

The Surfactant Effect in Semiconductor Thin-Film Growth

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I. Introduction

Progress in the fields of electronic and optical devices relies on the ability of the semiconductor industry to fabricate components of ever-increasing complexity and decreasing size. The drive for miniaturization has actually provided the impetus for much fundamental and applied research in recent

years. Nanoscale structures in 2, 1, or 0 dimensions, referred to as quantum wells, wires, and dots, respectively, are at the forefront of exploratory work for next-generation devices. In most cases these structures must be fabricated through epitaxial growth of semiconductor thin films, in either homoepitaxial (material A on substrate A) or heteroepitaxial (material A on substrate B) mode. There are usually two important requirements in this process. First, the film must be of high-quality crystalline material; second, a relatively low temperature must be maintained during growth. The need for the first requirement is self-evident, since highly defected crystals typically perform poorly in electronic applications; the imperfections, usually in the form of dislocations, grain boundaries, or point defects, act as electronic traps and degrade the electronic properties to an unacceptable level. The second requirement arises from the need to preserve the characteristics of the substrate during growth, such as doping profiles and sharp interfaces between layers, which can be degraded because of atomic diffusion when the growth temperature is high. These two requirements seem to be incompatible: In order to improve crystal quality, atoms need to have sufficient surface mobility so that they can find the proper crystalline sites to be incorporated into a defect-free crystal. On the other hand, excessive atomic mobility in the bulk must be avoided, which can be achieved only by maintaining lower than typical growth temperatures. These problems are exacerbated in the case of heteroepitaxial growth, where the presence of strain makes smooth, layer-by-layer growth problematic even when the temperature is high, since the equilibrium structure involves strain-relieving defects.

Early studies of the effects of contaminants and impurities on growth modes indicated that it is indeed possible to alter the mode of growth by the inclusion of certain elements, different from either the growing film or the substrate. For a discussion of epitaxial growth modes and the effect of contaminants, see the authoritative review by Kern *et al.*¹ A breakthrough in the quest for controlled growth of semiconductor films was reported in 1989 when Copel *et al.*² demonstrated that the use of a single layer of As can improve the heteroepitaxial growth of Ge on Si, which is otherwise difficult because of the presence of strain. Growth in this system typically proceeds in the Stranski-Krastanov mode; that is, it begins with a few (approximately three) wetting layers but quickly reverts to three-dimensional (3D) island growth. The eventual coalescence of the islands unavoid-

¹ R. Kern, G. Le Lay, and J. J. Metois, "Basic Mechanisms in the Early Stages of Epitaxy," in *Current Topics in Materials Science*, Vol. 3, ed. E. Kaldis, North-Holland Publishing Company (1979).

² M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, *Phys. Rev. Lett.* **63**, 632 (1989).

ably produces highly defective material. In the experiments of Copel *et al.*, the monolayer of As was first deposited to the Si substrate and continued to float during the growth of the Ge overlayers. The presence of the As monolayer in the system led to a drastic change in both the thermodynamics (balance of surface and interface energies) and the kinetics (surface and bulk mobility of deposited atoms), making it possible to grow a Ge film in a layer-by-layer fashion to unprecedented thicknesses for this system (several tens of layers). This remarkable behavior was termed the "surfactant effect" in semiconductor growth. Since then, a large number of experiments have confirmed this behavior in a variety of semiconductor systems (for early reviews see Refs. 3, 4, and 5).

We digress momentarily to justify the terminology. The typical meaning of the word *surfactant* is unlike its meaning here, which has led to some debate about the appropriateness of the term in the context of semiconductor thin-film growth. As defined in scientific dictionaries, *surfactant* is used commonly in chemistry to describe "a substance that lowers the surface or interfacial tension of the medium in which it is dissolved,"⁶ or "a material that improves the emulsifying, dispersing, wetting, or other surface modifying properties of liquids."⁷ While these physical situations and the effect itself are different from the systems considered in the present review, we adopt the term *surfactant* to describe the effect of adsorbate layers in semiconductor thin-film growth for two reasons. First, for a reason of substance: There are indeed some similarities between adsorbate layers in semiconductor thin-film growth and the classical systems to which the term applies; namely, in both cases the presence of this extra layer reduces the surface tension and changes the kinetics of atoms or clusters of atoms (small islands in semiconductor surfaces, molecules in classical systems) at the surface. Second, for a practical reason: The term *surfactant* has essentially become accepted by virtue of its wide use in semiconductor growth, and the need for consistency with existing literature forces it upon us. These reasons, we feel, justify and legitimize the use of the term in the present context.

Surfactants have been used to modify the growth mode of several systems, including metal layers in homoepitaxy and heteroepitaxy. In our view, the physics relevant to such systems is significantly different from that in the

³ E. Tournie and K. H. Ploog, *Thin Solid Films* **231**, 43 (1993).

⁴ K. H. Ploog and E. Tournie, *Diffus. Defect Data B, Sol. State Phenom.* **32-33**, 129 (1993).

⁵ E. Tournie, K. H. Ploog, N. Grandjean, and J. Massies, *IEEE 6th Conf. IPRM* (March 1994), 49.

⁶ L. L. Schram, *The Language of Colloid and Interfacial Science*, University of Calgary, Alberta, Canada.

⁷ See <http://www.sti.nasa.gov/thesaurus/S/word15290.html>, Official Scientific Thesaurus of NASA.

TABLE 1. EXAMPLES OF METAL-ON-METAL GROWTH MEDIATED BY SURFACTANTS

FILM/SUBSTRATE	SURFACTANT	REFERENCE
Ag/Ag(111)	Sb	10, 11, 12, 13, 14, 15
Cu/Cu(111)	O	16
Fe/Au(111)	Au	17
Fe/Cu(111)	C + O	18
Cu/Ru(0001)	O	19, 20, 21
Co/Cu(111)	Sb	22
	Pb	23, 24

case of semiconductors. Supporting this view is the fact that typically a small fraction of a monolayer is needed to produce the surfactant effect in metal growth, whereas in semiconductors typically a full monolayer of the adsorbate species (or what is the equivalent to full substrate coverage, depending on the surface reconstruction) is required. Presumably, in the case of metals a small amount of the adsorbate is sufficient to induce the required changes in surface kinetics^{8,9} by altering nucleation rates or step-edge barriers (for some representative examples of metal-on-metal growth mediated by surfac-

⁸ V. Fiorentini, S. Oppo, and M. Scheffler, *Appl. Phys. A* **60**, 399 (1995).

⁹ M. Breeman, G. T. Barkema, M. H. Lanelaar, and D. O. Boerma, *Thin Solid Films* **272**, 195 (1996).

¹⁰ H. A. Van der Vegt, H. M. van Pinxteren, M. Lohmeier, E. Vlieg, and J. M. C. Thornton, *Phys. Rev. Lett.* **68**, 3335 (1992).

¹¹ G. Rosenfeld, R. Servaty, C. Teichert, B. Poelsema, and G. Comsa, *Phys. Rev. Lett.* **71**, 895 (1993).

¹² J. Vrijmoeth, H. A. Van der Vegt, J. A. Meyer, E. Vlieg, and R. J. Behm, *Phys. Rev. Lett.* **72**, 3843 (1994).

¹³ J. A. Meyer, R. J. Behm, G. Rosenfeld, B. Poelsema, and G. Comsa, *Phys. Rev. Lett.* **73**, 364 (1994).

¹⁴ J. A. Meyer, J. Vrijmoeth, H. A. van der Vegt, E. Vlieg, and R. J. Behm, *Phys. Rev.* **51**, B14790 (1995).

¹⁵ J. A. Meyer, H. A. van der Vegt, and J. Vrijmoeth, E. Vlieg, and R. J. Behm, *Surf. Sci.* **355**, L375 (1996).

¹⁶ W. Wulfhekel, N. N. Lipkin, J. Kliewer, G. Rosenfeld, L. C. Jorritsma, B. Poelsema, and G. Comsa, *Surf. Sci.* **348**, 227 (1996).

¹⁷ A. M. Begley, S. K. Kim, J. Quinn, F. Jona, H. Over, and P. M. Marcus, *Phys. Rev.* **B48**, 1779 (1993).

¹⁸ N. Memmel, and E. Bertel, *Phys. Rev. Lett.* **75**, 495 (1995).

¹⁹ H. Wolter, M. Schmidt, and K. Wandelt, *Surf. Sci.* **298**, 173 (1993).

²⁰ M. Schmidt, H. Wolter, M. Nohlen, and K. Wandelt, *J. Vac. Sci. Technol.* **A12**, 1818 (1993).

²¹ M. Schmidt, H. Wolter, and K. Wandelt, *Surf. Sci.* **307-309**, 507 (1994).

tants see Table 1). In semiconductors, on the other hand, the entire surface must be covered by the adsorbate in order for the required changes in energetics and kinetics to be obtained. Because of this fundamental difference, in the present article we will concentrate on the surfactant effect in semiconductor systems.

In the following we first review the available information on the subject, from both the experimental (Section II) and the theoretical (Section III) points of view. We then present some theoretical arguments that we have advanced in an effort to create a comprehensive picture of the phenomenon (Section IV). Finally, we discuss our views on important issues that remain for future research on surfactants and comment on prospects for their use in the fabrication of electronic and optical semiconductor devices (Section V).

II. Experimental Observations

A wide range of systems have been studied where the surfactant effect was demonstrated. We classify these in three categories: growth of group-IV layers on group-IV substrates; growth of III-V compounds on III-V substrates; and mixed systems, including growth of elemental and compound systems on various substrates. This categorization has been inspired by the substrate features and the nature of the deposited species, which together determine the growth processes.

1. GROUP-IV FILMS ON GROUP-IV SUBSTRATES

In the first category, the substrate is either Si or Ge (in different crystallographic orientations), on which combinations of different group-IV elements are deposited (Si, Ge, C). In these systems the deposited species are mostly in the form of single group-IV atoms. The adsorbate layers consist of monovalent (H), trivalent (Ga, In), tetravalent (Sn, Pb), pentavalent (As, Sb, Bi), and hexavalent (Te) elements, or noble metals (Au). These adsorbates remove the usual reconstruction of the surface (the different versions of the (2×1) reconstruction for the Si and Ge(100) surfaces, the (7×7) and the $c(2 \times 8)$ for the Si and Ge(111) surfaces, respectively) and produce simpler

²² V. Scheuch, K. Potthast, B. Voigtländer, and H. P. Bonzel, *Surf. Sci.* **318**, 115 (1994).

²³ J. Camarero, L. Spendeler, G. Schmidt, K. Heinz, J. J. de Miguel, and R. Miranda, *Phys. Rev. Lett.* **73**, 2448 (1994).

²⁴ J. Camarero, T. Graf, J. J. de Miguel, R. Miranda, W. Kuch, M. Zharnikov, A. Dittschar, C. M. Schnieder, and J. Kirschner, *Phys. Rev. Lett.* **76**, 4428 (1996).

reconstructions that are chemically passivated. Characteristic examples are the (1×1) reconstruction (induced by H or As on the (111) surfaces); the $(\sqrt{3} \times \sqrt{3})$ reconstruction on the (111) surfaces with either one adsorbate atom per unit cell (induced by Ga or In) or three adsorbate atoms per unit cell (induced by Sn, Sb, Pb, Au); the (2×1) reconstruction of the (100) surfaces (induced by the trivalent and pentavalent elements or by H in the monohydride phase); and the (1×1) reconstruction of the (100) surfaces (induced by Te or by H in the dihydride phase). In these reconstructions the dangling bonds of the substrate atoms are saturated by the additional electrons of the adsorbate atoms, producing low-energy, chemically unreactive surfaces.

One important issue in these systems is the strain induced by the deposition of atoms with a different covalent radius than that of the substrate atoms. The normal growth mode in strained systems involves the formation of 3D islands that relieve the strain by relaxation at the island edges, either right from the initial stages of deposition (the so-called Volmer-Weber or 3D-island growth) or after the formation of a wetting layer (the Stranski-Krastanov growth). When surfactants are employed, it is possible to induce layer-by-layer growth in strained systems by avoiding the formation of 3D islands for film thicknesses much beyond what is obtained under normal conditions. The reduction of strain-induced islanding was, in fact, one of the early intended results of surfactant use and remains a goal pursued in several experimental studies. Even when surfactants are used, however, and the 3D-island mode of growth is suppressed, the strain in the heteroepitaxial film is still present and is usually relieved by the introduction of a network of misfit dislocations. The mechanism by which this happens is not known and remains to be analyzed by atomistic models.

It is natural to expect that diffusion of group-IV adatoms on the adsorbate-covered surfaces will be relatively easy because of the chemical passivation by the surfactant layer. Such a situation may lead to a substantial increase of the diffusion length of adatoms on top of the surfactant layer. Indeed, it has been reported experimentally that in Ge on Si heteroepitaxy certain elements, like Ga, In, Sn, and Pb, lead to an increase in the width of the depleted zone around islands.²⁵ At the same time, however, it has also been found that other elements, like As, Sb, Bi, and Te, lead to a decrease in the width of the depleted zone.²⁵ These observations were interpreted as indicative that the former type of surfactant (group-III and group-IV atoms) enhance the diffusion length while the latter type (group-V and group-VI atoms) reduce the diffusion length. Moreover, this interpretation has been

²⁵ B. Voigtländer, A. Zinner, A. Weber, and H. P. Bonzel, *Phys. Rev. B* **51**, 7583 (1995).

frequently invoked as an explanation of the suppression of 3D islanding in heteroepitaxy by group-V and group-VI surfactants.

Since it is generally easier for group-V and group-VI elements to provide a chemically passive surface, we argue that the above interpretation may not be unique. In fact, we show in Section IV that even if it were true, it would not explain the surfactant effect either in homoepitaxy or in heteroepitaxy. We propose an alternative interpretation of the experimental results, according to which the diffusion length is mostly irrelevant. Instead, the essential question is whether or not the surfactant layer passivates island edges. Some surfactants (group-III and group-IV elements) cannot passivate island edges, which then act as strong sinks of newly deposited atoms, while other surfactants (group-V and group-VI elements) passivate island edges as well as terraces, so that island edges do not act as adatom sinks and the width of the depleted zone is reduced. We show that this interpretation is consistent with the experimentally observed surface morphologies and island densities in the presence of surfactants. It also explains why group-V and group-VI adsorbates suppress 3D islanding in heteroepitaxy. The systems studied experimentally that belong to this category are listed in Table 2. The relative simplicity of the surface reconstruction induced by the surfactant and the fact that the deposited species is mostly single group-IV atoms make the systems in this category the easiest to analyze from a microscopic point of view. Indeed, most atomistic scale models of the surfactant effect address systems in this category.

2. III-V FILMS ON III-V SUBSTRATES

The second category consists of III-V substrates on which combinations of other III-V systems are deposited. The deposited species in this case are more complicated, since at least two types of atoms have to be supplied with different chemical identities. Under usual conditions the group-III species is deposited as single atoms, whereas the group-V species is deposited as molecules (dimers or tetramers) that have to react with the group-III atoms and become incorporated in the growing film. This is already a significant complication in growth dynamics and makes the construction of detailed atomistic growth models considerably more difficult. Moreover, the usual surface reconstructions of these substrates are more complicated and depend on deposition conditions (temperature and relative flux of group-III to group-V atoms). In the presence of surfactants both the surface reconstructions and the atomic motion are altered, but much less is known about the atomic-level details. The surfactants used in these systems include H, Be, B, In, Sn, Pb, As, Sb, and Te. In certain cases, the surfactant species is the same

TABLE 2. SYSTEMS IN THE FIRST CATEGORY OF SURFACTANT-MEDIATED SEMICONDUCTOR GROWTH: GROUP-IV FILMS ON GROUP-IV SUBSTRATES

FILM/SUBSTRATE	SURFACTANT	REFERENCE
Si/Si(100)	H	26
Si/Si(111)	Ga	25, 27, 28, 29, 30, 31
	In	25, 32
	Sn	33, 34, 35
	As	25, 28, 29, 30
	Sb	25, 28, 29, 30
	Au	36, 37
Ge/Si(100)	H	38, 39, 40, 41, 42, 43, 44,
	B	45
	In	46
	Sn	47, 48, 49
	Pb	50
	As	2, 51, 52, 53, 54, 55, 56, 57
	Sb	51, 53, 58, 59, 60, 61, 62, 63, 64, 65, 66,
		67, 47, 48, 68, 69, 70, 71, 72, 73, 74, 75,
		76, 77, 78, 79, 80
	Bi	79, 81, 82, 83
	Te	69, 70, 84, 85
Ge/Si(111)	H	86
	Ga	25, 39, 87, 88, 89
	In	25, 90
	As	25, 91, 92, 93
	Sb	29, 73, 94, 95, 96, 97, 98, 99, 100, 101
		25, 102, 103, 104
	Bi	105
	Au	37
Si/Ge(100)	H	106
	Sb	43, 69
	Ge	107
Si/Ge(111)	Sb	108, 109
Si _{1-x} C _x /Si(100)	H	110, 111
Ge _{1-x} Si _x /Si(100)	Sn	49, 112
	As	113
	Sb	114, 115
Si/SiGe(100)	As	51
	Sb	51
	Sb	116
Ge _{1-x} C _x /Si(100)	H	117
Si/Si _{1-x} Ge _x (100)	Sb	118
Sn/Ge(100)	Sb	119
Si _m Ge _n /Si(100)	Sb	120
Si _{1-x-y} Ge _x C _y /Si(100)	Sb	120

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as one of the atoms in the growing film (such as In in growth of InAs on GaAs), or one of the atoms in the substrate (such as Sb in growth of InAs on AlSb). Strain effects are important in these systems as well. Building high-quality III-V heterostructures has been one of the goals of many technologically oriented studies, and the use of surfactants has been beneficial in reducing the problems associated with strain. However, the more complex nature of these systems has prevented detailed analysis of the type afforded in group-IV systems. A compilation of experimental results for this category is given in Table 3.

TABLE 3. SYSTEMS IN THE SECOND CATEGORY OF SURFACTANT-MEDIATED SEMICONDUCTOR GROWTH: III-V FILMS ON III-V SUBSTRATES

FILM/SUBSTRATE	SURFACTANT	REFERENCE
GaAs/GaAs(100)	H	121, 122, 123
	Sn	124
	Pb	124
	Te	124, 125
InAs/GaAs(100)	H	126, 127
	In	128
AlGaAs/AlGaAs(100)	Be	129
	Sb	130, 131
InGaAs/GaAs(100)	Sn	132
	Te	133, 134, 135, 136
GaAs/InP(100)	H	127
InGaAs/InP(100)	H	137
GaAs/GaAs(111)	In	138
GaAs/GaInAs(100)	Te	139
InAs/GaInAs(100)	In	140
GaN/GaN(100)	As	141
GaN/AlGaN(100)	Si(CH ₃) ₄	142, 143
InAs/AlInAs(100)	In	144, 145
InAs/AlSb(100)	Sb	146
InAs/InPSb(100)	Sb	146
InAs/InGaAs(100)	In	147, 148, 149

3. MIXED FILM AND SUBSTRATE SYSTEMS

The final category consists of mixed systems in which group-IV films are grown on III-V substrates (for example, Si on GaAs) or vice versa (for example, GaN on Si). In these systems, in addition to the usual strain effects, one has to consider polarity effects, caused by the fact that at the interface different types of atoms are brought together and their dangling bonds contain different amounts of electronic charge that do not add up to the proper value for the formation of covalent bonds. It is possible that the surfactant layer plays an important role in reducing polarity problems as well as in modifying the energetics and in suppressing strain effects, as it does in the previous two categories.

Since the substrate and the thin film are rather different for systems in this category, we include in the same category a number of odd systems that involve the presence of insulating buffer layers (like CaF₂ in the growth of Ge on Si substrates) and the growth of metal layers (like In on Si, In on GaAs, Fe on Ge, Fe and Au on GaAs, and Ag on Si) or silicide layers (like CoSi₂ on Si), as well as the growth of technologically important semiconductors on insulators (like GaN on sapphire). All these cases are important for device applications, and it is interesting to study how surfactants can be employed to improve the quality of growth. However, the complexity of the structures involved and the several different species of atoms present make

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¹⁴⁹ K. H. Ploog, A. Trampert, and E. Tournie, *Physica Stat. Sol.* **A146**, 353 (1994).

TABLE 4. SYSTEMS IN THE THIRD CATEGORY OF SURFACTANT-MEDIATED SEMICONDUCTOR GROWTH: MIXED FILMS AND SUBSTRATES

FILM/SUBSTRATE	SURFACTANT	REFERENCE
Si/GaAs(111), (311)	H	150, 151
Si/GaAs(100)	As	152, 153
Ge/InP(100)	Sb	154, 155
Ge/GaF ₂ /Si(100), (111)	B	156
GaAs/Ge(100)	H	157
CoSi ₂ /Si(100)	As	158
Ag/Si(111)	Sb	159
In/Si(111)	H	160
In/GaAs(100)	Sb	161
Fe/Ge(100)	S	162
Fe,Au/GaAs(100)	Fe,Au	163
MnSb/GaAs(100)	H	164
GaN/Si(111)	As	165
GaN/SiC(100)	As	166
GaN/Al ₂ O ₃	Bi	167

- ¹⁵⁰ Z. Peng and Y. Horikoshi, *Appl. Phys. Lett.* **70**, 604 (1997).
¹⁵¹ J. M. Zhang, M. Cardona, Z. L. Peng, and Y. Horikoshi, *Appl. Phys. Lett.* **71**, 1813 (1997).
¹⁵² A. R. Avery, D. M. Holmes, J. L. Sudijono, T. S. Jones, M. R. Fahy, and B. A. Joyce, *J. Cryst. Growth* **150**, 202 (1995).
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¹⁵⁴ D. Rioux and H. Hochst, *J. Vac. Sci. Tech.* **A10**, 759 (1991).
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¹⁵⁷ Y. Okada, J. S. Harris, Jr., A. Sutoh, and M. Kawabe, *J. Cryst. Growth* **175**, 1039 (1997).
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¹⁶² G. W. Anderson, A. P. Ma, and P. R. Norton, *J. Appl. Phys.* **79**, 5641 (1996).
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¹⁶⁴ H. Ikekame, Y. Yanase, T. Ibarashi, T. Saito, Y. Morishita, and K. Sato, *J. Cryst. Growth* **173**, 218 (1997).
¹⁶⁵ G. Mendoza-Diaz, K. S. Stevens, A. F. Schwartzman, and R. Beresford, *J. Cryst. Growth* **178**, 45 (1997).
¹⁶⁶ G. Feuillet, P. Hacke, H. Okumura, H. Hamaguchi, K. Ohta, K. Balakrishnan, and S. Yosida, *Materials Research Society Symposia Proceedings*, eds. F. A. Ponce, T. D. Moustakas, I. Akasaki, B. A. Monemar, Materials Research Society, Pittsburgh, (1997), 257.
¹⁶⁷ R. Klockenbrink, Y. Kim, M. S. H. Leung, C. Kisielowski, J. Kruger, G. S. Sudhir, M. Rubin, and E. R. Weber, *Materials Research Society Symposia Proceedings*, eds. C. R. Abernathy, H. Amano, J. C. Zolper, Materials Research Society, Pittsburgh (1997), 75.

the detailed analysis of systems in this category rather difficult. We tabulate the experimental information for systems in this category in Table 4.

III. Theoretical Models

Following the experimental observations, a number of theoretical models have been studied in order to understand and explain the surfactant effect in semiconductor growth. We divide these models in three categories. In the first category we place models that have concentrated on the microscopic aspects, attempting to understand the atomic-scale features and processes involved in this phenomenon; models of this type typically employ sophisticated quantum-mechanical calculations of the total energy in order to evaluate the relative importance of the various structures and to determine the relevant activation energies involved in the kinetic processes. In the second category we place models that are more concerned with the macroscopic aspects of the surfactant effect, such as island morphologies and distributions as well as the effects of strain, without attempting to explain the details of the atomistic processes (although these may be taken into account heuristically). In the third category we place models that attempt to combine both aspects—that is, they try to use realistic descriptions of the atomistic processes as the basis for macroscopic models. Evidently, this last type is the most desirable but also the most difficult to construct. We review these three categories in turn.

4. MICROSCOPIC MODELS

Initial attempts at understanding the microscopic aspects of surfactant-mediated growth focused on the thermodynamic aspects; that is, they strived to justify why it is reasonable to expect the surfactant layer to float on top of the growing film. This was investigated by calculating energy differences between configurations with the surfactant layer buried below layers of the newly deposited atoms and configurations with the surfactant on top of the newly deposited atoms.² These energetic comparisons, based on first-principles calculations employing density functional theory, established that there is a strong thermodynamic incentive for keeping the surfactant layer on top of the growing film.

In a similar vein, calculations by Kaxiras¹⁶⁸ established that certain surfactants are more likely to lead to layer-by-layer growth than others,

¹⁶⁸ E. Kaxiras, *Europhys. Lett.* **21**, 685 (1993).

while a simplistic analysis of their chemical nature does not reveal such differences. These calculations used different types of surfactants on the same substrate and considered the relative energies of the various surface reconstructions induced by the surfactant layer. Specifically, three types of group-V atoms were considered as surfactants—P, As, and Sb—on the Si(111) surface for Ge or Si growth. The similar chemical nature of the three elements would argue for very similar surfactant behavior; however, the total energy calculations indicated that the three elements give significantly different reconstructions, some of which would lead to relatively easy floating of the surfactant layer while others would hamper this process. This is related to the manner in which, in a given reconstruction, the surfactant atoms are bonded to the substrate. For instance, in the energetically preferred reconstructions, the P and As atoms are bonded to the substrate with three strong covalent bonds each, while Sb atoms are bonded to the substrate with only one strong covalent bond per adsorbate atom. Based on these comparisons, Kaxiras proposed that Sb would work well on this substrate as a surfactant while P and As would not.^{168,169} This fact was subsequently verified experimentally.³⁰

A study of the same system by Nakamura *et al.*¹⁷⁰ (the Si(111) substrate with Sb as surfactant for Ge growth), based on the discrete variational approach and the cluster method to model the surface, reported that the presence of the surfactant strengthens the bonds between the Ge atoms on the surface. This effect, it was argued, leads to nucleation of stress-relieving dislocations at the surfaces, which is beneficial for layered growth of defect-free films. In this analysis neither the defects themselves nor any exchange and nucleation mechanisms were considered explicitly. Moreover, the bond-strengthening arguments are of a chemical nature, which may be useful in a local description of chemical stability but sheds little light on the dynamics of atoms during surfactant-mediated growth.

The chemical nature of Sb bonding on the Si(100) and the Ge(100) substrates was also investigated by Jenkins and Srivastava.^{171,172} In this work, first-principles density functional theory calculations were employed to determine the structure and the nature of bonding of Sb dimers in the (2 × 1) reconstruction, which, though interesting in itself, provides little direct insight into the process of surfactant-mediated growth.

The theoretical models considered so far addressed the problem of surfactant-mediated growth by considering what happens at the microscopic

level, but for entire monolayers—that is, by imposing the periodicity of the reconstructed surface in the presence of the surfactant. Subsequent atomistic models studied the equilibrium configurations and dynamics of individual adsorbed atoms or dimers, which is more appropriate for understanding the nature of growth on the surfactant-covered surface. A first example was an attempt by Yu *et al.*^{173,174,175} to justify how newly deposited Ge atoms on the As-covered Si(100) surface exchange place with the surfactant atoms in order to become embedded below the surfactant layer. In these calculations, based on total energy comparisons obtained from density functional theory, the metastable and stable positions of Ge dimers were established, indicating possible paths through which the newly deposited Ge atoms can be incorporated under the surfactant As layer. However, no explicit pathways were determined, and therefore no activation energies that might be relevant to growth kinetics were established. Furthermore, even though specific mechanisms for growth of needle-like islands by appending Ge dimers to a seed were discussed, the lack of calculated energy barriers for the exchange process and a large number of unproven assumptions involved in the proposed mechanisms means that they are of little help in understanding the surfactant effect. For instance, Yu *et al.*¹⁷³ claimed that Ge dimers are actually situated between, instead of on top of, As dimer rows, while in their proposed island growth mechanism they employed configurations that involve Ge dimers on top of the As dimer rows.

A similar type of analysis by Ohno,^{176,177} also using density functional theory calculations of the total energy, was reported for Si-on-Si(100) homoepitaxy using As as surfactant. Ways of incorporating the newly deposited Si dimers below the As layer were considered by studying stable and metastable positions and the rebonding that follows the exchange process. Again, though, actual exchange pathways and the corresponding activation energies relevant to growth kinetics were not considered. In this study it was shown explicitly how exchange of isolated Si dimers on top of the As layer is not exothermic, while the presence of two Si dimers leads to an energetically preferred configuration after exchange. This fact was used to argue that the Si dimer interactions are responsible for both their mutual repulsion and the initiation of the exchange. It appears, however, that these two effects—the strong repulsion of ad-dimers and the requirement of their

¹⁷³ B. D. Yu and A. Oshiyama, *Phys. Rev. Lett.* **72**, 3190 (1994).

¹⁷⁴ B. D. Yu, T. Ide, and A. Oshiyama, *Phys. Rev.* **B50**, 14631 (1994).

¹⁷⁵ B. D. Yu and A. Oshiyama, *Proceedings of the 22nd International Conference on the Physics of Semiconductors*, vol. 1, ed. D. J. Lockwood, World Scientific, Singapore (1995), 668.

¹⁷⁶ T. Ohno, *Phys. Rev. Lett.* **73**, 460 (1994).

¹⁷⁷ T. Ohno, *Thin Solid Films* **272**, 331 (1996).

¹⁶⁹ E. Kaxiras, *Mat. Sci. Eng.* **B30**, 175 (1995).

¹⁷⁰ J. Nakamura, H. Konogi, and T. Osaka, *Jap. J. Appl. Phys.* **35**, L441 (1996).

¹⁷¹ S. J. Jenkins and G. P. Srivastava, *Surf. Sci.* **325–354**, 411 (1996).

¹⁷² S. J. Jenkins and G. P. Srivastava, *Phys. Rev.* **B56**, 9221 (1997).

presence at neighboring sites for the initiation of exchange—are incompatible as far as growth is concerned. Both Yu *et al.*^{173,174,175} and Ohno^{176,177} dealt with mechanisms in which the basic unit involved in the exchange process is a deposited dimer, as was originally suggested by Tromp and Reuter.⁵⁴

An interesting microscopic study of surfactant mechanisms was reported by Kim *et al.*^{178,179,180} In this work, first-principles molecular dynamics simulations were employed to investigate the effect of Sb atoms at step edges on the Si(100) surface for Si homoepitaxy. This study examined the effect of Sb dimers on the step-edge barriers (also referred to as Schwoebel-Ehrlich barriers,^{181,182} for which we adopt here the acronym SEB, which is both descriptive and referential). These are extra barriers to adatom attachment to the step edge when the adatom arrives from the upper terrace, compared to the barriers for diffusion on the flat terraces. The authors found that the presence of Sb at the step edge gives a significant SEB for the attachment of a single Si atom but a much smaller SEB for attachment of a Si dimer by the push-over mechanism (in which the Si dimer at the upper terrace pushes the Sb dimer at the step edge over by one lattice constant and thus becomes incorporated in the bulk). This relative suppression of the SEB for dimer attachment leads to layer-by-layer growth as opposed to 3D island growth; consequently, Kim *et al.* argued, the presence of the surfactant Sb dimer at the step edge leads to layered growth. This is an interesting suggestion, but it remains to be proven correct for the system under consideration. Specifically, it is not clear whether a configuration with Sb dimers only at step edges of the Si(100) surface is stable. Typically, an entire monolayer is needed for the surfactant effect in similar systems, and the precise coverage is a crucial aspect of the effect. If the surfactant coverage is different from that assumed in the model of Kim *et al.*, the atomic processes at the step edge may be very different, leading to a different picture of the effect. Furthermore, kinetic Monte-Carlo studies are required to establish that the calculated energy barriers can actually lead to the predicted mode of growth,

since the density of Si adatoms (determined by flux, diffusion rate, and attachment-detachment rates) also influence the growth process.

Another detailed study of activation energies for diffusion and exchange processes in surfactant-mediated epitaxy was reported by Ko *et al.*¹⁸³ This study was also based on first-principles calculations of the energetics and addressed Si epitaxy on Si(100) with As acting as surfactant. In this work it was established that the exchange of a Si adatom with a sublayer As site involves an energy barrier of 0.1 eV, which is considerably lower than the energy barrier for diffusion (of order 0.5 eV) or the energy barrier for dimer exchange (of order 1.0 eV) which had been invoked as a possible mechanism in earlier studies of the same system (see Refs. 54, 173, 174, 175, 176, and 177). This is a very interesting suggestion, but falls short of providing a complete picture of the surfactant effect. Specifically, it is not clear how a single exchange step of the type investigated by Ko *et al.* can lead to a configuration that will nucleate the next layer of the crystal. This process may well involve additional important steps with different activation barriers, so that the barrier calculated, though important and interesting, may not be the determining step in the growth process. In fact, Ko *et al.* found that exchange of two individual Si atoms at neighboring sites leads to the formation of a protruding As dimer, which acts as a seed for further growth. This protruding As dimer binds additional Si adatoms and leads to the formation of a Si dimer, which eventually undergoes site exchange with a neighboring As dimer with an energy barrier of 1.1 eV. It then appears that it is this last step that is the determining one in growth, which leads back to the dimer-exchange picture discussed earlier, albeit now with a more detailed picture of how this process may be initiated by the barrierless exchange of single Si adatoms.

Two separate studies of growth on III-V surfaces addressed the surfactant effect in these systems. In the first, by Miwa *et al.*,¹⁸⁴ the dimer-exchange mechanism on III-V surfaces, using Te as the surfactant, was investigated using first-principles calculations. The authors found that InAs growth on GaAs(100) proceeds by complete dimer exchange between the In and Te layers on the As-terminated surface, while on the In-terminated surface the exchange between the Te layer and an overlayer of As is only partial. The second study, by Shiraishi and Ito,^{185,186} examined the equilibrium con-

¹⁷⁸ E. Kim, C. W. Oh, Y. H. Lee, K. Y. Lim, and H. J. Lee, *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, vol. 2, eds. M. Scheffler and R. Zimmermann, World Scientific, Singapore (1996), 1019.

¹⁷⁹ C. W. Oh, E. Kim, and Y. H. Lee, *Phys. Rev. Lett.* **76**, 776 (1996).

¹⁸⁰ E. Kim, C. W. Oh, Y. H. Lee, *Material Research Society Symposia Proceedings*, eds. S. M. Prokes, O. J. Glembocki, S. K. Brierly, J. M. Gibson, and J. M. Woodall, Materials Research Society, Pittsburgh (1997), 135.

¹⁸¹ R. L. Schwoebel and E. J. Shipsey, *J. Appl. Phys.* **37**, 3682 (1996); R. L. Schwoebel, *J. Appl. Phys.* **40**, 614 (1969).

¹⁸² G. Ehrlich and F. G. Huda, *J. Chem. Phys.* **44**, 1039 (1966); S. C. Wang and G. Ehrlich, *Phys. Rev. Lett.* **70**, 41 (1993).

¹⁸³ Y.-J. Ko, J.-Y. Yi, S.-J. Park, E.-H. Lee, and K. J. Chang, *Phys. Rev. Lett.* **76**, 3160 (1996).

¹⁸⁴ R. H. Miwa, A. C. Ferraz, W. N. Rodrigues, and H. Chacham, *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, vol. 2, eds. M. Scheffler and R. Zimmermann, World Scientific, Singapore (1996), 1107.

¹⁸⁵ K. Shiraishi and T. Ito, *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, vol. 2, eds. M. Scheffler and R. Zimmermann, World Scientific, Singapore (1996), 1103.

figurations of adatoms on the GaAs(100) surface with different As coverages, using first-principles total-energy calculations. This study concluded that preadsorbed Ga atoms create a "self-surfactant" effect by significantly influencing the adsorption energy of As dimers at various sites on the surface. In this analysis, energy barriers for diffusion and exchange mechanisms were not taken into account; consequently, the interpretation of actual growth processes was limited.

The most detailed study of actual atomistic mechanisms for diffusion and exchange was reported by Schroeder *et al.*¹⁸⁷ This work examined the motion of Si adatoms on the As-covered Si(111) surface, using first-principles total-energy calculations. The authors reported a very interesting pathway for exchange between the additional Si atom and an As surfactant atom with an energy barrier of only 0.27 eV. This is comparable to the diffusion barrier for the Si atom on top of the As layer, calculated to be 0.25 eV. The Si atom can undergo the reverse of the exchange process, and by so doing it can get on top of the As surfactant layer, a process that involves an energy barrier of 1.1 eV, according to the results of Schroeder *et al.* This leads to a rather complex sequence of events, with Si adatoms arriving at the surfactant covered substrate, diffusing, exchanging, undergoing the opposite of the exchange process and diffusing again, with the relevant energy barriers. The possibility of the opposite of the exchange process was first explicitly introduced in the work of Kandel and Kaxiras,¹⁸⁸ where it was called *de-exchange*. We adopt this term in the following as more descriptive of the opposite of the exchange process, since this undoes the effect of an exchange step rather than repeat it, as the term *re-exchange* (used in the work of Schroeder *et al.*) might suggest. The *de-exchange* process was shown by Kandel and Kaxiras to be crucial in maintaining the layer-by-layer growth mode in the presence of the surfactant (see more details below). They found that the *de-exchange* process has a higher activation energy (1.6 eV) than either exchange (0.8 eV) or diffusion (0.5 eV), although this was established by considering the exchange or *de-exchange* of entire monolayers of newly deposited atoms on top of the surfactant layer. Schroeder *et al.* showed that the same energy ordering also is valid for individual adatoms on top of the surfactant layer, but the actual barriers for individual adatoms are lower (1.1 eV, 0.27 eV, and 0.25 eV for *de-exchange*, exchange, and diffusion, respectively). This establishes unequivocally the importance of the *de-exchange* process.

¹⁸⁶ K. Shirasahi and T. Ito, *Phys. Rev. B* **57**, 6301 (1998).

¹⁸⁷ K. Schroeder, B. Engels, P. Richard, and S. Blügel, *Phys. Rev. Lett.* **80**, 2873 (1998).

¹⁸⁸ D. Kandel and E. Kaxiras, *Phys. Rev. Lett.* **75**, 2742 (1995); E. Kaxiras and D. D. Kandel, *Appl. Surf. Sci.* **102**, 3 (1996).

What is lacking from the work of Schroeder *et al.* is a sequence of steps that can actually lead to the formation of the next layer of deposited material. Specifically, even after the single Si adatom has exchanged positions with a surfactant As atom, the system is not in a configuration from which the repeated sequence of similar steps can lead to the formation of a new layer. In the system studied by Schroeder *et al.* this process may be quite complicated, since the Si(111) surface consists of double layers, the formation of which may involve additional energy barriers that supersede the one determined for the exchange of a single adatom.

5. MACROSCOPIC MODELS

There is a debate in the literature on whether the suppression of 3D islanding by surfactants in heteroepitaxy is an equilibrium effect or a kinetic one. While most researchers in the field take the kinetic approach, there has been some effort to explain the surfactant effect using thermodynamic considerations. According to the thermodynamic approach, the equilibrium state of the newly deposited material in the presence of a surfactant layer is a smooth flat film. The underlying assumption behind kinetic models is that even with surfactants the true equilibrium state of the system is that of 3D islands. The role of surfactants in this case is to induce layer-by-layer growth kinetically and to make the approach to equilibrium longer than realistic time scales. We will first give examples of the thermodynamic approach to the surfactant effect and then elaborate on some kinetic models.

Kern and Müller¹⁸⁹ calculated the free energy of the formation of a crystal of material A stretched to be coherent with a substrate of material B. They took into account effects of surface energy as well as surface stress and obtained the equilibrium shape of the crystal by minimizing its free energy with respect to its height and width. In their view, surfactants may reduce surface stress and surface energy, and hence lead to flatter islands and perhaps even to wetting of the substrate by the deposited material (which happens when the equilibrium island height vanishes). Kern and Müller viewed such surfactant-induced wetting as a transition from 3D growth to 2D layer-by-layer growth. This Kern-Müller criterion may indicate whether the effect of a certain surfactant is in the right direction to suppress 3D islanding. However, the researchers did not consider the possibility of 3D growth when the deposited material wets the substrate (Stranski-Krastanov growth mode). They also ignored strain relaxation, which reduces the cost of 3D-island formation. Thus, the

¹⁸⁹ R. Kern and P. Müller, *J. Cryst. Growth* **146**, 193 (1995).

question of whether the surfactant effect is a purely thermodynamic one is left unanswered.

A different equilibrium argument was proposed by Eaglesham *et al.*,⁴⁷ who argued that surfactants change the surface energy *anisotropy*, leading to the suppression of 3D islanding. They examined experimentally islands of Ge on Si(100) films with and without surfactants, and found that their equilibrium shape changes radically in the presence of surfactants and depends strongly of the specific surfactant used. For example, Sb as a surfactant favors (100) facets, whereas In favors (311) facets. Eaglesham *et al.* advanced the idea that if the surfactant favors facets in the same orientation as the substrate, the equilibrium shape of the islands generated will be flat. This will lead to earlier coalescence of islands and will enhance layer-by-layer growth. The mechanism proposed by Eaglesham *et al.* may have a significant impact on the growth mode, but it cannot be the main explanation of the surfactant effect, since the equilibrium morphologies observed in their experiments include 3D islands. Therefore, in their explanation of the surfactant effect they supplemented the equilibrium consideration with a kinetic one—that is, the reduction of the diffusion length induced by surfactants.

It seems quite difficult to explain the surfactant effect on the basis of thermodynamics alone. For this reason most researchers in the field make the assumption that surfactants suppress 3D islanding *kinetically*. Markov's work^{190,191,192} is an example of such a kinetic model. He developed an atomistic theory of nucleation in the presence of surfactants. The main results of this work are expressions for the nucleation rate and saturation density of islands. These quantities depend crucially on the difference between the energy barrier for adatom diffusion on top of the surfactant layer and the barrier for diffusion on a clean surface. If this difference is positive, surfactants decrease the diffusion length for adatoms and the saturation density of islands rises sharply. Such an anomalously high island density in the presence of surfactants has been seen experimentally in various systems, and it is viewed by many researchers (see Refs. 25, 28, 29, 52, 54, 70, 125, 126, 183, and 193) as the main mechanism by which surfactants change the growth mode of the film and suppress 3D islanding in heteroepitaxy. We will show in Section IV that this mechanism does not explain the surfactant effect.

An entirely different approach was taken by Barabasi.^{194,195} Rather than

look at the kinetics of the system on the atomic length scale, he viewed the growing film on a much coarser scale. He represented the local height of the film and the local width of the surfactant layers as continuous fluctuating fields, in the spirit of the KPZ model of kinetic roughening.¹⁹⁶ On the basis of the relevant symmetries of the system, he wrote down a set of coupled differential equations that describe the dynamics of these two fields. The quantity of interest in this approach is the width of the film surface and its dependence on system size. Typically, such a theory would predict a rough surface where the width diverges with system size. Barabasi found that surfactants can induce a flat phase where the surface width does not diverge with system size, and he associated this phase with a layer-by-layer growth mode. It is interesting to see that a theory on such a macroscopic length scale can capture effects that depend critically on processes that occur on an atomic scale. The drawback of this theory is that it is not clear what role lattice mismatch and strain play in the kinetics of the system. Also, in the rough phase the model predicts a self-similar structure for the surface. Experimentally, however, the morphology of a surface with 3D islands is not self-similar, and it is not clear whether this continuum theory can describe the experimental morphologies.

Barabasi and Kaxiras¹⁹⁷ extended this model to include two different dynamical fields—one representing the surfactant layer; the other the surface film layer. This allowed an investigation of whether subsurface diffusion, which had been neglected in the previous model, could change the behavior. It was found that subsurface diffusion essentially always leads to roughening and, if operative in real systems, would prevent layer-by-layer growth.

Most models of surfactant-mediated epitaxial growth emphasize the significance of adatom diffusion for the determination of the growth mode. Another atomic process of importance is attachment and detachment of adatoms from island edges. In fact, in Section IV we develop a model according to which surfactants suppress 3D islanding by passivating island edges, thus suppressing adatom detachment. It is therefore of interest to investigate the influence of island-edge passivation on surface morphology. Kaxiras first introduced the idea of island-edge passivation by the surfactant^{198,199} and carried out kinetic Monte-Carlo simulations on a very

¹⁹⁴ A.-L. Barabasi, *Phys. Rev. Lett.* **70**, 4102 (1993).

¹⁹⁵ A.-L. Barabasi, *Fractals* **1**, 846 (1993).

¹⁹⁶ M. Kardar, G. Parisi, and Y.-C. Zhang, *Phys. Rev. Lett.* **56**, 889 (1986).

¹⁹⁷ A.-L. Barabasi and E. Kaxiras, *Europhys. Lett.* **36**, 129 (1996).

¹⁹⁸ E. Kaxiras, *Thin Solid Films* **272**, 386 (1996).

¹⁹⁹ E. Kaxiras "Simulation of Semiconductor Growth Mechanisms in the Presence of Adsorbate Layers," in *Computational Materials Science*, ed. C. Y. Fong, World Scientific, Singapore (1997).

¹⁹⁰ I. Markov, *Phys. Rev. B* **50**, 11271 (1994).

¹⁹¹ I. Markov, *Phys. Rev. B* **53**, 4148 (1996).

¹⁹² I. Markov, *Mat. Chem. Phys.* **49**, 93 (1997).

¹⁹³ A. Sakai, T. Tatsumi, and K. Ishida, *Phys. Rev. B* **47**, 6803 (1993).

simple model to show that it can lead to morphologies compatible with experimental observations. Kandel also carried out a study of island-edge passivation effects.²⁰⁰ He investigated a simple model of submonolayer homoepitaxial growth in the framework of rate equation theory, using the critical island approximation (only islands of more than i^* atoms are stable, while smaller islands decay). The main result of this work is that the island density scales with flux, F , as F^χ with $\chi = 2i^*/(i^* + 3)$ when island edges are passivated, while $\chi = i^*/(i^* + 2)$ without island-edge passivation. This conclusion is important because the exponent χ can be measured experimentally and one can learn from its value whether island-edge passivation is operative or not in the experimental system at hand. For example, a value of $\chi > 1$ can occur only if the surfactants passivate island edges. Kandel's theory relies on a somewhat oversimplified picture of submonolayer growth, and the conclusions are yet to be verified with a more rigorous theory or by detailed simulations of the growth process.

IV. The Diffusion-De-Exchange-Passivation Model

To our knowledge the only attempt to construct a comprehensive model that includes both the microscopic aspects of atomic motion and a realistic description of the large length-scale evolution of the surface morphology was reported by the present authors.¹⁸⁸ The work of Zhang and Lagally²⁰¹ was another attempt to link the microscopics and the macroscopics of the effect of surfactants on thin-film growth. However, their work discussed homoepitaxial growth of metals, a subject interesting in its own right but beyond the scope of the present review article.

6. GENERAL CONSIDERATIONS

Before we embark on the construction of the theoretical model,¹⁸⁸ we briefly review the relevant experimental information since we do not claim that a single model captures every type of surfactant-mediated growth mode. We focus here on growth of elemental or compound semiconductors, in which a single species of atom controls the diffusion and exchange (or de-exchange) processes, and the surfactant produces a chemically passivated surface. We take as the canonical case a group-IV substrate (examples are Si(100) and Si(111)) and a group-III or group-V surfactant (these are

²⁰⁰ D. Kandel, *Phys. Lett.* **78**, 499 (1997).

²⁰¹ Z. Zhang and M. G. Lagally, *Phys. Rev. Lett.* **72**, 693 (1994).

actually the systems that have been studied most extensively experimentally, as is evident from Tables 2 through 4).

It appears that a full monolayer of surfactant coverage is required for growth of high-quality semiconductor crystals. This is different from the case of surfactant effects in the growth of metals, where a small amount of surfactant (typically a few percent of a monolayer coverage) is sufficient. The most direct evidence on this issue was provided by the experiments of Wilk *et al.*,³⁸ who studied homoepitaxial growth of Si on Si(111) using Au as a surfactant. These authors reported that the density of defects in the film correlates well with the surfactant coverage, with the minimum defect density corresponding to full monolayer coverage by the surfactant. This is a physically appealing result that can be interpreted as evidence that the better the passivation of the surface by the surfactant, the more effective the surfactant in promoting high-quality growth. In the following we will assume that full monolayer coverage of the substrate is the standard condition for successful surfactant-mediated growth of semiconductors.

The model we will now describe assumes that the surfactant effect is kinetic. As with all other kinetic models of surfactant-mediated growth, the underlying idea is that at equilibrium the heteroepitaxial system generates 3D islands even in the presence of surfactants. Surfactants make the approach to equilibrium very slow, so that 3D islands are not generated during the growth of the film. This means that surfactants kinetically suppress one or more microscopic processes, which are essential for the growth of 3D islands. The most important ingredient of any explanation of the surfactant effect is the identification of these processes. Almost all the explanations found in the literature identify the relevant process as adatom diffusion (see Refs. 25, 28, 29, 52, 54, 70, 125, 126, 183, and 193). The idea is that the energy barrier for exchange of an adatom with a surfactant atom, E_{ex} , is smaller than the barrier for diffusion of an adatom on top of the surfactant layer, E_d . An adatom therefore diffuses a very short distance before it exchanges, and after exchange it cannot diffuse (once it is underneath the surfactant layer). This suppressed diffusion mechanism explains the surfactant effect in the following way. The reduced diffusion length makes the density of islands nucleating on the surface very high. As a result, island coalescence occurs before any second-layer islands nucleate on top of existing first-layer islands. This is how, according to this mechanism, 3D islanding is suppressed.

As mentioned in Section II, support for this hypothesis comes from various experiments, particularly those of Voigtländer *et al.*,²⁵ who studied the effects of various surfactants on submonolayer homoepitaxial growth of Si on Si(111). The results were correlated with studies of the effect of the same surfactants on heteroepitaxial growth of Ge on Si(111). Voigtländer *et*

al. found that generally there are two types of surfactants. Group-III and group-IV elements tend to significantly decrease the island density in submonolayer homoepitaxy and lead to 3D islanding in heteroepitaxy. On the other hand, group-V and group-VI elements drastically increase the island density in submonolayer homoepitaxy and suppress 3D islanding in heteroepitaxy. If one interprets an increase in the island density as an indication of suppression of diffusion, these results confirm the mechanism discussed above.

Despite the appeal of the suppressed diffusion hypothesis, we propose that it may not be the entire story. Our concerns arise from the fact that group-V and group-VI elements chemically passivate the surface more efficiently than do group-III and group-IV elements. Intuitively, this should lead to faster diffusion on surfaces covered by the former elements, but the experimental results are consistent with the latter elements enhancing diffusion and the former ones suppressing it. To clarify this issue, we decided to examine more carefully the microscopic processes involved in the kinetics of surfactant-mediated epitaxy. Our investigation led to an entirely different explanation of the influence of surfactants on epitaxial growth modes.

A schematic representation of the possible atomic processes is shown in Fig. 1. The simplest process is, of course, diffusion of adatoms on top of the surfactant layer (Fig. 1(a)). A second important process is the exchange of adsorbed atoms with the surfactant atoms, so that the former can be buried under the surfactant layer and become part of the bulk. This process can take place either on a terrace or at a step (Fig. 1(b)). From thermodynamic considerations, we must also consider the process by which atoms de-exchange and become adatoms that can diffuse on top of the surfactant layer (Fig. 1(c)). Again, this process can take place on terraces or at surface steps. Finally, we have to consider separately surfactants that *cannot* passivate step edges, in which case both the exchange (Fig. 1(d)) and de-exchange processes (Fig. 1(e)) will be different than at passivated steps, since they no longer involve actual exchange events between adatoms and surfactant atoms. We refer to our model as diffusion-de-exchange-passivation (DDP), since these are the three processes that determine the behavior in surfactant-mediated epitaxy: Diffusion is always present; de-exchange obviously implies also the presence of exchange; and passivation (always present on terraces) may or may not be present at island edges, but its presence or absence is a crucial element.

7. FIRST-PRINCIPLES CALCULATIONS

In order to evaluate the relative contributions of these processes and their influence on the growth mode, the corresponding activation energies must be calculated. This is a difficult task because very little is known about the

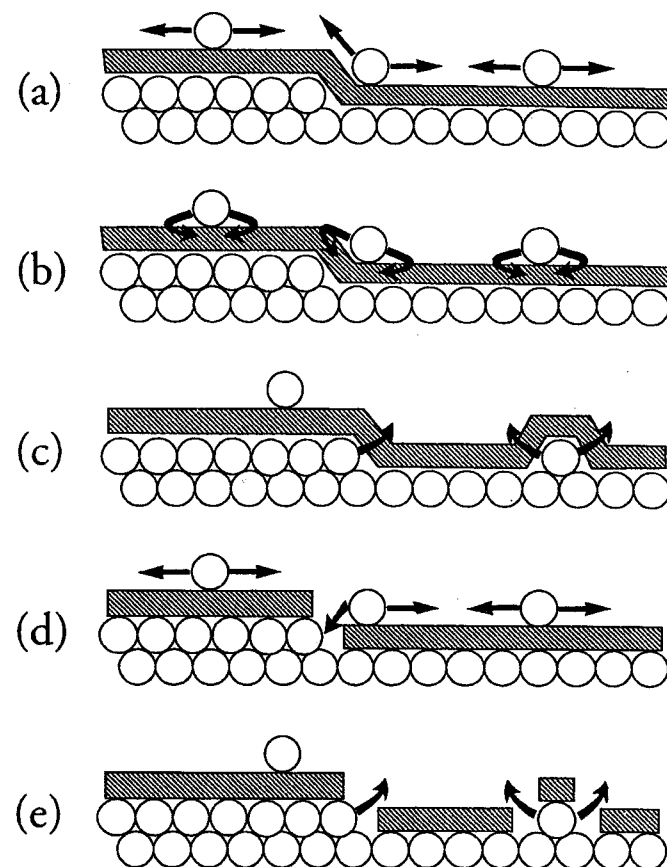


FIG. 1. Schematic illustration of important mechanisms in surfactant-mediated growth on a substrate (represented by white circles) with a full monolayer surfactant coverage (represented by continuous shaded area). (a) Diffusion on terraces and steps for surfactant that passivates step edges. (b) Exchange at terraces and passivated steps. (c) De-exchange at terraces and passivated steps. (d) Diffusion on terrace and exchange at nonpassivated steps. (e) De-exchange at terrace and at nonpassivated steps.

atomic configurations involved. We therefore begin by considering two idealized processes that involve entire monolayers; then we discuss how the corresponding activation energies can be representative and relevant for growth mechanisms, and obtain their values from first-principles calculations.

The first process we consider is diffusion on a surface covered by a surfactant monolayer. The representative system we chose to study consists

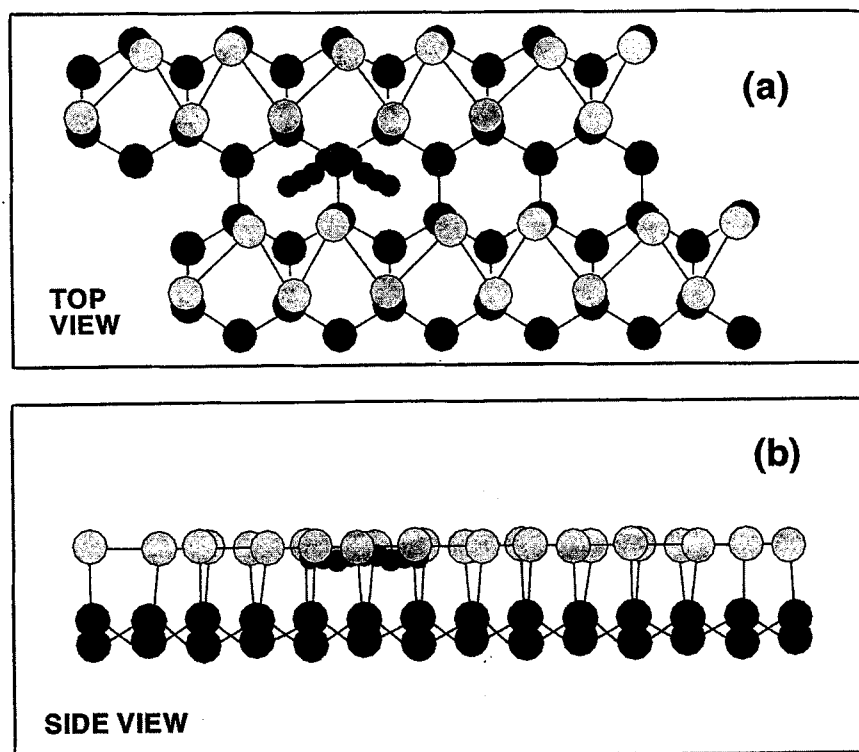


FIG. 2. Representative surface diffusion pathway, (a) top and (b) side views. The dark circles represent the substrate atoms; the light circles, the surfactant atoms. The smaller gray circle represents an extra atom deposited on top of the surfactant layer, at different positions. The geometries correspond to a Ge adatom on a Si(111) surface (the substrate) covered by a monolayer of Sb (the surfactant) in a (2×1) chain reconstruction.

of a Si(111) substrate, covered by a bilayer of Ge, with Sb as the surfactant. In this case, it was known that the structure of the Sb layer is a chain geometry with a periodicity of (2×1) , as shown in Fig. 2.¹⁶⁸ An additional Ge atom was then placed on top of the Sb layer, and the energy optimized for a fixed position of the Ge atom along the direction parallel to the Sb chains. All other atomic coordinates, including those of the Ge atom perpendicular to the Sb chain and vertical with respect to the surface, were allowed to relax in order to obtain the minimum energy configuration. The energy and forces were computed in the framework of density functional theory and local density approximation (DFT/LDA), a methodology that is known to provide accurate energetic comparisons for this type of system

(see in particular the reviews by Kaxiras^{202,203} on the application of such calculations to semiconductor growth phenomena). By considering several positions of the extra Ge atom along the chain direction and calculating the corresponding total energy of the system, we obtained a measure of the activation energy for diffusion in this direction. We found that the activation energy for diffusion along this path is 0.5 eV.

We next considered a possible exchange mechanism in the same system, through which the newly deposited Ge atoms can interchange positions with the surfactant atoms and become buried under them. To this end, we modeled the system by a full monolayer of Ge deposited on top of the surfactant layer (Fig. 3(a)). We studied a concerted exchange type of motion for the Ge-Sb interchange. In the final configuration (Fig. 3(e)) the Ge layer was below the Sb layer and the system was now ready for the deposition of the next Ge layer on top of the surfactant. The middle configuration, Fig. 3(c), corresponds to a metastable structure, in which half of the newly deposited Ge layer has interchanged position with the Sb surfactant layer. The configurations between the initial and middle geometries and the middle and final geometries, Fig. 3(b) and Fig. 3(d), respectively, correspond to the saddle-point geometries that determine the activation energy for the exchange. From our DFT/LDA calculations we found that the energy difference between structures 3(a) and 3(b) is 0.8 eV, and the energy difference between structures 3(c) and 3(d) is the same to within the accuracy of the results. Similarly, the energy difference between structures 3(c) and 3(b) and structures 3(e) and 3(d) is 1.6 eV. These two numbers correspond to the exchange activation energy (0.8 eV, going from 3(a) to 3(c) through 3(b), or going from 3(c) to 3(e) through 3(d)) and the de-exchange activation energy (1.6 eV, going from 3(c) to 3(a) through 3(b), or going from 3(e) to 3(c) through 3(d)) for this hypothetical process.

We discuss next why these calculations give reasonable estimates for the activation energies involved in surfactant-mediated growth. As far as the diffusion process is concerned, it is typical for semiconductor surfaces to exhibit anisotropic diffusion constants depending on the surface reconstruction, with the fast diffusion direction along channels of atoms that are bonded strongly among themselves. This is precisely the pathway we examined in Fig. 2. As for the exchange process, it is believed that the only way in which atoms can exchange positions in the bulk is through a concerted exchange type of motion, as first proposed by Pandey for self-diffusion in bulk Si.²⁰⁴ This motion involves the breaking of the smallest

²⁰² E. Kaxiras, *Surf. Rev. Lett.* **3**, 1295 (1996).

²⁰³ E. Kaxiras, *Comp. Mat. Sci.* **6**, 158 (1996).

²⁰⁴ K. C. Pandey, *Phys. Rev. Lett.* **57**, 2287 (1986).

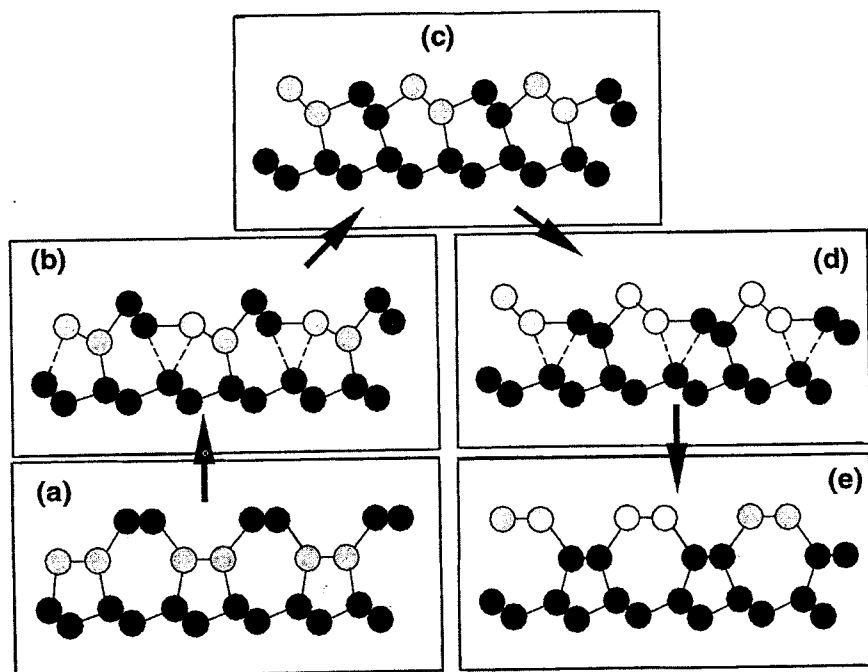


FIG. 3. Representative exchange pathway. The color scheme is the same as in Fig. 2. (a) Structure with one layer of newly deposited atoms on top of the surfactant layer. The geometries depicted in (b), (c), and (d) are the intermediate structures during a concerted exchange that breaks the surfactant layer on top of the newly deposited layer, shown as the final configuration in (e). Structure (c) is metastable, while structures (b) and (d) are saddle-point configurations. Solid lines linking the atoms correspond to covalent bonds, while dashed lines correspond to broken bonds. The geometries correspond to the same physical system as in Fig. 2.

possible number of covalent bonds during the exchange, which keeps the activation energy relatively low. In the case of bulk Si, the activation energy for concerted exchange is 4.5 eV.²⁰⁴ In the present case the activation energy is only 0.8 eV because, unlike in bulk Si, the initial configuration (Fig. 3(a)) is not optimal, having the pentavalent Sb atoms as fourfold coordinated (they would prefer threefold coordination) and the newly deposited Ge atoms as threefold coordinated (they would prefer fourfold coordination). In the final configuration (Fig. 3(e)), which has lower energy than the initial one, all atoms are coordinated properly (threefold for Sb, fourfold for Ge).

While we have argued that the above described atomic processes are physically plausible, we have not established their uniqueness or their supremacy over other possible atomic motions. In fact, the calculations of

Schroeder *et al.*,¹⁸⁷ discussed in Section III.5, are much more realistic concerning the exchange of single adatoms with surfactant atoms on terraces. However, those calculations refer to a single event, and the formation of an additional substrate layer could (and probably does) involve additional steps in the exchange process because of the double-layer nature of the Si(111) substrate. In our calculations, the structure of the layer below the surfactant is compatible with the lower half of the substrate double layer, so that the process of exchange can proceed with very similar steps to complete the double-layer growth. In this sense, we feel that the barriers we obtained are not too far from realistic values. To keep our discussion general we will consider the two sets of energy barriers as corresponding to a range of physical systems: The first set is suggested by our results ($E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, $E_{de-ex} = 1.6$ eV); the second, by the results of Schroeder *et al.* ($E_d = 0.25$ eV, $E_{ex} = 0.27$ eV, $E_{de-ex} = 1.1$ eV).

8. DE-EXCHANGE AND GENERALIZED DIFFUSION

It is clear that diffusion and exchange processes affect the morphology of the growing film. What about de-exchange processes? The energy barrier for de-exchange is significantly larger than the other two energy barriers. Are de-exchange events frequent enough to have any effect on the growth mode? Or, to be more quantitative, suppose an adatom exchanged with a surfactant atom; will it de-exchange before another adatom exchanges in its vicinity? To answer this question we assume that the time scale associated with a process with energy barrier E is $\nu^{-1} \exp(E/kT)$, where $\nu = 10^{13}$, sec^{-1} is the basic attempt rate, k is the Boltzmann constant, and T is the temperature. Even at the fairly low temperature of 350°C and with the large de-exchange barrier of 1.6 eV, the time it takes an atom to de-exchange is only 0.9 seconds. The time it takes to grow a layer at a typical flux of 0.3 layers/minute is 200 seconds. Therefore, an atom will de-exchange quite a few times before it will interact with additional atoms in the same layer. We conclude that de-exchange processes can influence the growth mode and should not be ignored.

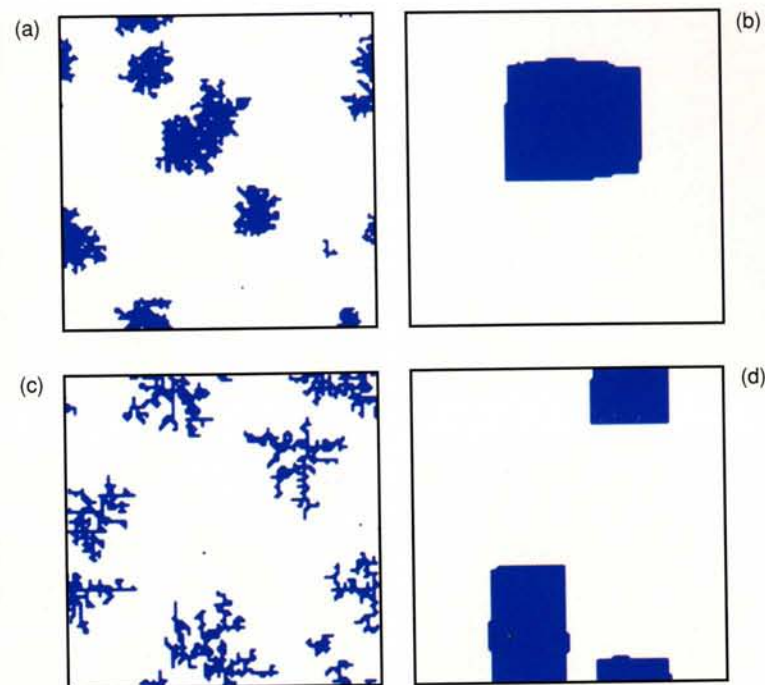
The above discussion changes our view of diffusion in surfactant-mediated epitaxy. The effect of diffusion cannot be understood simply by comparing E_d with E_{ex} , because after an adatom exchanges it may still continue to diffuse on top of the surfactant layer by de-exchanging with a surfactant atom. It is instructive to compare the effective diffusion constant, D_{eff} , which corresponds to this complex diffusion process, with the bare diffusion constant of an adatom on a surface (without surfactants), $D = \nu a^2 \exp(-E_d^{(b)}/kT)$. Here a is the lattice constant and $E_d^{(b)}$ is the energy barrier for bare diffusion.

To calculate D_{eff} , we consider the case $E_{ex} > E_d$ (a similar calculation can be done for the opposite case and yields an identical result). An effective diffusion hop consists of a de-exchange event followed by several microscopic diffusion hops and finally an exchange event. We calculate D_{eff} from the expression $D_{eff} = A^2/\tau_{eff}$, where τ_{eff} is the average time it takes to carry out an effective diffusion hop. A is the average distance an atom travels during such a hop, and it obeys the relation $A = a\sqrt{n}$, where n is the average number of microscopic diffusion hops the atom carries out between the de-exchange and exchange events. n is easily calculated as the ratio between the time for an exchange event and the time for a microscopic diffusion hop. This leads to the result $n = \exp[(E_{ex} - E_d)/kT]$. τ_{eff} is the time it takes to carry out a de-exchange event followed by an exchange event. Therefore, $\tau_{eff} = v^{-1}[\exp(E_{de-ex}/kT) + \exp(E_{ex}/kT)]$. The final expression for the effective diffusion constant is

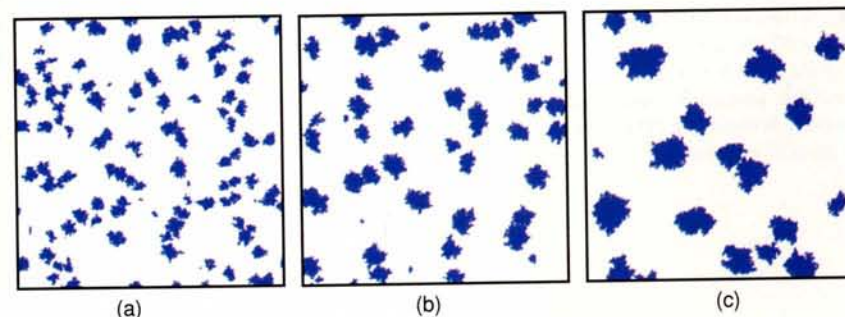
$$D_{eff} = D \frac{\exp[(E_d^{(b)} - E_d)/kT]}{1 + \exp[(E_{de-ex} - E_{ex})/kT]} \quad (4.1)$$

Clearly, a comparison of E_d with E_{ex} does not tell us much about the magnitude of D_{eff} . Passivation of the surface by the surfactant implies $E_d^{(b)} > E_d$ and $E_{de-ex} > E_{ex}$. Thus, both the numerator and the denominator are larger than 1, and the question is which is the larger of the two. For the values of energy barriers calculated from first principles (both ours and those of Schroeder *et al.*), $E_{de-ex} - E_{ex} \approx 0.8$ eV. The denominator of Eq. (4.1) is therefore a very large number (between 10^3 and 10^6 for typical temperatures). The numerator is much smaller, and therefore $D \gg D_{eff}$ —that is, diffusion is suppressed. This is not necessarily the case for all surfactants. For example, for surfactants that are less efficient in passivating the surface, $E_{de-ex} - E_{ex}$ may be comparable or even smaller than $E_d^{(b)} - E_d$, which would lead to diffusion enhancement. This may be the case for group-III and group-IV surfactants, which enhance diffusion according to experiments (see Refs. 33, 37, 50, and 205). It would be interesting to check this possibility with DFT/LDA calculations. One conclusion is that effective diffusion can be suppressed by surfactants even if $E_{ex} > E_d$; in other words, a surfactant can enhance diffusion on top of the surfactant layer and, at the same time, suppress effective diffusion, which takes into account de-exchange processes.

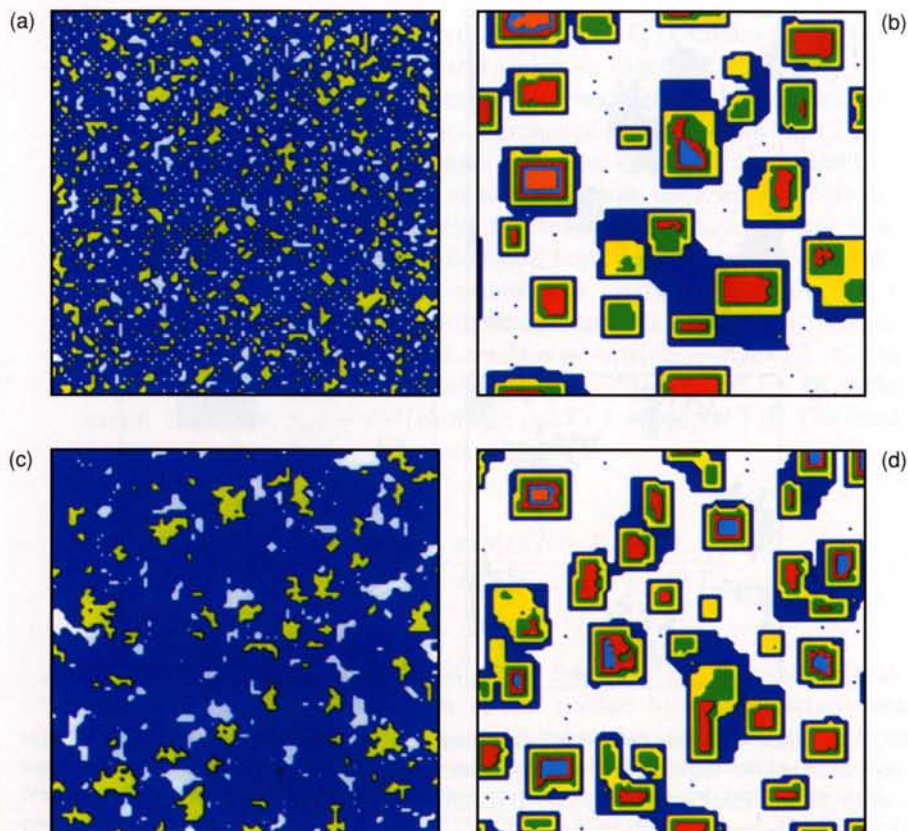
²⁰⁵ S. Iwanari, Y. Kimura, and K. Takayanagi, *J. Cryst. Growth* **119**, 241 (1992).



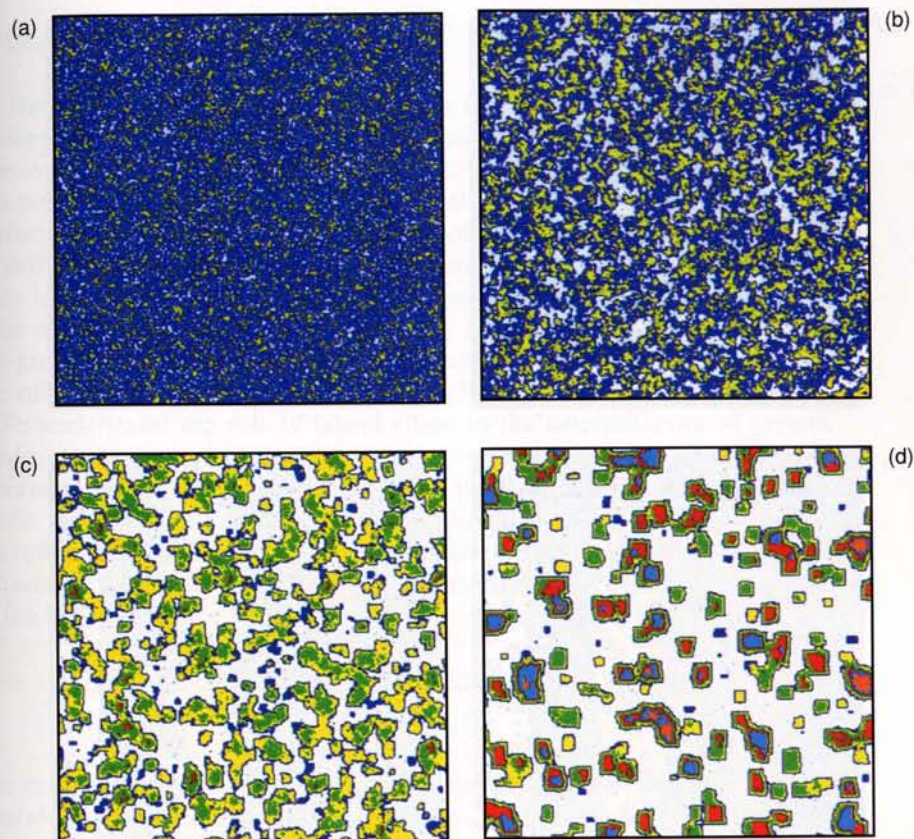
COLOR PLATE 1. Kinetic Monte-Carlo simulations of surfactant-mediated homoepitaxy in the DDP model, on a substrate of size 100×100 at a temperature of 600°C . A total of 0.15 monolayer of new material has been deposited. (a) Simulations with IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, $E_{de-ex} = 1.6$ eV, and $E_{det} = 3$ eV. (b) Simulations without IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, $E_{de-ex} = 1.6$ eV, and $E_{det} = 1.6$ eV. (c) Simulations with IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.3$ eV, $E_{de-ex} = 1.1$ eV, and $E_{det} = 2.5$ eV. (d) Simulations without IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.3$ eV, $E_{de-ex} = 1.1$ eV and $E_{det} = 1.6$ eV. IEP clearly increases the island density and significantly affects the island shape.



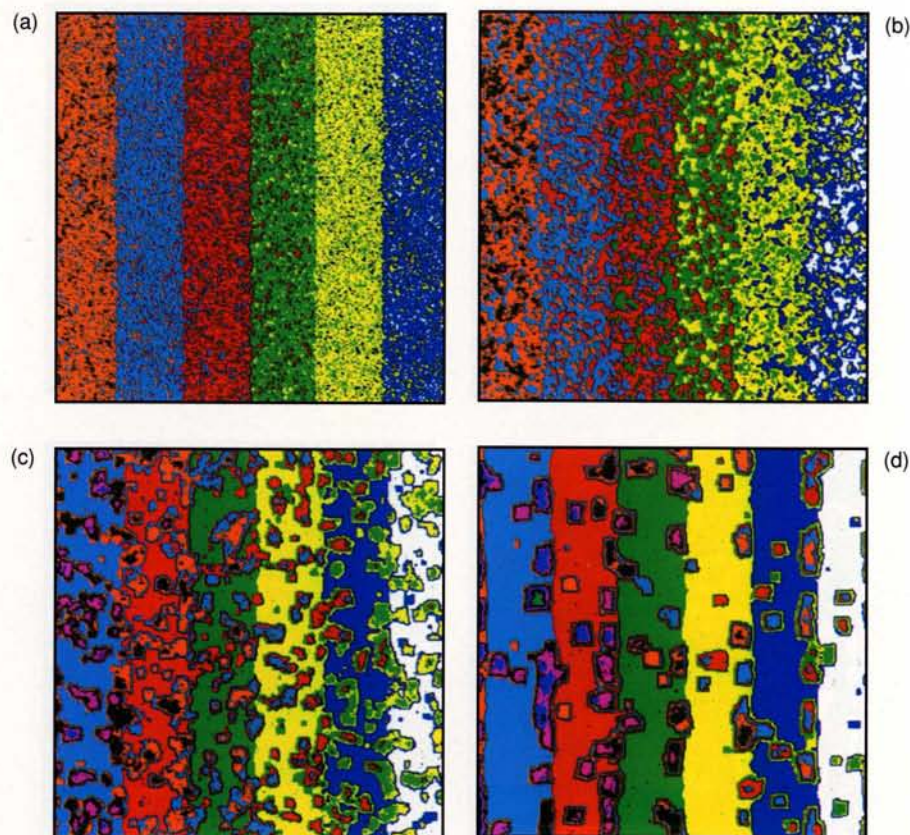
COLOR PLATE 2. Kinetic Monte-Carlo simulations of homoepitaxial surfactant-mediated growth in the DDP model, with IEP on a substrate of size 300×300 . The activation energies were $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, $E_{de-ex} = 1.6$ eV, and $E_{det} = 3$ eV. A total of 0.15 monolayer of new material has been deposited at (a) 600°C , (b) 700°C , and (c) 850°C . The high density of small islands at low temperature is evident, as well as the decrease of the island density with increasing temperature.



COLOR PLATE 3. Kinetic Monte-Carlo simulations of surfactant mediated heteroepitaxy in the DDP model, on a substrate of size 100×100 at a temperature of 300°C . A total of 1 monolayer of new material has been deposited. (a) Simulations with IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. (b) Simulations without IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. (c) Simulations with IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.3$ eV, and $E_{de-ex} = 1.1$ eV. (d) Simulations without IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.3$ eV, $E_{de-ex} = 1.1$ eV. Different colors indicate different surface heights. The surfactant that passivates island edges suppresses 3D islanding completely and induces layer-by-layer growth. Without IEP, 3D islands form on the film. They reach a height of 7 layers after deposition of 1 layer of material.



COLOR PLATE 4. Kinetic Monte Carlo simulations of heteroepitaxial surfactant-mediated growth in the DDP model, on a substrate of size 300×300 with IEP. The activation energies were $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. A total of 1 monolayer of new material has been deposited at (a) 300°C , (b) 350°C , (c) 400°C and (d) 450°C . The transition between layer-by-layer growth and 3D island growth takes place somewhere between 350°C and 400°C .



COLOR PLATE 5. Kinetic Monte-Carlo simulations of heteroepitaxial surfactant-mediated growth in the DDP model, on a vicinal substrate of size 300×300 with IEP. The activation energies were $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. A total of 1 monolayer of new material has been deposited at (a) 300°C, (b) 350°C, (c) 400°C, and (d) 450°C. The different colors indicate surface heights.

9. ISLAND-EDGE PASSIVATION

At this stage, it is tempting to claim that we have reached a much better understanding of the surfactant effect. However, we show next that this is not so. In fact, a more careful analysis shows that suppression of diffusion has nothing to do with the explanation of the surfactant effect, and that two surfactants, which lead to the same value of D_{eff} , may induce very different growth modes. This happens because different surfactants may vary drastically in their ability to passivate steps or island edges. We will see that the issue of island-edge passivation is crucially important to the morphology of the growing film and its surface. It is especially important for the ability of the surfactant to suppress 3D islanding in heteroepitaxy.

To understand the role of island edges in the determination of growth modes, we have to understand the reason for the formation of 3D islands in heteroepitaxial growth. The islands form because their presence facilitates strain relaxation much more efficiently than do flat layers. For example, Tersoff and Tromp²⁰⁶ calculated the elastic energy per unit volume, E_{el} , of a strained rectangular island of lateral dimensions s and t (measured in units of the lattice constant). They showed that

$$E_{el} \sim \left(\frac{\ln s}{s} + \frac{\ln t}{t} \right). \quad (4.2)$$

The energy of a narrow island is thus smaller than the energy of a wide one. Therefore, after a monolayer-high island has grown beyond a certain width, it is beneficial to grow another layer on top of it rather than to make it wider. The film then tends to grow in narrow and fairly tall 3D islands. The kinetic process that prevents the island from continuing to grow laterally is the detachment of atoms from the island edges. If such detachment processes are suppressed, the island will not reach its equilibrium shape, but will tend to be too wide and flat. It is quite obvious that surfactants that passivate island edges also suppress detachment events. Hence, they may change the growth mode from 3D islanding to layer by layer. Suppression of diffusion may not be sufficient to suppress 3D islanding, since detachment of atoms from island edges may lead to islanding even with very little diffusion. Passivation of island edges, on the other hand, can change the growth mode even if diffusion is not enhanced.

We now use our knowledge of the chemical nature of different surfactants to speculate about their ability to passivate island edges: Group-V atoms

²⁰⁶ J. Tersoff and R. M. Tromp, *Phys. Rev. Lett.* **70**, 2782 (1993).

(especially As and Sb) should be effective in passivating steps and island edges on the (111) and (100) surfaces of tetravalent semiconductors such as Si and Ge. This is because group-V atoms prefer to have threefold coordination, in which they form three strong covalent bonds with their neighbors, using three of their valence electrons while the other two valence electrons remain in a low-energy lone-pair state. This is precisely what is needed for passivation of both terrace and step geometries on the (111) and (100) surfaces of the diamond lattice which are characterized by threefold coordinated atoms. On the other hand, it is expected that elements with the same valence as that of the substrate, or noble metals, will not be effective in passivating step edges. In the case of the tetravalent semiconductors Si and Ge, for example, the elements Sn and Pb have the same valence, and while they can form full passivating layers on top of the substrate, they clearly cannot passivate the step geometries because they have exactly the same valence as that of the substrate atoms and hence can only form similar structures. Analogously, certain noble metals can form a passivating monolayer on the semiconductor surface, but their lack of strong covalent bonding cannot affect the step structure. We note that not all noble metals behave in a similar manner; some of them form complex structures in which they intermix with the surface atoms of the substrate (such as Ag on the Si(111) surface), in which case it is doubtful that they will exhibit good surfactant behavior.

10. KINETIC MONTE-CARLO SIMULATIONS

We have given a plausibility argument that surfactants suppress 3D islanding in heteroepitaxy by limiting atom detachment from island edges, not by suppressing diffusion. The complexity of the growth process does not allow us to give a more rigorous argument. However, our ansatz can be tested quite easily by carrying out kinetic Monte-Carlo (KMC) simulations of homoepitaxial and heteroepitaxial growth, in which all the relevant microscopic processes occur randomly with rates determined by the corresponding activation energies. Accordingly, we consider a system in which the processes examined above are operative and the activation energies corresponding to them are the ones obtained from the DFT/LDA calculations for the hypothetical cases illustrated in Fig. 2 and Fig. 3.

For simplicity, our simulation was carried out on a cubic lattice. Atoms land on the surfactant-covered surface with a flux of 0.3 layers/second (a typical value of the flux in experiments) and diffuse on top of the surfactant. They can exchange with surfactant atoms and become buried underneath the surfactant layer. A buried atom can de-exchange with a surfactant atom

and float on top of the surfactant layer again. This can happen provided the buried atom does not have lateral bonds with other atoms underneath the surfactant layer. If it is bonded laterally, we consider this atom as part of an island edge. An atom attached to an island underneath the surfactant layer can detach from the island edge and float on top of the surfactant layer. This detachment process is of major importance, as discussed above; however, it involves the breaking of lateral bonds between the detaching atom and the island edge, and this will be taken into account in the activation barrier for detachment. Also, we did not allow simultaneous breaking of two or more lateral bonds, so an atom attached to an island edge by more than a single lateral bond cannot detach. A diffusing atom can attach to a step or an island edge. The activation barriers for attachment and detachment processes depend on whether or not the surfactant passivates steps and island edges. Barriers for detachment from an island edge also depend on whether or not the island is strained.

We now describe the results of the simulations we did under various conditions. In each case we give a detailed list of the activation energy values. First, we studied homoepitaxial growth; that is, we considered a system without lattice mismatch and hence no strain effects. To investigate the influence of island-edge passivation (IEP) on surface morphology, we carried out KMC simulations of a surface of size 100×100 at a temperature of 600°C , and deposited on it 0.15 of a layer. The values of the activation energies used were $E_d = 0.5 \text{ eV}$, $E_{ex} = 0.8 \text{ eV}$, and $E_{de-ex} = 1.6 \text{ eV}$. The energy barrier for detachment from an island edge (provided only one lateral bond is broken) was $E_{det} = 3 \text{ eV}$ for a surfactant that passivates island-edges and $E_{det} = 1.6 \text{ eV}$ for a surfactant that does not. Typical morphologies are shown in Fig. 4(a) with IEP and Fig. 4(b) without IEP. Evidently, there is a marked difference between the growth process with and without IEP. First, surfactants that passivate island edges lead to a significantly higher island density in submonolayer growth. Second, with IEP the island edges are very rough, while without it the islands are faceted. As discussed above, experimental results indicate²⁵ that surfactants that suppress 3D islanding also increase the island density in homoepitaxy. The rough island edges are also observed experimentally. This gives strong support to the IEP ansatz. We note that the high density of islands induced by surfactants that passivate island edges is not a result of suppression of diffusion. Rather, it arises from the fact that adatoms can cross passivated island edges without attaching to them and then nucleate on a flat part of the surface, thus generating more islands.

In Figs. 4(c) and 4(d) we present results from similar simulations with another set of activation barriers: $E_d = 0.5 \text{ eV}$, $E_{ex} = 0.3 \text{ eV}$, $E_{de-ex} = 1.1 \text{ eV}$, $E_{det} = 2.5$ with IEP, and $E_{det} = 1.6$ without IEP. Although these barriers are

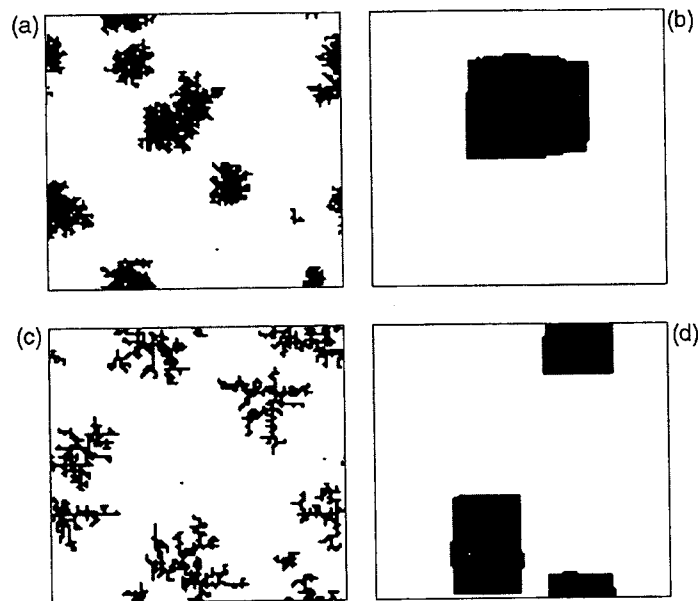


FIG. 4. Kinetic Monte-Carlo simulations of surfactant-mediated homoepitaxy in the DDP model, on a substrate of size 100×100 at a temperature of 600°C . A total of 0.15 monolayer of new material has been deposited. (a) Simulations with IEP, with the activation energies $E_d = 0.5 \text{ eV}$, $E_{ex} = 0.8 \text{ eV}$, $E_{de-ex} = 1.6 \text{ eV}$, and $E_{det} = 3 \text{ eV}$. (b) Simulations without IEP, with the activation energies $E_d = 0.5 \text{ eV}$, $E_{ex} = 0.8 \text{ eV}$, $E_{de-ex} = 1.6 \text{ eV}$, and $E_{det} = 1.6 \text{ eV}$. (c) Simulations with IEP, with the activation energies $E_d = 0.5 \text{ eV}$, $E_{ex} = 0.3 \text{ eV}$, $E_{de-ex} = 1.1 \text{ eV}$, and $E_{det} = 2.5 \text{ eV}$. (d) Simulations without IEP, with the activation energies $E_d = 0.5 \text{ eV}$, $E_{ex} = 0.3 \text{ eV}$, $E_{de-ex} = 1.1 \text{ eV}$, and $E_{det} = 1.6 \text{ eV}$. IEP clearly increases the island density and significantly affects the island shape. (See also color Plate 1.)

very different from the ones we used to produce Figs. 4(a) and 4(b), the morphologies are very similar. The change in the energy barriers has not influenced the island densities, nor has it affected the shape of the islands significantly. The only noticeable effect is that the shape of the islands in Fig. 4(c) is more fractal-like than that of the ones in Fig. 4(d). Note that in the first set of energy barriers $E_d < E_{ex}$, whereas in the second set the opposite holds. Thus, the relation between E_d and E_{ex} does not have a significant influence on the growth morphology. Based on these results, we expect the energy barriers we calculated using DFT/LDA and those of Schroeder *et al.* (see above) to lead to similar growth morphologies; that is, the difference between these two sets of activation barriers is irrelevant for the determination of the growth mode. The results of Fig. 4 support our generalized diffusion analysis. The two sets of energy barriers we used give the same

value for the effective diffusion constant, D_{eff} , according to Eq. (4.1). This is the reason the final surface morphologies are so similar.

It is also important to check the temperature dependence of the growth process in the case of surfactants with IEP. To this end we performed KMC simulations of a 300×300 lattice with activation energies identical to the ones used for Fig. 4(a). The resulting surface morphologies after deposition of 0.15 of a layer are shown in Fig. 5 for three different temperatures: 600°C ,

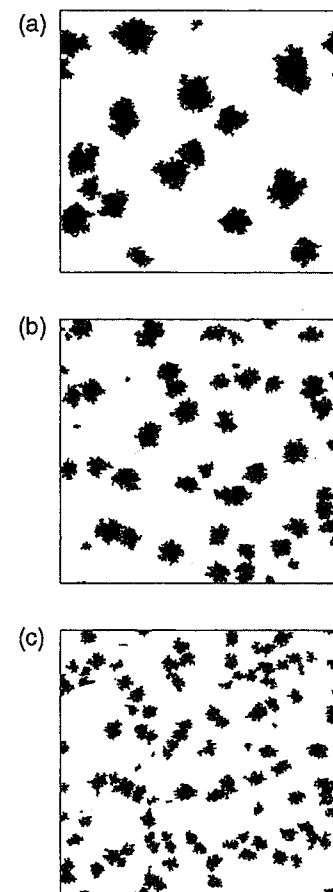


FIG. 5. Kinetic Monte-Carlo simulations of homoepitaxial surfactant-mediated growth in the DDP model, with IEP on a substrate of size 300×300 . The activation energies were $E_d = 0.5 \text{ eV}$, $E_{ex} = 0.8 \text{ eV}$, $E_{de-ex} = 1.6 \text{ eV}$, and $E_{det} = 3 \text{ eV}$. A total of 0.15 monolayer of new material has been deposited at (a) 600°C , (b) 700°C , and (c) 850°C . The high density of small islands at low temperature is evident, as well as the decrease of the island density with increasing temperature. (See also color Plate 2.)

700°C, and 850°C. At all three temperatures IEP leads to a high density of compact islands with rough edges. The island density decreases with temperature. All of these observations are consistent with experimental results.²⁵

Finally, we consider the effects of strain in surfactant-mediated heteroepitaxial growth. Strain is difficult to include in an atomistic calculation self-consistently. Here we will rely on the theory developed by Tersoff and Tromp²⁰⁷ for the elastic energy of strained islands on a substrate (see Eq. (4.2)). In analogy with this theory, we postulate that the effect of strain is to alter the strength of the bonds in elastically strained islands according to the expression of Eq. (4.2), which depends on the island size through the values of s and t . The most important consequence of this effect is a change in the activation energy for detachment of atoms from island edges, E_{det} , since this process involves the breaking of a lateral bond that is strongly affected by strain. E_{det} will now depend on the island size. The other barriers, having to do with processes that take place on top of the surfactant (diffusion and exchange on terraces and island edges), will be unaffected to the lowest order by the presence of strain. Therefore, the only important change in the kinetics comes from an island-size-dependent detachment rate, given by

$$E_{det} = \varepsilon_0 + \varepsilon_1 \left(\frac{\ln s}{s} + \frac{\ln t}{t} \right), \quad (4.3)$$

where $\varepsilon_0 = E_{de-ex}$ for surfactants that passivate island edges, and $\varepsilon_0 = 0$ when there is no IEP.

In our simulations we took the value $\varepsilon_1 = 3.0$ eV, which is a reasonable number for the typical strength of bonds and the amount of strain involved in the systems of interest (4% for the case of Ge on Si). As was done in the case of homoepitaxial growth, we first studied the effects of passivation of island edges on surface morphology. We simulated a system of size 100×100 at a temperature of 300°C, and deposited on it one layer. The values of the activation energies used were $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. The results are shown in Figs. 6(a) and 6(b) for the cases with and without IEP, respectively. Different surface heights are represented by different colors; white is the initially flat substrate. The system without IEP shows clear 3D islanding (Fig. 6(b)). Most of the substrate is exposed even after deposition of a full layer, and the deposited material is assembled in faceted tall islands (up to seven layers high). The surfactant that passivates island edges, on the other hand, suppresses 3D islanding completely (Fig. 6(a)). Most of the surface is covered by one layer (blue), with some small one-layer-high islands and holes in it.

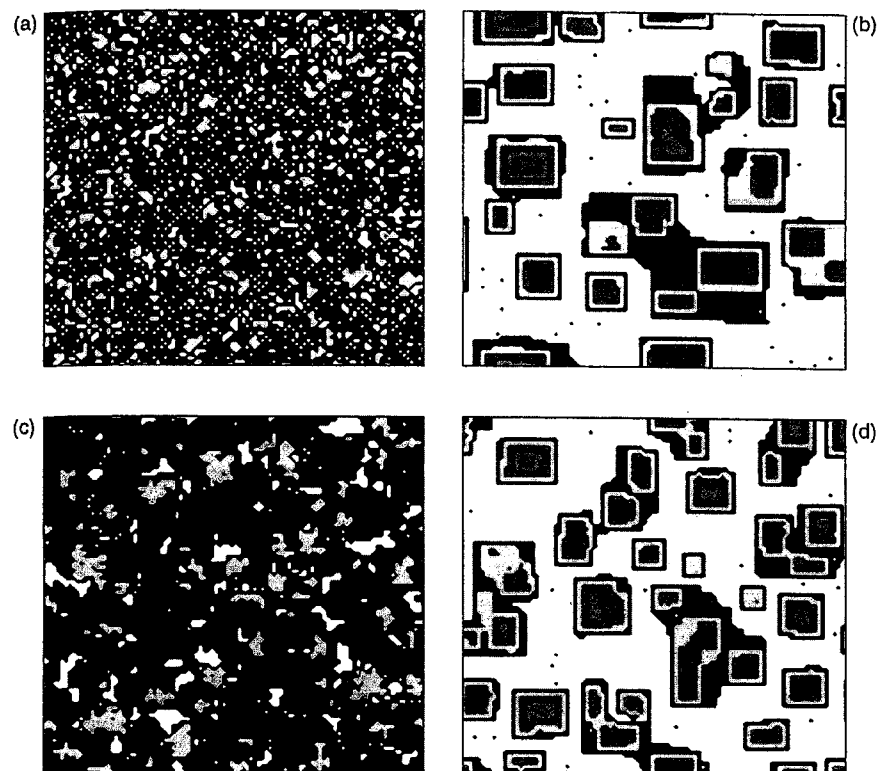


FIG. 6. Kinetic Monte-Carlo simulations of surfactant-mediated heteroepitaxy in the DDP model, on a substrate of size 100×100 at a temperature of 300°C. A total of 1 monolayer of new material has been deposited. (a) Simulations with IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. (b) Simulations without IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. (c) Simulations with IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.3$ eV, and $E_{de-ex} = 1.1$ eV. (d) Simulations without IEP, with the activation energies $E_d = 0.5$ eV, $E_{ex} = 0.3$ eV, and $E_{de-ex} = 1.1$. Different colors indicate different surface heights. The surfactant that passivates island edges suppresses 3D islanding completely and induces layer-by-layer growth. Without IEP, 3D islands form on the film. They reach a height of 7 layers after deposition of 1 layer of material. (See also color Plate 3.)

We also checked the influence of changes in the values of the activation barriers, by repeating the simulations with $E_d = 0.5$ eV, $E_{ex} = 0.3$ eV, and $E_{de-ex} = 1.1$ eV. The results are presented in Figs. 6(c) and 6(d) for the cases with and without IEP, respectively. The system without IEP does not show any change. In the case with IEP the densities of islands and holes decreased and their sizes increased accordingly, but the growth mode remained layer

by layer and 3D islanding was entirely suppressed. These results, together with the results on homoepitaxy, demonstrate convincingly that island-edge passivation, and not suppression of diffusion, is responsible for the surfactant effect.

To study the effect of temperature on the growth mode in heteroepitaxial growth with IEP, we simulated a system of size 300×300 , with the activation barriers $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. The resulting morphologies at temperatures of 300°C, 350°C, 400°C, and 450°C are shown in Fig. 7. In the first two cases, growth is essentially indistinguish-

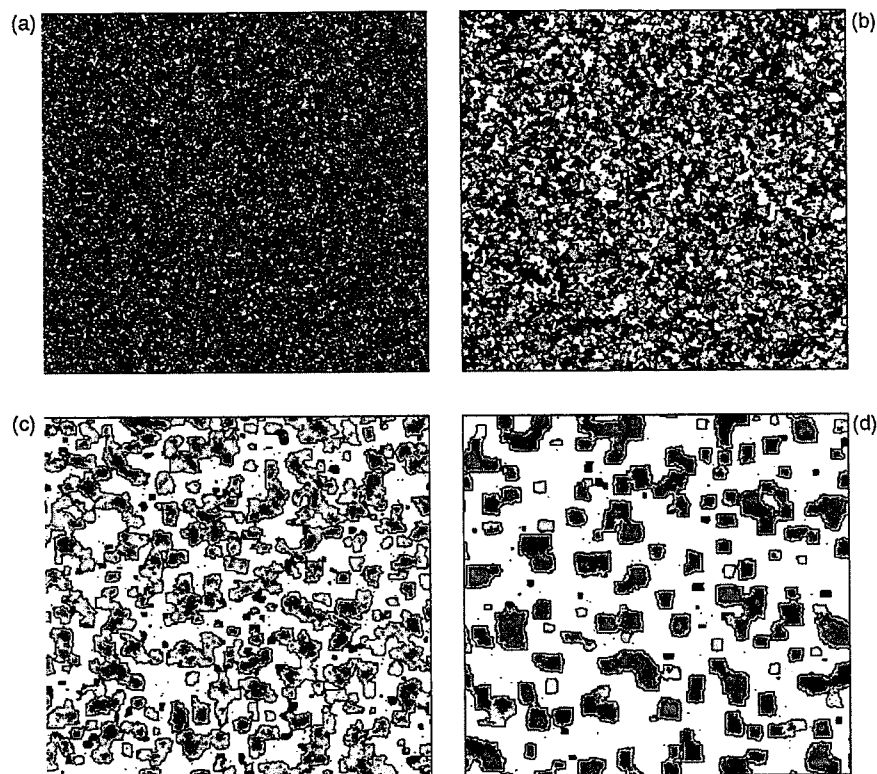


FIG. 7. Kinetic Monte-Carlo simulations of heteroepitaxial surfactant-mediated growth in the DDP model, on a substrate of size 300×300 with IEP. The activation energies were $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. A total of 1 monolayer of new material has been deposited at (a) 300°C, (b) 350°C, (c) 400°C, and (d) 450°C. The different colors indicate surface heights. The transition between layer-by-layer growth and 3D island growth takes place somewhere between 350°C and 400°C. (See also color Plate 4.)

able from the case of homoepitaxy, with a high density of small islands. However, at $T = 400^\circ\text{C}$, despite the small rise of only 50°C , a dramatically different growth mode is evident, with a large number of tall 3D islands and a substantial amount of the substrate left uncovered. This trend is even more evident at the higher temperature of 450°C . We also carried out simulations of heteroepitaxial growth on vicinal surfaces, with exactly the same parameters as those of Fig. 7, but we started from a system with atomic steps present on the substrate. Fig. 8 shows the results of these KMC simulations for the same temperatures as in Fig. 7. Again, the surfactant suppressed 3D islanding at low temperatures but not at high temperatures. This is precisely the type of abrupt transition from layer-by-layer growth at low temperature

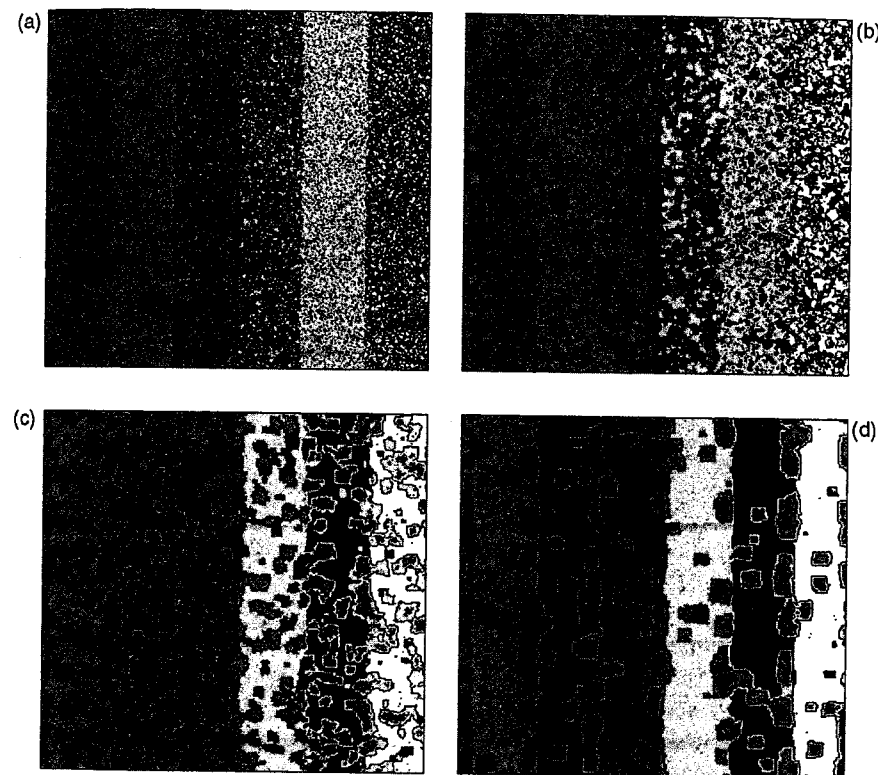


FIG. 8. Kinetic Monte-Carlo simulations of heteroepitaxial surfactant-mediated growth in the DDP model, on a vicinal substrate of size 300×300 with IEP. The activation energies were $E_d = 0.5$ eV, $E_{ex} = 0.8$ eV, and $E_{de-ex} = 1.6$ eV. A total of 1 monolayer of new material has been deposited at (a) 300°C, (b) 350°C, (c) 400°C, and (d) 450°C. The different colors indicate surface heights. (See also color Plate 5.)

to 3D island growth at higher temperature observed experimentally for the strained heteroepitaxial systems, such as Ge/Si with Sb as a surfactant.

V. Discussion

We have provided a critical review of the literature on surfactant-mediated semiconductor epitaxy, with an emphasis on comparisons between experimental observations and model calculations. Our main goal has been to arrive at a consistent explanation of the mechanism by which surfactants suppress 3D islanding in heteroepitaxial growth.

A vast number of experimental articles on the subject exist, and we have gathered most of them in tables according to the relevant combination of deposit-surfactant-substrate materials. The most important message, to be taken from these experimental studies is that in semiconductor epitaxy surfactants can be divided into two categories: the first category is surfactants that lead to an anomalously high island density in submonolayer homoepitaxy and also suppress 3D islanding in heteroepitaxy; the second category is surfactants that lead to step flow growth in homoepitaxy and are inefficient in suppressing 3D islanding in heteroepitaxy.

Explanations of the surfactant effect have focused on the relation between the activation energy for adatom diffusion on top of the surfactant layer and the barrier for exchange of an adatom with a surfactant atom. The rationale was that surfactants of the first category suppress 3D islanding and increase island density because they suppress diffusion. Suppression of diffusion was associated with relatively easy exchange processes. Surfactants of the second category, on the other hand, were thought to enhance diffusion, and exchange processes were expected to be relatively difficult.

Several first-principles calculations of the diffusion and exchange barriers have been carried out for various systems. In a typical calculation, specific paths for diffusion and exchange were proposed and total energies of the system in relaxed configurations along these paths were calculated. This allows fairly accurate estimates of the relevant energy barriers. Different studies arrived at different conclusions about the barriers mainly because the paths proposed were different. Thus, the main deficiency of these microscopic calculations is their inability to predict the correct kinetic path for the process under consideration.

We propose a new scenario for the explanation of the surfactant effect. According to our ansatz, neither the relation between diffusion and exchange nor the suppression of diffusion is relevant for the explanation of the surfactant effect. Instead, we argue that the efficiency of a surfactant is determined by its ability to passivate island edges. Surfactants that passivate

island edges also lead to an anomalously high density of islands and suppress 3D islanding. We supply ample evidence for this scenario. The most convincing evidence comes from kinetic Monte-Carlo simulations of the growth process and from the comparison of the results with experimental observations. Using realistic activation energies we show that a surfactant that suppresses diffusion, but does not passivate island edges, does not suppress 3D islanding. It also does not lead to a very high density of islands. Moreover, the islands generated in the growth process mediated by such a surfactant are faceted and do not have the rough edges observed in experiments. By contrast, island-edge passivation does lead to suppression of 3D islanding and to islands of a shape consistent with the experimentally observed shape. The temperature dependence of the island density, as well as the abrupt transition from layer-by-layer to 3D growth as the temperature is raised, is predicted correctly by simulations with IEP.

The evidence we provide for the validity of our scenario, although convincing, is far from a rigorous proof. In fact, it is based on a very simplified model that fails to take into account various aspects of the experimental system that may be important. For example, the use of an isotropic square lattice is not appropriate for all cases (the substrates with diamond lattice and (111) orientation have a hexagonal surface lattice, whereas those with (100) orientation have a square lattice but exhibit strong anisotropy in the directions parallel and perpendicular to the surface dimers). Nor do we account for the fact that in some cases the film grows in bilayers (as in (111) substrates) rather than in monolayers (as in (100) substrates). Finally, we do not properly treat the issue of critical island size, which may be very large in Si homoepitaxy or in heteroepitaxy of Ge on Si. For these reasons there is room for further discussion and more detailed modeling of surfactant-mediated thin-film growth.

There are various unresolved issues in surfactant-mediated epitaxial growth, which we have not discussed. Perhaps the most important is the issue of strain relaxation. Heteroepitaxial films grown in the layer-by-layer growth mode are initially highly strained and this strain energy must somehow relax after growth of a few layers. Indeed, dislocations appear in the film during surfactant-mediated heteroepitaxy. In some cases these dislocations do not thread the film and hence do not harm its epitaxial quality, but in other cases they do. It is therefore very important to study strain relaxation in the films. Some experimental studies have been carried out, but their description is beyond the scope of the present article. To the best of our knowledge, there has not been any detailed theoretical work on the problem.

Another important issue is that some of the surfactant layer inevitably becomes trapped in the growing film. This leads to unintended doping if the

surfactant is not isoelectronic with the deposited material. This could be beneficial if high levels of doping are desired, or detrimental if a film of high purity is desired. In any case, controlling the amount of the incorporated surfactant by carefully adjusting external conditions (such as flux rate, temperature, and surface preparation) is highly desirable.²⁰⁷ A better understanding of the surfactant effect, along the lines proposed here for the DDP model, will probably go a long way toward controlling the electronic properties of the film, which are strongly influenced by surfactant incorporation, strain relaxation defects, and surface morphology. Further research in these directions is necessary and essential before surfactant-mediated growth can become useful in practical applications.

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²⁰⁷ M.-H. Xie, J. Zhang, A. Lees, J. M. Fernandez, and B. A. Joyce, *Surf. Sci.* **367**, 231 (1996).