InP/GaAs self-assembled nanostructures: Modelization and experiment

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The initial stages of the three-dimensional metal organic vapor phase epitaxy growth of InP/GaAs have been studied by atomic force microscopy and Rutherford backscattering. The results are compared with the predictions of an equilibrium model that predicts an in-plane critical size for island formation. At low growth rates the model fits well the experiments while it needs to be further developed to include kinetic effects at higher growth rates. The experiments indicate a Stranski–Krastanow growth mode with a critical thickness of 2.1 ML. © *1996 American Institute of Physics.* [S0021-8979(96)08415-0]

The importance of semiconductor structures based on quantum confinement effects is increasing with the advances in the fabrication technology. Recently, great attention has been paid to the possibility of avoiding any postgrowth processing by exploiting self-organization phenomena during epitaxial growth. The idea is to perform epitaxy of highly mismatched material couples in conditions of three-dimensional (3D) growth and to control the size and the distribution of the resulting islands to obtain quantum dots and in some cases, as shown by Tersoff and Tromp,[1] even quantum wires. Eaglesham and Cerullo[2] first reported the possibility of relaxing the misfit elastic energy via a local deformation of the substrate, by means of coherent island formation. In many theoretical studies the instability of a uniformly stressed film against surface corrugation was investigated. In particular, Spencer *et al.*[3] and Gao[4] studied the conditions under which a perturbation can grow at the surface of a strained epilayer. They showed how the competition between the elastic relaxation and the increase of the surface energy determines a threshold characteristic length for the development of a surface perturbation. The characteristic length turns out to be inversely proportional to the square of the misfit. On the other hand, Tersoff and Tromp[1] used a crude analytical approximation of the elasticity equations to work out the optimum shape and size of a single faceted island sitting on a semi-infinite substrate under mismatch conditions.

In this work, we present a model that predicts a critical in-plane dimension for the development of 3D islands. The elasticity equations are solved with a perturbative method applied to the boundary conditions at the free surface. The substrate local deformation and the contribution due to the difference between the elastic constants of the islands and of the substrate are taken into account. To describe the evolution above the critical value, the elastic energy was numerically computed by means of the finite elements method (FEM) MARC Code.[5] This calculation allows us to determine the equilibrium dimension of a non-faceted island as the growth proceeds beyond the threshold for 3D growth. The InP/GaAs system was chosen to test the model due to its relatively low misfit (about 4%). In fact, although no quantum confinement is possible in this system, it has a higher characteristic length for the 2D–3D transition than other more investigated systems, such as InAs/GaAs.

The model considers that the determining factor for island formation is the stress-driven instability of the layer by layer growth that sets on after the deposition of one or more monolayers. The transition from a 2D layer to a 3D islanded structure occurs when the relaxation of strain energy associated with an increase of aspect ratio (height over base diameter) out balances the increase of surface energy due, essentially, to the increase of the surface area. As just above the 2D–3D transition the islands appear to be round shaped, in the model they are assumed to have a Gaussian surface profile where σ and h represent the standard deviation and the maximum height of a single island, respectively. The radius of the island base is assumed to be $r=2\sigma$, where the height drops to about $0.1\,h$. We stress, however, that the results presented in the following do not depend on the particular choice for the island shape. The aim of the calculation is to determine, in the thermodynamical limit, the size evolution of a 3D island. Details of the calculation will be reported elsewhere while here we summarize the main points.

In order to determine the strain energy of a single island with Gaussian profile over a substrate with different elastic constants, the calculation follows two steps: (i) taking the appropriate boundary conditions at the free surface, the strain energy density of a slightly undulating surface having a cosinusoidal shape is computed; (ii) the solutions corresponding to the Fourier components of the Gaussian profile, weighted by the Fourier transform, are superimposed. This is possible due to the linearity of the boundary conditions for

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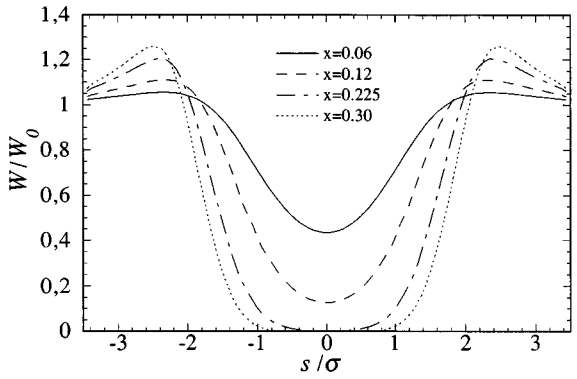

FIG. 1. The reduced strain energy density (W/W_0) at the island surface as calculated with finite elements method for different values of the aspect ratio x vs the reduced in-plane coordinate s/σ.

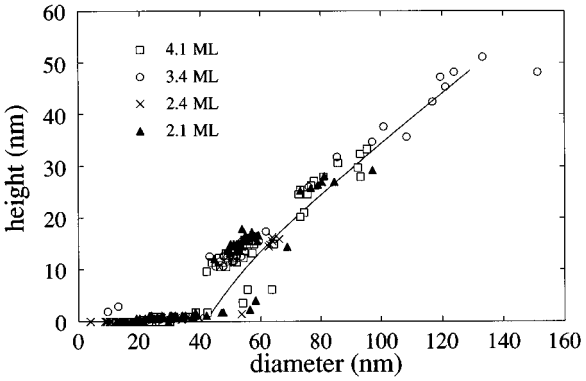

FIG. 2. Island height vs base diameter (4σ) for four samples grown at $v_g=0.16$ ML/s. The solid line shows the equilibrium dimensions predicted by the model.

aspect ratios $x=h/4\sigma \ll 1$ (i.e., at the very beginning of the instability development). In this approximation, the strain-energy relaxed with respect to a portion of a flat film with the same volume is given by

$$\Delta E = -8\pi\sqrt{\pi}\frac{E(1-\nu_s^2)}{E_s(1-\nu)}W_0\sigma^3x^2, \tag{1}$$

where ν and E are the Poisson ratio and the Young modulus of the film, ν_s and E_s being the corresponding quantities for the substrate and W_0 the strain-energy density per unit volume of a flat film. The first term of the series expansion of the surface energy variation is given by

$$\Delta\Sigma = 8\pi\gamma\sigma^2x^2, \tag{2}$$

γ being the surface energy per unit area of the growth plane. The minimum of the total energy at constant volume ($\sigma^3x=\text{const}$) is obtained for

$$\sigma=\sigma^0_{\min}=\frac{4E_s(1-\nu)}{3\sqrt{\pi}E(1-\nu_s^2)}\frac{\gamma}{W_0}, \tag{3}$$

which is independent of x. This result means that there is a critical in-plane dimension above which the relaxation of the strain energy dominates the increase of surface energy and the aspect ratio of the island tends to increase, i.e., the 3D morphology develops. Following Eq. (3) the model predicts a minimum equilibrium diameter for InP islands on (001) GaAs of 42–43 nm.

The FEM calculation of the strain field proceeds by simulating the mismatch between the island and the substrate by means of a fictitious difference in the temperature and thermal expansion coefficients of the two materials.[6] For small values of the aspect ratio, the numerical results reproduce well the analytical ones. Figure 1 shows the relative change of the strain energy density along the island surface for different values of the aspect ratio x. s is the in-plane coordinate normalized to σ. For $x=0.225$, the top of the island is completely relaxed and the extent of the relaxed surface area increases with further increase of the aspect ratio.

InP samples were grown on (001) GaAs substrates by metal organic vapor phase epitaxy in a low pressure Aixtron reactor at 580 °C. A GaAs buffer layer was always grown on top of the substrate. Most of the samples were deposited with a nominal growth rate of 0.16 InP monolayers (ML) per second.

Rutherford backscattering spectrometry (RBS) was used to calibrate the actual deposition rate. Moreover, the equivalent layer thickness was measured for each sample with a precision better than 0.2 ML.

The surface morphology of the samples was investigated by atomic force microscopy (AFM) with a Park Scientific Instruments microscope in the ''contact mode'' by using ''Ultralever'' tips of 10 nm nominal radius to minimize tip-surface convolution effects. Analysis of the AFM images was performed by NIH-Image[7] to measure the height and the base diameter of the islands. AFM analyses supported the Gaussian shape assumption, but for the biggest, faceted islands. Moreover AFM shows that in samples with a coverage of less than 2 ML only large terraces, separated by steps 1 ML high, are visible. From RBS and AFM analysis the threshold for the 2D–3D transition was found to occur after a deposition of 2.1 ± 0.2 ML. This result compares well to that of Ref. 8, where a critical thickness of 2.5 ML is found, and that of Ref. 9, where the 2D–3D transition for the similar misfit InP/InGaP system is found at 1.8 ML.

The results of the AFM size analysis of four samples, grown at 0.16 ML/s rate in the 2–4 ML thickness range, are collected in Fig. 2 where the height of all the islands is correlated to their diameter. The data indicate a critical diameter of about 40 nm, where the height of the islands suddenly reaches the value of 10–12 nm, i.e., an aspect ratio of 0.25–0.30. Some nanostructures with very small aspect ratio can also be identified. The solid line in Fig. 2 gives the equilibrium dimensions of the islands as predicted by our model with FEM.

The role of the kinetics, not taken into account in the model, was also investigated. Figure 3(a) shows the AFM 3D image of a 2.1 ML sample grown at $v_g=0.16$ ML/s. Few well-developed 3D islands (about 15 nm high) are evident while a large population of smaller structures is present. These small round-shaped structures are few monolayer thick (0.6–1.2 nm) and correspond to most of the data below 40 nm diam in Fig. 2. Upon further deposition, more 3D

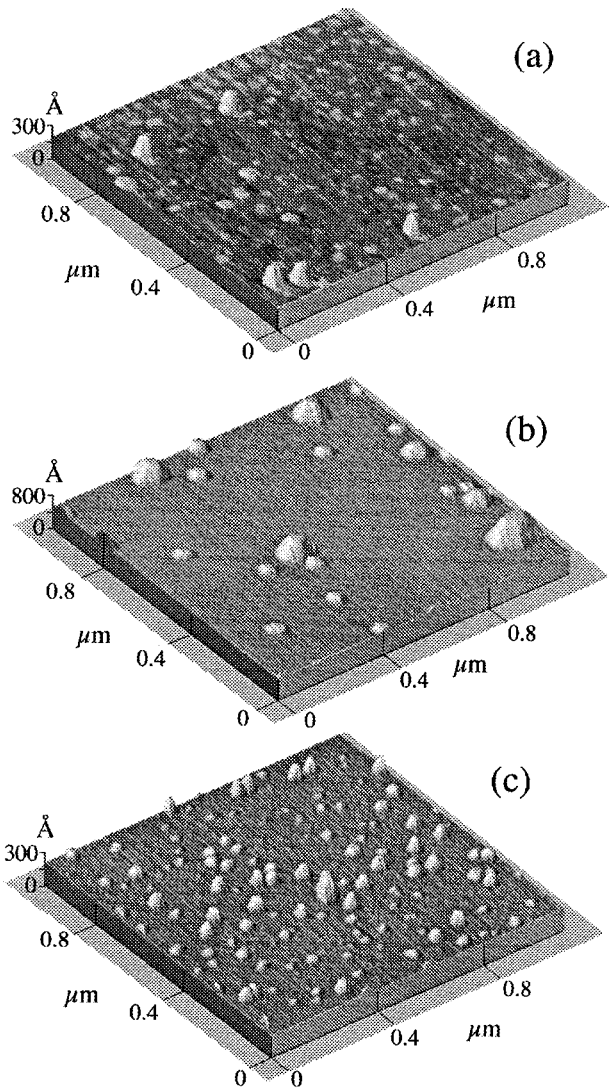

FIG. 3. AFM images of samples grown at $T=580$ °C. (a) $v_g=0.16$ ML/s, $t_g=14$ s; (b) $v_g=0.16$ ML/s, $t_g=25$ s; and (c) $v_g=0.60$ ML/s, $t_g=5$ s. The deposited InP dose, measured by RBS, is 2.1 ML in (a), 4.1 ML in (b), and 2.8 ML in (c).

islands develop with increasing dimensions as shown, for instance, by the sample of Fig. 3(b) ($v_g=0.16$ ML/s, 4.1 ML). In this sample the islands show a large spread in size, with some of them being very high (in the 50 nm range) and showing the beginning of faceting. Nevertheless, their density is low and a large part of the surface is not covered by islands. This is confirmed by AFM analyses performed with high resolution in the areas between the islands. Incidentally, RBS spectra recorded in depth-enhancing grazing incidence and emergence geometry[10] showed that two continuous InP ML still wet the substrate.

Growing at higher rates leads to a significantly different morphology as shown in Fig. 3(c) referring to a 2.8 ML sample grown at $v_g=0.6$ ML/s. Here, the density of the islands is higher than for the samples of Figs. 3(a) and 3(b) and is very close to the density of the small structures observed in the sample of Fig. 3(a).

This behavior suggests the following picture: the small structures are the ''seeds'' for the island formation, and their evolution is mainly controlled by the kinetics of the deposition process rather than by thermodynamics. The atoms that are aggregated in the seeds are still ''mobile,'' at least during the deposition, and they tend to minimize the energy by forming few big islands if they have enough time to move on the surface. On the other hand, for high deposition rates, the critical size for island formation is reached before substantial migration of the atoms on the surface has occurred and more islands of smaller height are formed.

In conclusion, we have determined the 2D–3D transition in the InP/GaAs system at 2.1 ± 0.2 ML. Above this critical thickness and at low growth rates, the island development and evolution is well described by a thermodynamical model. For high growth rates, kinetics dominates over equilibrium and higher densities of islands with less dispersed size distribution are obtained.

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