Monte Carlo simulation of In surface segregation during the growth of $In_xGa_{1-x}As$ on GaAs(001)

N. Grandjean, J. Massies, and M. Leroux
Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique, Rue B. Grégory-Sophia Antipolis, 06560 Valbonne, France
(Received 7 November 1994; revised manuscript received 24 May 1995)

The In surface segregation during the growth of $In_xGa_{1-x}As$ on GaAs(001) has been investigated through a Monte Carlo simulation taking into account the difference between the binding energies of InAs and GaAs and the effect of the epitaxial strain. Photoluminescence energies of quantum-well structures calculated from simulated composition profiles obtained at different temperatures are found to be in good agreement with the experimental ones. It is shown that Monte Carlo simulation is a very powerful way to predict the variation of the In composition profile as a function of growth parameters. It can, moreover, be easily extended to different materials, strain conditions, and surface morphologies.

Since its discovery,[1,2] surface segregation in III-V semiconductor alloys has been the subject of numerous studies, in particular in the $In_xGa_{1-x}As/GaAs$ strained material system[3–10] because of its considerable interest for optoelectronic and microwave device applications. It is now widely recognized that surface segregation effects are the ultimate limitation to the building of perfectly abrupt interfaces.[4–10] This limitation is well evidenced by the optical properties of $In_xGa_{1-x}As/GaAs$ quantum-well (QW) structures which are very sensitive to the potential profile at the interfaces.[4–6,8] A striking feature of these strained QW's grown under standard conditions is that their photoluminescence (PL) energy is significantly higher than that calculated by the envelope-function formalism for a perfect square well. It has been previously demonstrated that this blueshift is due to In surface segregation.[6,8] Indeed, during the growth, incoming In atoms are not all incorporated into the $In_xGa_{1-x}As$ well, because they ''float'' at the growing surface. Instead, they are incorporated into the GaAs barrier, reducing the effective width and the In content of the QW. Up to now, only a few attempts aimed at modeling the surface segregation in this important material system have been reported.[3,6,8,10] However, in these approaches a phenomenological parameter is involved and, therefore, they allow the *description* but not the *prediction* of the phenomenon as a function of growth materials and strain condition. Surprisingly, stochastic approaches, such as Monte Carlo (MC) simulations, which have proven very successful in the study of surface segregation in metallic alloys,[11] have not been applied to surface segregation effects in III-V semiconductor alloys to our knowledge.

The aim of this paper is to show that a MC simulation of the growth can provide a realistic description of the In surface segregation during molecular-beam epitaxy (MBE) of $In_xGa_{1-x}As/GaAs$ QW's by taking into account the binding energies of the constituents, the epitaxial strain, and the growth parameters. The reliability of this approach is demonstrated by comparing QW photoluminescence energies (calculated using the composition profiles deduced from the growth simulation) with the experimental values.

The samples consist in 6-ML-wide $In_{0.37}Ga_{0.63}As/GaAs$ QW's grown by MBE on GaAs(001) substrates after the growth of a buffer layer at 600 °C. The In composition was precisely calibrated using reflection high-energy electron-diffraction oscillations. The As_4 beam equivalent pressure was 5×10^{-6} Torr, and the growth temperature was measured by a pyrometer and corrected with respect to native oxide desorption from the substrate (580 °C). PL, excited by the 488-nm line of an argon laser, was performed at 9 K in a closed-cycle He cryostat, and detected with a liquid-nitrogen-cooled Ge detector.

Experimentally, we find that a 6-ML $In_{0.37}Ga_{0.63}As/GaAs$ QW grown under standard conditions (substrate temperature of 520 °C and growth rate of 0.48 ML/s for the well) exhibits a PL peak at 1.421 eV. This energy, corresponding to the e_1hh_1 excitonic transition, is significantly larger than that calculated for a perfect square well by the envelope-function formalism (1.376 eV if we assume an exciton Rydberg of 7 meV).[12,13] This blueshift is now well known, and is due to In surface segregation which reduces both the effective width and the In content of the QW.[6] The In segregation profiles responsible for the blueshift can be obtained from different models. One of these is a thermodynamical equilibrium model which was established a long time ago in metallic alloys.[14] It is described by a simple mass action law involving a segregation energy (E_s).[3,7,8] This model is easy to carry out, and can give the right segregation profile when the heteroepitaxial system is not too far from equilibrium (high growth temperature and low growth rate), but fails when kinetic restrictions apply. For example, to account for the reduction of the segregation with the lowering of the growth temperature, E_s must be strongly decreased together with the temperature, which is obviously unphysical. To turn over this difficulty, a model was proposed very recently by Dehaese, Wallart, and Mollot in which kinetics have been taken into account.[10] However, E_s cannot be

evaluated *a priori* from the characteristics of the growth constituents. More precisely, the bonding energies and the strain are not explicitly included in the determination of E_s, which therefore remains a phenomological parameter. E_s is in fact a fit parameter, and can only be adjusted *a posteriori* for each set of constituents and growth conditions. Another segregation model has been proposed in which the exchange process between In and Ga atoms on the topmost layer and the next layer is simply described through an exchange coefficient (R).[6] But once again, this model does not allow us to predict the segregation variation with the growth temperature. Indeed, R is purely phenomenological, and there is no explicit relation between R and T. Thus it appears that another approach is necessary if we want not only to fit but also to predict the QW energy levels as a function of growing species and growth conditions.

A more straightforward way to reach this aim is a MC simulation, which has been successfully applied to segregation in metal alloys.[11] Indeed, this method allows a microscopic description of the growth through the different hopping rates of each adatom, which are in fact the origin of the surface segregation process. We have used a MC simulation derived from the one proposed by Clarke and Vvedensky for the growth of GaAs on GaAs(001).[15] In a previous work,[16] we have shown that this approach, modified to take strain into account, correctly predicts the two-dimensional 2D-3D growth mode transition occurring in the $In_xGa_{1-x}As/GaAs$ system, proving the power of this growth simulation method. The hopping rate (h) is determined by the following expression: $h=h_0\exp(-E_d/kT)$, where h_0 is the adatom vibration frequency ($h_0=2kT/h$), E_d is the energy barrier to surface diffusion, and T the substrate temperature. Two terms contribute to the diffusion barrier E_d: a substrate contribution E and a contribution of the number of nearest neighbors in the $\langle 100\rangle$ and $\langle 1\bar{1}0\rangle$ directions, so that the energy barrier can be written as $E_d=E+pE_{\langle 110\rangle}+qE_{\langle 1\bar{1}0\rangle}$, where $E_{\langle 110\rangle}$ and $E_{\langle 1\bar{1}0\rangle}$ are the axis-dependent bonding energies with the nearest neighbors ($p,q\in\{0.2\}$).[17] The value of E is linked to the binding energy of the material ($E_{\mathrm{GaAs}}=1.73$ eV and $E_{\mathrm{InAs}}=1.53$ eV from Ref. 18), but is slightly smaller since the As surface coverage is less than one atomic monolayer. In order to investigate surface segregation processes, Ga and In atoms have been considered separately with $E=1.3$ and 1.15 eV for GaAs and InAs, respectively,[19] and $E_n/E=0.15$,[17] where E_n is the mean nearest-neighbor binding energy. The step energy anisotropy has been introduced in the simulation by taking an $E_{\langle 1\bar{1}0\rangle}/E_{\langle 110\rangle}$ ratio of ~ 6, following the work of Heller, Zhang, and Lagally.[20] The results presented here were obtained on a 50×50 square lattice with periodic boundary conditions in the two $\langle 110\rangle$ directions parallel to the surface.

For the set of experimental growth conditions given above, the calculated In concentration profile via MC simulation of the growth leads to an $e_1\mathrm{hh}_1$ transition energy of 1.397 eV for a 6-ML-wide $In_{0.37}Ga_{0.63}As/GaAs$ QW. This value is blueshifted with respect to the nominal one calculated for a perfect square well (1.376 eV), but is still significantly smaller than the experimental PL energy (1.421 eV). We conclude that the difference between GaAs and InAs binding energies is not sufficient to explain the extent of the In surface segregation. Other surface processes could reinforce this phenomenon, such as vertical exchange,[21] surface reconstruction, or the Schwoebel barrier. But, above all, we have to keep in mind that $In_xGa_{1-x}As$ ($x>0.25$) is highly strained on GaAs; in other words, that the In atoms could have some difficulties in being incorporated into the lattice. Indeed, it is well known that the size effect is an important driving force for segregation.[3,11,22–24] In order to include the strain effect in the MC simulation, the energy barrier E has been modified by adding a third term (E_e) which is an elastic energy contribution. This one affects the bond strength of the In adatom, and the energy barrier to surface diffusion is then decreased such as $E_d=E+pE_{\langle 110\rangle}+qE_{\langle 1\bar{1}0\rangle}-E_e$. In a previous work, we have shown that during the layer-by-layer growth of highly strained $In_xGa_{1-x}As$ on GaAs(001), elastic energy relaxation occurs mainly at the unit cells forming the free edges[16,25] of the 2D islands. An investigation by the finite-element method[16] of the highly strained island deformation also shows that most of the elastic energy relaxation occurs at the unit cells forming the free edges with a magnitude depending mainly on their local configuration. Therefore, in order to simplify the calculation we consider that the elastic energy relaxation is, in the first approximation, 2D-island size independent (see Ref. 26 for another approach to strain effects). For example, if $n=4$ (n is the number of nearest neighbors) no relaxation is possible, and the InAs unit cell is tetragonally deformed with $E_e^{(n=4)}=134$ meV according to elasticity theory. In the other cases, elastic relaxation occurs at the free edges of the InAs unit cell, and E_e decreases such that $E_e=E_e^{(n=4)}-E_r$, where E_r is the elastic relaxation energy defined as $E_r=\alpha_n E_e^{(n=4)}$.[16,25] The values of the coefficients α_n are deduced from a finite-element calculation.[27] The In composition profile now evaluated from this model is displayed in Fig. 1(a), and gives a PL energy of 1.419 eV, which is now in good agreement with the experimental value (1.421 eV). This clearly shows that strain plays a key role in the surface segregation process.[22–24] Of course, the relative importance of the difference in binding energy and of the strain cannot be deduced from any of the previously developed phenomenological models.

Let us now turn to the influence of kinetics on the surface segregation process. This phenomenon being at a maximum at thermodynamical equilibrium, it is possible to reduce the segregation process by keeping the system away from the equilibrium. For example, increasing the growth rate to 1.3 ML/s instead of 0.46 ML/s leads to a slight decrease of the PL energy, indicating that In surface segregation is weaker.[28] A MC simulation performed assuming such an increased growth rate predicts the right order for this redshift.

Actually, the temperature is the most efficient growth parameter to limit the segregation process kinetically, as has been experimentally demonstrated.[6] This is once again well accounted for by MC simulations, as illustrated in Fig. 1(b), giving the calculated In concentration profile of a 6-ML $In_{0.37}Ga_{0.63}As/GaAs$ QW grown at 395 °C.

The last point that we would like to address is the ability of a MC simulation to predict *quantitatively* the PL energy transition of a segregated structure as a function of the growth temperature. With this aim, a sample has been grown which contains four 6-ML-wide $In_{0.37}Ga_{0.63}As$ QW's separated by 500-Å GaAs barrier, but at four different substrate

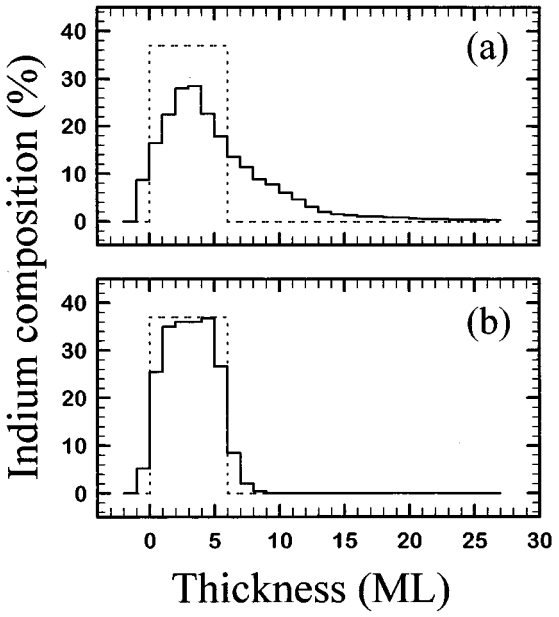

FIG. 1. Indium concentration profile of a 6-ML $In_{0.37}Ga_{0.63}As/GaAs$ QW at different growth temperatures without (dashed line) and with (full line) In surface segregation, as deduced from Monte Carlo simulation (growth rate: 0.5 ML/s). (a) $T=520\,^{\circ}C$. (b) $T=395\,^{\circ}C$.

temperatures ranging from 395 to 520 °C (with GaAs and $In_{0.37}Ga_{0.63}As$ growth rates of 0.3 and 0.48 ML/s, respectively, and an As_4 pressure of 5×10^{-6} Torr). Figure 2 displays the corresponding PL spectrum, where the resulting differences of In segregation are shown by the appearance of four well-resolved peaks. For these growth conditions, MC simulations have been performed, changing only the growth temperature. The e_1hh_1 transition energies calculated by the envelope-function formalism taking into account the

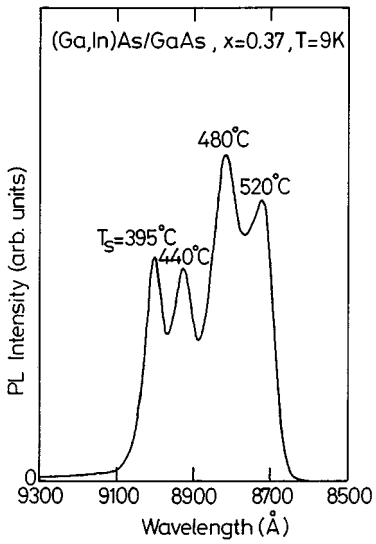

FIG. 2. 9-K photoluminescence spectrum of a 6-ML $In_{0.37}Ga_{0.63}As/GaAs$ QW's grown at four different temperatures (growth rate: 0.48 ML/s).

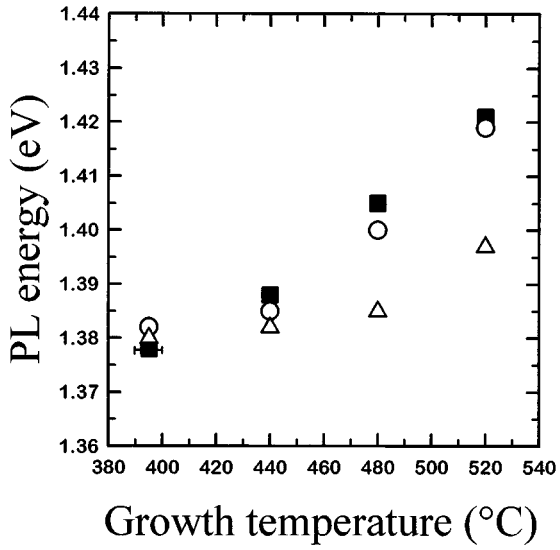

FIG. 3. Experimental 9-K PL energies of a 6-ML $In_{0.37}Ga_{0.63}As/GaAs$ QW grown at different temperatures (closed squares) and energies calculated from the segregation profiles provided by Monte Carlo simulation with (open circles) and without (open triangles) the strain effect (the error bar corresponds to an incertitude of $\pm5\,^{\circ}C$ on the growth temperature).

composition-dependent potential profiles deduced from MC simulations are reported in Fig. 3. Both MC simulations with (open circles) and without (open triangles) strain contribution have been performed. A good agreement between the experimental (closed squares) and calculated PL energies is obtained when the strain contribution is taken into account, confirming the key role of the size effect on the surface segregation process.

Finally it should be pointed out that the morphology of the substrate surface (e.g., the step density) can also be directly taken into account in the MC simulation. For example, the In surface segregation occurring for $In_xGa_{1-x}As/GaAs$ QW's grown on vicinal surfaces or high index surfaces can be evaluated in this way. It should also be emphasized that such a simulation tool can be used to study in more detail the surface segregation process by including in the MC model the surface reconstruction or other surface effects like the Schwoebel barrier.[29]

In conclusion, a simple Monte Carlo simulation has been performed to evaluate the effect of surface segregation on the In concentration profile at the $In_xGa_{1-x}As/GaAs$ interfaces. Compared to previous models, MC simulation makes it possible to take directly into account the type of material, the strain, and the growth conditions. This is demonstrated by the good agreement found between modeled and experimental photoluminescence properties of $In_{0.37}Ga_{0.63}As/GaAs$ QW's grown at different temperatures.

The authors would like to thank S. Taylor and E. Tournié for a critical reading of the manuscript, C. Chatillon, X. Wallart, F. Mollot, and F. Raymond for helpful discussions, and J. P. Faurie for strong support and interest. This work was supported by the CNRS-PIRMAT and the French Agency for Defense (DGA/DRET) under Contract. No. 93094.

[1] J. Massies, F. Turco, A. Saletes, and J. P. Contour, J. Cryst. Growth **80**, 307 (1987).
[2] J. Massies, F. Turco, and J. P. Contour, Semicond. Sci. Technol. **2**, 179 (1987).
[3] J. M. Moison, C. Guille, F. Houzay, F. Barthe, and M. Van Rompay, Phys. Rev. B **40**, 6149 (1989).
[4] J. M. Gérard, Appl. Phys. Lett. **61**, 2096 (1992).
[5] J. M. Gérard and J. Y. Marzin, Phys. Rev. B **45**, 6313 (1992).
[6] K. Muraki, S. Fukatsu, Y. Shiraki, and R. Ito, Appl. Phys. Lett. **61**, 557 (1992).
[7] M. Larive, J. Nagle, J. P. Landesman, X. Marcadet, C. Mottet, and P. Bois, J. Vac. Sci. Technol. B **11**, 1413 (1993).
[8] J. Nagle, J. P. Landesman, M. Larive, C. Mottet, and P. Bois, J. Cryst. Growth **127**, 550 (1993).
[9] J. F. Zheng, J. D. Walker, M. B. Salmeron, and E. R. Weber, Phys. Rev. Lett. **72**, 2414 (1994).
[10] O. Dehaese, X. Wallart, and F. Mollot, Appl. Phys. Lett. **66**, 53 (1995).
[11] See, for example, J. Eymery and J. C. Joud, Surf. Sci. **231**, 419 (1990), and references therein.
[12] G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Editions de Physique, Les Ullis, 1988).
[13] C. Lopez, R. Mayoral, F. Meseguer, J. A. Porto, J. Sanchez-Dehesa, N. Grandjean, C. Deparis, and J. Massies, Superlatt. Microstruct. **15**, 155 (1994).
[14] *Grain Boundary Structure and Properties*, edited by G. A. Chadwick and D. A. Smith (Academic, London, 1975).
[15] S. Clarke and D. Vvedensky, Phys. Rev. Lett. **58**, 2235 (1987).
[16] N. Grandjean and J. Massies, J. Cryst. Growth **134**, 51 (1993).
[17] T. Shitara, D. D. Vvedensky, M. R. Wilby, J. Zhang, J. H. Neave, and B. A. Joyce, Phys. Rev. B **46**, 6815 (1992).
[18] C. Chatillon, I. Ansara, A. Watson, and B. Argent, Calphad **14**, 203 (1990).
[19] The values of the energy barrier to diffusion (E) used in this work are not the same as the one used in Ref. 17. This is probably due to the quite different experimental conditions such as As_2 instead of As_4 as the As-element source and higher growth temperatures [see S. Clarke *et al.*, J. Cryst. Growth **95**, 28 (1989)].
[20] E. J. Heller, Z. Y. Zhang, and M. G. Lagally, Phys. Rev. Lett. **71**, 743 (1993).
[21] The vertical-exchange mechanism, known to occur in the surfactant-mediated growth [R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **68**, 954 (1992)], has been neglected here. Indeed, this process requires us both to break the In-As bond in the subsurface site, and the Ga-As bond in the surface site. The probability that the vertical exchange occurs is thus the product of the probabilities of each process, which is very low (breaking the In-As bond when In is in the subsurface site).
[22] R. A. van Santen and W. M. H. Sachtler, Adv. Catal. **26**, 69 (1977).
[23] P. Wynblatt and R. C. Ku, Surf. Sci. **65**, 511 (1977).
[24] M. P. Seah, J. Catal. **57**, 450 (1979).
[25] N. Grandjean, J. Massies, and F. Raymond, Jpn. J. Appl. Phys. **33**, L1427 (1994).
[26] C. Ratsch, A. Zangwill, and P. Smilauer, Surf. Sci. Lett. **314**, 937 (1994).
[27] The coefficients α_n depend on the number of nearest neighbors (n): $\alpha_n = 0.4,\ 0.25,\ 0{,}1,\ 0.03$, and 0 for $n = 0,\ 1,\ 2,\ 3$, and 4 (see Refs. 16 and 25).
[28] N. Grandjean, J. Massies, M. Leroux, J. Leymarie, A. Vasson, and A. M. Vasson, Appl. Phys. Lett. **64**, 2664 (1994).
[29] R. L. Schwoebel, J. Appl. Phys. **40**, 614 (1969).