# THERMODYNAMIC AND KINETIC ASPECTS OF GaAs GROWTH ON Si(100)

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A microscopic model of GaAs growth on Si(100) is discussed, which takes into account the role of kinetics and the morphology of the substrate. The model predicts that growth at the initial stages is dominated by GaAs islands nucleated at steps of the substrate, which begin forming upon deposition concurrently with layered growth on the terraces. This mode of growth does not fall within any of the traditional thermodynamic models of heteroepitaxial growth, and allows for different growth channels depending on deposition conditions. The predicted shape and structure of the GaAs seeds nucleated at Si steps are in agreement with recent experimental observations.

## INTRODUCTION

The growth of device-quality GaAs on Si substrates is a subject of great technological importance for the integration of optoelectronic devices.[1] At present, epitaxial growth of GaAs on Si substrates oriented slightly off the (100) crystallographic axis (by 2° to 6°) appears to be the most promising avenue towards achieving this technological goal.[2] Typically, growth begins on an As-terminated substrate in what appears to be a two-dimensional (2D) mode, with subsequent growth in a three- dimensional (3D) mode.[3,4] If this were strictly the case, this system would be an example of the Stranski-Krastanov (SK) mode of growth, whose traditional mechanism involves initial 2D pseudomorphic growth, followed by a stress driven transition to purely 3D island-like growth. In this paper we argue against the traditional SK mechanism for growth of GaAs on Si(100) and introduce a new model of growth that accounts in a natural way for experimental observations. Our model is derived from extensive microscopic first-principles calculations and makes specific predictions about the shape and structure of GaAs islands. The driving mechanism for this model is based on chemical an rehybridization reactions that take place at the nucleation stage, rather than on thermodynamic equilibrium arguments. This approach, that takes into account explicitly the substrate morphology and the substrate-overlayer interactions, provides the link between the microscopic nature of growth and the thermodynamic macroscopic description.

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## THERMODYNAMICS OF GROWTH

Heteroepitaxial crystal growth models fall in three different categories: 2D layered growth (known as the Frank-van der Merwe mode), 3D island growth (known as the Volmer-Weber mode) and initial 2D growth followed by 3D growth (the SK mode). These three modes exhaust the thermodynamic possibilities of growth and are determined by the relative energy of the interface $\sigma_I$ and of the free surfaces of the substrate $\sigma_S$ and the overlayers $\sigma_O$, which are treated as macroscopic parameters. The interface energy and the surface energy of the overlayers in general depend on the coverage. When $\sigma_S >> \sigma_O + \sigma_I$ wetting occurs leading to 2D growth. In the opposite limit, $\sigma_S << \sigma_O + \sigma_I$, there is complete lack of wetting and 3D growth occurs. The SK mode is an intermediate case ( $\sigma_S \sim \sigma_O + \sigma_I$ ) where a thin film initially wets the surface, after which layered growth is unfavorable and 3D growth follows.

There are two implicit assumptions in these growth models: first, that global equilibration is attainable during growth, and second that the substrate is homogeneous. These two assumptions make it possible to describe the system in terms of macroscopic parameters and, at the same time, avoid the complications that arise from kinetic effects. While these assumptions are reasonable when dealing with *macroscopic* features, they may be inappropriate when one attempts to model the microscopic aspects of growth. For instance, in a given system there may be several possible growth channels, all of which after several monolayers appear as SK growth. However,

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the specifics of the different channels can affect growth at the monolayer level and can be crucial in determining the *microscopic* features of the islands. Moreover, the conditions of deposition (temperature, relative abundance of species, etc.), that is, the *kinetics* of growth, could be the deciding factor between the different channels of growth. We propose that this is precisely the case during GaAs epitaxial growth on Si(100). Specifically, we develop a growth model which takes into account explicitly the topology of the Si substrate. The model predicts the formation of different types of GaAs 3D islands depending on substrate preparation and deposition conditions, in agreement with experimental observations.[5]

## MICROSCOPIC GROWTH MODEL

Our theory of GaAs growth on Si is based on the following premises:

(a) We concentrate only on the initial stages of growth, that is, what happens upon deposition of the equivalent of 3-4 monolayers of GaAs on the substrate. This is the stage which determines the characteristics of subsequent growth.

(b) We assume that global equilibrium is not attainable at the initial stages in the time-scales in which growth occurs. Rather, kinetics is very important and the type of growth observed depends on the specific conditions of deposition.

(c) For concreteness, we will assume conventional MBE parameters; that is, the substrate temperature, deposition rate, deposition configuration etc. are such that the following conditions prevail:

-the As sticking coefficient is low;

-the Ga sticking coefficient is unity;

-the flux of As is much greater than the flux of Ga, ensuring stoichiometric growth;

-the mobility of Ga is sufficiently large so that local quasi-equilibrium is possible. We note that all these quantities are inter-dependent. For example, if we define the mobility of Ga through a length scale over which Ga atoms move before being incorporated in a GaAs site, this length scale will depend on temperature, as well as on the flux rates of Ga and As, which also determine the sticking coefficients.

(d) The role of surface morphology, which turns out to be very important, is incorporated explicitly in the model. The most prominent features on Si substrates are terraces separated by steps, which are typically one or two layers high.

(e) Finally, we assume that kinetically allowed configurations that are electronically passive and have low energy are preferred during growth.

With these assumptions we proceed to investigate the possible avenues of growth of GaAs on Si(100) substrates. We begin with the energetics of local configurations on a flat region (terrace) of the substrate.[6] In conventional MBE, the Si substrate is usually covered by a monolayer of As, before the Ga source is opened. This results in a passive surface, in which all surface As atoms are three-fold coordinated, with two bonds to the substrate and one bond to another surface As atom, in an arrangement which satisfies the valency of As atoms. Next, Ga atoms are introduced to the surface. The most naive way to incorporate Ga atoms on top of the As layer is to break the As-As dimers and insert the Ga atoms between the As atoms, creating two Ga-As bonds and one Ga-Ga dimer on the surface. This succession of atomic planes corresponds to the zincblende bulk structure of GaAs. However, we have determined through first-principles quantum-mechanical calculations, that this arrangement of the Ga and As atoms on the surface would not persist under the kinetic conditions considered here. A configuration of much lower energy is obtained when half of the first layer Ga atoms are interchanged with As atoms from the layer directly below them.[6] This interchange results in formation of mixed layers, with equal amounts of Ga and As atoms in each layer, and Ga-As dimers on the surface. All like-atom bonds are eliminated in the mixed layers, and are replaced by unlike-atom bonds, which are energetically preferred. The atomic relaxations in the mixed layer structure are optimal, with surface As atoms assuming a pyramidal $p^3$ bonding configuration and surface Ga atoms assuming a planar $sp^2$ bonding configuration. The energy of the mixed layer structure is 1.3 eV per dimer lower than that of the pure layer configuration. The large energy gain upon formation of the mixed layers indicates that, at least *locally*, the mixed layers will dominate on the Si(100) substrate terraces. Since the system is not globally equilibrated, the tendency for mixed-layer formation will lead to a chemically disordered structure which will stunt the growth of zincblende GaAs on the terraces.

The obstacle of the mixed layers would be overcome if surface defects can suppress the tendency for intermixing. The most prominent surface defects on vicinal Si(100) are steps, which are typically one or two layers high. In the following, we will concentrate on double-layer steps (DLSs), because vicinal Si surfaces can be prepared containing exclusively DLS leading to a single domain configuration.[7,8] In addition, DLSs have the appealing feature that they naturally eliminate the formation of antiphase domains.[9] There are two types of DLSs: one in which the Si dimers on either side of the step are oriented perpendicular to the step direction (type A) and one in which the Si dimers are oriented parallel to the step direction (type B). Total-energy calculations indicate that type B DLSs are lower in energy on a clean Si surface.[10] The addition of an entire monolayer to the surface interchanges the character of DLSs (A becomes B and vice versa). Thus, if the initial Si substrate were prepared to contain exclusively type B DLSs, the As covered surface will contain steps with As-dimers oriented *perpendicular* to the step direction. However, this may not be the lowest energy configuration for the As covered surface. Although experiments indicate that deposition of As at low temperatures does indeed result in this type of configuration, deposition at higher temperatures (which would allow for atomic rearrangements, so that the As overlayer could perhaps attain a lower energy configuration) results in the As dimers being *parallel* to the step direction.[11]

We have constructed models of GaAs island growth on both type B and type A DLSs (these islands will be labeled according to the type of underlying Si DLS). Cross sections of these islands are shown in Figures 1 and 2. The exposed surfaces of type B islands are the (-1-1-1)-As-terminated surfaces of GaAs, whereas those of type A islands are the (111)-Ga-terminated surfaces of GaAs. The stages of formation of type B islands have been described in detail elsewhere.[12] The type A model is

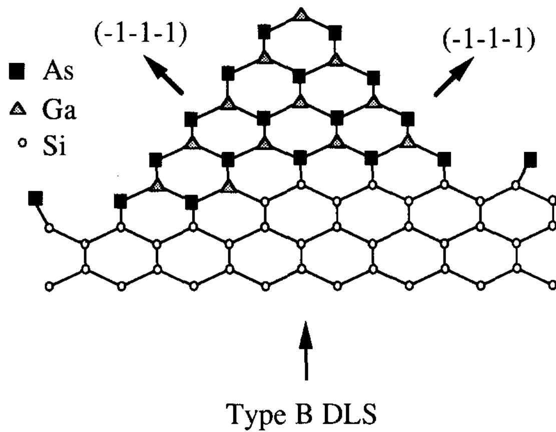


FIGURE 1: Cross section of GaAs seeds nucleated at type B DLS, with (-1-1-1)-As-terminated surfaces exposed.

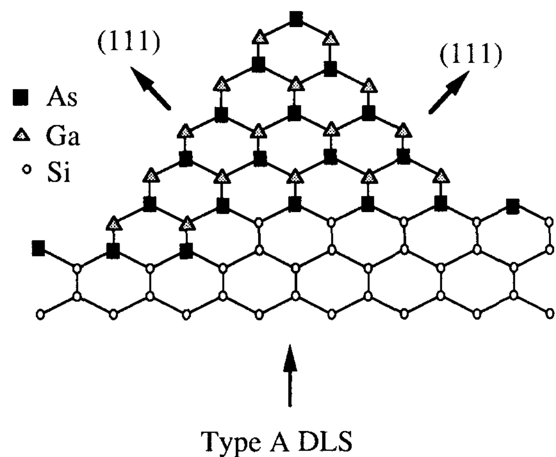


FIGURE 2: Cross section of GaAs seeds nucleated at type A DLS, with (111)-Ga-terminated surfaces exposed.

similar to the type B model, with the As and Ga atoms interchanged. Here we give a brief summary of the features that make these models particularly interesting. First, there is no intermixing in the DLS-nucleated GaAs islands, because it would lead to creation of like-atom bonds at the expense of unlike-atom bonds, which is not allowed energetically. Second, the structure of the islands is the zincblende structure of bulk GaAs, which ensures that growth of bulk material can be initiated. Finally, the DLS islands should have lower energy than the optimal layered structure containing equal amounts of Ga and As, because, for a given number of atoms, the step topology allows a higher number of covalent bonds to be formed than on the flat surface. We have verified the last argument through total-energy calculations, which show that the energy of the DLS-nucleated island is lower than that of the mixed layer configuration on a terrace by 1.5 eV per dimer unit.[12]

From the above arguments, it seems plausible that growth of GaAs begins by formation of islands nucleated at preferred DLS, provided that the substrate is prepared so that it contains an adequate number of DLSs. Typically, vicinal Si(100) substrates contain a mixture of single and double layer steps (the relative abundance of DLSs is enhanced by annealing).[8] There are strong experimental indications that growth is initiated by formation of elongated pyramidal islands and that the density of these islands is correlated with the density of steps on the Si surface.[13] Finally, recent high-resolution cross-sectional Transmission Electron Microscopy (TEM) images[14] indicate that the shape of the GaAs islands is exactly the shape predicted from DLS nucleated seeds shown in Fig. 1 or Fig. 2 (the TEM images cannot distinguish between the two types of islands, which have the same profile).

We shall attempt next to extract detailed predictions about the structure of DLS-nucleated islands. As noted earlier, these predictions will depend on the specific conditions prevailing during growth. We can identify in general two macroscopic variables that affect growth: temperature and pre-growth preparation of the substrate. Specifically, growth can be initiated either at low temperatures (~400 °C) or high temperatures (~600 °C) and on substrates preexposed either to As or to Ga (another variable is the molecular form of As used during growth - $As_2$ or $As_4$ - which could have an effect similar to that of raising or lowering the temperature). Thus, there are four combinations of conditions. Exposure of the Si surface to As at low temperature gives an As-terminated surface with steps of opposite character: If the Si substrate has type B DLSs, this will lead to GaAs islands with (-1-1-1)-As-terminated surfaces exposed. If the *same* Si surface is exposed to As at high temperatures, the As overlayer will have dimers parallel to the step direction,[11] which will lead to growth of GaAs islands with the (111)-Ga- terminated surfaces exposed. On the other hand, the exposed surfaces of the islands will be interchanged if the Si surface is precovered with Ga, given the assumption that the orientation of Ga dimers as a function of temperature behaves similarly to that of As dimers. These effects are summarized in Table I. Thus,

**TABLE I**

| | As-precoverage | Ga-precoverage |
|---|---|---|
| low T (~400 °C) | (-1-1-1)-As surface | (111)-Ga surface |
| high T(~600 °C) | (111)-Ga surface | (-1-1-1)-As surface |

TABLE I: Structure of GaAs seeds, as determined by their exposed surfaces, depending on the conditions of growth. The Ga-precoverage at high T assumes reorientation of the Ga dimers as in the case of As.

the exposed surfaces of the GaAs seeds can be chosen by appropriate combinations of precoverage and temperature. Since these surfaces have different chemical reactivity, which affects subsequent growth, Table I can be used as a guide for choosing the desired growth conditions.

One direct consequence of nucleation at DLS is a crystallographic rotation of the islands depending on growth conditions. The GaAs islands with (-1-1-1)-As or (111)-Ga-terminated surfaces will have the same elongated shape with their long axes running along the step direction, but the relative position of the Ga and As sublattices will be switched. This switching corresponds to a rotation of the crystallographic axes by 90° around the (100) direction. These effects should be observable by diffraction experiments (see e.g. Ref. 15) and would serve as a direct test of the nucleation model described.

Finally, what would clearly discriminate between SK growth and the model presented here, is the behavior of the system during deposition on the order of the first monolayer. According to the SK model, the very initial stages of deposition would result in *purely* 2D growth. In contrast, our model predicts that 3D GaAs seeds would start forming at steps *concurrently* with 2D growth on the terraces of the Si substrate.

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