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Stable and Metastable InGaAs/GaAs Island Shapes and Surfactantlike Suppression of the Wetting Transformation

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Contrasting behaviors are observed in InGaAs/GaAs island formation during vapor phase epitaxy: variation of group V partial pressures gives different critical thicknesses for the onset of the Stranski-Krastanow transformation, surface coverages, ratios between coherent and incoherent islands, and dissimilar morphologies upon annealing. The latter experiments show that small lens-shaped islands can be found in equilibrium if InGaAs surface energies are minimized, leading to the conclusion that AsH_3 can raise surface energies and act as an impurity-free "morphactant." [S0031-9007(98)07146-4]

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The importance of Stranski-Krastanow (S-K) coherent island formation as a mechanism for strain relaxation has been established in both Ge/Si [1] and InAs/GaAs [2,3] heteroepitaxy. In the S-K or wetting transformation, growth is initially two dimensional, until the film reaches a strain dependent critical thickness. Deposition beyond this critical thickness results in island formation and subsequent increases in island densities until saturation. Interest in S-K growth has been rekindled by the first reports of these strained islands to make defect-free, self-assembled, InGaAs/GaAs semiconductor quantum dots (QDs) [4–6]. Since then, a large number of studies have focused on strain relaxation by island formation. An improved understanding of the varying and often competing mechanisms that result in different morphologies during island nucleation will determine the successful utilization of these islands in zero-dimensional (0D) devices. Island shapes, aspect ratios, morphologies, and coherence (incoherence) all play a role into the electronic-optic-magnetic properties of self-forming semiconductor quantum dots.

Recent reports show ripening [7] behavior during island formation in Ge/Si and after annealing in InGaAs/GaAs QDs. An *in situ* study of the evolution of island growth in Ge/Si found an optimum range in uniformity [8] during the evolution to the stable dome-shaped configuration. Other reports show the coexistence of different types of islands [9] and a shape transition from small pyramid-shaped islands to dome-shaped islands [10]. In InGaAs/GaAs QD formation, ripening has also been observed upon annealing, which can be partially suppressed by steps in miscut substrates [11]. Ripening in QDs would have obvious disadvantages for applications of island-based devices; therefore, determining if stable islands can be achieved is of both practical and fundamental interest.

Studies using surfactants in the growth of Ge/Si have produced striking results, from the total suppression of the S-K transformation [12,13], to different critical thicknesses [14] and island shapes [15]. It is plausible that similar surfactantlike effects might explain the present controversy surrounding the different island shapes reported in the InAs/GaAs system.

Kinetic barriers for island formation have enabled 2D growth of InGaAs at low temperature [16]. Here we report a partial suppression of the S-K transformation; however, our results can be explained by an offset in the energetics driving the islanding transition. Annealing experiments done at high AsH_3 partial pressures (PP) show Ostwald ripening, but we also observe that small, high density, lens-shaped islands are unaffected by prolonged annealing if certain "optimum" values of group V PP are used during the island growth and subsequent anneals. These results establish that unfaceted InGaAs/GaAs (100) islands can exist in equilibrium.

InGaAs/GaAs structures were grown by metalorganic chemical vapor deposition. Details of the growth of InGaAs on GaAs (100) [17], the use of graded deposition rates in InGaAs growth [18], and the control of QD densities by varying group V PP (the ratio of AsH_3 pressure to the total gas pressures which includes group III precursors and H_2 carrier gas) [19] have been reported elsewhere. Large areas of uniform growth were obtained with H_2 flows of 17.5 standard liters/minute (slm), while a spatially graded deposition was obtained with H_2 flows of 5 slm. The nominal ternary compositions of the islands is $In_{0.6}Ga_{0.4}As$, the growth temperature was 550 °C, and the growth rate 0.5 to 0.75 monolayers (ML) per second. After island formation, uncapped structures were cooled to room temperature while maintaining the arsine PP to 400 °C. Force microscopy (FM) gave statistical

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information on island sizes and areal densities. Plan view transmission electron microscopy (TEM) and high resolution scanning electron microscopy (SEM) were also used for structural characterization in several samples.

Figure 1 shows the variation in surface coverage from nanometer size InGaAs as a function of arsine PP. Statistical information for two types of islands is presented: small coherent islands (QDs), and larger islands found to coexist with the QDs in different ratios, which are seen to depend critically on growth conditions. Figure 2 is a plan view TEM micrograph showing both types of islands in a sample grown under AsH_3 PP of 6×10^6. The larger islands are incoherent: They contain dislocations and show moiré fringes.

The solid diamonds and circles in Fig. 1 show the average diameters and the fractional surface coverages from these large islands, indicating that their density and sizes are also dependent on arsine flow. The fractional coverage for the small islands (QDs) is significantly higher for an "optimal" value in arsine PP, changing from a maximum of 25% for values of AsH_3 PP near 10^{-6} to only 5% for PP near 10^{-5}. Surface densities and dimensions for large islands are higher for the conditions that promote low coverage by small islands indicating opposing trends between small and large island coverages.

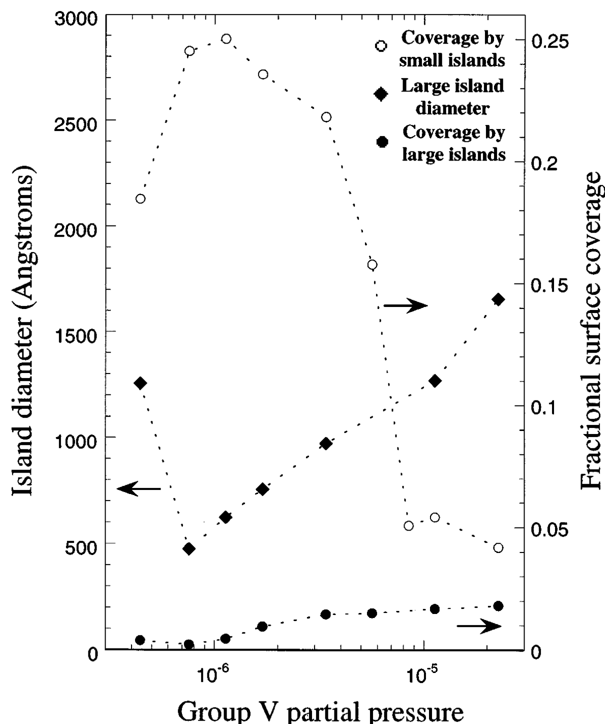

FIG. 1. Variations in InGaAs island coverages as a function of AsH_3 partial pressure (PP). Growth at 550 °C for 5 ML deposition at a growth rate of 0.5 ML/sec. Solid diamonds show the variation in diameter for large (often incoherent) islands. The fractional surface coverage is shown for small islands (hollow circles) and for large islands (solid circles).

A different type of experiment is presented in Fig. 3. Here depositions using a graded growth rate were used [18]. With this method, the structural evolution of island formation can be studied for a single growth, since a two-dimensional layer is obtained on one end of the sample strip and island coalescence at the other end. Two different graded growths were done for two different values of AsH_3 PP. This allowed determination of the 2D to 3D transitions for $In_{0.6}Ga_{0.4}As/GaAs$ for conditions of high and low AsH_3 PP. The island concentration curves shown in Fig. 3 indicate that different values for the 2D to 3D transition can be obtained in InGaAs/GaAs depending on arsine partial pressure. A larger critical thickness is obtained at high values of arsine partial pressure, indicating that high arsine flows can partially suppress, or at least delay, the onset of the S-K transformation.

In the next experiment, both growth and annealing of InGaAs islands were done under the two different values of AsH_3 PP, indicated by curves (a) and (b) in Fig. 3 (1.5×10^6 and 6×10^6). Annealing times were 60 min in both cases. The morphologies of the sample surfaces after such anneals are shown in Figs. 4(a), 4(b), and 4(c) for anneals at high Group V PP and in Figs. 4(d), 4(e), and 4(f) for anneals at low arsine PP. Despite such dramatic differences in morphology, all other growth conditions such as temperature, impurities, H_2 flow, deposition times, and growth rates were identical. As can be seen, lower coverages and larger sizes are found after

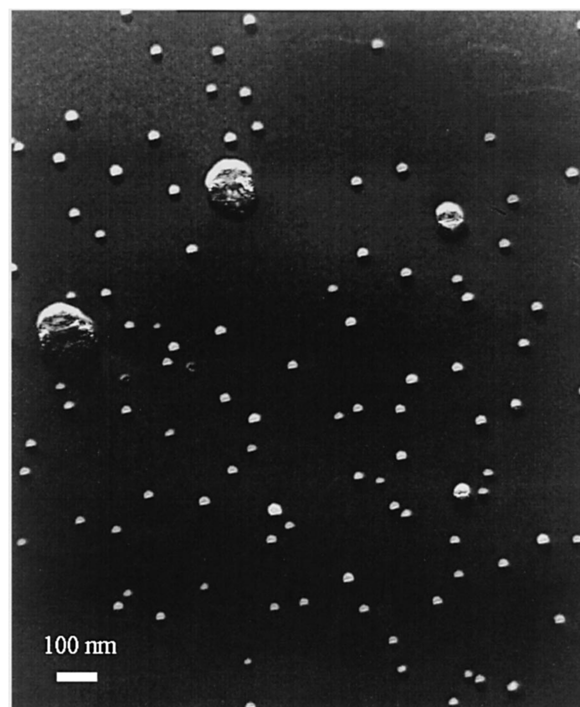

FIG. 2. Plan view TEM micrograph showing the morphology of the islands grown at high AsH_3 PP (6×10^6) without subsequent annealing or growth interruption.

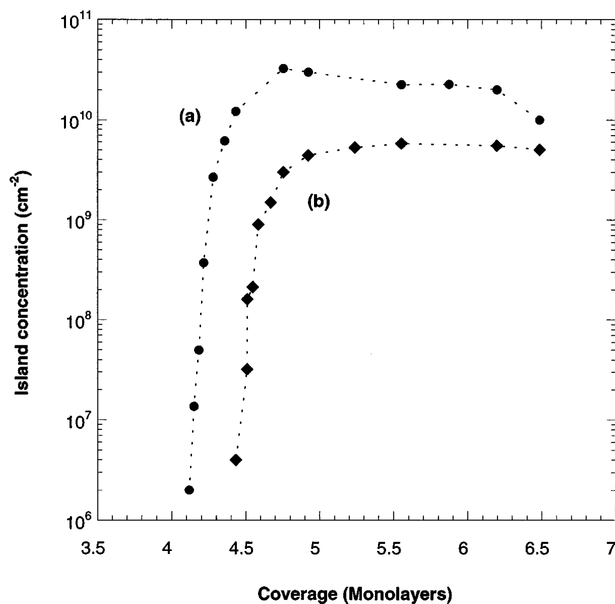

FIG. 3. Island concentrations as a function of coverage using conditions that produce a graded deposition. (a) At AsH_3 PP of 1.5×10^6 and (b) at AsH_3 PP of 6×10^6.

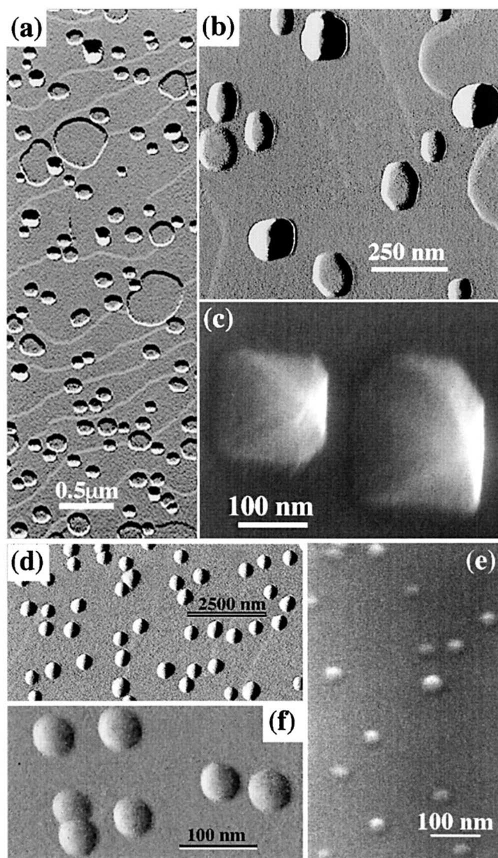

FIG. 4. (a),(b) FM images (deflection) and (c) high resolution SEM image of surface morphologies after 60 min anneals under high AsH_3 flows (PP of 6×10^6) (d),(e) FM images and (f) high resolution SEM micrograph of InGaAs islands annealed for 60 min under the same low AsH_3 flow that produces the maximum island densities shown in Fig. 1.

anneals at high AsH_3 PP, indicating significant differences in ripening behavior.

Several features can be seen from Figs. 4(a) and 4(b). The most prominent are the large, faceted dome-shaped islands similar to the ones reported for the growth of Si-Ge islands [10]. Vertical height measurements show these to have 10 times higher aspect ratios than the uniform lens-shaped islands shown in Figs. 4(d), 4(e), and 4(f). The other features shown in Figs. 4(a) and 4(b) were much flatter, with faceted elongated hexagonal islands and unformed large flat islands. The observation of different types of islands indicates that the system was still under ripening after 1 h anneals. Annealing conditions under low arsine PP produced instead islands in high concentrations, good size and shape uniformity, and smooth, continuously curved surfaces. The latter was verified by high resolution SEM and by FM using low cone angle tips.

Large islands are not present when the small islands show the largest converge; however, at arsine flows above and below this optimum value which promotes maximum island coverage, large islands were observed. Our observation of ripening at high arsine PP indicates that the large domed islands shown in Fig. 4(c) are a later stage of the large incoherent islands shown in Fig. 2, ripened at the expense of the smaller islands. The variation in average diameters for these large islands with arsine PP indicates the possibility that ripening and accelerated growth for incoherent islands is already occurring during the island formation or sample cooling. Incoherent islands experience a higher rate of growth. Such accelerated growth for strain relaxed islands was observed in Ge/Si (100) [20] and later explained [21] from differences between chemical potentials in strained and unstrained islands. Such dissimilar rates of growths have the effect of making the bimodal distribution in sizes more pronounced. This effect is also observed here for InGaAs/GaAs island growth. This is illustrated in Fig. 5, which shows islands grown under the same AsH_3 PP used for the island growth shown in Fig. 2. Growth was stopped shortly after the S-K transformation in Fig. 5(a), and after an additional 2 ML deposition in Fig. 5(b).

Figure 1 shows that maximum island coverage is obtained with an optimal value for AsH_3 partial pressure. The island coverage rises to its maximum value at AsH_3 PP near 10^{-6} and decreases for high values of AsH_3 PP. Different mechanisms might play a role on the island concentration shown on the right and left sides of the maximum value for coverage in Fig. 1. At very low group V PP, the possibility of group III reconstructed surfaces and their known effects on adatom mobilities must be considered.

We have shown that large variations in island density can be obtained with changes in the AsH_3 concentration; furthermore, dramatic differences are seen upon annealing. Our experimental results also indicate that the

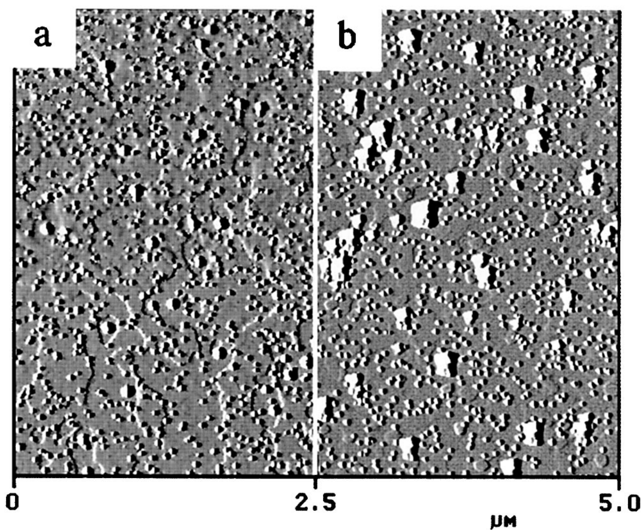

FIG. 5. InGaAs/GaAs evolution in bimodal behavior for deposition beyond saturation island densities. Estimated deposition: (a) 5.5 monolayers. (b) 7.5 monolayers.

conditions that promote low surface coverage also produce a later onset of the S-K transformation. Furthermore, the conditions that promote low island densities produce metastable island configurations causing ripening even during cooling with no annealing.

The differences in island coverage can be explained by considering the thermodynamic driving force in S-K island formation. In the formation of coherent S-K islands a reduction in strain energy is achieved at the expense of an increase in surface energy. The change in energy with formation of one island can be expressed as

$$\Delta E_{\mathrm{isl}} = \Delta E_{\mathrm{surf}} + \Delta E_{\mathrm{ela}} ,$$

where ΔE_{surf} is the cost in surface energy and ΔE_{ela} is the change in strain energy due to elastic relaxation. If the surface energy is lowered, islanding will be promoted for a fixed value of bulk elastic energy. Therefore, a decrease in island coverage suggests an increase in surface energy. This leads to the surprising conclusion that arsine can be used as an impurity free "surfactant." Impurities that raise surface energies were called "morphactants" [15] in a study that found different island shapes after prolonged annealing experiments which included the addition of different impurities used as surfactants in Ge/Si island growth. It appears then that an "excess" AsH_3 during growth can act in an analogous manner in the growth of III-V compounds. Prolonged annealing under high AsH_3 pressures decreases island density and induces faceting. All experimental observations presented here are compatible with the attribution of a surfactantlike action of AsH_3 in high concentrations.

Ripening has been predicted for unstable or metastable configurations [22] with the implication that no ripening occurs if the system is in equilibrium. Therefore we believe that the arsine flows that produce the highest density of small islands can be used to achieve equilibrium for growth of InGaAs islands on GaAs (100), since ripening is not observed even after prolonged annealing.

In conclusion, InGaAs/GaAs (100) island growth experiments done at different values of arsine flows have shown partial suppression of the S-K transformation and radical changes in island coverages and ripening behavior. It was found that the same conditions that promote low island coverage also cause a later onset of the S-K transformation, resulting in thicker films before island formation is observed. We have also shown that it is possible to achieve thermodynamically stable smooth unfaceted island growth when surface energies are minimized in the growth of InGaAs.

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