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Real-time RHEED investigation of indium segregation in InGaAs layers grown on vicinal GaAs(001) substrates

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The surface segregation of indium atoms was investigated *in situ* and in real time by reflection high-energy electron diffraction (RHEED) during molecular-beam epitaxy of InGaAs layers on misoriented GaAs(001) substrates. The strong damping of the RHEED oscillations was quantitatively related to the strength of the segregation process that was found to decrease with increasing miscut angle.

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I. INTRODUCTION

Indium (In) segregation during molecular-beam epitaxy (MBE) is one of the most serious problems to be solved in In-based ternary alloys because it limits the sharpness of the interfaces and strongly modifies the In-composition profile of thin heterostructures. The segregation of In atoms in InGaAs layers has already been intensively investigated during the last years[1–3] because this material is important to the optoelectronic and microwave industries. Most of the data encountered in the literature were obtained on GaAs(001) substrates, and only few results are available for vicinal surfaces that exhibit a small miscut angle with respect to the GaAs(001) plane and generally provide better optical and morphological properties of the layers.[4,5] A few years ago, Martini *et al.*[6] used a simple theoretical model taking into account the strain inhomogeneity at the GaAs steps[7] to interpret the blueshift observed in the photoluminescence (PL) spectra of InGaAs/GaAs quantum wells grown on vicinal GaAs(001) substrates and concluded that the segregation coefficient R introduced by Muraki and co-workers[8] was slightly smaller on misoriented substrates. Until then, it was assumed in the literature that In segregation was the same on vicinal and nominal substrates.[7,9,10] However, since the theoretical results are sensitive to the choice of the main physical parameters used in the calculations (band offset, electron and hole effective mass, binding energy of the exciton) and to the model itself, one might wonder whether such a small difference of segregation is really significant. Recently, the same group[11] proposed an experimental method allowing the *in situ* determination of In segregation by RHEED measurements during MBE growth of InGaAs on nominal GaAs(001) substrates. The strong decay of the RHEED oscillations was interpreted as a natural consequence of the segregation process of In atoms that accumulate at the surface and produce an extra scattering of the incident electron beam, thus leading to a strong decrease of the intensity of the specular spot. The damping of the RHEED oscillations could be fitted and provided a characteristic length that was identical to the segregation length introduced by Muraki and co-workers,[8] allowing the direct determination of the segregation coefficient that was in excellent agreement with the values of the literature.[11,12]

In spite of that, most of the works reporting on RHEED measurements performed during InGaAs heteroepitaxy still attribute the strong damping of the oscillations to the increase of the surface roughness generated by the strained growth. In the present paper, we investigate the RHEED oscillations of InGaAs epitaxial layers deposited on nominal and vicinal GaAs(001) substrates and show that their strong decay definitely comes from the segregation of In atoms and not from any surface-roughness enhancement. We also confirm that the segregation process on vicinal surfaces is slightly reduced with respect to the nominal surface, as previously suggested.[6]

II. EXPERIMENTAL DETAILS

The epitaxial layers were grown in a Gen. II MBE system on top of vicinal GaAs(001) substrates with a miscut of 0° (nominal), 1°, 2°, and 4° towards [110] (i.e., with steps terminated by gallium atoms). After oxide desorption at 580 °C, the substrate was degassed at 620 °C during 5 minutes and a 2000 Å thick GaAs buffer was grown at 570 °C. Then the sample temperature was ramped to 610 °C during 2 minutes in order to smooth the GaAs surface and was finally lowered to 515 °C to deposit 35 monolayers of $In_{0.13}Ga_{0.87}As$ material at a growth rate of 0.93 monolayer per second (ML/s). The RHEED measurements were carried out during InGaAs deposition with a 8 kV electron gun generating a focused electron beam along the [−110] direction of the GaAs(001) surface (i.e., parallel to the steps edge of the vicinal substrates) in order to be as sensitive as possible to the presence of two-dimensional (2D) islands nucleated on top of the terraces. The intensity of the specular beam was detected with a charge coupled device (CCD) camera connected to a computer.

III. RESULTS AND DISCUSSIONS

Under conventional growth conditions, GaAs homoepitaxy on a nominal (001) surface proceeds in the layer-by-layer growth mode, and the periodic intensity variation of the specular beam (yielding the so-called RHEED oscillations) is generally explained in terms of the roughening of the growth front by the nucleation of small 2D islands that merge to complete the monolayers one at a time. This periodic roughening of the surface induces a periodic scattering of the incident electron beam (due to the high density of steps generated by the edge of the 2D islands) that yields a minimum reflection of the electron beam (i.e., a faint specular spot) when half of the layer is deposited, and a maximum reflection (i.e., a bright specular spot) when the layer is completed. The amplitude of the RHEED oscillations slowly damps as the growth proceeds because the roughness of the growth front evolves with time and the total density of steps present on the surface reaches an equilibrium regime.[13]

The strong decay of the RHEED oscillations observed during InGaAs deposition on top of GaAs(001) is usually associated in the literature with the strained growth originating from the lattice mismatch between GaAs and InGaAs. Indeed, in that case, the nucleation of 2D InGaAs islands on the top layer before the completion of the underlying layer is energetically more favorable because they allow a partial relaxation of the strain at the islands edge and contribute to decrease the total energy of the surface,[14] unlike for GaAs homoepitaxy. Therefore, most of the works usually conclude that the strong decay of the RHEED oscillations during InGaAs heteroepitaxy is caused by the faster roughening of the surface. However, such an argument is not satisfactory because it is unable to account for the fast drop of the RHEED signal during InGaAs deposition on vicinal GaAs(001) substrates, as will be shown below.

On a vicinal substrate, the presence of a cut angle with respect to the nominal surface introduces a periodic array of monoatomic terraces whose width is a function of the angle. Hence, depending on the growth conditions, the surface-diffusion length of the group-III adatoms can be larger than the distance between two neighboring steps, and the atoms can thus directly incorporate at the edge of the natural steps, which act as a sink because they provide more dangling bonds and, consequently, minimize the total energy of the surface.[15] For such a step-flow growth mode, the nucleation of 2D islands on the terraces is no longer observed, and the existing step density (which is only due to the natural steps of the miscut substrate) is kept constant during growth, thus yielding a constant RHEED signal with no oscillations.[16] In this case, any decay of the RHEED intensity on a vicinal substrate might no longer be associated with any variation of step density.

Figure 1 shows several RHEED curves obtained during the growth of InGaAs on top of GaAs(001) substrates with a miscut angle of 0° (nominal), 1°, 2°, and 4° towards [110]. It can be seen that the number of RHEED oscillations in each curve decreases for larger values of the miscut angle, which is consistent with the increasing contribution of the step-flow mode with rising misorientation. The strong damping of the RHEED signal is clearly present on the nominal as well as on the vicinal substrates and is of the same magnitude for all of them, confirming that its origin cannot be attributed to any enhancement of the surface roughness caused by the strained growth, as is frequently suggested in the literature.

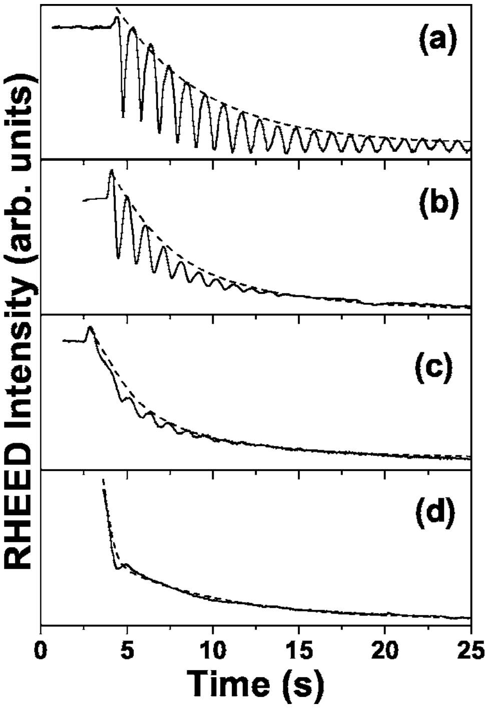

FIG. 1. RHEED oscillations during the epitaxy of $In_{0.13}Ga_{0.87}As$ on top of GaAs(001) substrates with a miscut angle of (a) 0° (nominal); (b) 1°, (c) 2°, and (d) 4° toward [110]. The dashed lines represent the best fits of the RHEED decay using Eq. (1).

Our interpretation of these RHEED data is the following: at the initial stage of the deposition of InGaAs on GaAs, most In atoms segregate to the surface and yield InGaAs layers with a low In content. As growth proceeds, more and more In atoms are incorporated into the layers until the nominal In content is reached. Since RHEED measurements mainly probe the last crystalline layer of the sample, the strong decay of the RHEED signal reflects the extra scattering of the incident electron beam by the In atoms incorporated in the top layer whose In concentration varies according to the model of Muraki and co-workers[8] and is a direct signature of the segregation phenomenon. As indium atoms have more electrons in their shells than the arsenic and gallium species, they provide a more effective scattering of the incoming electron beam because, for RHEED measurements on a semiconductor, electron-electron interaction is the dominant scattering process. Therefore, the intensity of the specular beam will be extremely sensitive to the presence of the In atoms in the top crystalline layer and will decrease proportionally to their concentration. Thus, fitting the strong RHEED damping with the formula

$$I = I_0 + I_1 \exp(-t/\tau), \tag{1}$$

as suggested in Ref. 11 (I represents the maxima of the RHEED oscillations, I_0 and I_1 are constants, t is the growth time and τ the decay constant that is actually the relevant fitting parameter) should provide a value of τ identical to the segregation length introduced by Muraki and co-workers[8] (after multiplying τ by the InGaAs growth rate), leading so to the segregation coefficient

$$R = \exp(-1/\tau). \tag{2}$$

The most important and interesting consequence of this interpretation is that it can be used to determine the In-segregation coefficient *in situ* and in real time on nominal as well as on vicinal substrates because we actually do not need to detect the RHEED oscillations themselves. Indeed, whatever the amplitude of the oscillations (large, weak, or even zero), only their upper envelope (i.e., the damping due to the increasing In concentration in each InGaAs layer) is necessary in the fitting procedure, as can be seen in Fig. 1 where the oscillations gradually vanish because of the increasing contribution of the step-flow mode. When the RHEED curves of Fig. 1 are fitted with Eq. (1), the values of R provided by Eq. (2) are 0.83, 0.80, 0.79, and 0.78 for the 0°, 1°, 2°, and 4° off surfaces, respectively. Since the experimental error of our R values is less than 0.01, these results definitely show that there is a slight, but real, reduction of the segregation strength on the vicinal substrates as previously suggested by Martini *et al.*[6] This is mainly due to the fact that the high density of steps influences the growth process[6,15] and acts as a sink for the group-III adatoms present at the surface, thus lowering their diffusion length and, consequently, the segregation effect.[17] The segregation reduction on vicinal substrates is generally extremely difficult to detect in PL measurements of InGaAs/GaAs quantum wells (it should yield a redshift of the optical emissions) because there is a competition with the inhomogeneous strain distribution at the GaAs steps that produces a blueshift.[6] Therefore, in the literature, the strength of In segregation was usually considered to be the same for nominal and vicinal surfaces. Our results prove that this is not the case and confirm that our experimental method is suitable to provide a quantitative analysis of the segregation process *in situ* and in real time without any need of extra *ex situ* measurements and theoretical calculations.

The smaller R values measured on vicinal substrates are directly related to the slight reduction of In segregation and cannot be explained by any variation of surface roughness or strain induced by the high density of natural steps present on such surfaces. Indeed, since the contribution of step-flow growth mode becomes more important for larger miscuts, the surface roughness usually decreases with rising misorientation. Therefore, any attempt to attribute the RHEED damping to the surface roughness (as erroneously done in the literature) should provide a larger segregation coefficient on the miscut substrates, which is in clear contradiction with our results. The same kind of argument can also be used with the strain on a vicinal substrate the first InGaAs layer must match the GaAs lattice parameter in the x-y plane [as on a nominal GaAs(001) surface] but also along the z direction (growth direction) because of the presence of the high density of natural GaAs steps. This extra strain (hydrostatic instead of biaxial) at the GaAs steps can be treated as a weak perturbative potential, since its influence can only be felt over a few unit cells away from the steps,[6,7] but its contribution becomes more important for larger miscuts. Therefore, if we try to interpret our RHEED results in terms of any strain variation,[18] one would expect larger segregation coefficients on the vicinal surfaces, which is not the case. Finally, our R values could only be obtained in a reliable and reproducible way when the maxima of the RHEED curves were fitted. This is mainly due to the fact that, at these points, the surface is flat and therefore any concentration of In atoms incorporated in the topmost crystalline layer will efficiently scatter the incoming electron beam, providing an extra scattering with respect to Ga atoms. However, when the minima or the intermediate points are used in the fitting procedure, the results are irreproducible mostly because, at the RHEED minima, the roughness is maximum and the scattering becomes more complex and more sensitive to the growth and surface conditions. Moreover, in our fitting procedure we do not need to subtract any contribution from the slight increase of surface roughness (after the completion of each monolayer) that usually yields a slow and symmetric decay of the RHEED signal, as observed during GaAs homoepitaxy. This is a direct consequence of the rapidly increasing concentration of In atoms in the InGaAs epilayers that produces a much stronger scattering of the incoming electron beam than the slowly increasing step density related to the surface roughness. Therefore, the numerical value extracted from our fitting procedure always gives the correct value of the segregation coefficient R.

It is worthwhile mentioning that the physical interpretation of the RHEED curves presented here is different from the one previously proposed by Martini and co-workers. In their first papers,[11,12] they suggested that the strong decay of the RHEED signal might come from the extra scattering of the incident electron beam by the increasing population of In adatoms accumulated at the surface of the sample as a consequence of the segregation process. Although In segregation does indeed create a floating layer of In adatoms, it cannot be at the origin of the large decrease of the RHEED signal because, as it was clearly observed in their RHEED experiments as a function of the growth temperature, the RHEED damping was stronger at lower growth temperature where segregation is known to be weaker (they indeed measured a smaller segregation coefficient). Therefore, according to their model, less In adatoms were supposed to be present at the surface and the scattering of the electron beam by the floating layer should be weaker, leading to a longer decay time of the RHEED signal and, consequently, to a larger segregation coefficient, which is clearly contradictory. As a matter of fact, these In adatoms are highly mobile on the surface and cannot scatter efficiently the incoming electron beam. On the other hand, the In atoms that are incorporated in the InGaAs layers have a fixed and well-defined position in the crystal lattice and are efficient scattering centers. In our interpretation of the RHEED data, we suggest that the RHEED signal is directly influenced by the concentration of In atoms that are actually incorporated in the top layer of the sample. Therefore, when segregation is weak (at low temperature for instance), the GaAs—InGaAs interface is sharper (more In atoms are incorporated) and the RHEED intensity decays rapidly, providing a small decay time and a small segregation coefficient as is indeed observed in the temperature data. When segregation is stronger (at higher growth temperature), less In atoms are initially incorporated in each InGaAs layer and the interface is wider, leading to a slower decay of the RHEED intensity (larger value of the decay time) and to a larger segregation coefficient, as expected. Therefore, the calculations of the segregation coefficient using the RHEED measurements are valid and physically consistent. The model is directly related to the segregation phenomenon because the electron beam probes the In concentration in the topmost InGaAs layer that varies during growth according to the phenomenological model of Muraki and co-workers.[8]

Recently this method was used by another group[19,20] to assess In segregation in AlSb/InAs(Sb) heterostructures deposited on GaSb substrates where, depending on the growth temperature, RHEED oscillations could be observed or not. In all the cases, their values of the segregation coefficient R were in excellent agreement with the ones estimated from other experimental techniques as high-resolution transmission electron microscopy and high-resolution x-ray diffraction, confirming that our technique can be applied for general investigation of surface segregation.

IV. CONCLUSIONS

As a conclusion, we showed that the RHEED oscillations during the MBE growth of InGaAs layers on nominal and vicinal GaAs(001) substrates exhibit a strong decay of their intensity that can no longer be attributed to any enhancement of the surface roughness caused by the strained growth, as generally reported in the literature. The strong damping is actually due to In segregation that generates a progressive incorporation of In atoms into the InGaAs layers that produces an extra scattering of the electron beam due to the fact that In atoms are more effective scattering centers. Our interpretation of the RHEED damping showed to be powerful and versatile because it allows real-time and *in situ* investigations of the phenomenon even when no RHEED oscillations are present, as for instance on vicinal substrates that became so important to microelectronics and optoelectronics. A slight reduction of In segregation was detected on vicinal substrates and results from the strong interaction between the group-III adatoms and the high density of natural steps present on such surfaces.

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