Surface segregation in (Ga,In)As/GaAs quantum boxes

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Three-dimensional coherent islands formed during the highly strained growth of $In_{0.3}Ga_{0.7}As$ on GaAs(001) are studied by scanning tunneling microscopy. High-resolution images evidence two different types of surface reconstructions between the top and the bottom of the islands. While a 2×4 GaAs(001)-like reconstruction is observed on the wetting layer, the top layer exhibits the $(2\times4)\alpha2$ phase, which is characteristic of the InAs(001) reconstructed surface. This is the consequence of In surface segregation leading to the formation of a monolayer of InAs at the island top. Finally, photoluminescence experiments exemplify the effect of segregation on the $In_xGa_{1-x}As$/GaAs quantum box optical properties. [S0163-1829(97)50116-0]

During the past few years, a considerable amount of work has been devoted to quantum boxes (QB's) due to their potential interest for optoelectronic device applications.[1–4] In particular, it has been recently demonstrated that they may open an alternative route toward the successful realization of III-V semiconductor laser diodes grown on silicon substrates.[5] Among the ways to achieve QB's, one of the simplest is to take advantage of the two-dimensional (2D)–three-dimensional (3D) growth mode transition occurring in highly strained epitaxial systems like $In_xGa_{1-x}As(x>0.25)$/GaAs(001).[6] In such a case, the (Ga,In)As islands, which are formed before reaching the critical thickness for plastic relaxation, are dislocation free and self-organized.[6,7] They can therefore be used as QB's by overgrowing a GaAs barrier.[8]

An important point, on which most of the material growth research is currently focused, is the control of the shape and size of QB's. Indeed, their distributions determine the photoluminescence (PL) peak linewidth which is at the heart of the performances of QB-based optoelectronic devices. With the aim of mastering the island formation, a lot of work has been devoted to the role of growth parameters such as substrate temperature,[9,10] growth rate,[11,12] V/III ratio,[12,13] or substrate misorientation.[14] Besides these parameters which govern the island formation, intrinsic growth phenomena can occur. For instance, it is now recognized that surface segregation of indium is a severe limitation to the building of perfectly abrupt III-V semiconductor interfaces. As a consequence, the optical properties of (Ga,In)As/GaAs quantum wells (QW's) are strongly dependent on the growth temperature.[15–18] In the case of InAs/GaAs QB's, theoretical calculations taking into account In surface segregation during the GaAs overgrowth indicate a blue shift of 20 meV of the transition energies.[19] Concerning the InGaAs/GaAs QB's, a significantly larger energy shift should be expected because surface segregation occur both during the island formation and the overgrowth process.

In this paper we report on a scanning tunneling microscopy (STM) investigation of (Ga,In)As coherent islands which develop on GaAs(001) surface. High-resolution images of both the top and the bottom of 3D islands have been obtained. Their analysis sheds light on the In surface segregation in 3D coherent islands. In order to illustrate the importance of this phenomenon on the electronic properties of InGaAs/GaAs QB's, PL measurements have been performed *versus* the temperature of the overgrown GaAs barriers.

The growth of (Ga,In)As alloys on GaAs(001) substrates was carried out in a molecular beam epitaxy (MBE) system equipped with *in situ* reflection high-energy electron diffraction (RHEED) and coupled to an ultrahigh vacuum STM (Omicron) facility. After growing a GaAs buffer layer (~1 μm) at 600 °C, $In_{0.3}Ga_{0.7}As$ was deposited at 520–530 °C. The indium composition was precisely calibrated by RHEED specular-beam intensity oscillations. The filled states STM images were taken with a sample bias voltage of -2 V and a tunneling current of 0.5 nA.[20] PL experiments were carried out at 10 K in a closed cycle He cryostat with an Ar laser excitation and a Ge detector.

The 3D islands formed during the highly-strained growth of (Ga,In)As on GaAs(001) have been already investigated by STM,[21,22] but to our knowledge, no high resolution images have been reported. The difficulty in imaging such rough surfaces like islanded epilayers is likely due to strong tip-island interactions resulting in noisy images.[23] In order to limit this phenomenon, islands with a relatively flat shape

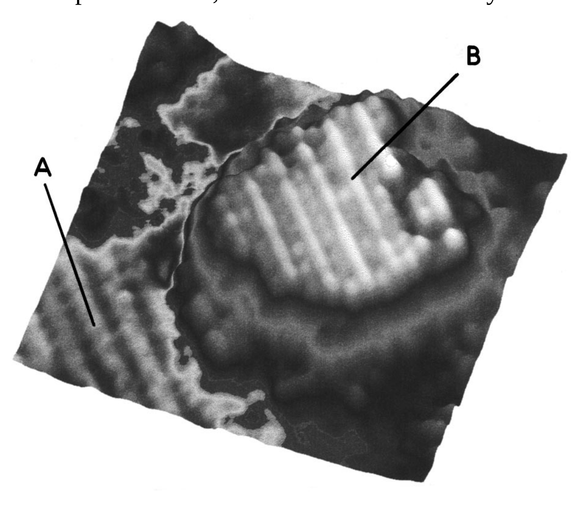

FIG. 1. STM image (200×195 Å^2) of an $In_{0.3}Ga_{0.7}As$ coherent island on GaAs(001). The dimensions of the island are 16 nm of lateral extension and 1.4 nm (5 ML's) high. Note that the wetting layer (A) and the top of the island (B) exhibit two different surface reconstructions.

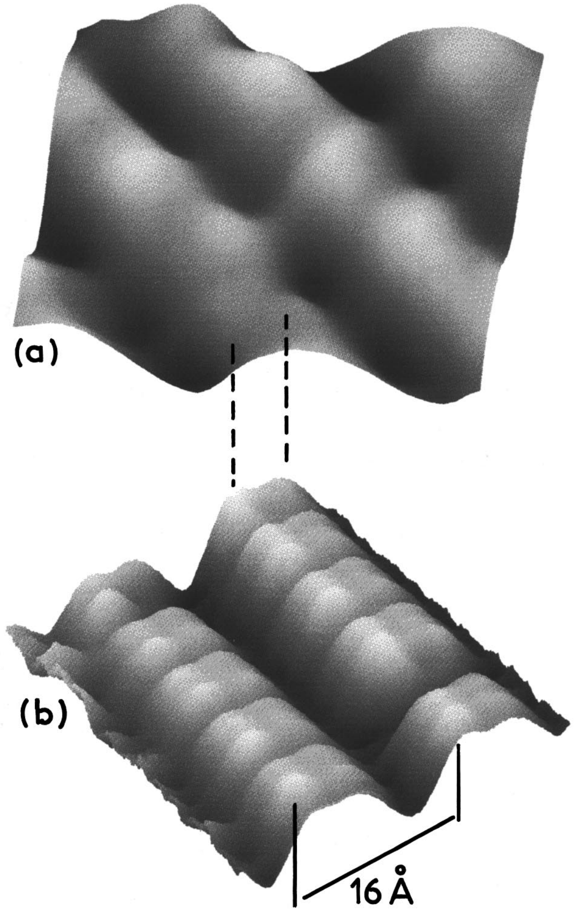

FIG. 2. (a) Zoom-in image (36×36 Å^2) of the surface reconstruction of the wetting layer (region *A* in Fig. 1). Bright streaks along the [1̄10] axis are separated by 16 Å and correspond to two As dimer rows. (b) STM image (33×40 Å^2) of a typical 2×4 reconstructed GaAs(001) buffer layer.

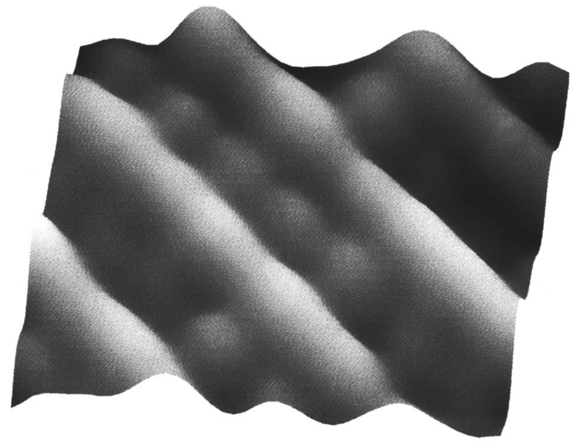

FIG. 3. Zoom-in image (48×51 Å^2) of the surface reconstruction of the island top (region *B* in Fig. 1). Bright streaks along the [1̄10] axis are separated by 16 Å and correspond to one As dimer rows.

were grown. This can be achieved when the In composition is slightly larger than the critical value of ∼25% above which the growth mode undergoes a 2D-3D transition. The growth must also be stopped just after this transition in order to avoid island coalescence. With these considerations in mind, 10 monolayers (ML's) of $In_{0.3}Ga_{0.7}As$ were deposited, corresponding to the critical thickness for islanding, as indicated by the appearance of a spottylike RHEED pattern. Though most of the STM scans performed on such a surface were generally very noisy, some areas were well defined. Figure 1 displays a STM image of an $In_{0.3}Ga_{0.7}As$ island from which both the top and the bottom are resolved. The dimensions of this island are small [16 nm of lateral extension and 1.4 nm (5 ML's) high], compared to an average island size of 70 nm in diameter and 6 nm high. Actually, we did not succeed in imaging larger islands with high resolution on the whole scan. Nevertheless, the considered island has the same aspect ratio (∼0.1) than the larger ones and the same morphology, i.e., the top is flat and corresponds to a (001) plane.

The main feature appearing in Fig. 1 is the difference in the surface reconstruction between the top of the island and the surrounding surface. Figure 2(a) displays a zoom-in image taken at the bottom of the island (wetting layer). Bright streaks oriented along the [1̄10] axis and separated by four lattice spacings (16 Å) are observed. The comparison with Fig. 2(b) corresponding to a 2×4 reconstructed GaAs(001) buffer layer surface allows us to conclude that the reconstruction of the wetting layer is also 2×4, the bright streaks observed in Fig. 2(a) being in fact two unresolved As dimer rows [which are clearly resolved in Fig. 2(b)]. This seems to indicate that the bare surface of GaAs, or at least, a strongly In-depleted (Ga,In)As wetting layer, is exposed around the island. If not, a 2×3 reconstruction characteristic of $In_xGa_{1-x}As$ ($x>0.1$) epilayer grown on GaAs should be observed.[24] This result is well accounted for by the island-induced stress field which favors In atom migration from the wetting layer toward the islands.[25] The important point here is that the surface reconstruction of the island top is clearly different (Fig. 3). The bright lines oriented along the [1̄10] axis are now much sharper, though always separated by ∼16 Å. They could correspond to only one As dimer instead of two As dimers in the case of the standard 2×4 GaAs(001) reconstruction.[26] Between these lines, bright points are supposed to be As dimers of the underlayer, since they are separated by 8 Å.[27]. These characteristics are actually typical of the $(2\times4)\alpha2$ surface reconstruction observed in the case of bulk InAs(001) surface.[28] This could be mainly due to the surface segregation of indium during the (Ga,In)As growth, leading to a strong enrichment of the In surface layer content. Indeed, it has been demonstrated that for 2D growth, a quasiequilibrium steady state situation is reached when ∼1 ML of InAs is present at the growth front.[29,30] Therefore, the $(2\times4)\alpha2$ InAs(001)-like reconstruction may be related to the presence at the island top surface of roughly one monolayer of InAs. However, an additional reason may be invoked to explain its formation since pseudomorphic (Ga,In)As layers, also terminated by ∼1 InAs ML,[29,30] exhibit a (2×3) surface reconstruction when deposited on GaAs substrates.[24] Having in mind that elastic strain relaxation is the driving force of the 2D-3D growth mode transition, the relaxation of the 3D island surface layer could play a key role in this phenomenon. Actually, the observation of well-defined surstructures both at the top and the bottom of an island allows us to measure the in-plane relaxation of the island terminated plane. Its average surface lattice parameter is relaxed by 2.2±0.1% with respect to the lattice of the wetting layer. It corresponds to the unstrained bulk param-

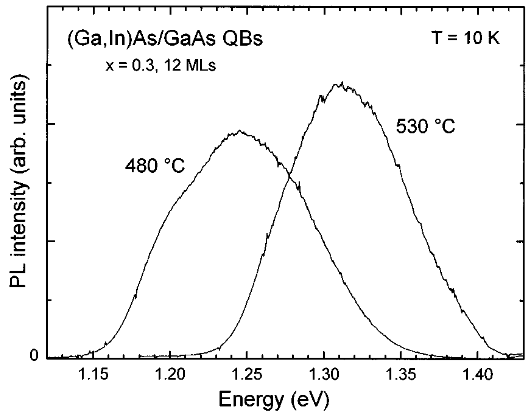

FIG. 4. 10 K photoluminescence spectra of $In_{0.3}Ga_{0.7}As$/GaAs QB's with two different temperatures for the GaAs overgrown barrier: 480 °C and 530 °C.

eter of the (Ga,In)As alloy at the nominal In composition of 30%, in agreement with previous results.[6,31] As a consequence, the InAs top layer experiences only a 5% compressive strain. It is supposed that this lower compressive strain compared to the case of InAs/GaAs (7%) may explain the formation of the $(2\times4)\alpha2$ surface reconstruction. Note that a monolayer of InAs on InP (3.2% of lattice mismatch) leads also to a (2×4) surface reconstruction.[32]

A particular attention must be paid to the In surface segregation occurring in the 3D (Ga,In)As islands because it should affect the optical properties of QB's. Two different samples have been grown in order to investigate the segregation effect on the transition energies of (Ga,In)As/GaAs QB's. In both samples, the dots are obtained by growing 12 ML's of $In_{0.3}Ga_{0.7}As$ at a constant temperature of 530 °C. Note that a constant temperature for the 3D island growth is required to avoid possible energy shifts due to different size distributions. Actually, the effect of the segregation is checked by overgrowing the GaAs barriers at two different growth temperatures: 530 °C and 480 °C.[33] The corresponding photoluminescence spectra are displayed in Fig. 4. The PL peak energy is strongly blueshifted by 65 meV when the growth temperature of the GaAs barrier is increased from 480 °C to 530 °C. This indicates a strong In redistribution from the island to the GaAs barrier during the overgrowth process. Besides the surface segregation, other phenomena should be considered such as strain-induced migration and lateral diffusion. Xie *et al.*[34] have shown that during the GaAs overgrowth process, In atoms are driven by the tensile stress above the island. In other words, In atoms do not diffuse laterally far away from the top of the islands, but on the contrary, are confined to the growth direction above the islands. Therefore, the lateral diffusion of indium in the overgrown barrier is rather low and does not strongly modify the indium composition shape in the in-plane directions. On the other hand, the vertical diffusion of In due to the surface segregation effect cannot be neglected since it is well known to deeply affect the transition energies of (Ga,In)As QW's (growth temperature induced blueshifts exceeding 40 meV are commonly observed).[15–18]

In order to exemplify the role of the surface segregation, the concentration profile of $In_{0.3}Ga_{0.7}As$/GaAs QB's has been estimated *versus* the overgrowth temperature (Fig. 5).

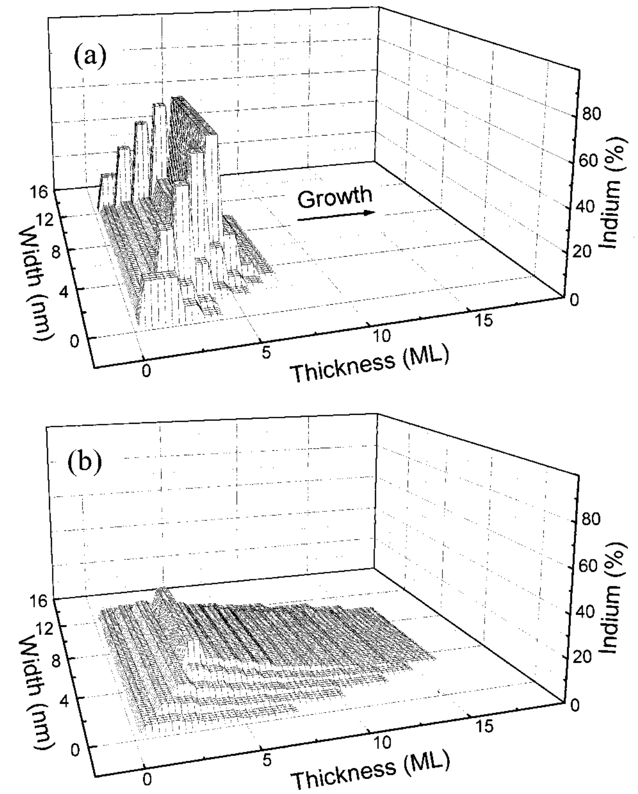

FIG. 5. Calculated In composition profile of an $In_{0.3}Ga_{0.7}As$/GaAs QB formed by the 3D island shown in Fig. 1 embedded in GaAs: with an overgrowth temperature of 480 °C (a) and 530 °C (b).

The segregation effect is calculated by using the model proposed by Muraki *et al.*[15] To account for the InAs monolayer observed by STM at the island top, the segregation coefficient R in the island must be at least 0.8, in good agreement with previous reports for the same temperature range.[35,36] The In segregation profile in the GaAs barrier is calculated by taking $R=0.83$ and 0.32, for 530 °C and 480 °C, respectively.[36] The nominal size and shape of the island are those obtained from STM measurements (Fig. 1). Actually, the blueshift of 65 meV observed in the PL spectra is not surprising regarding the evolution of the In concentration profile of $In_{0.3}Ga_{0.7}As$/GaAs QB's when the overgrowth temperature is increased from 480 °C [Fig. 5(a)] to 530 °C [Fig. 5(b)]. In fact, as a consequence of the segregation phenomenon during InGaAs growth, the whole surface of the island is In-enriched with a maximum at the top corresponding at least to 1 ML of InAs. This induces a potential deep localized at the surface of the InGaAs island. If GaAs is overgrown at low temperature, the In segregation into GaAs being negligible, indium accumulation remains at the island surface resulting in a potential deep at the interface [Fig. 5(a)]. In contrast, for GaAs overgrown at high temperature the surface segregation effect eliminates the In accumulation at the island top [Fig. 5(b)], i.e., the potential deep. This should result in a strong blueshift of the transition energy when increasing the overgrowth temperature from 480 °C to 530 °C. In order to be more quantitative, a simple analysis has been carried out. Taking advantage of the flat shape of the InGaAs islands (aspect ratio of ~0.1), we consider that the quantum confinement arises mainly from the quantization of the electron and heavy-hole wave functions along the growth axis. Moreover, the average diameter size of the islands being greater than 30 nm, the contribution of the additional lateral confinement is likely no larger than 10 meV referring to quantum wires.[37] The transitions energies of QB's are thus roughly estimated by adding 10 meV to the $e1-hh1$ energy of a QW of width corresponding to the average height of the islands. The calculation performed with an In nominal composition of 0.3, a well width of 5 nm, and an exchange coefficient of 0.83,[36] gives 1308 meV in agreement with the PL energy obtained for GaInAs QB's in the case of the 530 °C overgrowth temperature. When R is decreased to 0.32 (Ref. 36) to account for the overgrowth temperature of 480 °C, the calculated energy fall down to 1264 meV. This simple analysis indicates that the main part (44 meV) of the observed blueshift (65 meV) is well accounted for by In surface segregation (the discrepancy may come from the one-dimensional quantization model used and/or from other neglected effects such as strain-induced migration).

In conclusion, coherent islands formed just after the 2D-3D growth mode transition of $In_{0.3}Ga_{0.7}As$ on GaAs(001) have been studied by high-resolution scanning tunneling microscopy. The top surface of the (Ga,In)As islands is relaxed and reconstructed like the InAs(001) bulk surface. This leads to the conclusion that the 3D island terminated layer corresponds to ~ 1 ML of InAs due to the surface segregation of In. Photoluminescence measurements demonstrate that this phenomenon results in a strong blueshift of the QB transition energies *versus* the growth temperature.

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[1] M. Assada, Y. Miyamoto, and Y. Svetmatsu, Jpn. J. Appl. Phys. **24**, L95 (1985).
[2] J. N. Randall, M. A. Reed, and G. A. Frazier, J. Vac. Sci. Technol. B **7**, 1398 (1989).
[3] C. Weisbuch and G. Vinter, *Quantum Semiconductor Structures* (Academic, Boston, MA, 1991).
[4] N. Kirstaedter, N. N. Ledentsov, M. Grundmann, D. Bimberg, V. M. Ustinov, S. S. Ruvimov, M. V. Maximov, P. S. Kop'ev, Zh. I. Alferov, U. Richter, P. Werner, U. Gösele, and J. Heydenrenreich, Electron. Lett. **30**, 1416 (1994).
[5] J. M. Gérard, O. Cabrol, and B. Sermage, Appl. Phys. Lett. **68**, 3123 (1996).
[6] S. Guha, A. Madhukar, and K. C. Rajkumar, Appl. Phys. Lett. **57**, 2110 (1990).
[7] J. M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André, and O. Vatel, Appl. Phys. Lett. **64**, 196 (1994).
[8] D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. Denbaars, and P. M. Petroff, Appl. Phys. Lett. **63**, 3203 (1993).
[9] D. Leonard, M. Krishnamurthy, S. Farard, J. L. Merz, and P. M. Petroff, J. Vac. Sci. Technol. B **12**, 1063 (1994).
[10] G. S. Solomon, J. A. Trezza, and J. S. Harris, Jr., Appl. Phys. Lett. **68**, 991 (1995).
[11] J. M. Gérard, J. B. Génin, J. Lefebvre, J. M. Moison, N. Lebouché, and F. Barthe, J. Cryst. Growth **150**, 351 (1995).
[12] G. S. Solomon, J. A. Trezza, and J. S. Harris, Jr., Appl. Phys. Lett. **66**, 3161 (1995).
[13] H. Kitabayashi and T. Wako, J. Cryst. Growth **150**, 152 (1995).
[14] N. Ikoma and S. Ohkouchi, Jpn. J. Appl. Phys. **34**, L724 (1995).
[15] K. Muraki, S. Fukatsu, Y. Shiraki, and R. Ito, Appl. Phys. Lett. **61**, 557 (1992).
[16] J. Nagle, J. P. Landesman, M. Larive, C. Mottet, and P. Bois, J. Cryst. Growth **127**, 550 (1993).
[17] J. Leymarie, C. Monier, A. Vasson, A. M. Vasson, M. Leroux, B. Courboulès, N. Grandjean, C. Deparis, and J. Massies, Phys. Rev. B **51**, 13 274 (1995).
[18] N. Grandjean, J. Massies, and M. Leroux, Phys. Rev. B **53**, 998 (1996).
[19] J. Y. Marzin, J. M. Gérard, A. Izraël, D. Barrier, and G. Bastard, Phys. Rev. Lett. **73**, 716 (1994).
[20] Before STM measurements, the samples were quenched below 400 °C within 30 s under As_4 flux in order to limit the surface evolution. The possible As condensation, which can occur during the cooling down step, is removed by annealing for a few minutes the samples at 350–400 °C (with a growth chamber pressure lower than 2×10^{-10} Torr).
[21] C. W. Snyder, B. G. Orr, D. Kessler, and L. M. Sander, Phys. Rev. Lett. **66**, 3032 (1991).
[22] G. E. Cirlin, G. M. Guryanov, A. O. Golubok, S. Ya. Tipissev, N. N. Ledentsov, P. S. Kop'ev, M. Grundmann, and D. Bimberg, Appl. Phys. Lett. **67**, 97 (1995).
[23] Note that atomic resolution has been obtained for 3D Ge surfaces [see, e.g., Mo *et al.*, Phys. Rev. Lett. **65**, 1020 (1990)]. Actually, the relative concentration of (Ga,In) to As on the surface is also responsible for the difficulty in imaging III-As surfaces [see, e.g., R. M. Feenstra and J. A. Stroscio, in *Scanning Tunneling Microscopy*, edited by J. A. Stroscio and W. J. Kaiser (Academic, San Diego, 1993), p. 259].
[24] M. Sauvage-Simkin, Y. Garreau, R. Pinchaux, M. B. Véron, J. P. Landesman, and J. Nagle, Phys. Rev. Lett. **75**, 3485 (1995).
[25] A. Madhukar, J. Cryst. Growth **163**, 149 (1996).
[26] D. K. Biegelsen, R. D. Bringans, J. E. Northrup, and L.-E. Swartz, Phys. Rev. B **41**, 5701 (1990).
[27] D. J. Chadi, J. Vac. Sci. Technol. A **5**, 834 (1987).
[28] H. Yamaguchi and Y. Horikoshi, Jpn. J. Appl. Phys. **33**, L1423 (1994).
[29] R. Kaspi and K. R. Evans, Appl. Phys. Lett. **67**, 819 (1995).
[30] O. Dehaese, X. Wallart, and F. Mollot, Appl. Phys. Lett. **66**, 52 (1995).
[31] Y. Androussi, A. Lefebvre, B. Courboulès, N. Grandjean, J. Massies, T. Bouhacina, and J. P. Aimé, Appl. Phys. Lett. **65**, 1162 (1994).
[32] J. Massies, P. Devoldére, and N. T. Linh, J. Vac. Sci. Technol. **15**, 1353 (1978).
[33] In each sample, a growth interruption of 1 min is performed after the island growth to allow the change of the overgrowth temperature.
[34] Q. Xie, A. Madhukar, P. Chen, and N. P. Kobayashi, Phys. Rev. Lett. **75**, 2542 (1995).
[35] H. Toyoshima, T. Niwa, J. Yamazaki, and A. Okamoto, Appl. Phys. Lett. **63**, 821 (1993).
[36] Y. C. Kao, F. G. Celii, and H. Y. Liu, J. Vac. Sci. Technol. B **11**, 1023 (1993).
[37] Ch. Gréus, A. Forchel, J. Straka, K. Pieger, and M. Emmerling, J. Vac. Sci. Technol. B **9**, 2882 (1991).