Kinetically controlled critical thickness for coherent islanding and thick highly strained pseudomorphic films of $In_xGa_{1-x}As$ on GaAs(100)

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We have investigated the effects of surface-diffusion kinetics on the molecular-beam-epitaxy growth of highly strained $In_xGa_{1-x}As$ on GaAs(100). Experiments consisted of growing films at different substrate temperatures and characterizing them using reflection high-energy electron diffraction, scanning tunneling microscopy, and transmission electron microscopy. From a theoretical analysis we have obtained a criterion for a kinetically controlled critical thickness for coherent island formation that is in qualitative agreement with our experimental observations. The results of our study lead us to conclude that surface diffusion is a major factor determining the growth mode in strained-layer heteroepitaxy. As an example, it is shown that with limited kinetics (in this case, low temperatures) thick highly strained pseudomorphic layers may be grown.

To obtain optimal performances from electronic and photonic devices based on superlattices and heterojunctions, it is necessary to grow defect-free layers with morphologically and compositionally sharp interfaces. At the same time, in terms of physical properties, it is advantageous to fabricate structures from component materials which have significantly different band gaps and lattice constants. Unfortunately, the benefits of using dissimilar materials are often offset by difficulties in growth that lead to poor microstructure and consequently degraded electrical and optical properties. In semiconductor heteroepitaxial systems, elastic strain arising from a lattice mismatch greatly influences the growth and microstructure of an overylayer. For these systems, the traditional view of growth, derived from equilibrium theories,[1,2] is that a film that wets the substrate will grow uniformly and commensurately, strain energy increasing linearly with thickness, until reaching a particular thickness (i.e., critical thickness) beyond which it is energetically favorable for a network of dislocations to form. Such a discommensuration reduces the strain energy by partially accommodating the misfit. Experimentally, it is often observed that strain relaxation in semiconductor systems occurs at much larger thicknesses than predicted.[3] This has led to the incorporation of kinetic barriers that impede the nucleation and motion of dislocations into the theory.[4–9] The inclusion of such kinetic effects has resulted in better agreement with measurements of strain relaxation.

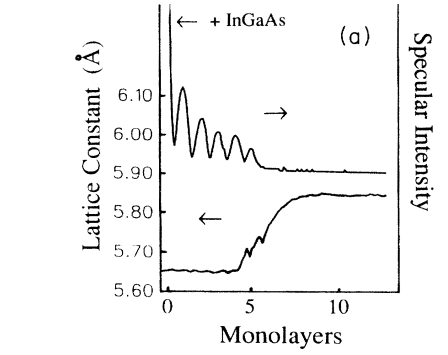
Despite successes, there remain some experimental and conceptual difficulties with the dislocation-based models. For example, recent studies of strained-layer epitaxy revealed microstructures containing coherent (undislocated) islands.[10,11] This is problematic because dislocations were normally thought to be a necessary precursor to island formation. Moreover, contrary to the assumptions of dislocation-based models, a uniform two-dimensional (2D) overlayer is not the lowest-energy configuration of a commensurate film in the thermodynamic limit.[12] In light of these discrepancies, we recently proposed a dislocation-free model for the growth mode and strain relaxation in the initial stages of strained-layer heteroepitaxy. It was based on strain relaxation through a morphological transformation occurring via the kinetically controlled evolution of a dislocation-free film toward a coherent island morphology.[13] In this paper we examine the role of kinetics (i.e., surface diffusion) in such a model.[14] Experimental data from reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM), and transmission electron microscopy (TEM) illustrate the dramatic effects surface-diffusion kinetics has on the growth mode and strain relaxation. It is demonstrated that under particular conditions, thick highly strained pseudomorphic films may be grown. These results lead us to introduce the concept of a kinetically controlled critical thickness for coherent 3D islanding. In addition, based on our ideas we discuss a simple, intuitive explanation for the case of layer growth followed by islanding, often referred to as a Stranski-Krastanow (SK) growth mode.

Our studies centered around the growth of highly strained $In_xGa_{1-x}As$ on GaAs(100). Experiments were performed in an ultrahigh-vacuum molecular-beam-epitaxy system equipped with *in situ* STM and RHEED. The ability to freeze in the growth front allowed for real-space STM characterization of the surface topography as it appeared during growth.[15] A charge-coupled-device detection scheme for RHEED analysis also enabled the evolution of the film to be studied in real time.[16] *Ex situ* characterization of the overlayers was accomplished using a JEOL 4000 and JEOL 2000 TEM.

We have investigated the growth of overlayers as a function of large misfits ($>2\%$), and temperature. For measurements at constant high temperatures, we observe that at a particular thickness a transition from 2D to 3D growth occurs. With decreasing misfit this characteristic thickness increases.[13] Presented in Fig. 1 are characteristic data depicting the high-temperature ($T\cong 520\,^{\circ}C$)

growth of 12 monolayers (ML's) of $In_{0.5}Ga_{0.5}As$ (3.5% misfit). The abrupt transition in the surface lattice constant at ~5 ML's, coincident with the damping of the RHEED specular intensity oscillations and the change in the diffraction pattern from streaked to spotty (not shown), is indicative of the beginning of island growth [Fig. 1(a)]. STM images reveal the islanded film [see Fig. 1(b)]. Previous studies showed that islands formed under these types of conditions were likely to be coherent.[11] In general, for fixed misfit, with decreasing growth temperature the onset for islanding occurs at increasing thicknesses and the transition becomes more gradual. Figure 2 displays the characterization of a 3.5% lattice-mismatched film grown at $T \cong 320$ °C. In contrast to the high-temperature growth, the specular intensity oscillations persist longer, the diffraction pattern remains relatively streaked, and the lattice-constant data reveal negligible strain relaxation even after depositing 50 ML's of material. Cross-sectional TEM micrographs [see Fig. 2(b)] reveal a crystalline film; thus, the thickness has not exceeded the epitaxial thickness (at $T = 320$ °C).[17] STM and lower-resolution TEM images (not shown) revealed a flat surface topography consistent with planar growth. Apparently, in the limit of low-temperature growth, island formation may be suppressed.[18] The combination of data in Fig. 2 is indicative of a pseudomorphically grown overlayer. These results lead us to consider whether low-temperature epitaxy may have the potential for producing good microstructure in semiconductor structures having large epilayer strains. In such a case, the benefits to device applications would be considerable.

Planar films grown at moderate and low temperatures are unstable to the formation of islands upon high-temperature annealing. This observation supports the view that an island film is a lower-energy configuration than a flat, uniformly strained film. This can be understood by considering that a strain-relieved coherent island reduces the elastic energy over its volume at a proportionally smaller cost of additional surface energy.[19] Since the volume contribution dominates, independent of the relative strength of surface to strain energies, a film



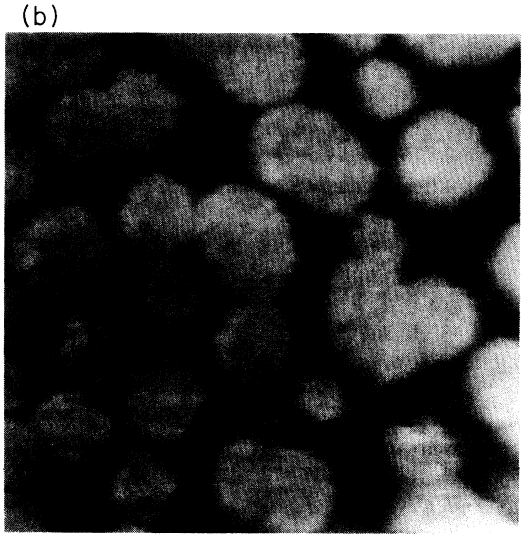


FIG. 1. RHEED and STM data characterizing the high-temperature ($T \cong 520$ °C) growth of $In_{0.5}Ga_{0.5}As$ (3.5% lattice mismatch) on GaAs(100). (a) Intensity oscillations of the specular beam and the corresponding surface lattice constant plotted as a function of epilayer thickness. $\phi = [110]$. (b) STM image of the overlayer obtained after depositing 12 ML's. The scan area is 150×150 nm^2. The height range (from black to white) is ~8 nm.

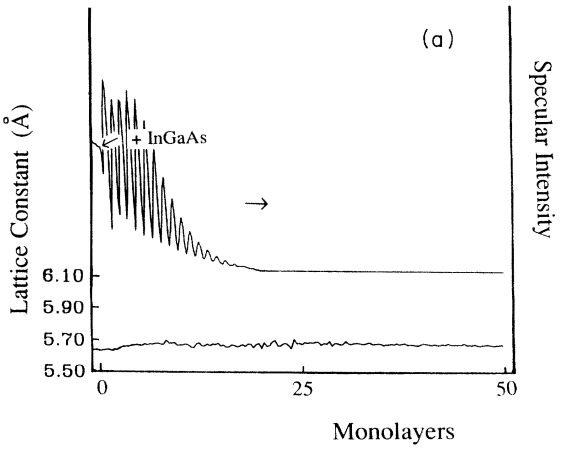


FIG. 2. RHEED and TEM data characterizing the low-temperature ($T \cong 320$ °C) growth of $In_{0.5}Ga_{0.5}As$ (3.5% lattice mismatch) on GaAs(100). (a) Intensity oscillations of the specular beam and the corresponding surface lattice constant plotted as a function of epilayer thickness. $\phi = [110]$. (b) Cross-sectional high-resolution transmission electron micrograph of a 50-ML-thick overlayer viewed along the [110] direction. The [110] structure is clearly seen, although the specimen thickness somewhat limits the quality of the image.

with large enough islands will have a lower energy than a 2D uniform film. It appears that 2D growth in this strained system results from kinetic barriers (i.e., limited surface diffusion). At low temperatures, atoms can only diffuse short distances before they are incorporated. Therefore, island formation is kinetically delayed or frozen out. Likewise, the nucleation and/or motion of dislocations in these films is significantly limited by kinetic barriers. Given the planar morphology and low temperatures, the barriers may be rather large. It is interesting to note that, whereas the film in Fig. 2 is not significantly relaxed, comparable low-temperature, planar films of Ge grown on Si(100) were nearly completely relaxed.[20] Moreover, 50 ML's does not appear to be the upper thickness limit for low-temperature pseudomorphic growth of $In_{0.5}Ga_{0.5}As$. Determining the thickness limits and investigating the mechanisms for the eventual strain relaxation of these films are interesting issues requiring further characterization. They are the subject of future work.

Our experimental observations point to surface diffusion as a primary factor controlling the facility with which a morphological transformation to a coherently islanded film may occur. In an attempt to understand this in more detail we have analytically modeled a strained overlayer in a way that incorporates surface diffusion. A (1+1)-dimensional film is segmented into lengths l, chosen to be equal to the surface diffusion length L given by $L=\sqrt{(D\tau)}$, where D, the surface diffusivity, depends exponentially on temperature, and τ is the time to deposit a monolayer. The volume of material, $V=Lt$, may be in the form of a uniform film with thickness t, or an island. In either case, the energy of the system is the sum of the strain energy and the surface energy, expressed as $E/V=\kappa\varepsilon^2 f(x)+\gamma_{\rm FV}\sqrt{x/V}$.[21] In this equation, ε is the misfit, $\gamma_{\rm FV}$ is the surface tension, and κ is the bulk modulus. Strain relaxation is incorporated in the strain energy term through the function $f(x)$, an empirical function determined from a numerical analysis. In the analysis, islands and the substrate are modeled elastically. The elastic constants of the film and substrate are approximated to be equal, and it is found that the mismatch is partly accommodated by straining of the substrate directly underneath the island.[10] f depends only on the aspect ratio x of the island height to width ($x=0$ for a uniform film), and it has the following functional form: $f(x)=(1.2)(0.075)/(x+0.075)$. Minimizing the energy of the islanded segment with respect to the island aspect ratio and comparing this with the energy of the uniform film, we obtain a critical thickness criterion, $t_c\approx\gamma_{\rm FV}^2/\kappa^2\varepsilon^4 L$. At $t=t_c$, there is a discontinuous change in the preferred aspect ratio from zero to a finite value. Thus, for $t<t_c$ we predict metastable elastically strained films will grow in a planar fashion; for $t>t_c$, coherent island formation should occur. Also predicted from our analysis is a minimum temperature,

$$T_{\rm min}=\left[\frac{k_B}{E_A}\ln\left[\frac{1.44D_0\tau\kappa^2\varepsilon^4}{\gamma_{\rm FV}^2}\right]\right]^{-1},$$

below which island formation is suppressed. In this expression, k_B is Boltzmann's constant, E_A is the activation energy, and D_0 is the surface diffusion constant. We emphasize that the basis for this critical thickness criterion is kinetics, not energetics; for near-equilibrium growth, t_c is essentially zero (see discussion below).

While the analysis above is in 1+1 dimensions, it captures most of the features observed experimentally in 2+1 dimensions. For example, it predicts that with decreasing temperature (i.e., L) conditions moving further from equilibrium, island formation should occur at increasing thicknesses or, disregarding statistical fluctuations, be suppressed completely.[22] Conversely, in the thermodynamic limit (i.e., near-equilibrium conditions) ($L\rightarrow\infty$), it is predicted that $t_c\rightarrow 0$.[23] This supports our view that beyond the wetting monolayers an islanded film is the thermodynamically stable configuration. Also, from the critical thickness criterion, we see that with decreasing misfit[13] or increasing surface tension the onset for islanding increases. Finally, although it appears from the above criterion that t_c should depend on the growth rate, our investigations revealed no change in the onset for islanding with a fivefold increase in the growth rate. This can be explained by considering that the incorporation time, which is much less than the time to deposit a monolayer, is the relevant time scale for surface diffusion.

The concepts discussed in this paper provide an explanation for a commonly encountered growth mode: layer growth of one or *many* monolayers, followed by island formation. This type of "generalized" SK growth will occur when the interfacial and chemical interaction energies of a substrate and epitaxial overlayer favor wetting, and when strain is involved so that a kinetically controlled critical thickness for islanding is applicable. For such a situtation, $t_c\rightarrow 0$ under near-equilibrium conditions, and islands will form immediately on the one or two wetting monolayers. On the other hand, for conditions further from equilibrium t_c may be rather large and islanding will be delayed for many monolayers.

It should be emphasized that our view is an alternative to dislocation-based models, but it does not preclude strain relaxation by dislocations. We might expect that at low temperatures and/or misfits, and/or high surface tensions,[18] $t_c(\text{island})>t_c(\text{dislocation})$. Hence, strain relaxation would occur through some type of dislocation mechanism. Furthermore, a coherently islanded film is not completely relieved, as there exists a nonuniform strain gradient. The tops of clusters are relaxed, while near the substrate the material is under strain. Therefore, at the edges of islands where the strain-energy density is highest, it is expected that homogeneous nucleation of dislocations will be facilitated, as kinetic barriers are significantly reduced.[24] Related to these considerations, the presence of islands may have an effect on the dislocation network morphology in thick films[24] and on the relaxation processes.[25] Supporting the latter are experiments suggesting that different modes of strain relief operate at high and low temperatures or misfits.[7,25] We expect islanding to play a role in the relief mechanisms at high temperatures and/or misfits, where it is most pronounced.

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[21]Without a loss of generality for a material such as $In_xGa_{1-x}As$ on GaAs, beyond the few-monolayer wetting layer, the substrate-vapor interface free energy γ_{SV} may be set equal to the film-vapor interface energy γ_{FV} and the film-substrate interface energy may be set equal to zero. In addition, the surface energy is expressed relative to the uniform film, which is set to zero.

[22]Comparison of the analytical predictions with experiment at fixed misfit and varying temperature is difficult because the onset for island formation is not abrupt beyond a small range of temperature extending from the congruent sublimation temperature of $In_xGa_{1-x}As$ ($T \sim 530\,^{\circ}\mathrm{C}$) to a few tens of degrees below. Thus, t_c is not well defined over a reasonable temperature range. Nevertheless, there is qualitative agreement in the high- and low-temperature regimes. Note also, an evaluation of T_{min} for quantitative comparison with experiment is problematic, as diffusion parameters are not accurately known.

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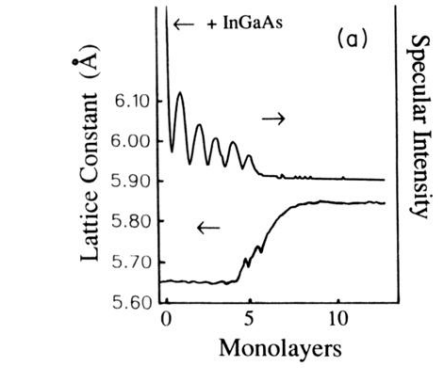
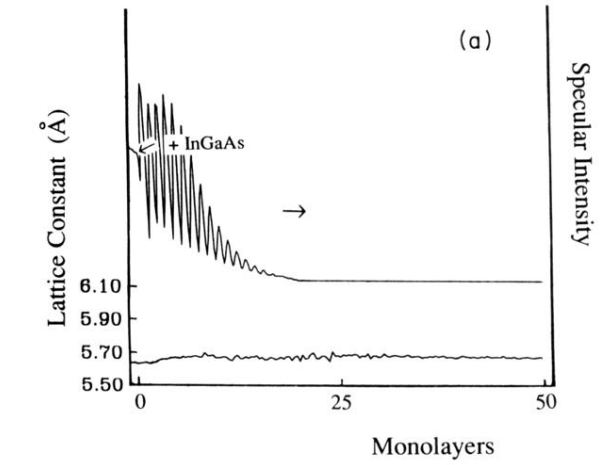


FIG. 1. RHEED and STM data characterizing the high-temperature ($T \cong 520\,^{\circ}\mathrm{C}$) growth of $In_{0.5}Ga_{0.5}As$ (3.5% lattice mismatch) on GaAs(100). (a) Intensity oscillations of the specular beam and the corresponding surface lattice constant plotted as a function of epilayer thickness. $\phi = [110]$. (b) STM image of the overlayer obtained after depositing 12 ML's. The scan area is 150×150 nm^2. The height range (from black to white) is ~ 8 nm.



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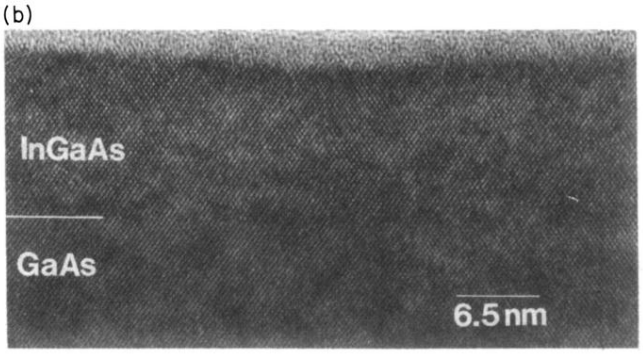

FIG. 2. RHEED and TEM data characterizing the low-temperature ($T \cong 320$ °C) growth of $In_{0.5}Ga_{0.5}As$ (3.5% lattice mismatch) on GaAs(100). (a) Intensity oscillations of the specular beam and the corresponding surface lattice constant plotted as a function of epilayer thickness. $\phi = [110]$. (b) Cross-sectional high-resolution transmission electron micrograph of a 50-ML-thick overlayer viewed along the [110] direction. The [110] structure is clearly seen, although the specimen thickness somewhat limits the quality of the image.