Epitaxial Growth and the Art of Computer Simulations

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The results of kinetic simulations of the aggregates formed during the deposition of atoms on a semiconductor surface are reviewed. Because the kinetic parameters are poorly known and the accuracy of the existing interatomic potentials has not been sufficiently tested, the goal has been to reach a qualitative understanding of the formation of unusual patterns during growth, such as the segregation of aluminum during the growth of aluminum-gallium-arsenide (AlGaAs) coherent tilted superlattices and the formation of thin, long, and parallel islands during the deposition of Si on an Si(100) surface. Kinetic mechanisms for these phenomena are proposed.

SMALLER, BRIGHTER, FASTER—THESE MODERN TRENDS IN electronic and photonic devices impose strict demands on crystal growth. Extremely small structures must be fabricated with high material uniformity and interface smoothness. This requirement demands control at an atomic level, and methods (such as molecular beam epitaxy) that were impractical not long ago are now used for device fabrication.

Scanning tunneling microscopy (STM) has reduced the space scale of crystal growth research to angstroms. Instead of observing the formation of chunks of matter, one can examine small atomic "clusters," the structure and stability of which are dominated by local chemical forces, and the shapes and sizes of which have regularities that cannot be explained by traditional nucleation theory.

These advances provide a theorist who wants to understand growth and segregation, in terms of atomic motion, with remarkable opportunities. One can theoretically study technologically important processes that involve a small number of atoms; the experiments provide both riddles to explain and sufficient detail to permit testing and improving of the models. Several groups (1) have answered the call, but in this article we describe only the work performed in our group at Santa Barbara.

The level of our investigations depends on how much is known about the system and on the kind of answers sought. If information is meager, we use kinetic Monte Carlo (KMC) simulations with simplified models. These simulations deposit atoms on the surface and move them from site to site with a frequency proportional to the corresponding rates. These rates are guessed through the use of all of the available experimental and theoretical information. Because this information is limited, we develop a minimal model in which the motion takes place on a lattice and the details deemed unessential

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are ignored. By varying the rates and comparing the results to the data, we find the physical features that are essential for reproducing the experimental observations. The results of such studies are interesting because the KMC procedure generates exactly the growth patterns that correspond to the postulated rates; these results are worth knowing even when the connection between a specific set of rates and specific materials has not been yet established.

If detailed STM measurements and reasonable interatomic potentials are available, we try to understand the growth process in greater detail. The potentials are used to estimate the jumping rates and their dependence on surface reconstruction and on the structure of the cluster formed with the neighboring atoms. These rates are used to generate, through KMC simulations, growth patterns that can be compared to those seen by STM.

Both approaches are purely kinetic and generate naturally the metastable structures formed during the growth. Because thermodynamics is the long-time limit of kinetics, the behavior predicted by thermodynamic arguments is correctly reproduced, if relevant.
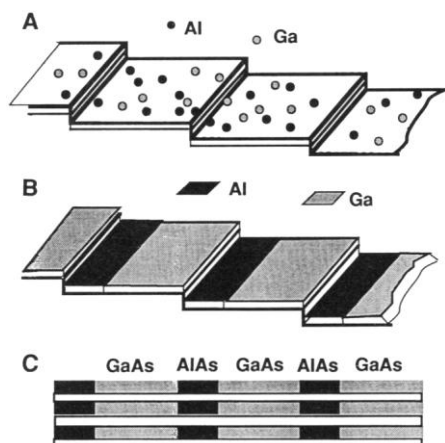
Although the computing methods are powerful, the input (limited data or insufficiently tested potentials) is of uncertain quality. In order to do useful work, we concentrate on those experimental observations that seem to defy common sense or experience and therefore require a qualitative explanation.

Coherent Tilted Superlattices

The experiment. Tsuchiya, Petroff, and Coldren (2) have proposed a striking scheme (Fig. 1) for growing what they call a coherent tilted superlattice (CTSL). The As face of a stepped GaAs(100) surface is exposed to a pulsed beam containing 30% Al and 70% Ga at an As pressure of 10^{-8} torr. The pulse length is designed to deposit an Al and Ga monolayer on the surface. There is evidence (2) that the Al atoms segregate at the step, that the Ga atoms occupy the remainder of the terrace, and that the border between the regions occupied by Ga and Al is smooth and parallel to the step (Fig. 1B). The Al and Ga monolayer is then covered with an As monolayer to produce a stepped surface similar to the one used at the start of the process. Repeating the procedure several times leads to the structure in Fig. 1C. If the material is uniform and the border is smooth, these stacks of extremely thin AlAs and GaAs wires should have high electron mobility and excellent optical properties (3).

An experienced "simulator" is likely to regard this growth scheme with skepticism. It is reasonable to believe that, under the right deposition conditions, Al segregates at the step in the early stages of deposition. However, in the later stages the Ga atoms occupying the center of the terrace should get in the way and prevent the stray Al atoms from reaching the Al island near the step. Furthermore, most (perhaps all) phase-segregation simulations performed so far lead to rugged boundaries between phases. A smooth border, such as the

Al-Ga border drawn (with an artist's license) in Fig. 1B, is unusual. The group at the Imperial College in London noted that "we have attempted to simulate this process using a wide range of parameters (substrate temperature, fluxes, diffusion and nearest-neighbor energies), but have so far failed to observe this form of step edge segregation for reasons we do not yet understand" (*4*, p. 1153).

It would be reassuring to show that the structure proposed above is compatible with reasonable kinetic models. One would also like to find out which properties of the system lead to the observed behavior.

Several other experimental observations (*2*) require an explanation. The Al segregation at the step takes place only in a narrow temperature range. If the steps are perpendicular to the dimer rows on the (100) GaAs terraces, the growth of CTSL is successful; if the steps are parallel to the dimer rows, growth fails.

The method of simulation. In order to simulate this process we used a KMC method (*5*). The atoms on the terrace move by site-to-site jumps on a square lattice. We postulated rates for all of the elementary processes involved, such as the site-to-site jumps, the jumps to leave or join a step or an existing adsorbate cluster, and so forth. The atoms were deposited on the surface and moved from site to site with a frequency proportional to the rate of the respective move: If the rate constant of the kinetic processes i was k_i, the largest rate was chosen as a reference and denoted k_r. The quantity $P_i = k_i/k_r$ was then used in a Monte Carlo program (*5, 6*) as the probability that the atom performs the jump i.

This procedure solves exactly the kinetic-diffusion equations corresponding to the rates in the model, including single-particle diffusion; dimer, trimer, and multimer formation and dissociation; sticking to and departing from the step; and so forth. This powerful algorithm solves exactly a set of transport differential equations, even though they cannot be written explicitly.

The KMC procedure differs from that of the ordinary thermal Monte Carlo algorithm that uses Boltzmann factors (*7*) to move the particles. The use of Boltzmann factors forces the system to evolve toward equilibrium, but the route of this evolution is, in most cases (*8*), physically meaningless (*9*). The KMC follows the actual path taken by the system and generates the correct nonequilibrium structures.

A gigantic time scale gap is faced by atomic level growth simulations. The atoms on a solid surface move on a scale of 10^{-15} s, whereas the deposition of a monolayer in epitaxy can take longer than 1 s. It is unlikely that a computer will soon be available that can move thousands of atoms for 10^{16} time steps. This gap can

be overcome in two stages. First, the adsorbed atom spends a lot of time oscillating at a surface site. On the scale of these oscillations the atom leaves its site very rarely (for example, once in 10^{-8} s). The rate of this rare event can be calculated (*10*) by methods that avoid following the atomic motion until the jump occurs; they generate the jump with the appropriate probability and follow the motion of the particle for a short time to see whether it reaches the final site or not. If good interatomic potentials are available, these calculations can provide the rates used in the KMC program, which then overcomes the remainder of the time gap. If, for example, the fastest rate of interest is of the order of 10^6 s^{-1}, then about 10^6 time steps are sufficient for completing the deposition of a monolayer. This calculation is manageable on existing computers.

Because of the methodology outlined above, the bottleneck in simulating processes relevant to epitaxy is no longer computer power but the lack of adequate and efficiently computable interatomic potentials. The most likely route for progress is the generation of semiempirical potentials that are used in simulations and refined by comparison with detailed STM experiments. The process is slow, tedious, and treacherous, but it is also very instructive.

The model. In order to apply the KMC method, we had to decide which elementary kinetic processes are important and guess their rates. To do this we had to use all available information (which is scanty), as well as folklore (which is abundant) and analogies to similar systems. Our first choice of rates (*5, 6*) produced an Al-Ga segregation very similar (Fig. 2A) to that proposed by Tsuchiya and co-workers (*2*), even though we did not vary the rates to fit the data. The patterns generated by the simulation were stable with respect to variations in the magnitude of the rates.

By experimenting with the model, we found two features essential (*5, 6*) for producing a CTSL. The Ga layer is fluidlike, whereas the Al layer has a greater rigidity; thus, the mobility of Ga on the As face of the GaAs(100) terrace is greater than that of Al, and the Ga-Ga and Ga-Al interactions are weaker than the Al-Al interactions. The islands formed on the terrace by the Ga atoms get in the way of the Al atoms traveling toward the step. However, if the Ga "islands" are fluidlike, they have a large number of mobile vacancies. An Al atom embedded in a Ga island can, whenever such a vacancy arrives near it, hop on the vacant site and thus migrate through the Ga layer. If the Ga-Ga interactions are increased or the temperature is lowered, the mobility of these vacancies is decreased dramatically, and the Al atoms do not have
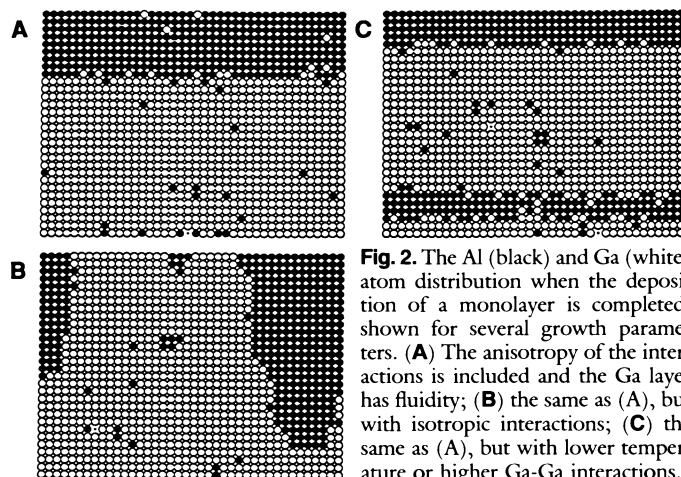
Fig. 2. The Al (black) and Ga (white) atom distribution when the deposition of a monolayer is completed, shown for several growth parameters. (**A**) The anisotropy of the interactions is included and the Ga layer has fluidity; (**B**) the same as (A), but with isotropic interactions; (**C**) the same as (A), but with lower temperature or higher Ga-Ga interactions.
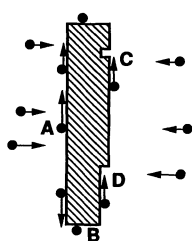
Fig. 3. The Al atoms (no Ga) form long Al islands oriented perpendicular to the dimer rows of the surface. The circles show Al atoms that will join the island. At C and D the growth process that repairs kinks or vacancies at the shore of the island is shown.

time to go through the Ga layer before the deposition of the monolayer is completed (5, 6) (Fig. 2C). This explains why the segregation of Al is so sensitive to temperature.

The second essential factor in CTSL formation is the anisotropy of the Al-Al interactions. The Al atoms adsorbed on the As face of the GaAs(100) terrace have two V-shaped, partly occupied orbitals that are not engaged in bonds and that point in well-defined directions; they are similar to the dangling bonds of an Si atom adsorbed on an Si(100) surface. If the line joining two adsorbed Al atoms is parallel to the dimer rows on the As surface, these orbitals point toward each other and the atoms interact strongly. If the same line is perpendicular to the dimer rows, the interaction is weaker. Because the Al-Al interactions influence the rate of an Al atom sticking to or leaving an Al island, the anisotropy of the interaction affects the growth pattern.

The importance of this effect, which is omitted in most simulations, and the mechanism through which it affects the growth patterns were established by experimenting with the model (5, 6). If the Al-Al interactions are made isotropic, the straight border between Al and Ga in Fig. 2A disappears and the Al domains take the shape in Fig. 2B. Extensive variation of the other parameters while maintaining the isotropy of the interactions failed to produce structures with flat borders.

The shape of the border is a property of the Al island, not of the Al-Ga interface. The model grows thin rectangular islands with smooth borders, oriented in a direction perpendicular to that of the As dimer rows on the substrate (Fig. 3), even if the surface has no Ga and no steps. This result is puzzling because the mobility of the Al atoms is much greater in the direction (shown by the horizontal arrows in Fig. 3) perpendicular to the island's long border. Examination of the motion generated by the simulations showed that the anisotropy of the Al-Al interactions caused the Al atoms that stick to the long side of an Al island (Fig. 3, site A) to run along the shore until they reached the head of the island and got stuck there (Fig. 3, site B). This effect also explains why the island's shore is so smooth. If the atoms running along the shore encounter a vacancy (Fig. 3, site C) or a kink (Fig. 3, site D), they get stuck there and repair the flaw. As a general rule, the growth of "perfect" structures is more efficient if the kinetics has a proofreading and error-fixing mechanism.

Aluminum manages to form thin islands with well-defined orientation even in the presence of the Ga atoms because the Ga-covered region has many vacancies that (at sufficiently high temperature) can move near the Al atoms stuck at the border, giving the Al atoms a chance to travel along it. The direction in which the long, thin Al islands grow is determined by the direction of the dimer rows on the terrace and not by the presence of a step: the thin island grows perpendicular to the dimer rows. If the step is perpendicular to the dimer rows, the island grows with its long side along the step. If the step is cut parallel to the dimer rows, Al forms thin, long islands perpendicular to the step.

Thus, only steps cut perpendicular to the dimer rows (within this model) are capable of "nucleating" good CTSLs.

The model determines exactly the growth pattern corresponding to a given kinetic scheme and allows the identification of a small number of properties responsible for the qualitative behavior observed experimentally. These conclusions are stable with respect to variations of the parameters that were not singled out as essential. In particular, changing either the rates of sticking to the step or the anisotropy of the diffusion coefficients did not affect the results qualitatively (6).

Fitting the data with a given model, however, is no guarantee that the model is correct. Further experimental work is needed [particularly by STM (11)] for a thorough test of the model.

Si Deposition on Si(100)

There is more information (12) about the Si(100) surface than about the GaAs(100) system: interatomic potentials have been developed and tested for 24 years, and the STM pictures show the growth patterns with atomic resolution. We provide kinetic explanations for the following phenomena: (i) The atoms deposited on the surface form (12–14) thin, long islands, with smooth borders and few defects, that are oriented perpendicular to the dimer rows of the substrate. (ii) Some of the one-atom-high steps are smooth, and some are rough (12–15). (iii) The deposition of one-half of an Si monolayer on an Si(100) surface with one-atom-high steps leads to a surface with two-atom-high steps (16).

For the remainder of this article, we attempt to provide kinetic explanations for a growth phenomenon by estimating the site-to-site jumping rates from an interaction potential (17) and then finding the jumps that are most effective in the formation of the observed growth patterns. The rates were obtained by calculating the energy barrier for the jump and using it in the Arrhenius formula with a pre-exponent of 10^{13} s^{-1}. The activation energy calculations were performed by finding the path of minimum energy for a given jump; while searching for this path all atomic positions were allowed to change. The value obtained depends strongly on the occupation of the neighboring sites, and calculations have been performed for a large number of neighbor configurations.

The growth after the deposition of Si on Si(100) is best described by thinking of each n-atom cluster as a distinct adsorbed species and of different conformations of n atoms as distinct isomers. The names conformer and isomeric conformer seem appropriate for these species. The kinetic stability of the conformers depends strongly on the number of atoms in them and on their specific isomeric structure; some are rarely seen on the surface, and others appear frequently (that is, magic numbers and "magic shapes" exist). The traditional nucleation theory, in which the free energy varies smoothly with cluster size and has a maximum, does not hold in this system. Nor is it possible to describe, by a simple diffusion equation, a system in which the concentration increases spontaneously and forms highly organized patterns. This is likely to be true for most semiconductor systems and for some metal-on-metal systems.

The surface atoms on the Si(100) surface pair up to form dimer rows (Fig. 4). An Si atom can be adsorbed on two strings of sites (18) (Fig. 4): the fast string, which consists of sites located along (on top of) a dimer row, and the slow string, which consists of sites located between the rows. The rate of the site-to-site jumps along a fast string is about six orders of magnitude as great as that along a slow string. The probability of jumping from a

fast to a slow string is low, and that of the reverse jump is even lower. As a result, the migration rate in the direction perpendicular to the dimer rows is much lower than that parallel to the rows.

The hopping rates are much larger than the deposition rate: at the temperature used in epitaxy (about 550°C) each atom performs an enormous number of site-to-site jumps in the time needed for the arrival, in the neighborhood of the atom, of a new atom from the gas phase. Numerical values for all of these rates can be found in (18). In this article we examine qualitative phenomena, such as the shapes of the growth patterns, which depend on the relative magnitudes of the rates (19).

Island growth at low coverage. The STM measurements (13, 14) show that the islands formed after the deposition of a sub-monolayer of Si on the Si(100) surface are thin, long, and parallel to each other and consist mainly of one or two dimer rows (Fig. 4). The preference for this shape is intriguing, especially because the thin islands are perpendicular to the direction of rapid migration. The kinetic stability of these islands is incomprehensible unless a mechanism is found by which the large number of particles reaching the island's long shore is transported to its short side.

The experiments also show that the long shores of these islands are very smooth; vacancies such as the one marked X in Fig. 4 are infrequent. This result is striking; the rate to migrate to the slow string sites is low, and one would expect that many such sites would remain empty, leading to vacancies.

In performing simulations with stochastic models, we found that nearly flawless structures are obtained not by building a model that avoids mistakes but by having a mechanism that discovers the errors and repairs them efficiently. One of our tasks is to find the error-repair mechanism that diminishes the number of vacancies in the islands.

Our calculations showed that most of the atoms deposited on the surface, at the early stage of deposition, are adsorbed on the fast strings (18, 19). After a large number of jumps along these strings, they hop onto the slow strings, on which they move slowly. The probability of leaving a slow string is low. The atoms

Fig. 5. A description of the exchange mechanism by which atoms located at the side of a dimer row are transported to the end of the row or are used to repair errors in the row. The crosshatched circles are the surface atoms, and the black circles are the adsorbed atoms. (**A**) A dimer row with an atom, labeled 1, at its side. (**B**) The configuration created by the exchange process involving the atoms 1, 2, and 3. A side view is shown at the top. (**C**) The two possible events after the exchange process: the atom moves along the dimer row either to fill the vacancy at V or to reach the end of the row. An atom at site 4 in (A) speeds up the exchange process or uses the atom at site 1 to start a new dimer row.
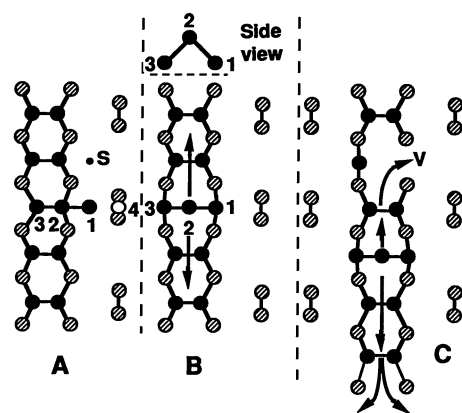
deposited next also run along the fast strings. They form weakly bound pairs with the atoms in the nearby slow string and strongly bound, low-mobility dimers with the atoms moving on the same fast string.

The atoms added later move rapidly along the fast string and form trimers, quadrimers, and larger clusters. Because the rate for reaching the sites on the slow string is low, a process must be found for how these sites are filled. The rate to move an atom from a fast to a slow string is substantially increased by the presence of other atoms on the neighboring sites, which lower the activation energy for the jump (20). This "collective" effect assists the atoms in occupying sites on the slow strings, but the rates are still lower than the rates for occupying the sites on the fast string. Errors will be made, and the island will have vacancies at some of the slow string sites. A correction mechanism is needed to diminish the number of these vacancies.

The kinetic steps described above have larger rates than all of the other atom movements we have tried. They are likely to lead to the formation of four to six atoms bound as dimers, which serve as nuclei for further growth of dimer row islands. The questions formulated at the beginning of this section now must be faced. Given that a short dimer row has been formed, how are the atoms arriving at its side transported to its end? And how are the expected vacancies in the slow string sites (for example, site X in Fig. 4) repaired? The answer is provided by the "exchange mechanism" described in Fig. 5.

The single atoms approaching the long shore of the island have no difficulty sticking to the shore at the sites 1 or S (Fig. 5A). The rates to leave the shore or to move along it are small. The most probable event, shown in Fig. 5B, involves the pair of atoms 1 and 2 that are initially (Fig. 5A) in the same plane. The pair tilts so that atom 2 climbs onto the dimer row (see Fig. 5B), and atom 1 takes its place in the dimer row. Once on top of the dimer row, atom 2 travels rapidly along it (Fig. 5C). If it finds an empty site along the row (such as V in Fig. 5C) it will fall in it; if not, it reaches the end of the row, descends onto the surface, and adds itself to the dimer row, elongating it. This scenario provides the error-correction mechanism and the transport mechanism that were sought.

The rate of the exchange mechanism is enhanced if a second
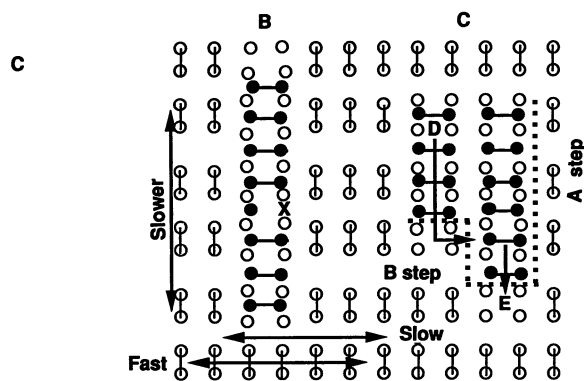
Fig. 4. The empty circles represent the surface atoms, and the solid circles represent the atoms deposited on the surface. The dimer bonds are indicated by lines joining the atoms. The surface atoms below the adsorbed ones are "undimerized." The horizontal arrows indicate the fast and the slow strings. A single dimer row island and a double dimer row island, which are frequently observed in STM pictures at low coverage, are shown. To save space, the islands in this schematic are shorter than those observed with STM. The dashed lines mark the two kinds of one-atom-high steps: the dimer rows on a terrace above a B step are perpendicular to the step; for an A step they are parallel.

atom is present at the site shown as an empty circle (site 4 in Fig. 5A); this atom is in the same plane as atoms 1, 2, and 3. The pair of atoms 1 and 4 also has a high probability to form a dimer and start a new dimer row near the original one. This process "nucleates" the double dimer rows (Fig. 4) observed experimentally (12).

Other kinetic phenomena. The kinetic steps described above explain how the atoms form thin, long islands with few defects. These steps must also be consistent with other phenomena observed on the Si(100) face. For example, this surface has two kinds of one-atom-high (13–15) steps (see Fig. 4). The B steps are rough, whereas the A steps are fairly smooth. This difference is consistent with our kinetic results. The dimer rows on the terrace above a B step [a B terrace (BT)] are perpendicular to the step (Fig. 4). The Si atoms on this terrace move rapidly along the dimer rows, reach the B step, and descend from it. Thus, they add to the step. Because to a first approximation the motion of atoms adsorbed on different dimer rows is uncorrelated, this mechanism leads to independent growth of the dimer rows rather than to a step-flow mechanism. Because these terraces are narrow, the fluctuations in the number of atoms adsorbed on each dimer row are large, leading to fluctuations in the length of the rows. Another important pathway for the growth of a BT is described by the arrows joining the points D and E in Fig. 4. An atom descending across a B step from a short string moves in the space between the kinks in the direction perpendicular to the kink walls. In doing so, it reaches the side wall of a longer kink and climbs on it through the exchange mechanism. Once on top of a dimer row in the long kink, the atom moves along the kink, descends from it, and adds to its end.

Both step propagation mechanisms described above tend to make a long kink longer: the first mechanism because there are more sites on a long kink, hence more atoms have a chance to add to the kink's end, and the second mechanism because it provides a way for atoms starting on a short kink to add at the end of a long one. This mechanism explains why a rough B step is kinetically stable.

The kinetic processes discussed here are also consistent with a phenomenon described by Hoeven *et al.* (16). If one-half of an Si monolayer is deposited on an Si(100) surface that has one-atom-high steps, the atoms move to form a surface with two-atom-high steps. To achieve this configuration, all of the atoms deposited on the BTs must move onto the neighboring terraces [which are located above an A step and are called A terraces (ATs)]. The rate calculations indicate that this movement is possible. As described above, the atoms on a BT move rapidly to reach the borders and climb up (through the exchange mechanism) or down onto the neighboring AT with reasonably high rates (20). The ones already on an AT move mostly parallel to the terrace edge, and their chance of reaching the edge is low. Furthermore, the rate to leave the AT is very small (21).

In evaluating these findings one must remember that the rates are estimated crudely and are based on energy calculation with a semiempirical potential (17). The potential fits well the properties of the bulk solid and liquid Si and the reconstruction of the Si(100) surface. It describes poorly the Si(111) surface and has mixed success in reproducing the structures of some of the Si clusters calculated with ab initio methods. This is not surprising because in the bulk solid and liquid the bonds are saturated, whereas in the clusters and at surfaces they are not. A relatively simple potential cannot be expected to describe how the interatomic forces change when the nature of the bonding changes.

The demands on computer power of these kinetic calculations are so extensive that the use of semiempirical potentials that can be evaluated rapidly is a foremost necessity. For two reasons the avenue pursued here is promising. First, the mechanism by which various growth patterns are formed is of interest. Most often these mecha-

nisms are likely to depend only on the rate constants of a few important jumps. Even for these jumps the precise magnitude of the rate constant is not always required. It is often sufficient that those processes that are faster in reality are also faster in the computer model. Second, the comparison of the patterns grown by the kinetic simulations to those observed by STM allows one to refine a "zeroeth" order model on the basis of the rates calculated from semiempirical potentials. A tedious but instructive iteration process would probably produce models having predictive power.

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19. Calculations made with Tersoff potential (D. Srivastava and B. J. Garrison, *J. Chem. Phys.*, in press) and those made with density functional theory [G. Brooks, P. J. Kelly, R. Car, *Phys. Rev. Lett.* 66, 1729 (1991); T. Myazaki, H. Hiramote, M. Okazaki, *Jpn. J. Appl. Phys.* 29, L1165 (1990)] give different numbers for some of the activation energies. However, the qualitative picture of the migration of a single atom on the surface is the same for all of the calculations. Extensive analyses of the data [Y. W. Mo, J. Kleiner, M. B. Webb, M. G. Lagally, in (1); Y. W. Mo and M. G. Lagally, *Surf. Sci.* 248, 313 (1991)] indicate a highly anisotropic migration rate.
20. Z. Zhang, Y-T. Lu, H. Metiu, *Surf. Sci.* 255, L543 (1991).
21. Z. Zhang and H. Metiu, unpublished results.
22. Supported by the NSF Science and Technology Center for Quantum Electronic Structures (QUEST) and by grants from the NSF, the Office of Naval Research, and the Air Force Office of Scientific Research. We benefited greatly from conversations with QUEST members A. Gossard, H. Kroemer, and W. Kohn and especially with P. Petroff and W. H. Weinberg. M. Lagally, R. Hamers, G. Comsa, M. Tringides, E. Vvedensky, and M. Wilby have generously shared information.