Oscillation of the Lattice Relaxation in Layer-by-Layer Epitaxial Growth of Highly Strained Materials

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It is shown that during the growth of $In_xGa_{1-x}As$ on GaAs, the strain-induced lattice distortion oscillates as a function of monolayer completion in both purely 2D and quasi-2D layer-by-layer growth regimes. This is explained by considering that nontetragonal elastic distortion occurs at the free edges of 2D monolayer islands. Numerical relaxation using a simplified model of interatomic forces gives the correct order of magnitude of the strain relaxation by this process.

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Considerable interest is currently being devoted to the epitaxial growth of lattice-mismatched heterostructures. This is because relaxing the lattice-match condition considerably enlarges the choice of materials which can be associated in order to obtain the desired physical properties. Moreover, at least for semiconductor materials, the built-in strain in the epitaxial layer, induced by the lattice parameter difference, introduces an additional parameter to help optimize the optoelectronic properties of the heterostructure. Indeed, a great deal of effort has been dedicated to the understanding of the first steps of the epitaxial growth of the prototypical Ge/Si and InAs/GaAs highly strained systems. In particular, several studies dealing with the interplay of elastic and plastic relaxation of the strain have been reported for these systems [1–6], which follow the so-called Stranski-Krastanov (SK) growth mode (layer-by-layer growth followed by 3D island formation). It was first demonstrated using transmission electron microscopy (TEM) that islands formed in the SK growth of Ge on Si are initially dislocation free [1]. This *coherent* SK growth was explained in terms of *elastic* deformation partially accommodating the lattice mismatch. Similar observations by TEM [2] and scanning tunneling microscopy (STM) [3] have been subsequently reported for $In_xGa_{1-x}As$ grown on GaAs. Significant lateral strain relief in coherent island growth is also qualitatively explained by free-edge elastic deformation. All these observations are somewhat in contradiction with current models of strain relaxation such as the one recently proposed by Price [4]: In this model, based on the *dynamic* study by reflection high-energy electron diffraction (RHEED) of the growth of $In_xGa_{1-x}As$ on GaAs, it is assumed that islands are nucleated by misfit dislocations.

In the present Letter, also based on a real time study of $In_xGa_{1-x}As$/GaAs growth by RHEED, we show that significant strain relaxation by nontetragonal *elastic* distortion occurs in *both* purely 2D layer-by-layer and quasi-2D (growth front roughening) growth regimes.

Experimental details are as follows. The growth of $In_xGa_{1-x}As$ was performed at 500 °C by molecular beam epitaxy (MBE) on GaAs(001). Just prior to the growth of the alloy, a GaAs buffer layer (0.5 μm) was grown under standard conditions. The growth was followed by RHEED (electron beam energy: 20 keV) using a high-sensitivity charge-coupled-device camera based video recording system. A precise determination of both diffraction intensity and lattice parameter variations (within 0.08%) was made possible by RHEED image acquisition and dedicated analysis software [7].

As is now well established, the growth of $In_xGa_{1-x}As$ on GaAs follows a SK-like growth mode for $x > 0.2$, the 2D-3D growth mode transition being easily detected by RHEED [3,8]. The 2D growth regime is classically associated with the observation of RHEED intensity oscillations, while the 2D-3D transition is characterized by a sharp decrease of the specular beam intensity [8] (and more generally of the 2D diffraction features) due to the change from reflection diffraction on a flat surface to transmission diffraction through 3D islands. This typical behavior is shown in Fig. 1. When considering the distance between streaks associated with a 1×1 unit cell RHEED pattern, this gives the in-plane surface lattice parameter $a_{\parallel}$ [4,7]. When the lattice mismatch is considerable, i.e., $x > 0.25$, the streak separation varies abruptly

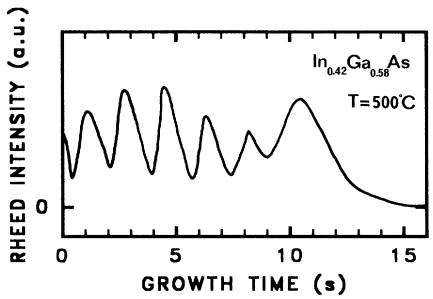

FIG. 1. Typical RHEED intensity oscillation observed during the growth of a highly strained InGaAs layer on GaAs (growth temperature 500 °C). The growth is layer by layer (2D nucleation growth mode) up to 6 monolayers (ML), and then becomes highly 3D.

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at the so-called critical thickness commonly associated with misfit dislocation generation which allows a rapid strain relaxation. However, looking at a finer scale, we observe that $a_{\parallel}$ actually varies from the beginning of the growth within one monolayer. This is exemplified in Fig. 2, where we have reported the variation of $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ [based on the (110) interplanar spacing at the surface] during the growth of $In_{0.42}Ga_{0.58}As$ on GaAs up to the critical thickness of six monolayers (ML). It can be seen that the $a_{\parallel}$ variation oscillates in such a way that it is maximum (minimum) for half (complete) monolayer coverage, i.e., in opposite phase with the specular beam intensity oscillation [9]. Another important feature is that while the $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ value returns to nearly zero after each monolayer completion for the first three monolayers, this is not the case for the subsequent monolayers: An increasing permanent relaxation superposed on the oscillatory deformation is observed up to the critical thickness for which a drastic variation occurs.

How can we explain these observations? In the usual treatment of the pseudomorphic growth regime (coherent strained layers), the biaxial stress imposed by the GaAs lattice parallel to the interface results in an elastic tetragonal distortion of the $In_xGa_{1-x}As$ unit cell, the magnitude of which is assumed to be given by the continuum elasticity theory. Using this approach it is obvious that we cannot explain the oscillatory behavior of the in-plane $In_xGa_{1-x}As$ parameter [10]: As shown schematically in Fig. 3(a), purely tetragonal deformation does not allow a variation of $a_{\parallel}$. This brings us to the conclusion that nontetragonal deformation takes place at the free edges of 2D islands [Fig. 3(b)]. Since the free-edge density is maximum for roughly half monolayer coverage, the $a_{\parallel}$ variation is then also maximum there, as is experimentally observed (Fig. 2) [11].

In order to understand the dynamical behavior of strain relaxation during growth of highly strained layers, we have thus to consider local instead of macroscopic properties of the crystal lattice. This was also the conclusion of the work recently reported by Brandt *et al.* [5], demonstrating the failure of the continuum elasticity theory to predict the correct magnitude of the tetragonal distortion at the monolayer level. To simulate strain relaxation in the fractional monolayer range, we have thus used a simplified version of the valence force field model, which is the most natural description of interatomic forces [12]. In this type of model, the interatomic forces are resolved into bond-stretching and bond-bending forces [13]. In our simplified model, we approximate monolayer islands by a linear chain in which only the bottom As atoms are rigidly fixed to the GaAs semi-infinite lattice, as schematically depicted in Fig. 4. In this figure, k_1 and k_2 are the force constants for bond stretching of the In(Ga)-As and As-As surface dimer bond, respectively, while k_3 corresponds to the In(Ga)-As bond bending. The monolayer "island" shape is calculated neglecting the substrate deformation [14] by numerical relaxation from the initial stage corresponding to biaxial compression of the bulk-type InGaAs lattice to the equilibrium situation where the force sum $\sum f_i$ is zero. The relation between the force constants k_1 and k_3 is taken from the work of Martin [12] ($k_3 = 0.042 k_1$). By assuming as a first approximation that the force constants are proportional to the binding energy, k_1/k_2 is deduced from the ratio between the $(In_{0.42}Ga_{0.58})$-As bond energy and the

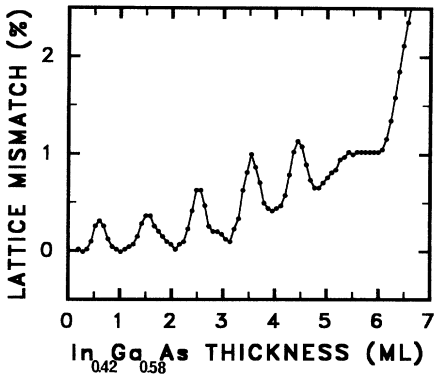

FIG. 2. Lattice-mismatch $[\Delta a_{\parallel}/a_{\parallel}^{GaAs} = (a_{\parallel}^{InGaAs} - a_{\parallel}^{GaAs})/a_{\parallel}^{GaAs}]$ variation as a function of $In_{0.42}Ga_{0.58}As$ thickness in monolayers (ML). The $a_{\parallel}$ variation is deduced from integral order streak spacing on the outside of 3D Bragg diffraction features (a standard 3-point curve smoothing procedure has been applied to the raw data in order to reduce the noise level somewhat). Note that up to critical thickness (6 ML) where strong relaxation occurs by dislocation generation, $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ oscillates as a function of monolayer completion and is maximum for half monolayer coverage. Note also that while for the first three monolayers, $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ returns to nearly zero after each monolayer completion, this is not the case for subsequent monolayers.

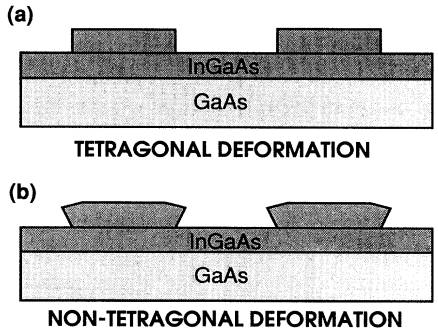

FIG. 3. Schematic representation of the situation corresponding to 2D nucleation growth mode of InGaAs on GaAs for a surface coverage $\theta = 0.5$: (a) considering only tegragonal deformation and (b) adding elastic nontetragonal distortion at free edges of 2D islands. In this case the mean value of $a_{\parallel}$ at the surface is no longer equal to $a_{\parallel}^{GaAs}$. We return to purely tetragonal deformation ($a_{\parallel} = a_{\parallel}^{GaAs}$) for $\theta = 1$.

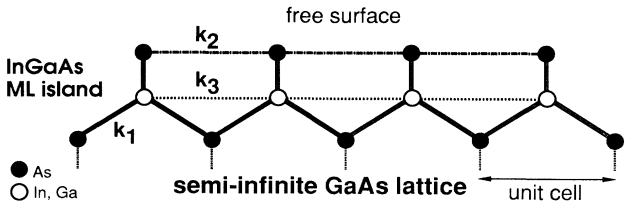

FIG. 4. Simplified model of interatomic forces in a 1D "island" of InGaAs on GaAs. k_1 and k_2 correspond to force constants for bond stretching while k_3 is for bond bending.

As-As surface dimer energy. Taking 1.59, 1.41, and 0.2 eV for the bond energies of Ga-As, In-As, and As-As, respectively [15,16], we obtain $k_2 = 0.067 k_1$ [17]. Using these relations between $k1$, $k2$, and $k3$, we can now evaluate the elastic strain relaxation associated with islands of a given size and vice versa.

After the deposition of the equivalent of four complete monolayers, we note that $\Delta a_{\parallel}/a_{\parallel}^{GaAs} = 0.4\%$ instead of 0% for 1-3 ML (Fig. 2), presumably because of the extra relaxation associated with the growth front roughening. At this stage of the growth, a deposited monolayer is probably distributed over at least two levels at the surface and thus the step density and the correlated strain relaxation increase significantly. To account for a $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ of 0.4% with islands of one monolayer height distributed over two levels, numerical relaxation with the above model gives the lateral extent of the islands as 16 unit cells (6.4 nm) for the $n = 4$ level and 12 unit cells (4.8 nm) for the overlying $(n+1)$ level, with the mean lateral extent of the islands being 5.6 nm and the mean height 0.5 nm [18]. This is in fact very close to what is observed by STM [3] for the growth of $In_{0.4}Ga_{0.6}As$ on GaAs(001): After 4 ML were deposited the lateral extent of the islands is 3-5 nm and the corrugation is 0.5 nm. We can therefore apply our model with some confidence to evaluate the 2D island mean size necessary to account for the $a_{\parallel}$ relaxation observed for half monolayer coverage in the purely layer-by-layer growth regime. For the first half monolayer deposited we observe a $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ of 0.3%, which is found to correspond to elastic relaxation of one monolayer high islands of 11 unit cells of lateral extent (4.4 nm) and covering half the surface. Variations of $a_{\perp}$ and $a_{\parallel}$ across such an island are given in Figs. 5(a) and 5(b). As expected, the $a_{\parallel}$ relaxation is only important near the free edges of the island. When the island size is sufficiently increased, the unit cells at the center of the island are in a purely tetragonal distortion situation and we find an extension of $a_{\perp}$ of 6.5% for InAs on GaAs. Considering that our model corresponds to uniaxial strain, this gives a variation of 13% for the actual biaxial strain situation. This value is considerably higher than the one predicted by the continuum elasticity theory, giving only a variation of 7.3% for $a_{\perp}$, but is in good agreement with the experimental determination by TEM (12.6%) recent-

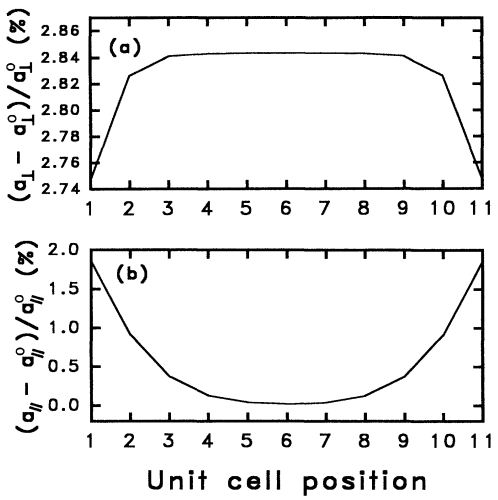

FIG. 5. Variation of $\Delta a_{\perp}/a_{\perp}^{InGaAs}$ (a) and $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ (b) from edge to edge of a 1D "island" of length 11 unit cells. This island size allows a variation of $a_{\parallel}$ of 0.6% within the island and therefore of 0.3% for the mean value of $a_{\parallel}$ variation corresponding to a surface coverage $\theta = 0.5$. Note that this $a_{\parallel}$ variation is the one experimentally observed for half monolayer deposition of InGaAs on GaAs (see Fig. 2).

ly reported by Brandt *et al.* [5] for a monolayer of InAs sandwiched in GaAs. In fact, as concluded also by these authors, the In-As bonds directly at the interface are stretched in order to conserve their bulk bond length.

Finally, a word of discussion should be given about the comparison of the growth behavior of highly covalent materials such as the III-V compounds and of more ionic materials (e.g., II-VI). We have shown here that elastic deformation plays an important role in the strain relaxation of $In_xGa_{1-x}As$ on GaAs. In fact, energy minimization through elastic relaxation is the driving force of the growth front roughening, and then of the 2D-3D growth mode transition. Indeed, for highly strained layers (high indium content) this transition occurs before the critical thickness (plastic relaxation by dislocation) [5,7], while it is no longer observed for low strain ($x < 0.2$) [8]. The situation is very different for II-VI materials. For the growth of CdTe on ZnTe ($\Delta a/a = 6\%$), there is no 2D-3D transition: Growth remains layer by layer even after the critical thickness (6 ML) [19]. Why does elastic relaxation not promote 3D island formation in these materials? This may simply be because when islands coalesce dislocations are formed more easily since, as the bonds are more ionic, the bond-bending force constant is lower, and thus there is greater deformation at the edges of the islands.

In conclusion, we have shown by a real time RHEED study of the strained growth of $In_xGa_{1-x}As$ on GaAs that periodic strain relaxation occurs when the growth proceeds in a layer-by-layer fashion. This relaxation increases at the beginning of each monolayer growth, is

maximum for half monolayer coverage, and then decreases up to the completion of the monolayer. This is explained by nontetragonal elastic distortion at the free edges of the 2D islands which develop and merge during the monolayer growth. When the growth begins to diverge from the ideal 2D mode, an increasing permanent relaxation occurs which is also accounted for by elastic deformation of islands and then distributed over different levels (growth front roughening). In this type of covalent material, energy minimization through elastic relaxation is in fact the driving force of the 2D-3D growth mode transition. A simple model based on interatomic forces gives, by numerical relaxation, a correct description of these phenomena.

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[1] D. J. Eaglesham and M. Cerullo, Phys. Rev. Lett. **64**, 1943 (1990).
[2] S. Guha, A. Madhukar, and K. C. Rajkuma, Appl. Phys. Lett. **57**, 2110 (1990).
[3] C. W. Snyder, B. G. Orr, D. Kessler, and L. M. Sander, Phys. Rev. Lett. **66**, 3032 (1991).
[4] G. L. Price, Phys. Rev. Lett. **66**, 469 (1991).
[5] O. Brandt, K. Ploog, R. Bierwolf, and M. Hohenstein, Phys. Rev. Lett. **68**, 1339 (1992).
[6] B. G. Orr, D. Kessler, C. W. Snyder, and L. Sander, Europhys. Lett. **19**, 33 (1992).
[7] N. Grandjean, J. Massies, and V. H. Etgens, Phys. Rev. Lett. **69**, 796 (1992).
[8] A. Marti Ceschin and J. Massies, J. Cryst. Growth **114**, 693 (1991).
[9] Such an oscillatory behavior of the InGaAs lattice parameter can also be seen in the Fig. 2 data of the following reference (but without comment of the authors): C. W. Snyder, D. Barlett, B. G. Orr, P. K. Bhattacharya, and J. Singh, J. Vac. Sci. Technol. B **9**, 2189 (1991).
[10] This is not surprising since a fractional monolayer cannot be considered as a continuous elastic medium.
[11] It should be noted that we cannot be sure that we measure the actual mean $a_{\parallel}$ parameter variation. Since the in-plane lattice parameter varies from the center (where it should be equal to that of GaAs) to edges of 2D islands, some asymmetric broadening of the streaks, which may affect the determination of their position, should occur. From sample to sample we observe a difference in $a_{\parallel}$ for half and complete monolayer coverage ranging from 0.3% to 0.5%. This scattering can reflect the lack of precision we have in determining the actual value of the mean $a_{\parallel}$. In fact it is more probably associated with the fluctuation of the mean island size. Indeed we have checked that broadening effects are very limited.
[12] See, for example, R. M. Martin, Phys. Rev. B **1**, 4005 (1970), and references therein.
[13] P. N. Keating, Phys. Rev. **145**, 637 (1966).
[14] This seems justified (to a first approximation) at least for the very first monolayers of InGaAs when the growth regime is still 2D or quasi-2D (our model is proposed to explain the lattice relaxation behavior in this regime). In this case the strain energy is homogeneously distributed over the entire substrate surface. However, when highly 3D islands are formed (i.e., beyond 6 ML), substrate deformation can no longer be neglected (see, for example, Refs. [1] and [2]).
[15] R. Ludeke, R. M. King, and E. H. C. Parker, in *The Technology and Physics of Molecular Beam Epitaxy,* edited by E. H. C. Parker (Plenum, New York, 1985), p. 555.
[16] J. M. McCoy and P. A. Maksym, J. Cryst. Growth **111**, 178 (1991).
[17] The As-As mean surface bond energy is taken as half of the dimer bond energy.
[18] For the sake of simplicity, we consider that 2D islands are isotropic to evaluate $\Delta a_{\parallel}/a_{\parallel}^{GaAs}$ at the surface from the calculated 1D island $a_{\parallel}$ mean relaxation.
[19] J. Cibert, Y. Gobil, Le Si Dang, S. Tatarenko, G. Feuillet, P. H. Jouneau, and K. Saminadayar, Appl. Phys. Lett. **56**, 292 (1990).