Surfactant Mediated Crystal Growth of Semiconductors

Daniel Kandel and Efthimios Kaxiras
Department of Physics and Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

(Received 10 July 1995)

The influence of surfactants on semiconductor thin film growth is studied by means of a mesoscopic model combined with first principles calculations. We introduce a new kinetic mechanism that explains how surfactants induce layer-by-layer growth. The experimentally observed high density of 2D islands is a natural consequence of the chemical passivation of *step edges*, as well as flat surfaces, by the surfactant. In heteroepitaxial growth, we take strain effects into account, which leads to layer-by-layer growth at low temperatures and three-dimensional growth at high temperatures, in agreement with experiments.

PACS numbers: 68.55.–a, 68.35.Bs

One of the goals of cutting-edge technology in electronic devices is growth of *smooth, defect-free* layers of one semiconductor on top of a different substrate. This technologically driven desire stumbles on a fundamental physical limitation: The lattice mismatch between the overlayers and the substrate introduces strain into the film. The film then grows in the Volmer-Weber or Stransky-Krastanow modes, in which three-dimensional (3D) islands are formed that relax the strain, but at the same time introduce an unacceptable number of defects and imperfections. The resulting material is useless for technological applications. Overcoming this limitation is of crucial practical importance, and represents a unique challenge to our understanding of the fundamental processes of growth. A simple solution would be to limit the tendency of the system to form 3D islands by lowering the temperature so much that diffusion is greatly reduced, preventing the atoms from finding energetically preferred positions. Suppression of diffusion, however, also leads to a high density of defects.

A significant breakthrough was achieved recently by using surfactants [1–4]: Before growing material A on top of a substrate of material B (a process called heteroepitaxy), a layer of a third material, the surfactant, is deposited on the substrate. With the appropriate choice of this third material, the surfactant layer floats on top of the growing film during deposition of material A, without significant incorporation of surfactant atoms into the film. Moreover, growth now proceeds in the layer-by-layer (Frank–van der Merwe) mode at relatively high temperatures, leading to films of high epitaxial quality. More recently, the method has been applied to the growth of material A on a substrate of the same type (homoepitaxy) [5–7]. In spite of several years of intensive research, the physical mechanism by which the surfactant alters the mode of growth remains unresolved. In this Letter we propose a simple model that captures the essential features of surfactant mediated growth, both for heteroepitaxy and homoepitaxy.

Surfactant atoms saturate surface dangling bonds and chemically passivate the surface. As a result, the energy of the system is lower when the surfactant layer is on top rather than buried under newly deposited A atoms. The surfactant therefore tends to float on top of the film. To understand how this happens, we have to consider the kinetic exchange process between surfactant atoms and newly deposited atoms. Two parameters control the exchange process: The energy barrier for exchange, E_{ex}, and the barrier for diffusion of A atoms on top of the surfactant layer, E_d. Models of surfactant mediated epitaxy [8–11] distinguish between two limiting cases (in either case, A atoms cannot diffuse once they have been buried under the surfactant, following an exchange event): In the first case, scenario I, the probability of an exchange is much smaller than the probability of a diffusion hop (i.e., $E_d < E_{\mathrm{ex}}$). In this case an atom diffuses a long distance before it exchanges, and hence the diffusion length is very large. The second limiting case, scenario II, occurs when the exchange probability is comparable to the probability of a hop (i.e., $E_d \approx E_{\mathrm{ex}}$). This would lead to a small diffusion length where an A atom exchanges with a surfactant atom near its point of impact on the surface.

Both scenarios have been considered in order to account for experimental results in surfactant mediated homoepitaxy. In Si homoepitaxy on Si(111) with Sn as a surfactant, step flow growth is observed [5], in which Si atoms diffuse long distances on top of the surfactant layer until they exchange preferentially at edges of surface steps, in accord with scenario I. On the other hand, in Si homoepitaxy on Si(111) with Sb as a surfactant, high density of small 2D islands is observed during growth [6]. This could be interpreted as evidence for scenario II, where the surfactant reduces the diffusion length considerably. It is generally believed (see, e.g., [8,9]) that surfactants that lead to layer-by-layer growth in heteroepitaxy act according to scenario II, suppressing diffusion which would lead to the energetically favored 3D islands. The purpose of this work is to point out that theoretical considerations and first principles calculations make scenario II implausible. In fact, as we demonstrate below, a reduced diffusion length is *not necessary* in order to explain either the high density of small 2D islands or the suppression of 3D islanding.

0031-9007/95/75(14)/2742(4)$06.00

There is a basic conceptual problem with scenario II. It requires that the exchange barrier be comparable to the diffusion barrier (see above), which is presumably very small because of the chemical passivation of the surface by the surfactant. On the other hand, exchange processes involve interlayer atomic motion and breaking of chemical bonds. It is difficult to imagine a situation where the barrier for such a process is as small as the diffusion barrier. At present, there is essentially a complete lack of information on exchange barriers. In order to obtain some reliable numbers that can lend credence to the above arguments, we performed first-principles quantum mechanical calculations for a hypothetical exchange barrier. We considered the case of a Si(111) substrate with a bilayer of deposited Ge and a layer of Sb as the surfactant in a (2×1) chain reconstruction. It has been established that this is the optimal structure for this particular system [12], consistent with experimental observations [7]. A monolayer of Ge was next deposited on top of the surfactant. We then determined an exchange pathway that allows the entire layer of newly deposited Ge atoms to exchange positions with the surfactant layer. Since this is a concerted type of exchange mechanism, the calculated barrier will be a *lower bound* for any realistic process. We find that this lower bound is 0.8 eV, while the activation energy for diffusion of Ge atoms on an unpassivated Ge(111) surface is 0.5 eV [13]. Thus, the true exchange barrier is significantly higher than the diffusion barrier.

Assuming the above results are representative, they rule out the possibility that the surfactant suppresses diffusion, and support the ansatz that enhanced diffusion is a *universal* feature of surfactant mediated growth on semiconductor surfaces. The following question now arises: How can this be compatible with the high density of small 2D islands observed in certain experiments [6,8]? To address this question, we introduce a detailed atomistic model of surfactant mediated growth kinetics. We propose that the difference between surfactants that lead to step flow and those that lead to a high density of 2D islands is in the way they bond to surface steps. If surfactant atoms bond weakly to step edges, they do not passivate the steps. Hence, the exchange barrier at step edges is significantly smaller than the barrier on the flat surface. This case is similar to scenario I. If, however, the surfactant atoms bond strongly to step edges, these are passivated as much as the flat surface is. Accordingly, the two exchange barriers are comparable. Since exchange kinetics is controlled by the energy barrier, exchange at a step edge is not *a priori* preferred over exchange on a flat surface. Thus, although diffusion on top of the surfactant is enhanced, the atoms do not "see" the step edges and may still exchange on the flat part of the surface creating more 2D islands. Note that step edges are still preferred for exchange *a posteriori*, in the sense that the energy gain is larger for exchange at a step edge than on a flat surface. Such a step edge effect is, in fact, very plausible from a microscopic point of view. On the Si(111) substrate, it is possible to construct fully passivated step edges with Sb atoms, which are pentavalent and naturally prefer threefold coordination. This is compatible with STM experiments on this system. Contrary to this, it is not possible to construct fully passivated steps with Sn atoms, which are tetravalent, same as the substrate atoms. Thus, the two surfactants, Sn and Sb, will exhibit different behaviors on the same substrate.

Before addressing the effect of strain we consider another process, which, according to our first principles calculations, cannot be ignored. This is the process of deexchange in which an A atom buried underneath the surfactant layer exchanges with a surfactant atom and floats on top of the surfactant. The barrier for this process within our calculation (see above) is $E_{\mathrm{dex}} = 1.6$ eV when the atom underneath the surfactant has a minimal number of neighboring A atoms. The process of deexchange can be suppressed if additional A atoms exchange at neighboring sites creating lateral A-A bonds under the surfactant layer, since the cost of breaking these bonds will be high. In order to form structures that involve several A-A bonds, a relatively high external flux of A atoms is required. This is an issue of competing time scales; with a typical flux of 0.2 layers/min, the time it takes to grow a layer is 300 sec. Assuming the time scale associated with deexchange can be expressed as $\tau_{\mathrm{dex}} = \nu^{-1} \exp(E_{\mathrm{dex}}/kT)$ with $\nu \sim 10^{13}\ \mathrm{sec}^{-1}$, our estimate for τ_{dex} at $T = 600\,^{\circ}\mathrm{C}$ is 0.0002 sec. Hence a deexchange process typically occurs before other A atoms from the flux bind the buried atom permanently to the substrate.

To investigate the interplay between the processes described above, we carried out kinetic Monte Carlo simulations of growth on a square lattice with one layer of surfactant, which keeps floating during growth. With each lattice site (i,j) we associate a variable $h(i,j)$, which we define as the height of the surfactant atom at that site. Throughout the simulation we maintain the relation $|h(i,j) - h(i',j')| < 2$ for all pairs of nearest neighbor sites; this is a restricted solid-on-solid (RSOS) condition [14]. Within the simulation, atoms land on the surface with a flux of $F = 0.005$ atoms per site per second. They diffuse on top of the surfactant with a diffusion barrier $E_d = 0.6$ eV. They can exchange with surfactant atoms, and the barrier for this process is $E_{\mathrm{ex}} = 1.0$ eV, independent of whether the atom is at a step edge or on a flat surface (i.e., the surfactant in this case is of the type that passivates the step edges). An A atom of the layer below the surfactant can deexchange with a surfactant atom with energy barrier $E_{\mathrm{dex}} = 2.0$ eV, provided it does not have lateral A-A bonds prior to deexchange. Neither exchange nor deexchange can occur if they violate the RSOS condition. All processes have the same basic time scale $1/\nu = 10^{-13}$ sec. This simulation mimics homoepitaxial growth since no strain effects are taken into account. The energy barriers are such that, for the system sizes and temperatures we studied, at most one A atom is exposed on top of the surfactant at any given time. This simplifies the simulation considerably, but does not impose significant physical constraints in the system.

Figure 1 shows configurations of a system of 300 × 300 sites after growth of 0.15 of a monolayer, starting from a flat surface. Growth at two different temperatures, $T = 600\,^{\circ}\mathrm{C}$ [1(a)] and $T = 850\,^{\circ}\mathrm{C}$ [1(b)], clearly shows a high density of islands that decreases when the temperature is raised. The islands are two dimensional, and their edges are very rough in agreement with STM observations on the system Si/Sb/Si(111) [6]. Thus our model reproduces the qualitative behavior of the density of islands observed in experiments without suppressing diffusion.

Strain may affect any of the energy barriers of our model. Most significantly, however, it makes a new process possible. This is the process of deexchange of an A atom that *does* have a lateral A-A bond when it is still underneath the surfactant layer. Breaking of this bond becomes probable because it is weakened in the presence of strain. We incorporate this additional deexchange process in the RSOS simulations with an energy barrier that depends on the shape and size of the island on top of which the exchanging atom resides:

$$E'_{\mathrm{dex}} = E_{\mathrm{dex}} + \epsilon\left(\frac{\ln l_1}{l_1} + \frac{\ln l_2}{l_2}\right). \tag{1}$$

l_1 and l_2 are the lengths of the island in the X and Y directions, respectively, along lines that cross at the position of the A atom. The strain term in (1) is analogous to the expression found by Tersoff and Tromp [15] for the elastic energy gain due to strain relaxation in a rectangular island of side lengths l_1 and l_2. This is a very crude way of taking strain effects into account. However, it captures the essential physics (at least for growth of a few layers), namely, that strain relaxation is more effective in small islands. It also incorporates the correct functional dependence of the strain energy on the linear island size ($\ln l/l$). We also considered strain-induced changes in barriers for exchange and deexchange, but these had no significant effect on the growth mode, and are therefore ignored in the following.

Typical configurations from our simulations including strain effects are shown in Fig. 2. Here we used $E_d = 0.4$ eV, $E_{\mathrm{ex}} = 0.8$ eV, $E_{\mathrm{dex}} = 1.6$ eV, and $\epsilon = 3.0$ eV with a flux of $F = 0.005$ atoms per site per second. These numbers are very close to theoretical estimates (see earlier discussion and [16]). In all four pictures the coverage is one layer. The different colors correspond to different heights of the surface (green is the initial surface). At $T = 350\,^{\circ}\mathrm{C}$ [Fig. 2(a)] a smooth layer grew on top of the initially flat surface. Small 2D islands and holes are observed on the layer, with rough edges similar to island shapes in homoepitaxy (see Fig. 1). The same behavior

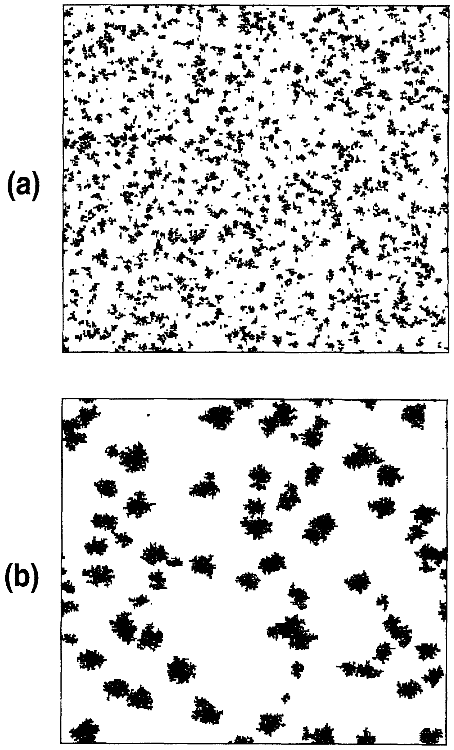

FIG. 1. Configurations of a 300 × 300 system after surfactant mediated homoepitaxial growth of 0.15 of a monolayer at (a) $T = 600\,^{\circ}\mathrm{C}$ and (b) $T = 850\,^{\circ}\mathrm{C}$.

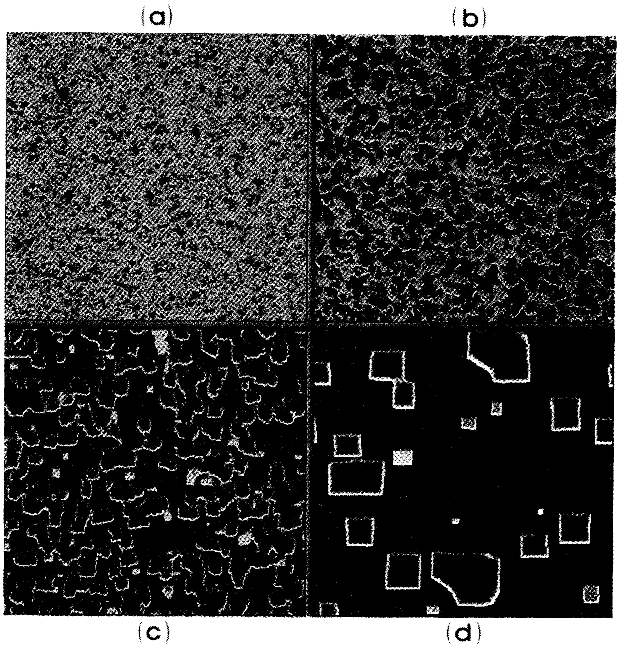

FIG. 2 (color). Configurations of a 300 × 300 system after surfactant-mediated heteroepitaxial growth of 1 monolayer at (a) $T = 350\,^{\circ}\mathrm{C}$, (b) $T = 400\,^{\circ}\mathrm{C}$, (c) $T = 450\,^{\circ}\mathrm{C}$, and (d) $T = 600\,^{\circ}\mathrm{C}$. Different surface heights are represented by different colors; green is the initially flat surface.

is observed at $T = 400\,^\circ\mathrm{C}$ [Fig. 2(b)] with 2D islands of larger size. In both cases growth occurs in a layer-by-layer mode with 3–4 layers exposed. This morphology remains the same after growth of more than 10 layers. The morphology of the surface is dramatically different for growth at $T = 450\,^\circ\mathrm{C}$ [Fig. 2(c)]. Here a very large portion of the initial surface remains exposed. The islands are much taller than at lower temperatures (about 5 layers tall compared to 1), and they have a square shape with smooth edges. We conclude that at a critical temperature $T_{3\mathrm{D}}$ (with $400\,^\circ\mathrm{C} < T_{3\mathrm{D}} < 450\,^\circ\mathrm{C}$) a transition in the growth mode has occurred from layer-by-layer to 3D islanding. Figure 2(d) demonstrates growth at an even higher temperature ($T = 600\,^\circ\mathrm{C}$) with fewer and taller islands (10–12 layers). These results are qualitatively very similar to experimental observations. For example, in the system Ge/Sb/Si(111) a transition of the type we find was observed [17] at $T_{3\mathrm{D}} \approx 650\,^\circ\mathrm{C}$.

The behavior of our system can be understood very simply. At low temperatures it is impossible to break a lateral A-A bond even on top of the highly strained initial surface, and there is no difference between growth on top of a completed layer and a small island. The critical nucleus size is 1 everywhere on the surface. The equilibrium tendency to form 3D islands is thus kinetically suppressed, and the crystal grows in the layer-by-layer mode. When the temperature is raised, it becomes possible to break A-A bonds on top of large islands (or a completed layer), but not on top of small islands, which are strain relaxed. The critical nucleus size changes to 3 on top of large islands, but remains 1 on top of small ones. Hence nucleation of stable islands occurs much more frequently on top of small islands than on a completed layer, and the equilibrium tendency towards 3D islanding is restored. Our model is not detailed enough to produce realistic critical nucleus sizes. Nevertheless, we believe the qualitative dependence of the critical nucleus on island size and on temperature is reproduced correctly.

While our simple lattice model does not address the material-dependent strain relaxation due to dislocations that appear in thick layers [3,4,18], it explains very successfully how and under what conditions a surfactant may prevent strain relaxation via 3D islanding at the initial stages of growth.

We thank A. Zangwill for helpful discussions. This work was supported by the Office of Naval Research Grant No. N00014-95-1-0350.

[1] M. Copel, M.C. Reuter, E. Kaxiras, and R.M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
[2] M. Copel, M.C. Reuter, M. Horn-von Hoegen, and R.M. Tromp, Phys. Rev. B **42**, 11 682 (1990).
[3] M. Horn-von Hoegen, F.K. LeGoues, M. Copel, M.C. Reuter, and R.M. Tromp, Phys. Rev. Lett. **67**, 1130 (1991).
[4] M. Horn-von Hoegen, M. Copel, J.C. Tsang, M.C. Reuter, and R.M. Tromp, Phys. Rev. B **50**, 10 811 (1994).
[5] S. Iwanari and K. Takayanagi, J. Cryst. Growth **119**, 229 (1992).
[6] B. Voigtländer and A. Zinner, Surf. Sci. Lett. **292**, L775 (1993).
[7] M. Horn-von Hoegen, J. Falta, M. Copel, and R.M. Tromp, Appl. Phys. Lett. **66**, 487 (1994).
[8] R.M. Tromp and M.C. Reuter, Phys. Rev. Lett. **68**, 954 (1992).
[9] J. Massies and N. Grandjean, Phys. Rev. B **48**, 8502 (1993).
[10] B.D. Yu and A. Oshiyama, Phys. Rev. Lett. **72**, 3190 (1994).
[11] T. Ohno, Phys. Rev. Lett. **73**, 460 (1994).
[12] E. Kaxiras, Europhys. Lett. **21**, 685 (1993); E. Kaxiras, Mater. Sci. Eng. B **30**, 175 (1995).
[13] E. Ganz, S.K. Theiss, I.-S. Hwang, and J. Golovchenko, Phys. Rev. Lett. **68**, 1567 (1992); E. Kaxiras and J. Erlebacher, Phys. Rev. Lett. **72**, 1714 (1994).
[14] The role of the RSOS condition is to force the angle between the edges of 3D islands to be smaller than 90°, as is the case in experiments.
[15] J. Tersoff and R.M. Tromp, Phys. Rev. Lett. **70**, 2782 (1993).
[16] R.D. Meade and D. Vanderbilt, Phys. Rev. Lett. **63**, 1404 (1989).
[17] B. Voigtländer and A. Zinner, J. Vac. Sci. Technol. A **12**, 1932 (1995).
[18] F.K. LeGoues, M. Copel, and R. Tromp, Phys. Rev. Lett. **63**, 1826 (1989); Phys. Rev. B **42**, 11 690 (1990).

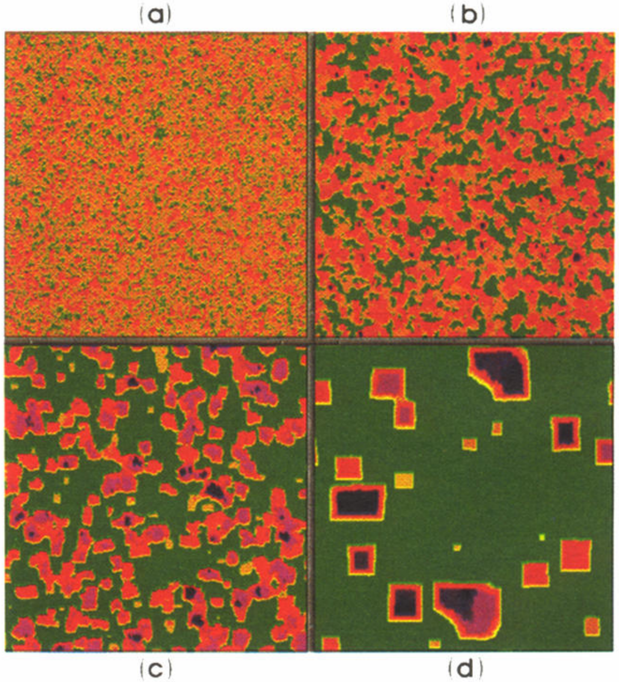

FIG. 2 (color). Configurations of a 300 × 300 system after surfactant-mediated heteroepitaxial growth of 1 monolayer at (a) $T = 350\,^{\circ}\mathrm{C}$, (b) $T = 400\,^{\circ}\mathrm{C}$, (c) $T = 450\,^{\circ}\mathrm{C}$, and (d) $T = 600\,^{\circ}\mathrm{C}$. Different surface heights are represented by different colors; green is the initially flat surface.