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## TOPICAL REVIEW

# Surfactant-mediated growth of semiconductor materials

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## Abstract

During epitaxial growth of semiconducting materials using either molecular beam epitaxy or organometallic vapour deposition, the addition of a surfactant can enhance two-dimensional layer-by-layer growth. This modified growth process is now called the surfactant-mediated growth (SMG) method. It has had an important impact on the development of technologically important materials in device applications, such as heterostructures used for laser applications. Recent developments that use surfactants to improve doping profiles in semiconducting systems and antisurfactants (ASMG) to grow quantum dots further ensure that SMG/ASMG will play a major role in the future development of optoelectronic materials and nanoparticles. In this paper, we review important earlier experimental work involving the SMG method as well as some recent developments. Theoretical work involving first-principles methods and kinetic Monte Carlo simulations are discussed but confined only to the surfactant effect.

## 1. Introduction

Since the first success of growing superlattices by Esaki's group at IBM [1], epitaxial growth methods, such as molecular beam epitaxy (MBE) [2] and organometallic vapour deposition (OMVD) [3], have been developed for growing layered samples. These samples can be either metals or semiconductors. In this review, we shall confine our focus to the growth of semiconductors. These epitaxial growth methods always start with a semiconducting substrate. Adatoms, which can be either the same species as the substrate or a different one, are then deposited on top of the substrate. If the adatoms are different from the substrate, the sample is called a heterostructure. A typical example of a heterostructure is germanium (Ge) grown on a silicon (Si) substrate [4]. On the other hand, if both adatoms and substrate are the same species then growth of a pure sample will occur. Growth of gallium arsenide (GaAs) on a GaAs substrate ([5] and references therein) is a typical example.

Experimentally, three different types of epitaxial growth have been observed. If the growth maintains the two-dimensional (2D) form, this results in a layer-by-layer growth mode or the Frank–van der Merwe (F–M) mode (see, e.g. [6]). However, because of either the lattice constant mismatch between the substrate and the adspecies or the presence of defects such as vacancies and dislocations, three-dimensional (3D) growth, i.e. the formation of islands, will appear. If a wetting layer exists on top of the substrate before islands are formed, it is called the Stranski–Krastanov (S–K) mode [7]. If islands are formed directly on the substrate, this is the Volmer–Weber (V–W) mode [8]. In general, any growth modes should involve both equilibrium and nonequilibrium processes. If a steady state is considered, a *simple-minded* argument about which mode is dominant during the growth is based on the energetics associated with the growth process. In particular, there are three important surface energies: (1) the surface free energy of the substrate,  $E_s$ ; (2) the interface free energy,  $E_i$ ; and (3) the surface energy of the heteroepitaxial layer,  $E_h$ . The interface free energy,  $E_i$ , is the strain energy induced by the lattice mismatch between the substrate and the heteroepitaxial layer. The mode of growth depends upon the competition among these three free energies. If the growth layer thickness is less than some critical thickness, then  $E_s$  is dominant and the F–M mode is favoured. For large lattice mismatch and thicker growth layers,  $E_h$  controls the growth mode and the V–W mode will subsequently ensue. If the substrate is wetted and there is a strain between the substrate and the wetting layer, then  $E_i$  is most important and the S–K mode governs the growth process. Depending on the growth requirements, the issue of controlling one mode over the other has been impugned by experimental groups. For quality device applications that require materials to be grown epitaxially, the F–M mode is definitely favoured. Consequently, this requirement has led to the development of the surfactant-mediated growth (SMG) method.

Among the artificial semiconducting materials, the idea of growing Ge on top of Si to form Ge/Si heterostructures has attracted much of the attention because it was anticipated that these materials could be integrated into the existing Si-based technology, which has led to many experimental efforts devoted to growing Ge/Si superlattices and heterostructures in the late 1980s. Ideally, it is desirable to sustain the two-dimensional (2D) growth process so that perfect superlattices or heterostructures can be fabricated. However, it was found that at most six layers of Ge can be grown on top of the Si(001) surface before the sample exhibits islands or other defects, such as dislocations [9]. The reason is that there is a 4% lattice constant mismatch between the growing species (Ge) and the substrate (Si). Thus, islands are formed on the surface and interrupt the ideal layer-by-layer growth. In 1989, Copel *et al* [4] were the first to demonstrate the use of an additional species, such as arsenic (As), covering the surface before depositing Ge atoms. They found that the thickness of the 2D Ge layer could be increased by a factor of two without exhibiting the formation of islands or dislocations. The F–M growth mode of Ge on Si(001) is then significantly enhanced due to the additional species now called a surfactant. It drastically affects the epitaxial growth process of Ge on Si. Therefore, a new scheme to improve 2D growth, at least for homopolar materials, has been discovered. The SMG method has been further extended to the growth of pure samples and heterostructures made of III–V and II–VI semiconductors. Typical examples are GaAs/cadmium telluride (CdTe) [10], GaAs/zinc telluride (ZnTe) [11] heterostructures and GaAs pure samples [5, 12]. More recently, this method has been used to improve doping profiles in semiconducting systems [13].

The idea of using a surfactant has not been restricted to sustaining the F–M growth mode. Because of the tremendous potential of using quantum dots in information storage, fabrication of light sources, and various medical applications, the growth of quantum dots has attracted much attention recently. Quantum dots with sizes in the nanometer scale are of particular interest and have become the backbone for the development of today's cutting-edge nanotechnology. In order to expedite the formation of quantum dots, a third species

called an antisurfactant is also introduced on the substrate. The function of this antisurfactant is in contrast to the SMG in the sense that it encourages the V–W growth mode to happen sooner. Several experimental groups [14, 15] have utilized this so-called antisurfactant-mediated growth (ASMG) process to grow quantum dots.

These two growth methods are expected to play essential roles for the development of future semiconductor technologies. Therefore, we shall review the characteristics of experimental features in SMG and ASMG in section 2. In addition, we have included discussions about the possible mechanism or mechanisms of SMG and ASMG based on experimental measurements. Theoretical efforts towards an understanding of the microscopic mechanism or mechanisms in SMG will be reviewed in section 3. In section 4, we shall conclude with discussions on the prospects of SMG and ASMG methods.

## 2. Experimental work and the unique feature of surfactant-mediated growths

In this section, we shall briefly describe the experiments that use SMG method to grow not only Ge/Si heterostructures on two different Si surfaces, but also GaAs homoepitaxy samples. In addition, we shall mention another recent application that improves the doping profiles in semiconducting systems. The description of the ASMG method will follow.

### 2.1. Surfactant-mediated growth

**2.1.1. Ge on Si(001).** As we mentioned earlier, Copel *et al* [4] were the first to demonstrate the effect of the surfactant by using As to enhance the 2D growth of Ge on Si(001). Without the surfactant, the growth is known to be restricted to at most six monolayers (ML) without showing any 3D islands or other defects (such as dislocations) [9]. As the Ge coverage increased, these authors used transmission electron microscopy (TEM) to confirm the presence of 100 Å thick Ge islands. The growth mode was identified as the S–K mode. However, with a constant flux of As atoms, the Ge film can be grown to 15 ML thick. By using core level photoemission spectroscopy, they found that intensities of the  $2p_{1/2}$  and  $2p_{3/2}$  lines associated with As atoms do not diminish as the layer thickness increases. They therefore concluded that As atoms were always migrating to the growth front and they did not form any alloy or other compounds with host atoms.

Many other elements have also been used as surfactants for growing the Ge/Si heterostructures. An excellent list of different surfactants has recently been given by Kandel and Kaxiras [16], and more recent work using Sb was performed by Power *et al* [17].

**2.1.2. Ge on Si(111).** In 1999, Tsong [18] and his collaborators investigated the growth of Ge on the Si(111) surface with lead (Pb) serving as the proposed surfactant. The experiment was done at room temperature in an ultra-high vacuum chamber. The authors used scanning tunnelling microscopy (STM) to examine the surface morphology. Before the deposition of Ge atoms, they prepared a  $1 \times 1$  Pb/Si(111) surface that was unreconstructed with each Si atom at the top of the substrate terminated by a Pb atom. When the Ge atoms were deposited, they found that these atoms do not attach to the step edges of the Si substrate. Instead, 2D Ge islands were formed. To find out how the 2D Ge islands are nucleated, further experiments were carried out [19]. With the flux kept at  $(1/28)$  bilayer (BL)  $\text{min}^{-1}$ , they found no Ge island formed if the deposition time,  $t_d$ , was less than 4 min. This is equivalent to a critical coverage,  $\Theta_c$ , of 0.14 ML. When  $t_d$  was equal to 4 min, nucleation of ramified large 2D Ge islands was observed. The height of the island was about 3.2 Å, which is equal to the BL step height of the substrate. Because no corrugation was observed on top of the islands and because they could resolve a  $1 \times 1$  structure with a good tip, they concluded that Pb atoms covered 2D

Ge islands. Furthermore, at high temperature (80°C) or low flux (0.003 ML s<sup>-1</sup>), fractal Ge islands were formed. On the other hand, at low temperature (room temperature) and high flux (0.0067 ML s<sup>-1</sup>), compact 2D Ge islands were observed when the coverage reached 1.2 $\Theta_c$ . In addition, they observed that the shape of 2D islands changed with the Ge coverage, deposition flux, and temperature.

*2.1.3. Growing GaAs along the [100] direction.* The application of SMG is not limited to the growth of group IV materials. Massies and Grandjean [5] were the first to extend the SMG method to a III–V semiconductor, GaAs, along the [100] direction. They tried two species, Te and Pb, as surfactants. Only the Te atom, not the Pb atom, acted as an effective surfactant during the epitaxial growth of GaAs.

Throughout the SMG process, they covered the GaAs(100) surface with less than a complete ML (0.6 ML) of Te before switching on the As atomic beam. They determined that the As coverage has to be larger than one ML and the presence of Ga atoms is necessary. The enhanced layer-by-layer growth of GaAs was then determined by comparing the reflection high energy electron diffraction (RHEED) measurements with and without the surfactant. They also found that: (1) Te atoms migrated to the growth front, similar to the behaviour of As atoms in the growth of Ge/Si; and (2) a Te atom was initially bonded to two Ga atoms at the top of the substrate. This position is now called the bridge site.

In summary, from the experiments in which Ge/Si heterostructures and pure GaAs materials are grown, a unique feature in all of SMG methods emerges. That is, the surfactant always migrates to the growth front. They neither form an alloy (a compound) with constituent atoms of the substrate nor are they embedded in the substrate.

*2.1.4. SMG improving doping profiles in semiconducting systems.* Recently, a group at the University of Utah [13] found that SMG could also improve doping profiles. They doped zinc (Zn) in GaAs by using the OMVD method, where Zn atoms can diffuse deep into the sample if antimony, Sb, is utilized as a surfactant. They also found that the presence of Sb, but not Te or phosphorus, P, enhanced the impurity (in this case, indium) concentration. Detailed information about the configurations of the surfactant during the growth and how it functions have not yet been reported.

## 2.2. Antisurfactant-mediated growth

*2.2.1. Growing GaN quantum dots in Al<sub>x</sub>Ga<sub>1-x</sub>As.* As we continue to delve into the regime of nano-technology, the demand for high quality quantum structures has been on the increase. For example, arrays of quantum dots require a consistency in the dot size. In laser applications, epitaxial growth of quantum dots has been plagued by the presence of so-called threading dislocations (TDs). To improve the consistency of quantum dot sizes, Tanaka *et al* [14, 15] have successfully fabricated GaN quantum dots on an Al<sub>x</sub>Ga<sub>1-x</sub>N alloy surface using an antisurfactant. By adding a small amount of Si (3.2 mmol to 32.0 mmol), they found that the GaN growth mode changed from a 2D step-flow mode to a 3D island formation. An image taken from an atomic force microscope revealed the formation of uniform nano-sized (4–5 nm) GaN quantum dots. Furthermore, by using a cross-sectional TEM, they found that the TD density is greatly reduced in the GaN over-layer when Si is used as an antisurfactant.

## 3. Possible mechanisms for surfactant-mediated growth

In this section, we review possible mechanisms proposed by experimental groups based on their observations, even though some of them may be controversial. We discuss them here

in the hope that they can stimulate new approaches to help understand the complex growth processes.

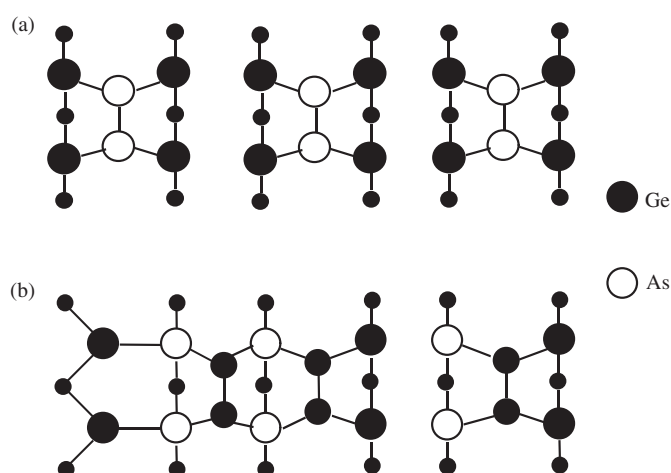
### 3.1. SMG of Ge on Si(100)

Based on their experimental results, Copel *et al* [4] proposed that surfactant atoms lower surface free energetics of both Ga and Si. In this particular case, the As-capped surface leaves no dangling bond due to the extra valence electron per As atom as compared to the case of a Si-terminated surface. To quantify this assertion, a series of first-principles calculations were carried out on Si/Ge/As and Si/As/Ge surfaces. The energy of the Si/Ge/As surface is found to be lower than the Si/As/Ge surface by 0.6 eV per surface dimer. Therefore, they concluded that an As-terminated surface is more favourable such that Ge adatoms on top of the As layer will exchange with As atoms. This induces a large reduction of the diffusion length (or the mobility of Ge atoms), thereby inhibiting the island formation. Later, Tromp and Reuter [20] used low energy electron microscopy (LEEM) to image growth patterns of similar systems with and without a surfactant. They found that the incorporation of Ge atoms on an As-covered Si(100) surface proceeds in a highly local manner, with minimum surface diffusion. Based on this experimental result and the favourable energetics in eliminating dangling bonds, they proposed a microscopic mechanism for the exchange process—the two-dimer correlated exchange mechanism. The process is depicted in figure 1.

Initially, two Ge dimers are located above As dimers. By pushing down and moving to the right with respect to their initial positions, Ge dimers can exchange with As dimers. Later experiments carried out by Boshart *et al* [21] using a scattered MeV ion energy distribution with transmission ion channelling method confirmed that dimers are involved in the exchange mechanism. However, they were skeptical about the above-mentioned exchange model by Tromp and Reuter [20]. Therefore, how the exchange happens remains an issue to be resolved.

### 3.2. SMG of Ge on Si(111)

Chang *et al* [19] proposed an exchange-reaction rate limited mechanism to explain their results of transforming from compact to fractal forms of Ge islands at high temperatures and low



**Figure 1.** The two-dimer correlated exchange mechanism proposed by Copel *et al* [4], where Ge is indicated by open circles and As is represented by filled circles.

flux conditions. This behaviour is distinct from the traditional theory that accounts for the transformation under low temperature and high flux environment. They suggested that the exchange process is between Ge clusters and Pb atoms. The critical size of the Ge cluster is about ten atoms. The involvement of Ge clusters induces a high barrier for the exchange-reaction and thus limits the reaction rate. They, therefore, assumed that the exchange barrier is greater than the diffusion barrier for nucleation and growth of Ge islands. How the exchange process proceeded in reality is not addressed in their study.

### 3.3. SMG of GaAs

When Massies and Grandjean [5] did their experiments of growing GaAs with Te and Pb as surfactants, they interpreted that the surface diffusion length, SDL, of the growing species is modified by the presence of the surfactant. This is a different perception from the energetic point of view adopted by Copel *et al* [4]. A surfactant is reactive if it reduces the SDL. For example, Te is reactive when deposited on GaAs. In contrast, a surfactant that increases the SDL, such as Pb, is called a nonreactive surfactant. Massies and Grandjean also made an interesting suggestion to account for the distinct behaviour of these two types of surfactants. A nonreactive surfactant is located at an interstitial site and forms a surfactant–semiconductor complex through weak bonding with surface atoms. They claim that it is easier to form the surfactant–semiconductor complex at the surface due to the presence of dangling bonds. On the other hand, a reactive surfactant, which is located at the bridge site, forms stronger bonds with the semiconductor than the nonreactive type. The reactive surfactant then exchanges with the growing species by breaking existing bonds and forming new bonds. This process eventually leads to a higher diffusion barrier of the growing species, thus reducing its SDL.

Based on various experimental works on this subject, there are several different views of the role played by a surfactant. Some prefer the view that a surfactant changes the energetics on the surface while others feel that the diffusion process on the surface is being modified to improve the 2D growth mode. Kandel and Kaxiras [16] have tried to unify these different views by suggesting that the 2D growth mode is being enhanced as a consequence of the following reasons. The exchange barrier,  $E_{ex}$ , between a surfactant atom and an adatom of the growing species is less than the diffusion barrier,  $E_{diff}$ , for an adatom on top of the surfactant layer. After the exchange, the adatom is locked (no diffusion occurs). The reduction of the SDL therefore enhances the island density nucleated on the surface. Island coalescence occurs before any second layer islands can be created. Finding a way to determine the exchange barrier,  $E_{ex}$ , from a microscopic point of view has become one of the crucial tasks in the understanding of the role played by a surfactant.

## 4. Possible mechanisms for antisurfactant-mediated growth

To enhance the growth of GaN quantum dots with Si serving as a surfactant, Tanaka *et al* [14] interpreted that Si atoms form new bonds with nitrogen atoms at the top of the substrate. With the Si coverage less than one ML, the Si–N bonds are found to mask the  $Al_xGa_{1-x}N$  surface with one ML thickness. GaN deposition is limited in the nano-masking region because of the low sticking coefficient of GaN precursors. Nanoholes are thus formed and 3D growth of GaN happens in these regions.

Furthermore, the ASMG has been used to terminate TDs [15]. The explanation proposed by Tanaka *et al* [15] is that N atoms are found at step edges and at cores of TDs. Nitrogen dangling bonds can easily form bonds with Si (antisurfactant) atoms. Therefore, the formation of Si–N bonds provides a mechanism to terminate TDs.

## 5. Theoretical efforts to understand the mechanism or mechanisms

We shall confine our discussions to the theoretical efforts towards understanding SMG processes. Not much work has been done on the ASMG method at this point. We shall first mention a macroscopic approach to the growth favoured by many experimentalists even though it has not been applied to SMG or ASMG. Then, we shall present some first-principles studies that are attempting to gain more understanding of the mechanism or mechanisms. Finally, the kinetic Monte Carlo (MC) method will be discussed, but only briefly because [16] gives a detailed account of this.

### 5.1. Energetic approach

We mention this approach because it especially appeals to many experimental groups and has been applied to many epitaxial growth problems. The energetic approach to studying epitaxial growth was initiated at the beginning of the 1990s (see, e.g. [22]). In this particular scheme, the free energy of the system is the most important quantity. Depending on circumstances, the free energy can have different forms. For example, in [14], the free energy of the ASMG process is attributed to three contributions:

$$F = E_s + E_h + E_i, \quad (1)$$

where  $E_s$  is the surface free energy of the substrate,  $E_h$  is the energy of the heteroepitaxial layer or the film, and finally  $E_i$  is the interface free energy. For 3D growth of quantum dots, the following inequality holds:

$$E_s \leq E_h + E_i. \quad (2)$$

Apparently, it is a simple approach to gain a macroscopic insight into the growth processes. Furthermore, it will bring in-depth understanding of such processes if each component can be determined from its microscopic origin. However, such an understanding is very difficult to attain, which is why this approach has not been quantitatively applied to either the SMG or the ASMG methods.

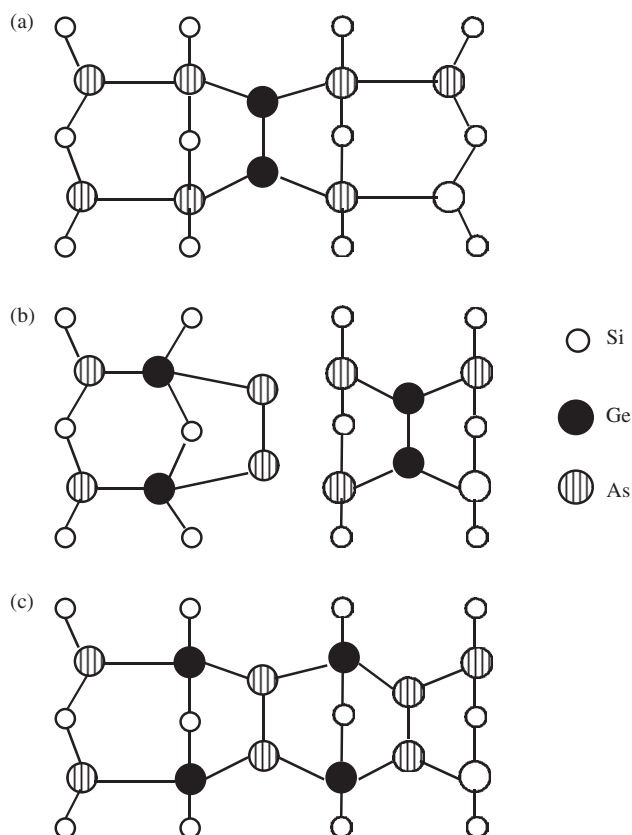
### 5.2. First-principles total energy approach

There have been several first-principles total energy calculations [23–27] relevant to the SMG method. Most of them used the self-consistent pseudopotential method (see, e.g. [28] and references therein) in conjunction with the local density approximation (LDA) [29] within density functional theory (DFT) [30].

**5.2.1. Ge/Si(100).** To understand their experimental results, Copel *et al* [4] reported first-principles calculations of the energetics for different configurations of As, Ge and Si on top of the Si(100) surface. The energy differences between  $\dots\text{Si/Si/Ge}$  and  $\dots\text{Si/Ge/Si}$  or  $\dots\text{Si/Si/Ge/As}$  and  $\dots\text{Si/Ge/Si/As}$ , where ‘ $\dots\text{Si}$ ’ stands for Si multi-layers, are of the order of 0.1 eV. However, the difference is of the order of 0.5 eV for  $\dots\text{Si/Ge/Si/As}$  and  $\dots\text{Si/Ge/As/Si}$  or  $\dots\text{Si/Ge/As}$  and  $\dots\text{Si/As/Ge}$ . Because a full one ML coverage of the top layer was considered to participate in the exchange process, their results do not explain the microscopic process of the exchange. Other calculations to address the microscopic process of the exchange mechanism were performed by Ohno [24] and Ko *et al* [25]. Both groups were concerned about the single site exchange.

The microscopic two-dimer exchange process proposed by Trump and Reuter [20] has stimulated several theoretical calculations [23, 31] and prompted further experimental study of



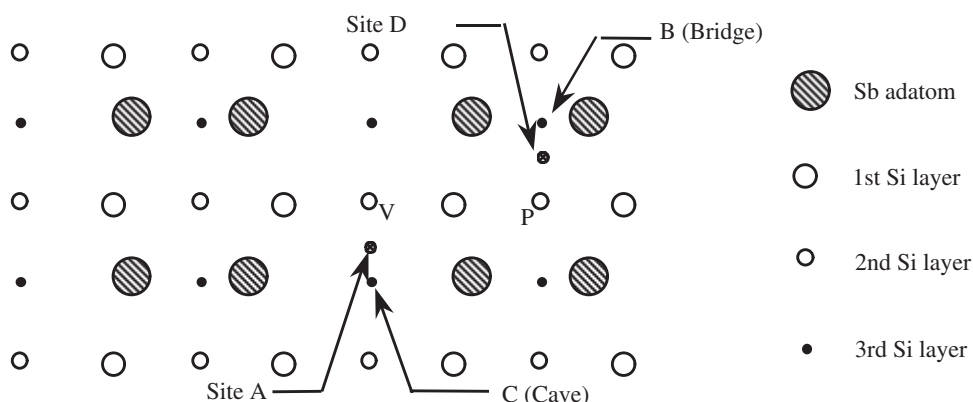


**Figure 2.** A Ge-dimer exchanges with an As-dimer: (a) the initial configuration; (b) the intermediate configuration with an additional Ge dimer on top of As dimers; (c) the final configuration for the exchange of As dimers with Ge atoms.

Sb serving as a surfactant [21]. Based on a simple argument of reducing dangling bonds, Yu and Oshiyama [23] suggested that a single Ge dimer exchanging with an As dimer is energetically more favourable than the two-dimer exchange process. The single-dimer exchange process suggested by Yu and Oshiyama [23] is illustrated in figure 2.

However, the intermediate steps (figures 2(a) and (b)) of the exchange process were not considered in their calculations. This is important because of the bond switching between the lower layer of Si atoms and the As and the Ge dimers. In addition, Boshart *et al* [21] claimed that the initial configuration (figure 2(a)) is not consistent with their data for the low (0.15 ML) and high (0.68 ML) coverages of Ge.

The initial configuration of Sb on the Si(100) surface has also been studied by Jiang *et al* [31], who used the first-principles all electron discrete variational  $X\alpha$  method. Instead of using a slab geometry to model the surface, they used a cluster approach. They started with a cluster of 35 Si atoms, and added 32 hydrogen (H) atoms to saturate any dangling bonds on the surface. Their findings of asymmetric (buckled) Si dimers at the surface were consistent with other first-principles results [32]. Next, they determined the possible single sites for Ge on top of Sb. A cluster with a total of 81 atoms (37 Si atoms, 8 Sb atoms, and 36 H atoms) was used. The Sb adatoms were arranged in the form of dimers. Figure 3 shows the possible Ge sites, and their corresponding energies are summarized in table 1.



**Figure 3.** Possible single Ge sites on top of the Sb covered Si(100) surface. Si is shown as open circles and Sb by large shaded circles.

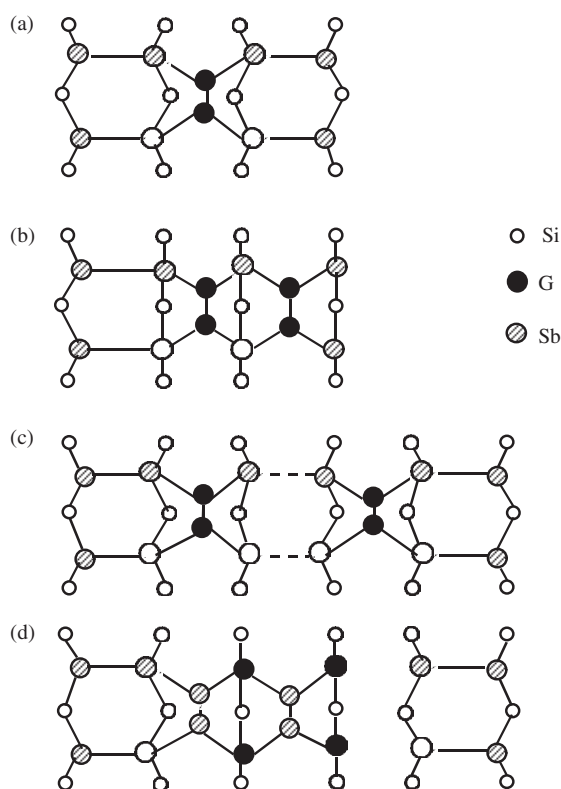
**Table 1.** Relative adsorption energies of Ge at different sites with respect to site A. The Ge adsorption energy at site A is 3.14 eV.

Positions	Relative adsorption energy (eV)
A	0.0
B (bridge site)	0.783
C (cave site)	0.965
D	0.818
P (pedestal site)	0.691
V (valley bridge site)	0.892

Finally, they modelled the low coverage (0.15 ML) and the high coverage (0.68 ML) of Ge. The energetically favoured single Ge dimer site at low coverage is shown in figure 4(a). It is similar to Yu and Oshiyama's model [23], except that Sb atoms remain in the dimer form. This recent result is consistent with the experimental determination of the bond length between two Ge atoms by Boshart *et al* [21]. For high coverage, two Ge dimers are formed and the most favourable initial configuration is shown in figure 4(b). In addition, these authors did examine one of the possible final configurations (figure 4(c)). However, the pathway from the initial to the final configurations is not given in their model.

Kim *et al* [33] used a four layer slab model to characterize the  $4 \times 2$  Si(100) surface and determined that the diffusion barrier of a single Ge atom on one ML of Sb-covered surface is 0.04 eV smaller when parallel to the dimer rows than when perpendicular to the dimer rows. Furthermore, they modelled the experimentally observed  $\{311\}$  facet using a rebonded double layer step. The stepped surface was simulated by a triclinic supercell consisting of 54 Si atoms. H atoms were used to saturate Si dangling bonds at the bottom layer. Using the Car–Parrinello approach [34] to examine the exchange pathway, they found that the dimer exchange process involving the pushing-out and the rolling-over processes gave a larger diffusion barrier ( $\geq 2$  eV) than the dimer surface diffusion barrier (1.1 eV). They, therefore, rejected such an involved exchange process and instead proposed a mechanism utilizing only the pushing-out process between two Ge dimers. This pathway is depicted in figure 5.

The process goes as follows: it starts with a Ge dimer on top of the Sb layer (figure 5(a)). The Ge dimer is then pushed down and to the left. This process involves breaking Ge–Sb bonds and strengthening Sb–Sb weak bonds (figure 5(b)). Subsequently, the two Sb atoms bonded

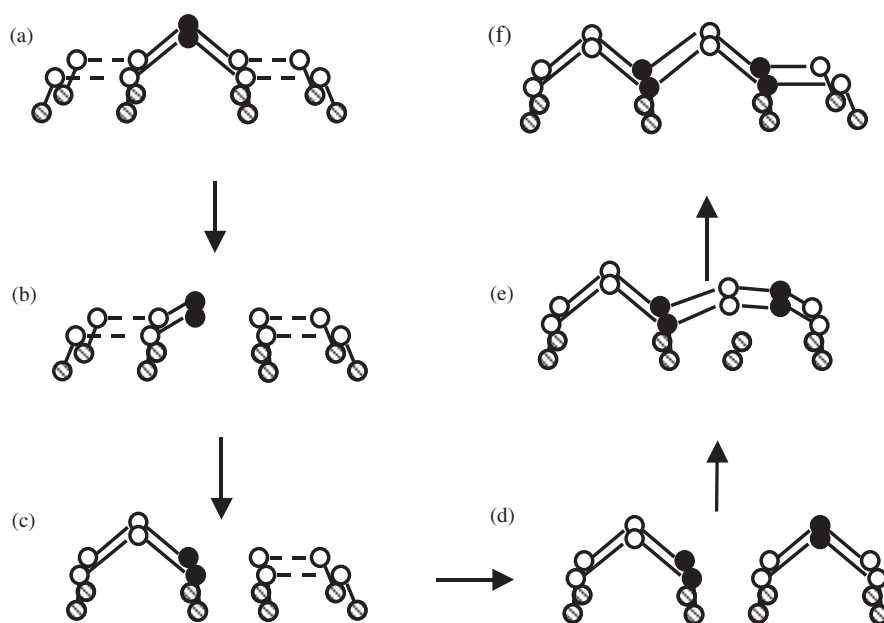


**Figure 4.** The most favourable initial configuration for: (a) a single Ge dimer; and (b) two Ge dimers on top of Sb dimers. Dashed lines indicate weak bonds. (c) Two Ge dimers at the nearest neighbour sites. (d) The configuration after the exchange.

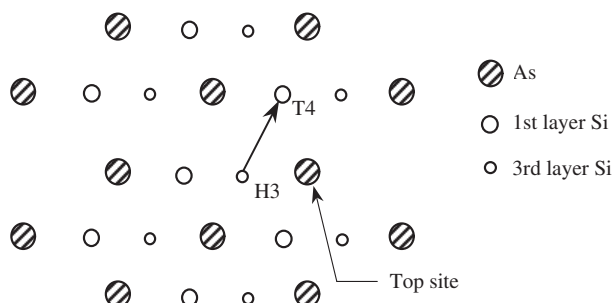
to Ge atoms are pushed out, causing the Sb–Si bond breaking and the Ge–Si bond formation (figure 5(c)). The authors then considered another Ge dimer deposited on top of Sb atoms (figure 5(d)). The newly arrived Ge dimer pushes itself down and causes its left neighbouring Sb atoms to be pushed up. Finally, the two Ge dimers form a layer on top of the Si atoms, which causes Sb atoms to eventually migrate to the top layer (figures 5(e) and (f)). The reliability of this process is still questionable due to the accuracy of the simulations: (1) the calculations were performed with a plane-wave energy cutoff of 8.0 Ry, which may not be enough; (2) the starting configuration is adopted from the one given in [23] which is debatable [21].

**5.2.2. Si/Si(111).** A very nice work concerning Si growth on Si(111) with As serving as the surfactant was given by Schroeder *et al* [27] who used norm-conserved pseudopotentials [35], LDA [29], and plane waves as basis functions. The cutoff energy is 13.69 Ry. This is more than most of the earlier calculations. Their model consists of a full ML of As on top of a Si(111) substrate and a Si adatom.

The energies of three possible Si adatom positions on the As layer were compared (figure 6). The three positions are: on top of an As atom (the top site), on top of the Si located at the first layer of the substrate, T4, and above the Si atom located in the third layer of the substrate, H3. The H3 site was found to have the lowest energy. They then examined the possible diffusion pathway from H3→T4. The Si adatom can move from H3→T4 through a trough in the energy surface that has a barrier height of 0.25 eV. This is smaller than the 0.76 eV



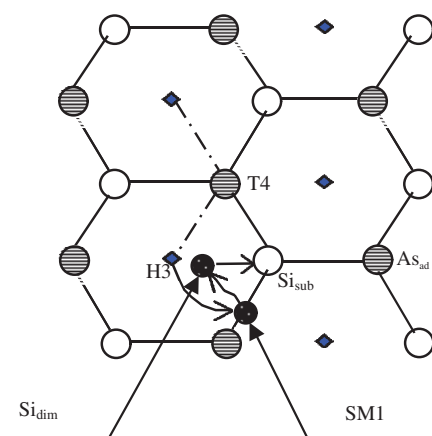
**Figure 5.** The pushing-over process for two Ge dimers. Ge is shown as filled circles, Sb by shaded circles and Si by open circles.



**Figure 6.** Two possible sites for Si on top of the As layer (shaded circles). The line with an arrow indicates the pathway in the trough from H3 to T4.

diffusion barrier on a clean Si(111)  $7 \times 7$  surface. The fact that the H3–T4 barrier height is lower supports the suggestion that surfactant atoms can passivate Si dangling bonds at the top of the surface and therefore lower the diffusion barrier.

Finally, they investigated the exchange process between the Si adatom ( $\text{Si}_{\text{ad}}$ ) at H3 and a nearby As surfactant ( $\text{As}_{\text{sub}}$ ). To determine the pathway for the exchange process,  $\text{Si}_{\text{ad}} + \text{As}_{\text{suf}} \rightarrow \text{Si}_{\text{sub}} + \text{As}_{\text{ad}}$ , they first tried to find an energy minimum along the direct pathway. One local minimum was found for the Si adatom halfway between the initial site, H3, and its final substitution site,  $\text{Si}_{\text{sub}}$ . They called this minimum a ‘dimer’ because the Si adatom forms a dimer with an As atom with the centre of mass close to a T4 site. However, there is a barrier of more than 1.0 eV for the adatom travelling from site H3 to this ‘dimer’ minimum. Therefore, they pursued an alternate pathway involving a side minimum. The exchange goes as follows: the Si adatom at H3 moved first to SM1, a side minimum (figure 7), with an energy barrier of 0.27 eV. At this point, the vertical height of the Si atom decreased



**Figure 7.** A possible exchange path of a Si atom on Si(111) with As serving as a surfactant.

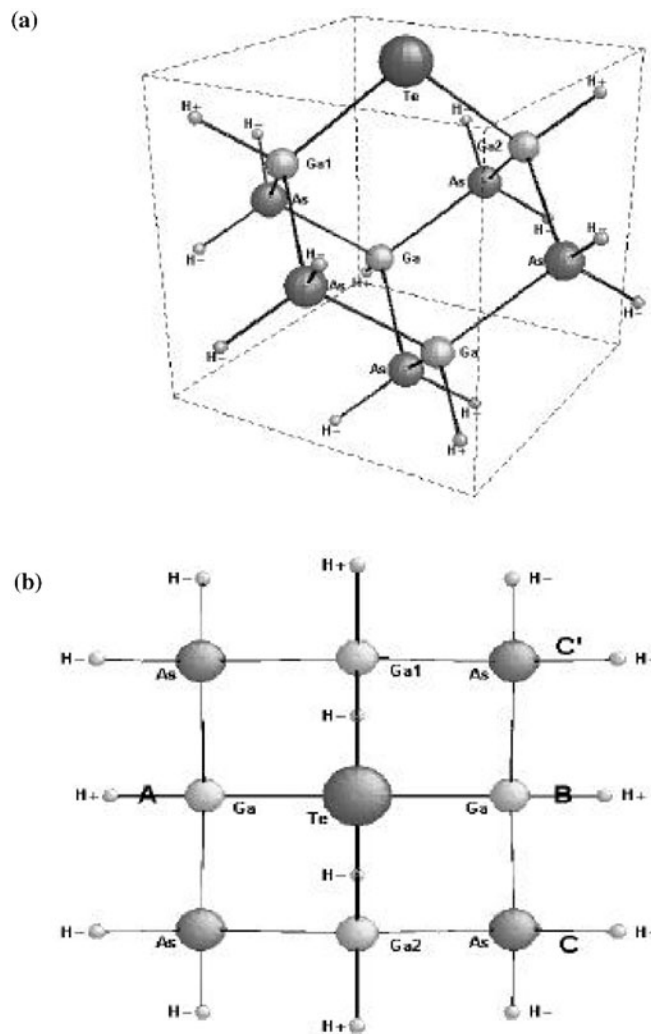
and one of the Si–As bonds was broken. Then, the Si adatom moved to the dimer position. This step cost 0.15 eV and resulted in a Si–As dumb-bell aligned parallel to the surface whose centre of mass was close to the top layer. In this configuration, the Si and As atoms maintained their respective coordination numbers. However, the bond angles were stretched. Finally, the Si adatom in the dimer form pushed the As atom out of its position. The corresponding barrier was 0.11 eV. This pathway is summarized in figure 7. When the Si adatom was at its final site ( $\text{Si}_{\text{sub}}$ ), it had four neighbours and an energy gain of 0.8 eV.

Schroeder *et al* also examined the reverse process,  $\text{Si}_{\text{sub}} + \text{As}_{\text{ad}} \rightarrow \text{Si}_{\text{ad}} + \text{As}_{\text{sub}}$ , where the activation energy is found to be 1.1 eV. They called this process ‘reexchange’. It is the same process suggested by Kandel and Kaxiras [16]. However, in [16], it was called ‘deexchange’ and the authors asserted that it is an important process to maintain the layer-by-layer growth at finite temperatures.

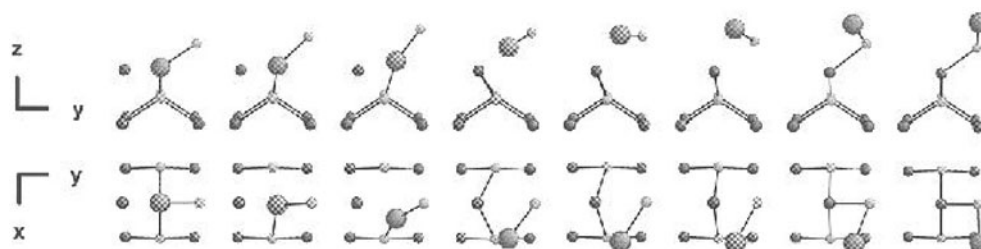
**5.2.3. Te on GaAs(100).** Several studies using the pseudopotential method and LDA with plane waves as basis function (see, e.g. [36]) have been carried out to examine both the energetics of Te on GaAs(100), and the growth of Te compounds, such as CdTe, on the GaAs surface. The surfactant effect of Te on GaAs was considered in [26]. These authors assumed a complete one ML coverage of Te atoms on the GaAs(100) surface. On top of each Te atom was an As atom. The total energy of this configuration was compared to the case in which each Te atom was exchanged with its respective on-top As atom. The results favoured Te atoms forming the top layer. Although the calculated energetics favoured the exchange between Te atoms and As atoms, it is unlikely for this kind of exchange process to happen in reality. From the bonding point of view, As atoms are bonded to Ga atoms. The bond orientations between consecutive layers in the [100] direction make a 90° rotation. The direct exchange between a surfactant (Te atom) and an on-top As adatom of the growing species will render the surfactant atom in the wrong position after the exchange and the process will not be able to continue. Consequently, the growth process will terminate instantly. Furthermore, a full-layered coverage of Te atoms on top of the GaAs(100) surface is not consistent with experimental observation [5].

At present, the only theoretical investigation of the microscopic exchange process between a Te atom and an As atom on top of the GaAs(100) surface based on experimental observation was carried out by Consorte *et al* [37]. They used a cluster model to study the growth process. A 24-atom cluster was used to simulate the local environment of a Te atom on a GaAs(100)

surface. The position of the Te atom was taken from Massies and Grandjean [5], in which the Te atom was at a bridge site and was bonded to two Ga surface atoms. According to [38], there exist two metastable sites on the  $2 \times 4$  clean Ga terminated (100) surface—one is an interstitial site in front of the bridge site and the other is the site for a Ga adatom to form the next Ga layer. Consorte *et al* assumed that an As atom that would eventually be incorporated into the surface was initially located at an interstitial position near the Te atom. In addition, a Ga adatom was assumed to be located at its bulk position. Theoretically, the initial position of the As atom is not a proper site in the GaAs bulk structure, but both the assumed position of the As atom and the presence of the Ga atom are consistent with the experimental observation. The measured coverage of As atoms is more than one ML and the presence of Ga atoms is needed for the exchange process to proceed. With more than one ML coverage, some of the As atoms will have to occupy some metastable sites. This initial configuration is shown in figure 8.



**Figure 8.** The initial configuration of Te, As, and Ge for an exchange process: (a) the cluster model in 3D view; (b) the same model viewed from the [001] direction.



**Figure 9.** A snapshot series of a pathway for the exchange process between the surfactant, Te, and the As adatom with the presence of a Ga atom. The top panel is the side view and the lower panel is the top view. The large sphere is the Te atom, the dark small sphere is the As adatom, and the light small sphere is the Ga adatom. For clarity, most of the substrate atoms have been omitted.

By moving the As atom towards the initial position occupied by the Te atom and the Te atom to its final position at the same time, their calculations showed no barrier higher than 0.014 eV, which is the degree of accuracy one can obtain from such calculations. It is in qualitative agreement with the experimental observation that the exchange process happens very fast. The final position of the Te atom is one layer higher than the position of the Ga adatom and is rotated by  $90^\circ$  with respect to its initial position. At this new position, the Te atom is ready to repeat the exchange process and to help grow the next layer. The full microscopic pathway is illustrated in figure 9.

Because the Ga–As bond is stronger than the Ga–Te bond, the proposed exchange process actually gains energy. This excess energy can in turn increase the kinetic energy of the Te atom. If the Ga atom was not present nearby during the process, the Te atom would move away and the exchange process would be stopped.

In summary, this model study shows: (1) how the Te surfactant atoms segregate to the growth front in such a way that they occupy new As substitutional sites and can thus perpetuate the layer-by-layer growth; (2) why Ga adatoms are needed in the growth process; and (3) that the exchange process is very efficient, i.e. it is short-ranged with no energy barrier more than the accuracy of the calculations.

*5.2.4. Criteria for an element to be used as a surfactant.* In [37], the authors pointed out three factors for an element to serve as a surfactant on a particular semiconductor surface. First, the surfactant atom must occupy a bridge site. Second, it must be weakly bonded to the surface atoms and thus have a longer bond length than the host atom that replaces it. Finally, the surfactant atom must be larger than the substrate atoms for it to segregate to the growth front rather than diffusing into the surface.

### 5.3. Monte Carlo simulations

In order to treat surface problems using first-principles methods, models can only handle a small number ( $\sim 100$ ) of atoms. Although classical molecular dynamics simulations can alleviate this size problem, they suffer from a lack of proper phenomenological potentials that should be coordinate-number (environment) dependent (i.e. they should not be determined from the bulk properties). In addition, classical molecular dynamics can only simulate growth conditions in a very short period of time (of the order of  $10^{-9}$  s). These bottlenecks leave MC simulations as a method to treat growth phenomena involving thousands of atoms and a reasonable timescale. By using a few adjustable parameters that characterize the energy barriers, it is possible to

semi-quantitatively understand some features appearing in the growth process. Before the development of the SMG method, MC simulations were used to study the 2D island formation in the sub-monolayer coverage regime. The diffusion-limited aggregate (DLA) theory that was successful in explaining pattern formation [39] was a result of MC simulations. In essence, this theory is based on the assumption that an impinging adatom hits the surface and sticks to the edge of an existing island in the form of a fractal.

The pattern formation of 2D islands during the initial stages of SMG, which was observed in [19], has been investigated by Liu and collaborators [40, 41]. They used the kinetic MC simulations based on the exchange reaction limited assumption proposed by Chang *et al* [19]. A large exchange barrier was assumed when an impinging atom exchanged with a surfactant atom. Three parameters were introduced to characterize three basic energy barriers. These barriers are for: (1) the diffusion of mobile adatoms on the surfactant terrace; (2) the exchange of mobile atoms with surfactant atoms; and (3) the aided exchange of stuck adatoms with surfactant atoms. The results explain the formation of fractal islands at low deposition flux or high temperatures. This formation is transformed to compact islands when the flux is decreased while the temperature is increased. An excellent review concerning the kinetic MC simulation is given by Kandel and Kaxiras [16].

## 6. Prospective and important issues to be addressed

We have reviewed the experimental work using SMG and ASMG to grow heterostructures/pure samples and quantum dots, respectively. In addition, there is experimental evidence that SMG can improve doping profiles in semiconducting systems [13]. A very recent experiment also showed that ASMG could reduce the density of TDs [15]. We anticipate that both SMG and ASMG methods will have an important impact on the development of technologically important materials. For example, one area that will be tremendously impacted is the epitaxial growth of magnetic half-metals on top of semiconductors with or without doping magnetic transition metal elements. Currently, samples with half-metal layers of approximately 30 nm thickness were grown on GaAs [42] under lattice matched conditions. If surfactants can be found to improve the 2D growth of lattice mismatched heterostructures, fabrication of high spin moment and high Curie temperature materials for spintronic applications will be greatly facilitated.

If ASMG can be used to grow new nanosamples that are more uniform in size, the growth of arrays of quantum dots will be significantly accelerated. The results will have a profound effect on future manufacturing of nanodevices.

The SMG and ASMG methods also present experimental and theoretical challenges in understanding the microscopic processes happening between surfactant atoms and growing atoms. So far, there is no theoretical work on the subject of antisurfactants in the literature.

As we illustrated in the discussion of possible exchange mechanisms, it is clear that the role played by a surfactant is far from being understood at this time. There are many fundamental questions to be answered. For example, even on one particular surface, why should some species be excellent surfactants while others are not [5]? The initial site of the surfactant on the surface can play a role. But in many cases the site can involve surface reconstruction, which itself can be controversial [21, 23]. For example, there is a  $3 \times 1$  and  $2 \times 1$  reconstruction controversy for Te on GaAs(100). The former was determined to be more favourable by Massies and Grandjean [5], whereas the latter was supported in [43] and has been used in most theoretical studies [26]. We [44] recently found that for Te on clean GaAs(100), the  $3 \times 1$  reconstruction [5] is energetically more favourable than the  $2 \times 1$  reconstruction. However, the presence of a growing species can induce a different type of surface reconstruction. Therefore,



an unambiguous determination of the surface reconstructions of SMG and ASMG is definitely necessary for a fundamental understanding of the role played by the surfactant/antisurfactant.

On the theoretical side, it would be desirable to secure a basic understanding of the processes involved in SMG and ASMG methods. It would be a tremendous step forward in the basic understanding of these methods if the first-principles approaches could provide information about statistical energetics that could be applied to large scale MC simulations. It would also be beneficial if one by-product of this increased theoretical understanding is to provide a logical guidance in selecting a surfactant and an antisurfactant for SMG and ASMG methods, respectively, instead of the trial and error scheme adopted by the experimentalists.

In summary, SMG and ASMG methods provide rich areas of research that will be valuable in growing future technologically important materials. The understanding of growth processes involved, especially from the microscopic point of view, will have an important impact on other subjects in surface physics.

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