is the surface diffusion constant, c_0 is the adatom concentration in the absence of a flux, and R is the radius of the (circular) terrace. By measuring the rate at which single-layer etch pits fill in, we estimate $F = 2.8 \times 10^{-3}$ bilayers/s for a disilane pressure of 3×10^{-7} Torr. Measured values of Dc_0 above T_c range from 10^7 [17] to 10^8 s^{-1} [18,19]. With these values, Eq. (4) implies $\Delta\mu/k_BT$ has a value in the range 2×10^{-4} to 2×10^{-3} the center of the terrace, in good agreement with the data shown in Fig. 3. Thus, the values of $\Delta\gamma$ determined from the domain configurations are consistent with a reasonable estimate of the adatom density based on the known flux.

Our analysis shows that a supersaturation during growth or etching changes the difference in free energy between the 7 × 7 and '1 × 1' phases, $\Delta\gamma$. The configuration of domains provides a novel way of determining $\Delta\gamma$, or $\Delta\mu$, without reference to kinetic parameters. A convenient way to understand the influence of the flux is to interpret the change in $\Delta\gamma$ as a change in the phase-transition temperature, T_c. Specifically, expanding the surface-free energy difference to linear order about equilibrium at T_c, we can write $\Delta\gamma = (T - T_c)\Delta S + \Delta\mu\,\Delta\rho$, where ΔS is the entropy difference between the '1 × 1' and 7 × 7 phases, about $0.013\,k_B$ per '1 × 1' cell [6,7]. Thus, a change in μ is equivalent to a change in T_c given by $\Delta T_c = -\Delta\mu\,\Delta\rho/\Delta S$. For the configuration shown in Fig. 2, a flux of 2.8×10^{-3} bilayers/s corresponds to a lowering of T_c by 3 K at the center of the terrace. For comparison, typical growth rates used in semiconductor manufacturing are 2 orders of magnitude larger, leading to a much more significant change in T_c. Clearly, an external flux can have a dramatic effect on the structure of a surface during growth. In fact, in the absence of a surface stress difference (i.e., no elastic relaxation), at temperatures slightly below T_c a flux would cause the surface to transform from 7 × 7 to '1 × 1' [20]. By care-

fully measuring surface structure during growth, the influence of supersaturation on structure can be quantified and related to fundamental thermodynamic parameters.

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