

Growth and Equilibrium Structures in the Epitaxy of Si on Si(001)

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Scanning-tunneling-microscopy measurements of submonolayer growth of Si on Si(001) show anisotropic island shapes. From coarsening experiments it is determined that these shapes are a consequence of the growth kinetics. They can be explained by a lateral accommodation coefficient for atoms arriving at the edge of islands that differs by an order of magnitude at the ends and at the sides of dimer rows.

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Because of its atomic resolution, scanning tunneling microscopy offers the possibility to investigate the microscopic mechanisms of crystal growth and surface ordering processes at a detail heretofore unachievable. There have recently been several reports of the growth of Si on Si(100) that either show directly^{1,2} or require³ an anisotropic island shape during growth. Several possibilities have been advanced for these shapes: (1) They are an equilibrium crystal shape^{1,3,4} caused by adatom interactions that differ in different directions;⁵ (2) they are caused by anisotropic surface diffusion;^{6,7} and (3) they are a nonequilibrium structure caused by aspects of the growth dynamics.^{7,8} In particular, Ref. 8 considers the collective motion of densely packed adatoms and proposes that the opening of dimer bonds in the underlying layer, to accommodate the new layer, differs in two directions, causing the anisotropic structure.

We demonstrate here, by appropriate measurements at submonolayer coverages and during the initial stages of growth, that the shapes are not equilibrium structures and are not a consequence of anisotropic diffusion, but rather that an anisotropic lateral accommodation coefficient must be responsible for most of the growth-shape anisotropy. This phenomenon appears not to have been previously considered; it is the 2D analog of 3D growth shapes observed in bulk crystal growth.

The growth of a homoepitaxial (*A-on-A*) system can be described in terms of the kinetics of island formation when two phases coexist, the islands and the 2D vapor. The three fundamental stages of ordering in two-phase coexistence are nucleation, growth, and coarsening. Consider a homogeneous disordered phase that is quenched (e.g., by changing the coverage suddenly) to a state in which, at equilibrium, islands and the 2D vapor phase coexist. Immediately after the quench, the system will be a supersaturated low-density homogeneous disordered state. Nucleation of islands takes place randomly. If the disordered phase is continually replenished (e.g., by continued deposition), the supersaturation is maintained, and all islands will grow by diffusion and condensation of atoms at the edges of existing islands. If the deposition is interrupted, growth *per se* will cease when the mean supersaturation is eliminated and the islands

are in local equilibrium with their vapor. Subsequent ordering takes place by coarsening, in which small islands disappear at the expense of larger ones. The process is driven by the difference in boundary free energy of islands of different sizes, which cause variations in local vapor pressures, and hence, concentration gradients. The mechanisms involved in coarsening are therefore 2D evaporation, monomer diffusion driven by a concentration gradient, and 2D condensation. Coarsening is a slower process than growth, because it requires, in addition to the activation energy for diffusion, the (generally larger) activation energy to desorb an atom from the island.

During both the growth and coarsening stages any island will continually seek to minimize its boundary free energy and adopt its equilibrium shape, which, at finite temperatures, may be a circle or an ellipse. The aspect ratio of the ellipse is proportional to the free energy and thus reflects (at least at low temperatures) the ratio of strengths of adatom interactions in the relevant directions. An equilibrium shape can be assured only for a system in equilibrium with its vapor (as many atoms leaving an island as arriving), which can occur only in the final stages of coarsening. Earlier in the growth process, there is always an imbalance in flux, and hence no requirement for equilibrium shapes. In such situations "growth shapes" may form, determined by the ease of growth of particular facets (in 3D) or sides (in 2D). The ease of growth in particular directions is most easily understood in terms of an anisotropic accommodation coefficient for arriving species. The more the accommodation coefficient differs in different directions, the more anisotropic the growth shape will be. Growth and the evolution toward the equilibrium shape are competitive processes: The more rapid the growth is (i.e., the higher the steady-state supersaturation) the more the growth shape may differ from the equilibrium shape.

Using scanning tunneling microscopy (STM), appropriate experiments have been performed to distinguish between growth and equilibrium shapes in Si epitaxy on Si(001). It is shown that the major part of the anisotropy¹⁻³ is a growth shape. Limits are set on the equilibrium shape anisotropy and hence the anisotropy in

free energy. A value for the required accommodation coefficient anisotropy is suggested.

Si was deposited onto well-cleaned Si(001) by evaporation from another Si wafer. The substrate preparation⁹ leaves the surface with a minimum concentration of defects. Typically wafers have a slight misorientation, producing a surface with $\sim 500\text{-\AA}$ -wide terraces, separated by single-atomic-height steps; and hence both (2×1) and (1×2) domains. Depositions were made to coverages of a fraction of a monolayer at several temperatures between room temperature and 500 K. The island shapes were monitored after deposition and after subsequent annealing. All measurements were made at room temperature, which required quenching those samples that were treated at higher temperatures. Figure 1 shows island shapes and distributions at two temperatures. It should be noted that islands form during deposition at room temperature, implying that diffusion of monomers is sufficiently large on the surface to do so. On the other hand, all distributions are stable at room temperature, implying that coarsening is a much slower process than growth, as expected from earlier arguments. In fact, from the stability of islands and terrace edges, a simple Arrhenius argument suggests that the lateral

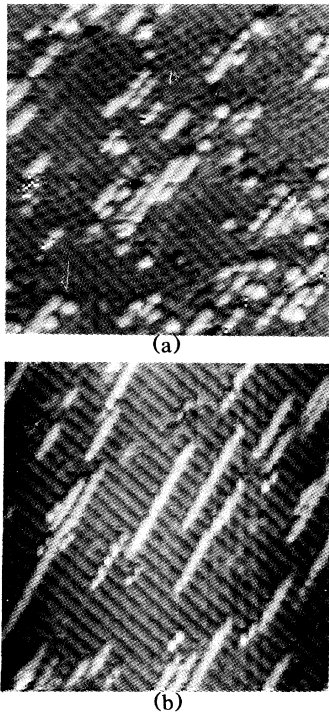


FIG. 1. STM micrographs of island shapes and distributions for growth at a rate of $1/200$ ML (monolayer) per second to a coverage of 0.2 ML at (a) 300 K and (b) 475 K. Islands are long in the direction of a dimer row. The anisotropy depends on deposition rate and substrate temperature. Scale, $230\times 230 \text{ \AA}^2$.

desorption energy of an atom must be greater than 1 eV. Deposits made at higher temperatures can, in principle, change their shape toward greater equilibrium during cooling; our experiments show that this is a negligible effect at our cooling rates. In any case, the effect would be in the direction that would require the initial island shapes to be even more anisotropic.

Because of the anisotropy of the substrate (i.e., dimer rows), it has been suggested⁷ that the self-diffusion coefficient of Si on Si(001) is likely to be anisotropic. Even if this is so, one needs to address if it can lead to anisotropic island shapes. It is relatively straightforward to argue on physical grounds that it cannot, by considering an initially uniform distribution of monomers diffusing at different rates in orthogonal directions and stopping when they meet each other or an existing island. We have made Monte Carlo calculations to confirm this reasoning. The Monte Carlo calculations explored both the effects of anisotropic bond energies and anisotropic hopping diffusion. The model considers the arrival of atoms at a slow rate and an isotropic and large probability of sticking. The binding energy of atoms in orthogonal directions can be varied, as can the arrival rate from different directions. No preferential motion along the edge of an island is allowed; an island can seek its equilibrium shape only through desorption from the edge (involving a Boltzmann factor of the binding energy of an atom at the edge) and readsorption at a different position. This condition minimizes the rate of approach to equilibrium and thus emphasizes the effect of kinetic factors. If the binding energies are made anisotropic, the equilibrium shape of the island, as expected, directly reflects this anisotropy. To test for the effect of diffusional anisotropy, the binding energies were made isotropic and the shape of islands was monitored as a function of time for both (1) an initial supersaturation of monomers that was allowed to decay and (2) a supersaturation that was maintained by continued deposition. Diffusion coefficients in orthogonal directions were then varied up to a factor of 20. No shape anisotropy was observed at any time; if the binding energies were made large, reducing the rate of approach to the equilibrium shape, the structure appeared somewhat like a diffusion-limited aggregate, but still showed no shape anisotropy. Initial measurements show that, in any case, the diffusional anisotropy in Si(001) appears to be less than a factor of 2.²

To test if the islands have equilibrium shapes, structures such as those shown in Fig. 1 were annealed. Results are shown in Figs. 2 and 3. For all initial conditions that we have studied, shapes become more isotropic upon annealing. Figure 2 shows islands with an aspect ratio of about 2 or 3, which therefore provides an upper limit to the free-energy anisotropy. There appears to be no dependence of the degree of anisotropy on island size, suggesting that other energy terms, such as strain ener-



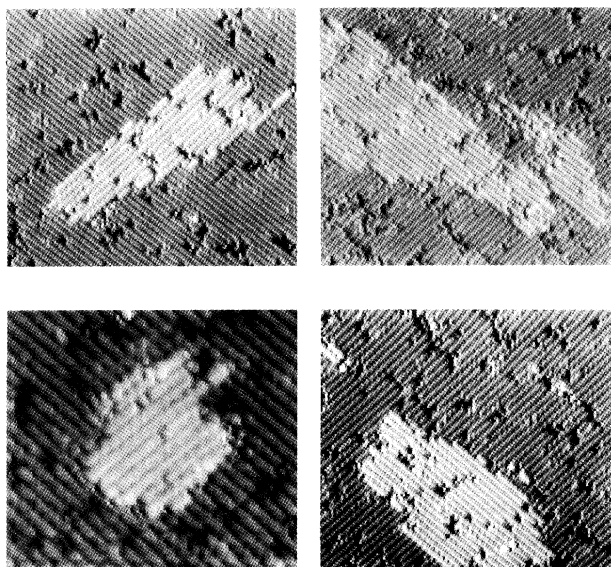


FIG. 2. STM micrographs of island shapes after annealing structures such as those shown in Fig. 1 at ~ 600 K for 2 min with the flux off. Islands grow, become more widely dispersed, and adopt a more rounded shape. Scale is $320 \times 320 \text{ \AA}$, except lower left which is $160 \times 160 \text{ \AA}^2$.

gy, do not control the shape. Figure 3(a) shows STM images of islands formed during the deposition of half a monolayer of Si onto Si(001) at 300°C . Figure 3(b) shows the same surface after a 10-min anneal at 300°C . Again the shapes after annealing are anisotropic by only a factor of 2 or 3, while before annealing the anisotropy is greater than 10. We cannot conclude from Figs. 2 and 3(b) that the shapes shown there are at equilibrium. Because of the limited terrace size ($\sim 500 \text{ \AA}$) on the substrates, there is a continued loss of atoms to edges, and further annealing will eventually lead to terraces free of islands. Therefore true equilibrium cannot be reached if any information on islands is desired, and the free-energy ratio in orthogonal directions estimated above is a maximum. If it can be assumed that the entropy is small, then the observed anisotropy also reflects the maximum adatom interaction⁵ ratio in orthogonal directions.

As Figs. 1 and 3(a) show, the shape anisotropy during growth is as large as 10–15. It can be explained simply by an anisotropic accommodation coefficient. Accommodation can be understood microscopically in terms of the pathways and transition probabilities for energy transfer so that an arriving atom can stick to an existing island. The problem is similar to accommodation of atoms on a surface from the 3D gas phase.¹⁰ If the accommodation coefficient of an approaching atom at the side of a growing dimer chain is much less than it is at the end of the chain, atoms will effectively reflect off the side and stick only on the ends. This causes the chain to grow longer.

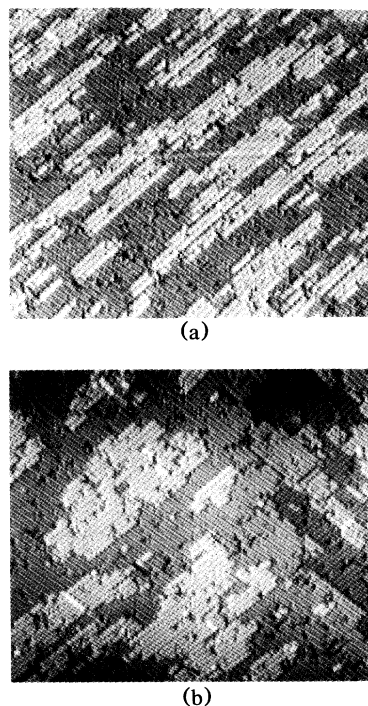


FIG. 3. STM micrographs of island structure for deposition of 0.5 ML of Si at $1/20$ ML/sec and 575 K ; (a) as deposited and (b) after annealing for 10 min at 575 K . Scale is $500 \times 500 \text{ \AA}^2$. Islands become more rounded with annealing.

In the limit that this kinetic process completely dominates the process of seeking the equilibrium shape (e.g., at very high supersaturations in the 2D vapor phase), the island shape anisotropy directly reflects the anisotropy in the accommodation coefficient. Thus the accommodation coefficient at sides and ends of Si dimer rows may differ by a factor of 10 or more. A possible alternative explanation of accommodation is based on an anisotropy in sticking of monomers. Such a scenario would require that the binding energy of a monomer arriving at an edge be much smaller and more anisotropic than that of an atom already incorporated into the two different types of island edges that bound the island structure.⁵

Anisotropic accommodation will naturally affect growth in actual molecular-beam-epitaxy (MBE) situations. In fact, the observation that double-height steps form during MBE of Si on slightly vicinal Si(001) (Ref. 11) can only be explained, we believe, by anisotropic accommodation. Given a finite probability for level crossing by deposited atoms, the terraces with dimer rows running parallel to the edge will grow slowly, due to a smaller accommodation coefficient, while the terraces with dimer rows running perpendicular to the edge will grow rapidly. At suitable deposition rates and temperatures, the latter type will catch up with the former and create a double step. Whereas, in principle, the phe-



nomenon could also be explained by an equilibrium argument with highly anisotropic and small edge desorption energies and high migration barriers,¹² our experiments show that this is unphysical for Si on Si(001).

In many respects, the "evaporation" shape of a crystal is closely related to the growth shape. Consequently, the conclusions drawn here may have considerable bearing on the structure of terrace edges in vicinal surfaces. Their structure, including edge roughness¹³ and, in particular in vicinal Si(001) miscut toward [110], the precise angle at which the single-to-double-atomic-height-step transition occurs, may depend on surface processing conditions. Furthermore, any accommodation coefficient less than 1 will also affect determination of surface diffusion coefficients made from observing the behavior of reflection-high-energy-electron-diffraction intensity oscillations with temperature.^{14,15}

In conclusion, we have shown that anisotropic island shapes in the growth of Si on Si(001) are to a large degree a growth structure and not an equilibrium effect or the consequence of anisotropic diffusion. At growth temperatures $T \approx 500$ K the 2D accommodation coefficient must differ by an order of magnitude or more in orthogonal directions. It is likely that other observed anisotropic island shapes¹⁶ are also growth structures and that this result can be generalized to many more structures evolving in a highly nonequilibrium manner.

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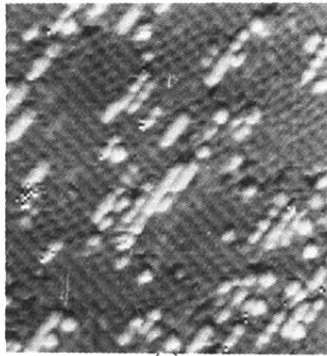
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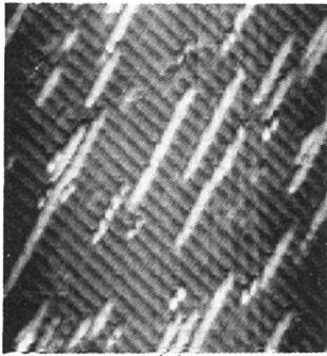
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(a)



(b)

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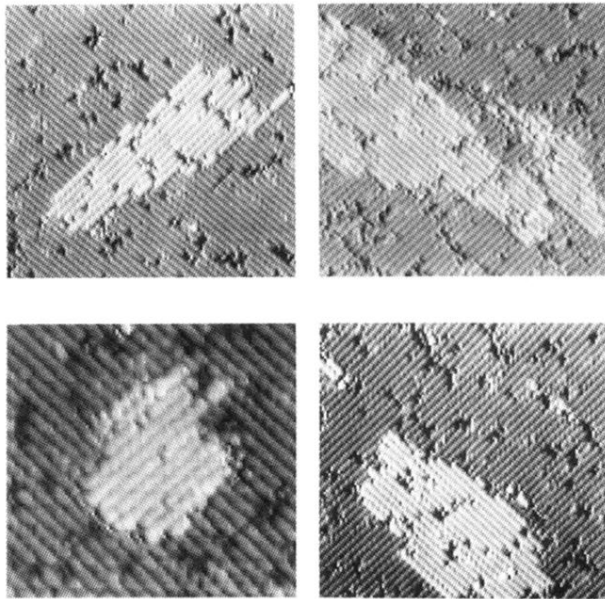
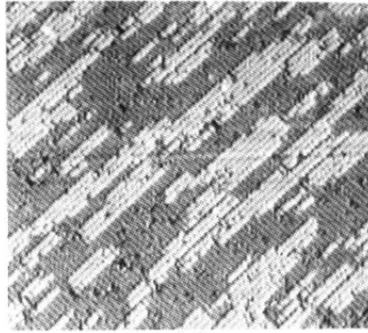
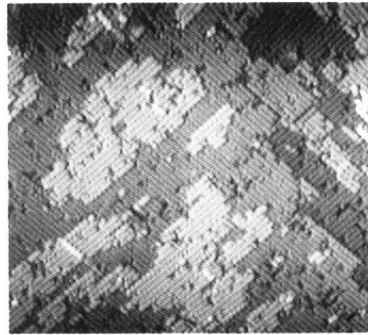


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