Probing the Lateral Composition Profile of Self-Assembled Islands

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(Received 18 December 2002; published 13 May 2003)

We apply a selective etching procedure to probe the lateral composition profile of self-assembled SiGe pyramids on a Si(001) substrate surface. We find that the pyramids consist of highly Si intermixed corners, whereas the edges, the apex, and the center of the pyramids remain Ge rich. Our results cannot be explained by existing growth models that minimize strain energy. We use a model that includes surface interdiffusion during island growth, underlining the paramount importance of surface processes during the formation of self-assembled quantum dot heterostructures in many different material systems.

DOI: 10.1103/PhysRevLett.90.196102 PACS numbers: 68.65.Hb, 81.07.Ta, 81.15.Hi

The analysis of composition profiles of self-assembled semiconductor islands is valuable for the understanding of growth phenomena in these nanostructures. The knowledge of the material distribution inside the island provides information about the validity of different growth models. Good control over the interdiffusion is also of fundamental importance for applications in electronic devices because predictions about any optical and electronic properties in such devices are only reliable if the correct material distribution is known and can enter into the modeling. The SiGe system is a particularly simple system for the investigation of growth and interdiffusion processes since these phenomena are not complicated by the presence of a third component like, for example, in III/V materials.

The compositional state of self-assembled Ge islands has been the subject of intense research [1–8]. It was found that nominally pure Ge islands are substantially intermixed with Si when grown at temperatures above $\approx 550\,^{\circ}\mathrm{C}$, but the exact intermixing process has not been clarified. While some authors explained the observed intermixing by strain enhanced volume interdiffusion at the basal interface between islands and Si substrate [1,2], other authors attributed the alloying to surface interdiffusion processes [6,8]. The distinction between different growth models was complicated by the fact, that experimental methods for analyzing the composition of Ge islands have put forward either averaged concentration values for whole islands [1–4] or one-dimensional concentration profiles [5–7]. Here, we demonstrate that the lateral composition profile of self-assembled Ge islands can be determined by selective wet chemical etching. The experimentally found lateral composition profile cannot be explained by strain enhanced intermixing but is in good agreement with a growth model that for the first time is governed by surface interdiffusion during growth.

In this Letter, we investigate self-assembled, coherent islands with 6 ML of Ge grown at 560–600 °C using solid source molecular beam epitaxy (MBE). At this substrate temperature, the islands grow in a bimodal distribution of pyramids [9] and dome [10] islands. The growth procedure for the samples was as follows: The undoped Si substrate was chemically cleaned, introduced to the MBE chamber and deoxidized at 950 °C. After growth of a 100 nm Si buffer layer at a Si growth rate of 0.1 nm/s, the germanium was deposited at a growth rate of 0.05 ML/s. After Ge deposition, a growth interruption of 500 s was inserted before the samples were cooled to room temperature. After removal from the MBE chamber, the islands were wet chemically etched in a hydrogen peroxide solution. The morphology of the islands before and after etching was analyzed by scanning the surface with atomic force microscopy (AFM; Digital Instruments Nanoscope III in tapping mode).

In Fig. 1 we show AFM height images of a sample that was grown at 560 °C. Figure 1(a) shows the as-grown surface decorated with a typical bimodal distribution of pyramids and dome islands. The upper part shows a 3D rendered magnification of the single pyramid island

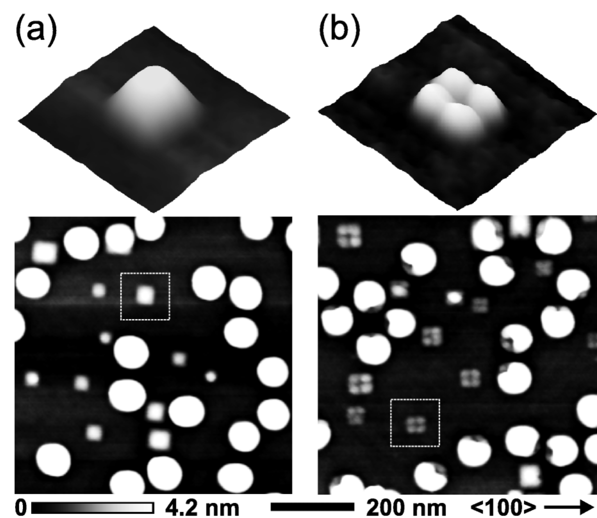

FIG. 1. AFM images of domes and pyramids grown at 560 °C (a) before etching and (b) after etching for 2 min in 31% H_2O_2 solution.

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marked by the dashed square. The domes have an average height of 12 nm whereas the {105}-faceted pyramids have a height between 2.5 and 5 nm. The dome islands appear mostly white because their height exceeds the displayed color scale. The same sample was wet chemically etched after the measurement. We have shown previously [7] that selective wet chemical etching in diluted hydrogen peroxide can be used to investigate the intermixing in Ge islands. Etching in 31% H_2O_2 removes SiGe material with a high Ge content and effectively stops at a Ge concentration of 65% $\pm$ 5%, leaving a surface of that composition that may again be analyzed using AFM. Therefore, by using selective etching we are able to uncover and analyze a surface of constant composition inside the islands. We checked that the etchant reliably stops at a fixed composition. For this purpose we etched several pieces of the same sample for different times (1 to 40 min). The surface morphology looked almost identical for all samples, thus underlining the high selectivity of the used etchant.

Figure 1(b) shows the sample in Fig. 1(a) after etching. The most striking observation is the pronounced change in shape which is obtained after etching the pyramids. The height is reduced and four small mounds remain in the corners of the former pyramid. A deep depression is observed in the middle of the pyramid. Figure 1(b) implies that the pyramid corners are enriched with silicon and cannot be removed by the etching. On the contrary, the edges and the center of the pyramid consist of Ge rich material and are strongly etched. As a result, two grooves are etched into the pyramid and form a crosslike shape inside the island. This particular shape is mainly observed for the smaller pyramids. The larger pyramids and also the dome islands have intermixed stronger with Si and only a small part is etched away [1]. The dome islands exhibit an anisotropic shape with only one etched corner. High resolution scanning tunneling microscopy (STM) images show that these islands have transformed from pyramids into domes [11]. Transition structures (most probably identical to those reported in [12]), which cannot be distinguished from dome islands in AFM, show a very asymmetric shape in STM. The apex of these transition structures is not centered with respect to the pyramid base. It is therefore expected that the asymmetries during the transition from pyramid to dome cause a very asymmetric Ge profile, which results in the observed etch profile.

We explain the observed composition profile by surface interdiffusion during growth. Since *ab initio* simulations of three-dimensional island growth are clearly not feasible in the near future, we propose here a phenomenological growth model that is based on only a few assumptions. Our model is based on the interplay of two rates r_{Ge} and $r_{D,WL}$: r_{Ge} is the rate of Ge atoms, which are deposited on the surface from the incoming flux and are incorporated into the island, $r_{D,WL}$ is the rate at which atoms from the wetting layer migrate into the island. It is well known that the wetting layer contains Si [13] and after island formation a thinning of the wetting layer is observed [14]. As a result, the diffusion of wetting layer atoms inevitably leads to some Si incorporation into the islands. The composition profile depends crucially on how far the Si atoms will diffuse on the island. For simplicity, we assume that the Si diffusion on and around the pyramid is characterized by a single, isotropic diffusion length L_D. The corresponding diffusion length of Ge is much larger (at least larger than the island size), since otherwise the growth of perfectly faceted islands could not be observed. Figure 2(a) summarizes the important parameters used in our simulation. In Fig. 2(b), we plot a top view of the pyramid and several Si atoms diffusing on the wetting layer. The schematic shows that a sufficiently short diffusion length causes an accumulation of Si atoms in the pyramid corners. The reason for this accumulation is of purely geometric origin: Wetting layer atoms can reach the pyramid corner from two sides while they can reach the edge only from one side. The simulation is perfomed for a cubic lattice and the pyramid grows with 11.3° contact angles corresponding to {105} facets. The growth cycle is simulated as follows: The Ge atoms arriving on the pyramid are counted and we add a complete layer of Ge atoms each time enough Ge atoms have arrived to finish a facet by deposition or indiffusion.

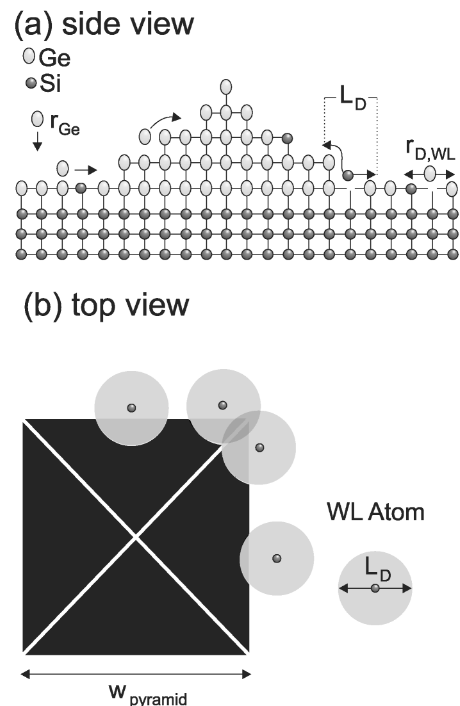

FIG. 2. Simulation parameters for the phemonenological growth simulation which includes interdiffusion with a Si-intermixed wetting layer. If a short Si diffusion length is assumed, the pyramid corners will be Si enriched because diffusing atoms can reach the island from two sides.

Between adding successive Ge layers, the Si indiffusion is simulated by randomly choosing a site on a step edge of the pyramid and then isotropically picking an atom in a distance r away from that site with $P(r) = \exp(-r/L_D)$, where $P(r)$ is the probability of choosing an atom in a distance r. If the chosen atom is in the wetting layer, it is added to the island. If the atom is a Si atom, it is incorporated at the chosen destination, while if it is a Ge atom, it is used to finish the facet. We repeated the whole growth simulation a number of times and as a result we calculated the probability of finding a Si atom for each atomic site in a three-dimensional pyramid.

In Fig. 3 we show the simulation result obtained for an island with 360 atoms base width and 37 atoms height. The diffusion length in this simulation was 90 atoms, the Si concentration in the wetting layer was fixed at 20%. The growth was simulated with the rates $r_{\mathrm{Ge}} = 100 r_{D,WL}$. After the pyramids reached a certain volume, the experimental growth interruption was simulated by continously decreasing r_{Ge} down to $r_{\mathrm{Ge}} \approx r_{D,WL}$, that is the rate of incoming atoms was decreased during the growth interruption compared to the rate of indiffusing atoms. The plotted surface represents the sites in the pyramid where the probability of finding a Si atom is 35% or higher, i.e., we plot a surface of constant $\mathrm{Si}_{0.35}\mathrm{Ge}_{0.65}$ composition. As observed in experiment, the isocomposition profile in the pyramid exhibits a depression in the middle and Si rich corners. The depression in the middle is caused by the fact that, because of the initially small volume of the pyramid, only a few diffusion events occur until a new layer on the pyramid is completed, while in the later stages a large number of Si atoms is incorporated into the pyramid between the completion of successive layers. We calculated the isocomposition profiles for a range of rates and diffusion lengths. We also performed simulations, where the ratio between r_{Ge} and $r_{D,WL}$ was fixed for the whole growth cycle. The basic shape of the isocomposition profile was similar in all cases provided that the Si diffusion length was small compared to the island base width.

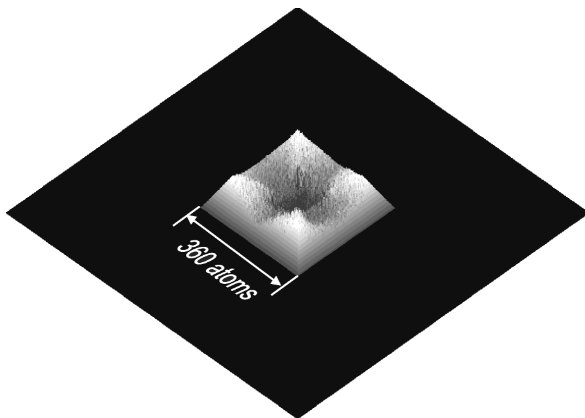

FIG. 3. Isocomposition (65% Ge) surface plot of an interdiffused pyramid growing on a wetting layer with 20% Si content. A Si diffusion length of 90 atoms is assumed.

Compared to the surface diffusion considered here, volume diffusion is very small. This can be seen experimentally by the deep depression in the middle of the island which indicates that this area is not intermixed although there is significant strain at the basal interface to the Si substrate in the center of an island [15]. Very sharp interfaces between SiGe alloys and the pure Si substrate material have been observed in energy-dispersive x-ray [6] measurements demonstrating that interdiffusion at the basal interface is negligable. Finally, we discuss the limitations of our model. We modeled isotropic diffusion although the diffusion on a reconstructed surface will certainly be anisotropic and may also be unequal on the {105} facet than on the $M \times N$ reconstructed wetting layer. For the wetting layer, we expect the two-dimensional grid of dimer vacancy lines and dimer row vacancies present in the $M \times N$ reconstruction to reduce the diffusional anisotropy compared to, e.g., a 2×1 reconstructed Si(001) surface. For the current model, the assumption of isotropic diffusion is therefore adequate. We have not made an attempt to add more details to the growth model since it would have obscured the fact that a good agreement with experiment for the investigated case is already reached using the current, extremely simple and traceable model.

In the following we verify that the observed composition profile cannot be explained by an elastic strain energy minimization. A nonuniform composition in self-assembled islands has been attributed to strain enhanced intermixing by which the islands are able to minimize their elastic strain energy [16]. We simulated the strain in a freestanding SiGe pyramid on top of a wetting layer for different composition profiles. The Ge content averaged over the full pyramid volume was 77% in all cases. The strain distributions were calculated applying a finite element method (FEM). The FEM calculations have been performed using the elastic constants of Si and Ge [17] and including the anisotropy of elastic properties. The elastic strain energy was calculated by integrating over the pyramid volume and also, with equivalent results, by integrating over a volume including the pyramid, wetting layer, and substrate. We compare the elastic strain energy for three profiles: The first profile is a constant composition, in the second profile the Ge content increases towards the pyramid apex, and for the third profile we assumed the experimentally observed Si enrichment in the pyramid corners. If the intermixing is driven by energetics, the strain energy of the third profile should be lower than both alternative models. However, we found no reduction of strain energy in the third model compared to the constant composition pyramid. This is because a reduced strain in the Si rich corner is compensated by an increase in strain in the middle of the pyramid baselines. In contrast to this, the model where we assumed a Ge

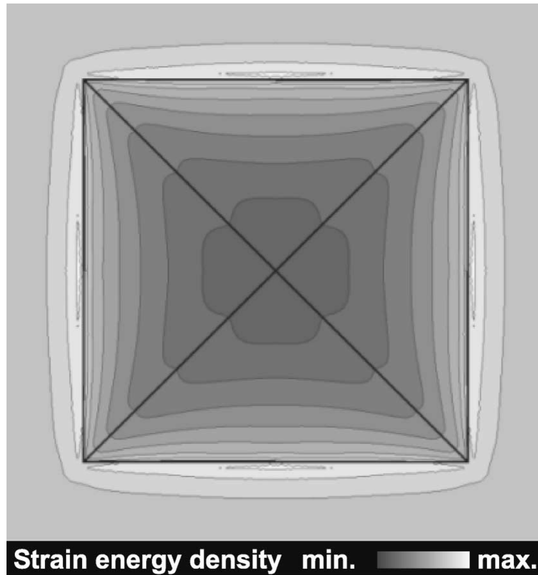

FIG. 4. Strain energy distribution in the wetting layer below a pyramid. The thick black lines indicate the shape of the simulated pyramid.

enrichment toward the apex had a significantly lower strain energy than the constant composition model. We have plotted the strain energy density in the wetting layer below a constant composition pyramid in Fig. 4 (the thick black lines indicate the shape of the simulated pyramid). The shape of the strain energy distribution bears no resemblence to the observed composition profile. The regions of highest strain energy are not in the basal corners of a pyramidal island, but in the middle of the base edges [18]. Therefore, if the observed profile tends to minimize the strain, we should expect increased diffusion of Si atoms into the edges and not into the corners of the pyramid. The disagreement between strain energy distribution and observed etch profile also rules out that the etching rate is significantly influenced by strain effects.

In summary, we have shown both experimentally and theoretically that the intermixing in self-assembled SiGe pyramids proceeds by surface diffusion. By using selective wet chemical etching, we showed that nominally pure Ge pyramids are highly intermixed in the corners. The observed Si enrichment in the corners was reproduced in a simulation, which relies on surface diffusion during growth only. By calculating the strain energy of SiGe pyramid islands with different composition profiles, we verified that the intermixing process is not governed by strain energy minimization but instead is caused by kinetic considerations.

The authors acknowledge the help of G. Bauer, A. Hesse, and M. Sztucki during FEM calculations. We also thank G. Costantini for helpful discussions and K. von Klitzing for his continuous support and interest. This project was partly supported by SIGENET (EC Project No. IHP-RTN-99-1).

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