Model of epitaxial growth of GaAs on Si(100): Nucleation at surface steps

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A microscopic model of epitaxial growth of GaAs on Si(100) is proposed, which explains how double-layer steps on the Si(100) surface act as nucleation sites in the initial stages of growth. On the flat terraces of Si(100), there is a strong tendency towards the formation of mixed layers of Ga and As, which inhibit growth of zincblende GaAs. The bonding topology of the surface steps supresses this mixing, and drives the growth of ideally bonded GaAs in a three-dimensional mode with islands forming along the steps edges. Total-energy calculations indicate that the proposed model for nucleation of GaAs at double-layer steps on the surface is energetically stable.

I. INTRODUCTION

Epitaxial growth of semiconductors has been the subject of intense research in recent years.[1] This is in large part due the potentional technological importance of micro-fabricated materials. In particular, the growth of GaAs on Si(100) surfaces has received much attention. However, in spite of all the experimental work that has been done, there is still no understanding of the fundamental mechanisms involved in the epitaxial growth of crystals. From the theoretical point of view, very few studies have been done and little progress has been made. This is due to the complexity of the problem, which involves both kinetics and energetics, and requires a description that couples microscopic processes with macroscopic behavior.

In this paper we focus on a simple, but basic question, which can be addressed theoretically: What is the microscopic configuration of the first few layers of GaAs when it is epitaxially grown on a Si(100) surface? We find that growth does not occur on the flat terraces of Si(100), and that double-layer steps (DLS) on the surface play a crucial role in promoting the growth of ideally bonded GaAs in a three-dimensional mode (3D). Using basic physical and chemical concepts regarding the bonding topology of the Si(100) surface, and its interaction with Ga and As atoms, we construct a microscopic model that describes the initial stages of growth. This model provides a natural explanation for some of the observed properties of the epitaxial growth of GaAs on Si(100).

Experimental studies have shown that on vicinal Si(100) surfaces GaAs initially grows in an islandlike or 3D mode, with islands forming in the vicinity of surface steps.[2–4] This GaAs islands run along the direction of the steps, which remain stationary as growth proceeds. This 3D growth mode is in contrast to the usual planar or two-dimensional epitaxial mode which proceeds by step motion. The model proposed in this paper can explain the fundamental mechanism that drives the 3D growth of GaAs on Si(100). According to the model, the bonding configuration of DLS on the Si(100) surface leads to the nucleation of GaAs islands with ideal or zincblende bonding topology, and promotes 3D growth. Thus, the 3D growth mode is different from the conventional 3D growth modes driven by strain or absence of wetting.[5] When growth is initiated on the flat terraces of Si(100), chemical and rehybridization reactions lead to the formation of a mixed bilayer of GaAs with wurtzite structure, inhibiting any further growth. The bonding structure of the steps prevents these reactions to occur, and pins the first bilayer of GaAs to have the zincblende bonding topology. Our model provides a stage-by-stage description of the growth process. Previous attempts at a microscopic description of growth has concentrated on the flat terraces of the surface.[6] To the best of our knowledge, DLS have only been considered in the context of eliminating antiphase domains in the GaAs overlayers (for a review of this see Ref. 6).

The rest of the paper is organized as follows. First, we briefly summarize results of first-principles total-energy calculations of monolayer and bilayer coverages of GaAs on Si(100). One conclusion of this study is that growth on the flat terraces is inhibited by a strong tendency to the formation of mixed layers of Ga and As. Next, a stage-by-stage description of the model is presented, explaining the role that DLS play. We present results of total-energy calculations based on a tight-binding model which indicate that DLS are low-energy nucleation sites. Finally we discuss some general consequences of the model.

II. GROWTH ON FLAT TERRACES OF Si(100)

In a previous work, Kaxiras and Joannopoulos[7] calculated total-energies of monolayer and bilayer coverages of Ga and As on flat terraces of Si(100). These were first-principles calculations carried out within the framework of local-density functional theory, using pseudopotentials and a

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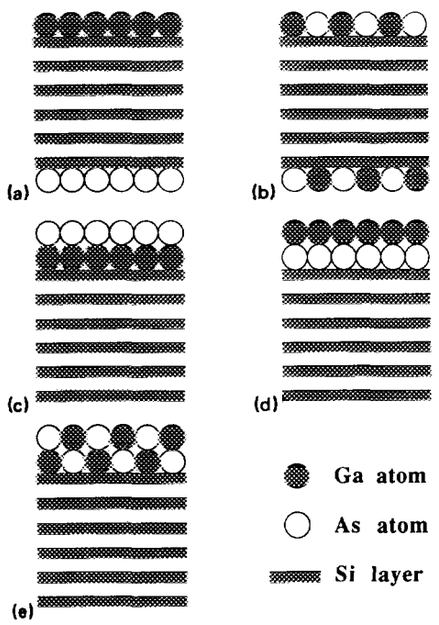

FIG. 1. Schematic representation of Ga and As overlayers on Si(100). The Si(100) surface is represented with a slab geometry. (a) Pure monolayer coverage, (Ga)[Si](As). (b) Mixed monolayer coverage, (GaAs)[Si](GaAs). (c) Bilayer coverage with pure layers and As-exposed surface, (As)(Ga)[Si]. (d) Same as (c) with Ga-exposed surface, (Ga)(As)[Si]. (e) Bilayer coverage with mixed layers, (GaAs)(GaAs)[Si].

plane-wave basis set. The geometries studied in this study are shown in Fig. 1, and the corresponding calculated energies are given in Table I. Note that on each case the number of As and Ga atoms is the same, and, therefore, direct energy comparisons are possible without the need to use chemical potentials. Here we will focus only on a few conclusions regarding these results. A detailed discussion is presented elsewhere.[7] The configuration with the lowest energy corresponds to a mixed monolayer with equal amounts of Ga and As atoms, which form pairs with a (2×1) surface periodicity [Fig. 1(b)]. Each Ga–As pair relaxes so that the As atom moves up to a geometry close to its preferred p^3 bonding, and at the same time the Ga atom has local geometry close to its preferred sp^2 bonding. The surface is electronically passive, since each Ga and As atom contributes three electrons to covalent bonding, and the As atoms retain a lone pair of electrons. There are no dangling bonds on the surface.

Growth of zincblende GaAs along the [100] direction requires alternating planes composed exclusively of Ga or

TABLE I. Total-energies of the various Ga–As overlayer configurations shown in Fig. 1. Energies are given relative to the lowest energy configuration. Units are eV/(2×1) surface unit cell.

(a) (Ga)[Si](As)	0.8
(b) (GaAs)[Si](GaAs)	0.0
(c) (As)(Ga)[Si]	2.2
(d) (Ga)(As)[Si]	2.8
(e) (GaA)(GaAs)[Si]	1.5

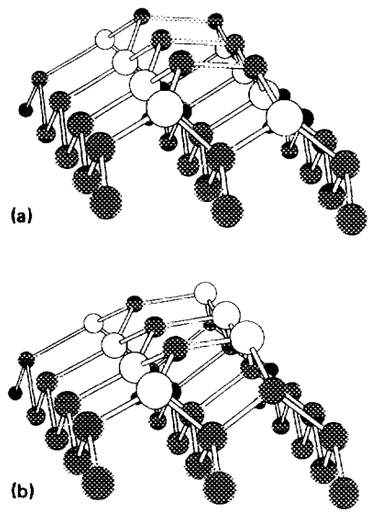

FIG. 2. Perspective view of the bonding configuration of (a) Ga dimers on As covered Si(100), and (b) mixed GaAs bilayer on Si(100). These structures correspond to Figs. 1(d) and 1(e), respectively. As in Fig. 1, Si atoms are shaded circles, Ga atoms are solid circles, and As atoms are open circles.

As atoms. The two possible bilayer structures having this stacking arrangement, shown in Figs. 1(c) and 1(d), have higher energy than the mixed bilayer structure of Fig. 1(e). In typical experimental growth conditions[8] the Si surface is initially covered by As. Then Ga is incorporated onto the surface. The resulting structure, corresponding to Fig. 1(d), is unstable to the formation of a mixed bilayer, with an energy gain of 1.3 eV/(2×1) surface unit cell (see Table I). This represents a very large energy difference. The structures corresponding to the initial As-covered Si surface terminated by Ga dimers, and the mixed bilayer configuration [Figs. 1(d) and 1(e), respectively], are shown in more detail in Fig. 2. Similarly to the case of the mixed GaAs monolayer structure, the low energy of the mixed bilayer structure results from the relaxation of the GaAs surface pairs (hybridization), and the absence of any dangling bonds. The mixed bilayer of GaAs has the structure of locally strained wurtzite, which is separated from the stable zincblende structure of bulk GaAs by a large energy barrier. Thus, growth of zincblende GaAs on the flat terraces of Si(100) is inhibited by the formation of a low-energy mixed GaAs bilayer in the initial stages of growth.

Any model of growth of GaAs on Si(100) has to explain how this tendency towards mixing is suppressed. In order to understand this mixing mechanism we interpret the low energy of the mixed overlayer structure in an alternative way. In the pure-layer configuration of Fig. 2(a), the number of Ga–As bonds/(2×1) surface unit cell is four, and there is one Ga–Ga bond. In the mixed bilayer geometry, shown in Fig. 2(b), there are five Ga–As bonds, but no Ga–Ga bonds. This bond between like atoms has been replaced by a Ga–As bond, resulting in a large energy reduction. Thus, there is a strong driving force towards the formation of mixed GaAs overlayers whenever bonds between like-atoms can be replaced by bonds between unlike-atoms. These ideas will be

used to construct our model of growth, which is discussed in the next section.

III. GROWTH AT DOUBLE-LAYER STEPS

Following the experimental evidence that growth of GaAs on Si(100) initiates in the vicinity of surface steps, as discussed in the Sec. I, and our conclusion from the previous section that mixing inhibits growth of bulklike GaAs on the flat terraces of Si(100), we have studied possible mechanisms for nucleation of GaAs at steps on the Si(100) surface. Next we will describe our model for growth, where DLS act as nucleation sites which promote growth of zincblende GaAs. This description will follow the same sequence as in the usual experimental setup in molecular-beam epitaxy (MBE).

We begin with a clean Si(100) surface, which when cut slightly off-axis from the (100) plane, necessarily contains steps. These can be in general one or more atom high. Of the various step configurations, we focus only on DLS, which have the appealing feature that they eliminate antiphase domains. Moreover, theoretical calculations[9,10] indicate that DLS of the form shown in Fig. 3(a) are the lowest energy steps on Si(100), and in fact surfaces can be prepared with only DLS present.[11] Along this step there is a row of threefold coordinated atoms (shown with darker shading) which do not participate in dimer formation. These atoms are, therefore, more reactive and less stable energetically.

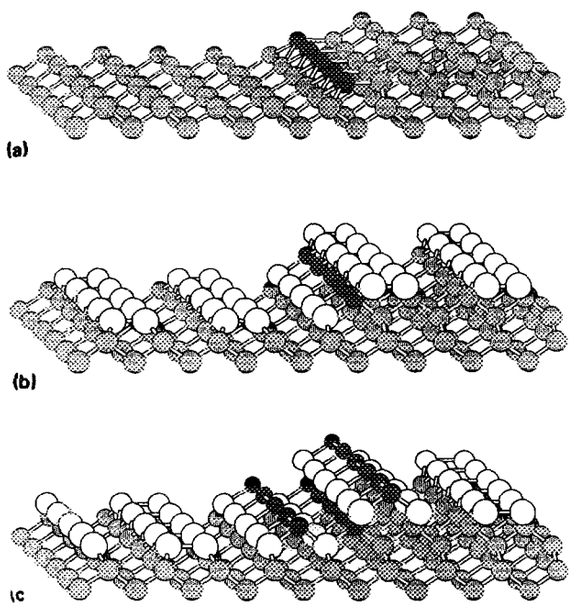

FIG. 3. Three stages of growth of GaAs at a DLS on Si(100): (a) The clean Si(100) surface with a DLS. The Si dimers on either side of the step are oriented parallel to the step. The threefold coordinated Si atoms at the step shown by a darker shading do not participate in dimer formation and should be more reactive. (b) The As-covered configuration. The row of threefold coordinated Si atoms at the step of the clean surface have been substituted by As atoms. The displaced Si atoms (shown by darker shading) are now fourfold coordinated and are bonded to three surface As atoms. (c) The Ga-and-As covered step configuration. Note that adding more Ga atoms on either side of the step would permit mixing which would inhibit (100) growth. Thus, preferred growth proceeds by growing larger and larger overlayers directly on the step along the (211) direction.

The first thing that occurs is that the surface is covered with As. On the flat regions of the Si substrate the As atoms break the existing Si dimers and form new As dimers.[12] To obtain the optimal configuration at the steps themselves, we propose that the threefold coordinated Si atoms at the step edge are interchanged with As atoms. After an appropriate amount of extra As is incorporated to complete coverage of the surface, all the Si atoms in the resulting configuration are fourfold coordinated, and all the As atoms are threefold coordinated. Thus this As-covered surface, including the steps, is electronically passive and is probably energetically stable. We note that, prior to the As-for-Si substitution, the Si atoms at the step are exposed and have locally the same configuration as in the Si(111) surface. In this case, it has been shown that is favorable for As atoms to replace the entire uppermost layer of Si atoms.[13] In a different context, substitution of As for Si atoms has been proposed[14] to reduce the effects of polarity in layered growth on the flat terraces of Si(100). We expect that the configuration shown in Fig. 3(b) is most likely the equilibrium ground state of the As-covered vicinal Si(100) surface.

The next step in the growth process consists of depositing Ga on the surface. On the flat terraces, the Ga atoms will break the As dimers, and form the low-energy mixed bilayer discussed in the previous section. This will inhibit growth of zincblende GaAs. When the incoming Ga atoms are incorporated at the As-covered steps, the bonding configuration of these steps prevents mixing to occur and promotes 3D growth of GaAs with ideal bonding topology. To see this, first consider the row of Si atoms along the step. Each of these Si atoms is surrounded by three As atoms [see Fig. 3(b)]. Electronegativity arguments[15] indicate that it is energetically favorable to replace these Si atoms by Ga atoms. The removed Si atoms diffuse to bulk positions of lower energy, or to equivalent surface sites. The resulting structure after the Ga-for-Si substitution includes pairs of fourfold coordinated Ga and As atoms at the step edge, as shown in Fig. 3(c). Additional Ga atoms arrive at the surface and are incorporated between As dimers on either sides of the steps. Each Ga becomes threefold coordinated, with two bonds to As atoms and one bond to a second Ga atom. The As atoms on either side of the step remain threefold coordinated. This structure is, therefore, electronically passive. *Notice that because the Ga and As atoms on the rows that run along the step edges are fourfold coordinated, mixing cannot occur.* Any interchange of atoms cannot create more Ga–As bonds at the expense of Ga–Ga or As–As bonds. Avoidance of mixing is crucial if the growth of zincblende GaAs is to continue.

To substantiate our claims about the stability of the Ga and As covered step configuration, we have carried out total-energy calculations to compare the energy of the step structure with a geometry where the Ga and As atoms are incorporated on the flat terraces. These calculations were done within a tight-binding theory, which incorporates rehybridization effects upon atomic relaxation.[16] In this model the energy difference between two structures is expressed as the difference between the band structure and ionic repulsion energies:

$$\Delta E_{\text{tot}} = \Delta E_{\text{bs}} + \Sigma_i U_i \Delta N_i.$$

The first term in this equation is the difference in band-structure energy, which is the sum over the eigenvalues of a one-electron tight-binding Hamiltonian. In our calculations, the tight-binding parameters are taken from Harrison's solid state table.[17] The second term represents a sum over ion–ion interaction energies, where U_i is the energy of a bond of type i (e.g., Ga–Ga bond) and N_i is the number of such bonds in the system. The ionic repulsion energies U_i for Si–Si and Ga–As are obtained by fitting the cohesive energy of the corresponding crystal structures,[16] and the remaining constants are fitted to the first-principles energy calculations of KJ.[7] The system is relaxed by allowing bond angles to vary, but bond lengths are held fixed. This incorporates the essential features of rehybridization, particularly the formation of sp^2 and p^3 bonds. The structures considered have unit cells with ~ 120 atoms, a number large enough so that the empirical approach we have taken to calculate total-energies is necessary. Nevertheless, we reiterate that the essential rehybridization and bonding effects are included in the calculations.

We compare the energy of the relaxed step configuration shown in Fig. 1(c), with the energy of the optimal arrangement of the same number of Ga and As atoms on a flat terrace of the Si(100) surface. The terrace configuration involves mixing of Ga and As. However, since the ratio of Ga to As atoms at the step is not 1:1, the corresponding terrace configuration cannot be fully mixing. Nevertheless, we have included the full energy/GaAs pair gained upon mixing (1.3 eV/surface Ga–As pair), thereby deliberately underestimating the energy of the terrace configuration. The final result is that the energy of the step configuration is *lower* than the energy of the terrace configuration by 1.5 eV/unit length (3.81 Å) along the step. This is a very large energy difference (even if the reliability of the calculation is good only within 20%, we can arrive at the same conclusion). To test the robustness of the calculation, we have carried out calculations where an additional row of Ga dimers is placed on the surface. We find that the energy difference remains essentially unchanged.

IV. DISCUSSION AND SUMMARY

The exposed plane at the step is not the (100) plane, but rather the (211) plane. For GaAs this is not a polar plane, and has been previously proposed as an alternative orientation for the Si substrate[18] in order to eliminate polarity effects associated with growth of GaAs on Si surfaces along the [100] direction. It is reasonable to assume then that growth will continue along the [211] or a neighboring direction, rather than along [100].[19] This leads to three-dimensional growth with GaAs forming along the edges of the DLS, in agreement with experimental observations of the initial stages of growth.[2–4] No special cut of the surface is needed to promote growth, but only a sufficient density of DLS which is readily obtained by using vicinal Si(100) surfaces. Still, it could be speculated that a miscut leading to the largest number of DLS would be ideal. This corresponds to the (311) plane. Of course, determination of the optimal cut requires consideration of additional issues like strain, defects and temperature. A different misorientation like (511) or (711) may prove to be better than (311).

To briefly summarize, we have proposed a new model for GaAs growth on vicinal Si(100) surfaces. The model is based on DLS on the Si surface acting as nucleation sites for GaAs islands. A stage-by-stage justification of the step-nucleated growth is presented, including some of the details of the associated reactions. An As-covered step configuration is identified, which we believe is energetically stable, which is crucial in eliminating mixing at the neighborhood of the step. Total-energy calculations within a tight-binding formalism show that the unmixed step configuraion is energetically favored over the optimal mixed terrace configuration. It is concluded from the above arguments, that 3D growth is promoted along the [211] (or a neighboring) direction, perpendicular to the step planes. We note the 3D mode of growth is driven by the specific bonding properties of the surface DLS. This is different than the conventional 3D growth driven by strain or absence of wetting. The coalescence of the islands leads to thick, bulklike, GaAs layers. The usual problems of dislocations and lattice strain associated with these thick layers lie beyond the scope of our work and have not been addressed here.

ACKNOWLEDGMENTS

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[19]It has been pointed out (see Ref. 14) that intermixing can lead to a neutral interface for GaAs on Si(100), and thus polarity is in fact not a problem. Still, it is reasonable to assume that growth is more likely to proceed along nonpolar planes.