Surface Stress and Thermodynamic Nanoscale Size Selection

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Using the Si(111) surface as an example, we show how temperature can be used to tune the size of domains during a surface phase transition. From analysis of the measured stable domain sizes, we determine key material parameters and clarify the close relationship between nucleation and thermodynamic size selection. More generally, the model we developed describes nanoscale self-assembly processes in contact with a reservoir (for example, liquid- or vapor-phase epitaxy).

Nanoscale fabrication has driven renewed interest in self-organization and self-assembly at surfaces (*1, 2*). Surface stress is expected to play a critical role in fabricating devices with highly uniform and predictable electrical, magnetic, or optical properties. For example, theories of elastic relaxation at surfaces predict the formation and stabilization of periodic structures with well-defined equilibrium sizes (*3–6*). In these analyses, the equilibrium feature size is determined by balancing the elastic energy gain associated with relaxation at the phase boundary against the energy cost of creating the boundary. It has been more difficult to establish the link between stress and morphology in experiments, because key kinetic or thermodynamic parameters necessary for a quantitative interpretation are often unknown. Furthermore, the extended periodic structures that many theories predict (*4–7*) can be difficult to produce and equilibrate experimentally, further complicating a quantitative analysis.

Here, we present detailed experimental and theoretical analysis of tunable and reversible size selection near the first-order structural phase transition of the Si(111) surface. When heated above $T_c = 1135$ K, the surface converts from the complex 7 × 7 structure (*8*) to a nearly-disordered "1 × 1" phase. In a recent analysis of a vicinal Si(111) surface with uniformly-spaced $\langle 11\bar{2} \rangle$ steps, it was shown conclusively that surface stress leads to phase coexistence near T_c (*9*). Although the area-fractions of each phase can be tuned by changing the temperature, the periodicity of the resulting "striped" phase is fixed by the step density (*10*). Here, we investigate a simple geometry where steps do not impose an artificial periodicity: an isolated domain on a large, step-free terrace. We find that the interplay between elastic relaxation, surface free energy, and the phase boundary creation energy leads to novel and distinct phenomena that have not been previously recognized: isolated 7 × 7 domains that are stable [or metastable (*11*)] above T_c, and whose equilibrium size can be tuned by changing the temperature. In contrast to many epitaxial systems [e.g., SiGe quantum dots (*12*)], the uniform size of the domains is due to a well-defined local minimum in the free energy as a function of size, and is not related to kinetic effects. Tunable size selection is possible because the area fraction of each phase is not fixed during a phase transition. Surface domains individually optimize their size by exchanging material with a reservoir [i.e., the bulk (*13*)]. In the absence of such a reservoir, nanoscale objects, such as structural domains and quantum dots, can only change size through the long-range exchange of material with other such objects. This collective coarsening process can be extremely slow for large or well-separated structures (*12*).

In order to make a quantitative comparison between theory and experiment, our theoretical approach differs from those developed for periodic configurations (*4–7, 9*). First, using isotropic continuum elasticity theory, we compute the formation energy of an isolated domain as a function of its size, which allows us to analyze an experimental configuration that is relatively easy to produce and equilibrate. Extension of our real-space approach to arbitrary configurations of domains (including periodic configurations) is straightforward. Second, we explicitly account for the anisotropy of the phase boundary energy, which gives rise to triangular-shaped domains (rather than circular "droplets"). Finally, because the relative fractions of each phase change during a phase transition, temperature, rather than coverage, is the externally controllable parameter. More generally, the resulting theory describes a growth environment in which there is exchange of material between the surface and an external reservoir.

Our experiments were performed on large step-free areas of a lithographically patterned Si(111) surface. Low-energy electron microscopy (LEEM) (*14*) measurements were made using a microscope constructed at IBM with a lateral spatial resolution of better than 5 nm (*15*). Surface temperatures were measured by focusing the light emitted from the sample (at ~1135 K) onto a silicon photodiode, which was calibrated using an infrared pyrometer. The extreme sensitivity of this method allows changes in temperature to be measured with an accuracy of 0.05 K. Images of an isolated domain at the center of a 4 μm by 12 μm terrace are shown in Fig. 1. An isolated domain is formed by cooling from well above T_c (i.e., from the uniform "1 × 1" phase) until a single 7 × 7 domain is nucleated. If more than one domain is nucleated, or if the nucleated domain is situated near a step, the process is repeated. We characterize the size of the domain by L, the length of a side. In order for large (~1 μm) domains to remain close to equilibrium, heating and cooling rates must be kept below 0.01 K/s. We find that isolated 7 × 7 domains adopt a stable size that depends on temperature. As the temperature is raised, the size decreases. Below a critical size of about 200 nm, domains are unstable and decay away. Measurements of the equilibrium size as function of temperature are shown in Fig. 2.

The measurements are reproduced in a model that includes elastic relaxation at the phase boundaries. The formation energy of an isolated triangular 7 × 7 domain at the "1 × 1" surface can be written as

$$E(L) = \frac{\sqrt{3}}{4}\Delta\gamma L^2 + 3\beta L + U(L) + E_c \quad (1)$$

where L is the length of a side of the domain, $\Delta\gamma$ is the free energy difference between the 7 × 7 and "1 × 1" phases, and β is the energy per unit length of the phase boundary (in the absence of elastic relaxation effects). $U(L)$ is the elastic relaxation energy of a domain of size L. As we show below, $U(L)$ is negative and stabilizes 7 × 7 domains above T_c. E_c is a corner-energy term assumed to be independent of L. The temperature dependence of $\Delta\gamma$ is determined by the entropy difference between the "1 × 1" and 7 × 7 phases, ΔS: $\Delta\gamma = \gamma_{7\times7} - \gamma_{1\times1} = (T - T_c)\Delta S$ (*9*). We treat ΔS as independent of T over the ~10 K interval of phase coexistence.

The discontinuity in surface stress at the phase boundary results in forces on the atoms at that boundary, giving rise to elastic relaxation (*3, 4, 9*). For Si(111), these "force monopoles" are directed toward the interior of the 7 × 7 domains, as shown in Fig. 1 (*16*). The magnitude of the force per unit length along the boundary λ is equal to the difference in surface stress between the 7 × 7 and "1 × 1" phases. Using transmission electron microscopy, Twesten and Gibson measured $\lambda = 30 \pm 5$ meV/Å^2 (*16*). We compute the elastic relaxation energy U by summing the interaction between all pairs of force monopoles at the boundary. For isolated triangular domains, the

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elastic energy can be conceptually divided into two contributions

$$U(L) = 3(1-\sigma)F_0L\left[1 - \ln\left(\frac{L}{a}\right)\right] + 3F_0L[(1 - \sigma)\ln(3) + \sigma] \quad (2)$$

where σ is Poisson's ratio, and the force F_0 is a function only of the elastic properties of the surface: $F_0 = (1 + \sigma)\lambda^2/\pi\ M$, where M is Young's modulus. Using the parameters measured by Twesten and Gibson, $F_0 = 3.56$ meV/nm (*16*). The first term in Eq. 2 comes from the elastic interaction between force monopoles on the same side of the domain. The interaction energy decreases with increasing domain length, and thus favors large domains. The interaction between monopoles on different sides of the domain is included in the second term. Because these force monopoles are nearly antiparallel, the interaction between sides is repulsive, and increases with increasing domain length. The distance a is a short-range elastic cutoff that prevents a divergence of the elastic energy at small distances (*3, 4*).

The domain energy has a particularly simple form when β is expressed in terms of a characteristic length, L_0, defined by $3\beta L_0 + U(L_0) = 0$. L_0 is the domain size for which the elastic energy gain balances the cost of creating the boundary (excluding the corner energy E_c). As we show below, L_0 can be directly measured. With $\beta = -U(L_0)/3L_0$, Eq. 1 becomes

$$E(L) = \frac{\sqrt{3}}{4}\Delta\gamma L^2 - 3(1-\sigma)F_0L\ln\left(\frac{L}{L_0}\right) + E_c \quad (3)$$

In Fig. 3, $E(L) - E_c$ is shown for several values of $\Delta\gamma = \Delta S(T - T_c)$. At small L, $E(L)$ increases with increasing L. If $\Delta\gamma$ is larger than a maximum value ($\Delta\gamma_0$, defined below), the energy increases monotonically with size, and phase coexistence will not occur. However, for $\Delta\gamma < \Delta\gamma_0$, 7 × 7 domains can be stable above T_c; above a critical nucleus size, L_c, at which $dE/dL = 0$, an increase in size is accompanied by a decrease in the formation energy. At large L, the energy again increases due the L^2-dependence of the surface energy term. At intermediate L, $E(L)$ has a well-defined minimum at L_s. That is, the stable domain size can be reversibly controlled by varying T. As T is lowered, L_s increases, diverging as T approaches T_c (i.e., $\Delta\gamma \rightarrow 0$). The curves in Fig. 3 show that stable domains above T_c are not necessarily energetically favorable (*11*). If the stable size, L_s, is less than about 2.7 L_0, the formation energy is still positive, and the domains are metastable.

Both the critical nucleus size, L_c, and the stable domain size, L_s, are defined by the condition $dE/dL = 0$. The energy is at a maximum at the critical nucleus size and at a minimum at the stable domain size. L_c increases with temperature, while L_s decreases. They coincide at a size given by the condition that both the first and second derivatives of $E(L)$ are zero, which occurs precisely at $L = L_0$ (Fig. 3). This provides a direct physical interpretation of L_0 as the smallest possible stable domain size, which we measure to be about 200 nm. The temperature, T_0, above which a domain of size L_0 becomes unstable is given by:

$$\Delta S(T_0 - T_c) = \Delta\gamma_0 = 2\sqrt{3}(1 - \sigma)\frac{F_0}{L_0} \quad (4)$$

The large value of $L_0 = 200$ nm corresponds to an extremely small free-energy difference between the phases: $\Delta\gamma_0 = 6.15$ μeV/1 × 1 cell. Note that $\Delta\gamma_0$ is the largest free-energy difference between phases for which phase coexistence will occur: if $\Delta\gamma > \Delta\gamma_0$, the surface reverts to the "1 × 1" phase.

The entropy difference between the phases can be determined from measurements of the equilibrium size as function temperature. An equation relating both L_c and L_s to temperature is obtained from the condition $dE/dL = 0$

$$\Delta S(T - T_c) = \Delta\gamma_0\left(\frac{L_0}{L}\right)\left[1 - \ln\left(\frac{L_0}{L}\right)\right] \quad (5)$$

At each temperature within the range of phase coexistence, there are two values of L for which Eq. 5 is satisfied; the smaller value is L_c, whereas the larger is L_s. Equation 5 shows explicitly how both the equilibrium size and critical nucleus size are related to fundamental and measurable parameters. In Fig. 2, we show a fit of Eq. 5 to the measured domain size as a function of temperature, corresponding to $\Delta S = 0.013 \pm 0.003\ k_B$ per 1 × 1 cell. The surprisingly small value of ΔS agrees well with our previous estimate from measurements of the width of striped domains on a stepped surface (*9*). From ΔS, we determine T_0 relative to T_c: $T_0 - T_c = \Delta\gamma_0/\Delta S = 5.3$ K. Equation 5 also implies that the critical nucleus size decreases from 200 nm at T_0 to about 10 nm at 900 K, in good agreement with scanning tunneling microscopy measurements of Hoshino *et al.* (*17*). This agreement suggests that the entropy difference be-

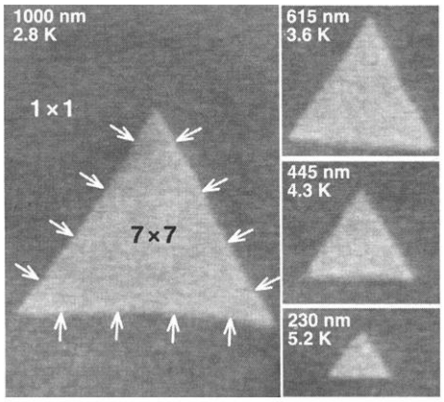

Fig. 1. Bright-field LEEM images (10 eV) of isolated 7 × 7 domains at four temperatures above T_c. The 7 × 7 areas of the surface appear bright, whereas the "1 × 1" regions are darker. Each panel is labeled by L, the side length of the domain, as well as the approximate value of $T - T_c$. Arrows indicate the orientations of "force monopoles" at the boundary between the phases.

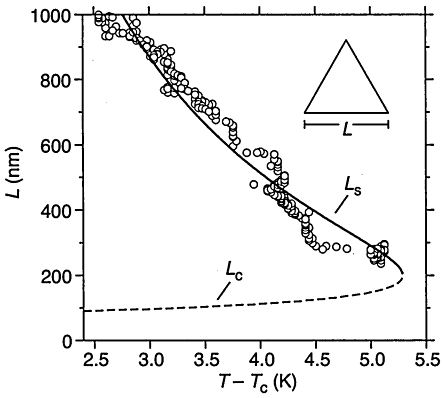

Fig. 2. Measured stable domain size L as a function of temperature. Domain sizes can be reversibly tuned by heating and cooling. The solid line indicates the size of stable 7 × 7 domains, whereas the dotted line corresponds to the critical nucleus size (Eq. 5). The determination of temperatures relative to T_c is described in the text.

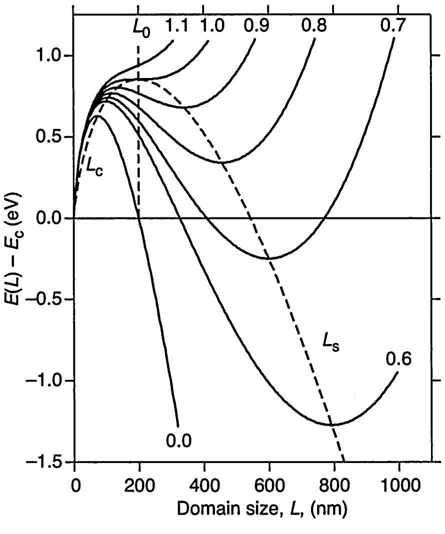

Fig. 3. Formation energy, relative to E_c, of an isolated triangular 7 × 7 domain as a function of size L for several temperatures (solid curves). Each curve is labeled by the ratio $r = \Delta\gamma/\Delta\gamma_0$, which is proportional to $T - T_c$. For $r > 1$, there is no stable minimum, and phase coexistence will not occur. The smallest stable domain, $L_0 = 200$ nm, occurs at $r = 1$. As r is reduced, the equilibrium size grows, diverging at $r = 0$. The critical nucleus size L_c and stable domain size L_s are shown as dashed curves. The same energy curves also describe an isolated "1 × 1" domain on a 7 × 7 surface below T_c, with r proportional to $T_c - T$.

tween the phases is not strongly T-dependent in this temperature range.

Our analysis has focused on phase coexistence, where surface free energy plays the role of the chemical potential (*18*). One could achieve the same advantages in heteroepitaxial structures, such as quantum dots, by having them in equilibrium with a reservoir of controlled chemical potential μ_{res}, e.g., an ambient vapor at a specified partial pressure. For two-dimensional structures, elastic relaxation lowers the free energy relative to that of a uniform film for some range of island sizes. The chemical potential μ_0 of the uniform film plays the role of T_c here. For $\mu_{res} < \mu_0$, individual islands of a particular size are stable and do not grow. (The stable island size diverges as μ_{res} approaches μ_0.) As μ_{res} is decreased, the island size shrinks, until below some critical value μ_{min} the islands become unstable and disappear. This point defines the minimum stable island size, analogous to L_0. Thus, growth from a reservoir allows reversible and direct control of the island size, as well as the potential to circumvent kinetic limitations associated with coarsening.

Finally, we note that many properties of ensembles of domains are directly related to the energetics of an isolated domain. For example, not only isolated domains, but also groups of domains near equilibrium have a well-defined size, as shown in Fig. 4. Because the interaction between domains is repulsive, domains that are metastable when isolated ($L < 2.7\ L_0$) are necessarily metastable as part of a group. Thus, the configuration shown in Fig. 4 (with $L \approx 500$ nm) has a higher energy than the uniform "1 × 1" phase. Direct numerical computation of the elastic energy, including elastic interactions between domains, supports this conclusion. The hysteresis observed in the nucleation of 7 × 7 domains (*19*) is also explained by Eq. 3. Because the critical nucleus size is large and the nucleation kinetics are slow, nucleation near T_c is extremely unlikely. In practice, nucleation occurs only when T is well below T_c, where the critical nucleus size is small.

Our analysis of the stability of isolated 7 × 7 domains shows that size selection is directly linked to elastic relaxation at phase boundaries. For a range of temperatures above T_c, 7 × 7 domains are stable with well-defined equilibrium sizes. However, if the equilibrium size is less than about 2.7 L_0, the configuration is metastable, and conversion to the "1 × 1" phase is still energetically favorable, although kinetically hindered. The domain size must be very large—greater than about 550 nm—in order for elastic relaxation effects to offset the energy cost associated with the (unfavorable) 7 × 7 phase. Our analytical theory shows that the nucleation, formation energy, and size selection of isolated domains can be described in terms of a small number of measurable parameters. Knowledge of these parameters in strain-mediated self-assembly systems will be required for a detailed understanding and control of size selection at surfaces.

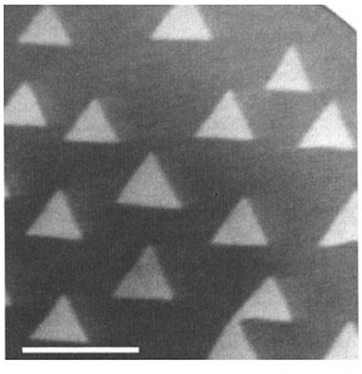

Fig. 4. Bright-field LEEM image (10 eV) of a near-equilibrium domain configuration above T_c. The bright areas indicate the 7 × 7 structure, whereas dark areas correspond to the "1 × 1" structure. All of the domains shown in the figure are metastable. The small variation in size among the domains is due to elastic interaction between the domains and a step outside the field of view. Scale bar, 1 μm.

References and Notes

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10. In the striped geometry, the boundary length is independent of T. Consequently, the area fraction of each phase does not depend on the phase boundary creation energy.
11. We use the word "stable" to describe both stable and metastable domains above T_c. However, because the kinetics of nucleation are slow at the Si(111) surface, metastable domains are for all practical purposes stable.
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18. To make clear the correspondence with the familiar free energy $F = E - \mu N$, we could have written Eq. 1 as $F = E - \gamma_{1\times1} A$, where $E = \gamma_{7\times7} A + 3\beta L + U(L) + E_c$, and A is the domain area. The "reservoir" of area is the surrounding "1 × 1" phase, and its surface energy plays the role of the corresponding chemical potential μ.
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Continuous Wave Operation of a Mid-Infrared Semiconductor Laser at Room Temperature

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Continuous wave operation of quantum cascade lasers is reported up to a temperature of 312 kelvin. The devices were fabricated as buried heterostructure lasers with high-reflection coatings on both laser facets, resulting in continuous wave operation with optical output power ranging from 17 milliwatts at 292 kelvin to 3 milliwatts at 312 kelvin, at an emission wavelength of 9.1 micrometers. The results demonstrate the potential of quantum cascade lasers as continuous wave mid-infrared light sources for high-resolution spectroscopy, chemical sensing applications, and free-space optical communication systems.

The mid-infrared portion of the spectrum, covering approximately the wavelength range from 3 to 12 μm, is sometimes referred to as "underdeveloped" because of its lack of convenient coherent optical sources. Especially when compared to the visible or near-infrared spectral range, where interband semiconductor lasers are now produced very economically with continuous wave (CW) output power of tens of milliwatts, this assertion holds true. In the mid-infrared, a new class of semiconductor lasers—intersubband quantum cascade (QC) lasers (*1*)—has become a promising alternative to interband diode lasers (*2*, *3*) in the past 7 years. In these devices, photon emission is obtained by electrons making optical transitions between confined energy lev-

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