Quantum-dot-induced ordering in $Ga_xIn_{1-x}P$/InP islands

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Thin layers of $Ga_xIn_{1-x}P$ grown on top of self-assembled InP quantum dots has been studied using transmission electron microscopy (TEM), scanning tunneling microscopy (STM), and low-temperature scanning tunneling luminescence (STL). STM reveals that the overgrowth is highly uneven, in which elongated $Ga_xIn_{1-x}P$ islands covering the dots are formed. TEM and high-spatial-resolution STL show that the quantum dots locally induce domains with higher degree of ordering in the islands. The luminescence from these domains is observed as a strong $Ga_xIn_{1-x}P$ peak at an energy below the emission from the $Ga_xIn_{1-x}P$ barrier material.

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I. INTRODUCTION

Semiconductor quantum dots (QD's) are investigated as possible candidates for novel nanoscale optoelectronic devices. Together with the progressing development of low-dimensional structures the characterization techniques have been improved, and it has recently become possible to investigate the luminescence from single III-V semiconductor QD's.[1–5] The InP/$Ga_xIn_{1-x}P$ system exhibits strong emission of light in the longer wavelength region of the visible spectrum and is thus interesting for several applications.[6–8]

However, the $Ga_xIn_{1-x}P$ alloy has a very complex nature both structurally and optically. Transmission electron microscopy[9] (TEM) and scanning tunneling microscopy[10] (STM) investigations have shown that under certain conditions atomic long-range ordering may occur in the $Ga_xIn_{1-x}P$ alloy.[11] The most frequently observed ordered phase is the CuPt structure, which is a monolayer superlattice of alternating Ga-rich $Ga_{x+\eta/2}In_{1-x-\eta/2}$ and In-rich $Ga_{x-\eta/2}In_{1-x+\eta/2}$ atomic planes perpendicular to the $[1\bar{1}\bar{1}]$ and $[\bar{1}11]$ directions, where η is the ordering parameter.[12] The atomic ordering takes place in domains extending from a few 100 nm to a few micrometers, wherein the ordering (η constant) is believed to be uniform.[13] The size, shape, and degree of ordering of these domains are strongly related to the growth conditions[7] as well as to substrate misorientation.[14–16]

Atomic ordering has been shown to significantly change the band gap energy and thus the optical properties of $Ga_xIn_{1-x}P$.[7,14] In low-temperature macro-photoluminescence (macro-PL) spectra two distinct luminescence peaks are commonly observed. Whereas the high-energy emission exhibits features typical for a band-to-band excitonic recombination, the low-energy emission shows a more complex behavior[13,15–17] and its microscopic origin is debated.[17]

The samples in this study consisted of InP quantum dots embedded in $Ga_xIn_{1-x}P$, grown by metal-organic vapor phase epitaxy (MOVPE). We have performed detailed studies of the photon emission from the $Ga_xIn_{1-x}P$ surrounding single QD's, primarily using scanning tunneling luminescence (STL). The findings are compared to TEM and PL measurements, revealing how single InP dots locally induce domains with higher degree of ordering in the overgrown $Ga_xIn_{1-x}P$.

II. EXPERIMENTS

In this study a variable-temperature, ultrahigh-vacuum (UHV) STM was used in which sample temperatures down to 20 K can be obtained. The system is equipped with an *ex situ* laser source and an optical detection system allowing for combined STL and PL studies without changing the sample position.[18] The STM tips were made from tungsten wire by electrochemical etching. Prior to measurements the tips were cleaned *in situ* by Ar^+-ion sputtering and radiative heating. The PL was obtained using a frequency-doubled Nd:yttrium aluminum garnet (YAG) laser emitting at 532 nm. The emitted light was detected using a liquid-nitrogen-cooled charged coupled device (CCD) camera, in the case of spectral measurements, or a GaAs photomultiplier during photon mapping.

The TEM experiments were performed using a JEOL 4000EX microscope with point-to-point resolution of 0.16 nm, operated at an acceleration voltage of 400 keV. The [110] cross-section samples for TEM investigations were prepared in the standard manner by cleaving, mechanical grinding, and polishing followed by Ar^+-ion milling until electron transparency was reached.

InP QD's were grown in Stranski-Krastanow growth mode by MOVPE. The growth runs were carried out in a low-pressure (100 mbar), rf-heated reactor. Trimethylgallium (TMG), trimethylindium (TMI), PH_3, AsH_3, and Si_2H_6 precursors were used with H_2 as the carrier gas. First, a 250-nm-thick $Ga_xIn_{1-x}P$ layer was grown, lattice matched to the (001)GaAs substrate. On top of the $Ga_xIn_{1-x}P$, 2 ML of GaP were grown and the dots were then grown by deposition of 3 ML (0.5 ML/s) InP at 580 °C. After 12 s annealing the samples were overgrown with nominally 20 nm or 30 nm $Ga_xIn_{1-x}P$ and then cooled to room temperature. The $Ga_xIn_{1-x}P$ layers were highly Si doped ($n=10^{18}$ cm^{-3}). Further details of the growth have been presented elsewhere.[19,20]

To enhance surface properties for STM and STL measurements, the samples were sulphur passivated by immersion into a 2% ammonium sulphide solution kept at 55 °C for 30

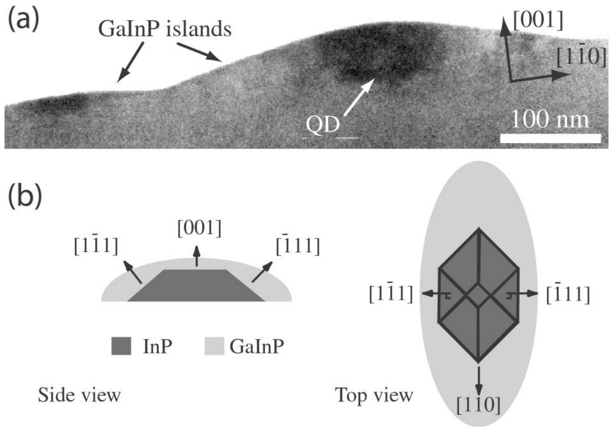

FIG. 1. (a) A [110] cross-sectional TEM micrograph of InP QD's overgrown with nominally 20 nm of $Ga_xIn_{1-x}P$ showing how the $Ga_xIn_{1-x}P$ islands have merged together. The two darker areas indicate the presence of local strain fields in and around the InP QD's. (b) Schematics of the InP dot and $Ga_xIn_{1-x}P$ island geometries.

min. The samples were then baked at 120 °C for 12 h in the load lock before transfer into the UHV chamber.

III. RESULTS

TEM was performed on the samples to determine the structure of the overgrown material. Figure 1 shows a TEM micrograph of nominally 20 nm capped InP QDs. Figure 1(a) demonstrates that the surface morphology has local thickness variations, with large $Ga_xIn_{1-x}P$ islands covering the dots. The height of the $Ga_xIn_{1-x}P$ on top of the InP dot is about 9 nm.

We have earlier showed that the $Ga_xIn_{1-x}P$ nucleates on the side facets of the dots[18] and with increasing $Ga_xIn_{1-x}P$ deposition the islands increase in size [see Fig. 1(b)]. The islands grow preferentially in the [110] direction and at a nominal cap layer thickness of about 20 nm the $Ga_xIn_{1-x}P$ islands have started to coalesce,[21] as can be seen in Fig. 1(a).

The shape of the QD is not affected by the overgrowth, in agreement with earlier measurements by Georgsson *et al.*[22] The fully developed dots have heights of about 15 nm and base widths of 45 nm and 60 nm in the $[\bar{1}10]$ and [110] directions, respectively. Furthermore, the side facets were shown to be low-index planes of {001}, {110}, and {111} types.

The bulk $Ga_xIn_{1-x}P$ (the 250 nm below the InP dots) and material in between the InP dots are only weakly ordered in the $[1\bar{1}1]$ and $[\bar{1}11]$ directions and the degree of ordering varies slightly in these areas, as could be seen by Fourier transforming the different areas in the TEM images (not shown). In contrast, the $Ga_xIn_{1-x}P$ surrounding the InP dots shows large variations in the degree of ordering. On the $[1\bar{1}0]$ and $[\bar{1}10]$ sides of the island large domains with highly ordered $Ga_xIn_{1-x}P$ are seen in the $[1\bar{1}1]$ and $[\bar{1}11]$ directions, respectively (see Fig. 2). However, on the [110] and $[\bar{1}\bar{1}0]$ sides of the island the $Ga_xIn_{1-x}P$ is less ordered

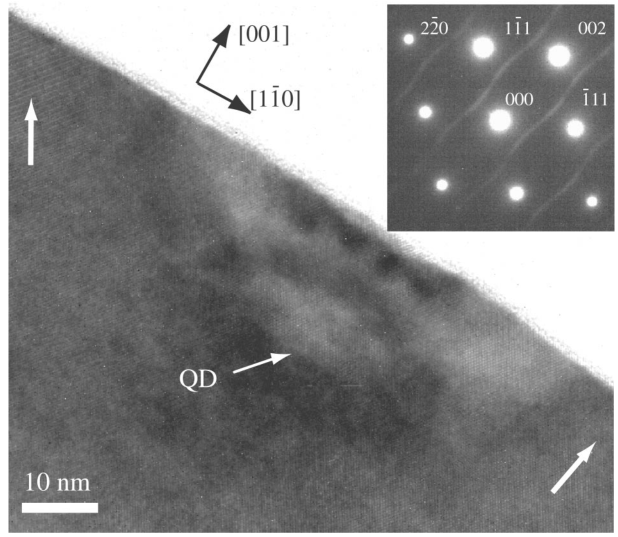

FIG. 2. A [110] cross-sectional TEM micrograph of a single InP QD overgrown with nominally 20 nm of $Ga_xIn_{1-x}P$. White arrows indicate domains with higher degree of ordering in the $Ga_xIn_{1-x}P$ islands. The inset shows the diffraction pattern for the sample.

than the bulk material. These variations in ordering degree can be explained by monolayer steps on the surface of the $Ga_xIn_{1-x}P$ islands. Steps parallel to the [110] and $[\bar{1}\bar{1}0]$ (so-called *B* steps) foster the formation of ordering, whereas steps parallel to the $[1\bar{1}0]$ and $[\bar{1}10]$ (so-called *A* steps) hinder ordering.[23] High strain fields, which are due to the lattice mismatch between the InP QD's and the $Ga_xIn_{1-x}P$ matrix, also prevent ordering and no ordering is visible in the brighter and darker gray areas on the sides and on top of the InP dot (see Fig. 2). The ordered $Ga_xIn_{1-x}P$ is only observed about 10 nm away from the InP dot.

Macroscopic PL was performed *in situ* to obtain information of the luminescence properties of the sample, as shown in Fig. 3. Three main peaks can be identified in the spectrum: emission from the GaAs substrate at 1.5 eV, a broad emission peak at slightly higher energy, and luminescence from the $Ga_xIn_{1-x}P$ barrier material. The emission peak at 1.6 eV originates from a large number of QD's. The central dot luminescence energy is in agreement with earlier measurements by Pistol *et al.*[24] The peak at 1.94 eV is attributed to

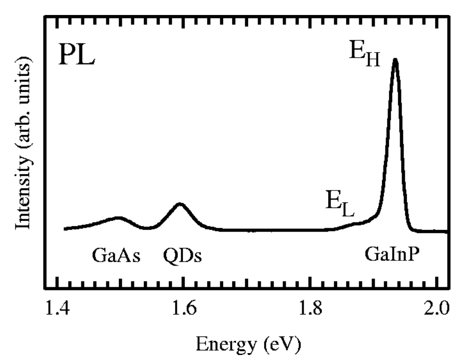

FIG. 3. PL spectrum acquired at 20 K of the sulphur-passivated sample of InP QD's overgrown with nominally 30 nm $Ga_xIn_{1-x}P$.

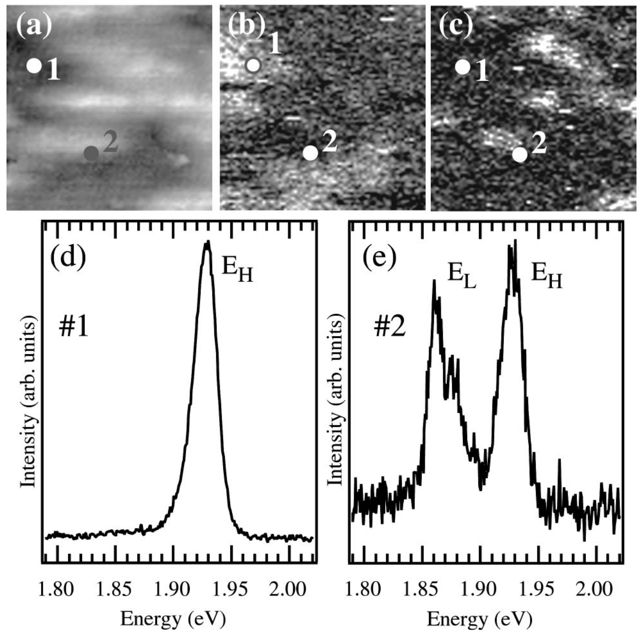

FIG. 4. (a) A constant-current topograph of a sulphur-passivated sample of InP QD's overgrown with nominally 30 nm $Ga_xIn_{1-x}P$ ($I_{tunneling}=0.1$ nA, $V_{sample}=-8$ V). For the same region of the sample photon maps at 1.94 eV (b) and 1.57 eV (c) were acquired for 15 min with a sample bias of -10 V and a current of 10 nA. All images are 600 nm×600 nm, and all measurements were done at 20 K. The spectra in (d) and (e) were acquired at the STM tip positions indicated in the images.

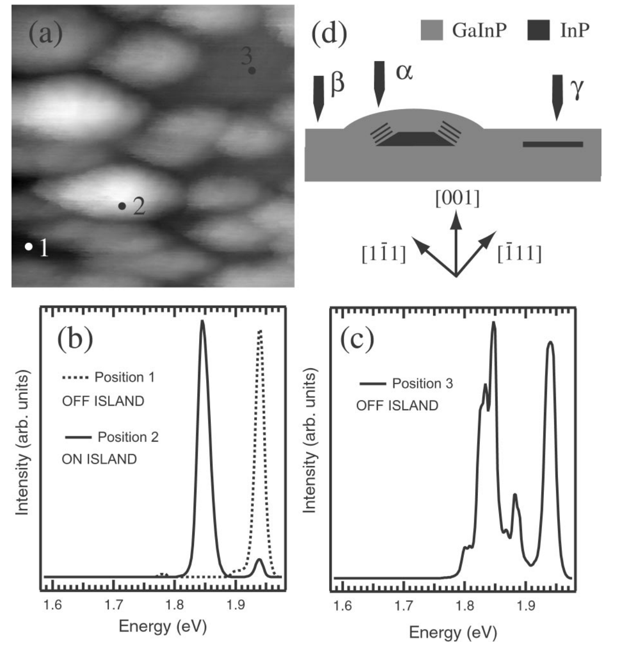

FIG. 5. (a) A constant-current topograph of a sulphur-passivated sample of InP QD's overgrown with nominally 20 nm $Ga_xIn_{1-x}P$ ($I_{tunneling}=0.1$ nA, $V_{sample}=-6$ V). The tip positions during acquisition of the STL spectra in (b) and (c) are indicated in the STM image. The acquisition time was 1 min using a sample bias of -6 V and a tunneling current of 10 nA. In (d) a model of the sample structure and different locations of the STM tip is shown. The STM image is 1 μm×1 μm, and all measurements were done at 20 K.

the excitonic band-to-band transition of the $Ga_xIn_{1-x}P$ bulk and will be denoted E_H. In addition, a weak emission shoulder can be observed at a slightly lower energy. This weak luminescence, denoted E_L, can be attributed to emission arising from domains with higher degree of ordering in the $Ga_xIn_{1-x}P$ cap layer, as will be further discussed below.

To be able to study single individual $Ga_xIn_{1-x}P$ islands and InP QD's we increased the spatial resolution by using STL. Figure 4(a) shows a constant-current topograph of InP QD's capped with nominally 30 nm $Ga_xIn_{1-x}P$, in which the bright features correspond to overgrown QD's. The density of islands can be estimated to be about 10^9 cm^{-2}, in agreement with STM and atomic force microscopy of uncapped samples grown under the same conditions. Indicated in Fig. 4(a) are the two positions used when acquiring the luminescence spectra shown in Fig. 4. The spectrum in (d) was acquired by positioning the tip at a position without any island. The tip was positively biased, 7 V, relative to the sample, the tunneling current was 5 nA, and the acquisition time was 3 min.

Under these conditions the Fermi level of the tip is below the valence band edge of the $Ga_xIn_{1-x}P$ and we extract electrons from the sample. This is equivalent to injecting holes, which recombine with electron in the sample and photons are emitted. The strong luminescence peak seen in Fig. 4(d) has the same energy as E_H in the PL spectrum. The E_H peak is thus likely to be dominated by emission from the $Ga_xIn_{1-x}P$ bulk material, since the PL technique has a large excitation volume. However, if instead the tip is positioned on an island, having sample voltage of -8 V and a tunneling current of 10 nA, a prominent E_L peak is observed [see Fig. 4(e)], in addition to the E_H peak seen in (d).

To determine the spatial extent of the E_H peak prominent in all spectra above, we have performed monochromatic photon mapping. Figure 4(b) shows a photon map acquired at an energy of 1.94±0.06 eV of the same sample region as in (a). The E_H intensity varies spatially on a 100 nm scale, and the observed length scale is consistent with the TEM results, which were performed on the same sample. For reference, a photon map was acquired at a detection energy of 1.57 ±0.06 eV, the energy of dot emission seen in the PL; see Fig. 4(c).[21] It can be concluded by comparison with the constant-current topograph that all of the islands here contain a QD with emission in the relevant energy range. Thus, it is evident that the dots are typically situated in the center of the island. Furthermore, the two photon maps are complementary, where the E_H peak is only detected in regions in between the GaInP islands.

The same type of measurements were performed on a 20 nm capped sample, which in TEM was seen to have the same structure as the 30 nm capped samples, but the individual $Ga_xIn_{1-x}P$ islands are easier to distinguish [see Fig. 5(a)]. Indicated in Fig. 5(a) are the tip positions during STL measurements. When the tip is positioned in between the islands (spectrum No. 1) only one peak at 1.94 eV with a small shoulder at lower energy can be seen. If instead the tip is positioned on the side of the island (spectrum No. 2), a strong luminescence peak can be detected at 1.85 eV together with an additional faint peak at 1.94 eV. The full-width-at-half-maximum (FWHM) values of the two main peaks in spectra Nos. 1 and 2 are 17 meV and 24 meV, respectively. PL results from the same sample (not shown) give the same FWHM for the E_H peak, which suggests that the E_H peak is broadened by local variations in the bulk $Ga_xIn_{1-x}P$,[15] as was confirmed by TEM.

We can conclude that the $Ga_xIn_{1-x}P$ peak varies in energy depending on the location of the STM tip during the excitation. A competition between two spectral elements has also been observed on a larger length scale by Smith *et al.*[13]

In addition, several sharp peaks are sometimes observed, as shown in Fig. 5(c), when the STM tip is positioned in between islands, e.g., position 3 in Fig. 5(a). The E_H peak is observed at an energy of 1.94 eV, in agreement with the STL spectra 1 and 2 in Fig. 5(b).

IV. DISCUSSION

The TEM investigations show that as a result of the $\{111\}$ side facets of the InP dot, large regions with pronounced ordering are formed in the $Ga_xIn_{1-x}P$ cap layer. Similar observations have been made for intentionally oriented or processed samples.[16,25] From the STL spectra and photon maps it is evident that the E_H was dominating in regions in between the $Ga_xIn_{1-x}P$ islands, whereas the E_L was found to be related to the $Ga_xIn_{1-x}P$ islands. Furthermore, the E_L peak is more prominent if the tip is positioned on the side of the island, Fig. 5(b), since the $Ga_xIn_{1-x}P$ directly above the InP QD's is not ordered. Accordingly, when we position the STM tip on a single island, luminescence from the highly ordered region is detected; see position α in the model in Fig. 5(d). On the other hand, at tip positions similar to location β, only the E_H peak is detected. This emission is also observed in the PL and is attributed to the $Ga_xIn_{1-x}P$ bulk material, since it is independent of the location of the STM tip.

At some locations off the islands, marked γ in Fig. 5(d), very rich and complicated spectra were observed. Several groups have reported that the sharp emission at low energy observed in PL measurements is quantum-dot-like states associated with the domain boundaries present in the $Ga_xIn_{1-x}P$.[13,16,17,26] Smith *et al.* showed that the low-energy-band PL emission and the associated quantum-dot-like luminescence may also originate from other defects within the ordered domain.[13] Furthermore, Kops *et al.* have reported that micro-PL investigations of partially ordered $Ga_xIn_{1-x}P$ reveal, in contrast to the macro-PL, that the low-energy emission consists of two parts: a broad underlying PL band and superimposed narrow emission lines.[16] They concluded that these narrow emission lines originate from zero-dimensional InP quantum disks naturally formed at In-In antiphase boundaries embedded in the $Ga_xIn_{1-x}P$.

In our TEM investigations we do not detect any InP wetting layer. This is plausible, since a thin layer of GaP is grown prior to the InP deposition to improve the QD size homogeneity and the GaP is likely to intermix with the thin wetting layer. However, at larger flat areas residues of the wetting layer or partially formed QD's may be present and consistently we sometimes detect strong luminescence from these. The peak positions and their linewidths are in rough agreement with theoretical and experimental results for InP quantum wells by Carlsson *et al.*[19,20]

V. SUMMARY

In summary, STM imaging reveals that the overgrowth has local thickness variations, forming large $Ga_xIn_{1-x}P$ islands on top of the QD's. TEM images show that domains of highly ordered $Ga_xIn_{1-x}P$ are preferentially formed parallel to the $(\bar{1}\bar{1}1)$ and $(1\bar{1}\bar{1})$ facets of the rather large InP QD's. The high spatial resolution of the STL together with the surface topography identified that these domains are the origin of the E_L, about 90 meV, below the E_H peak of the $Ga_xIn_{1-x}P$. In addition, a rich structure could also be seen in between the islands which probably reflects InP low-energy regions where carriers are trapped. The sharp emission lines were shown to be very position dependent.

This study shows that for refining the growth of optically useful QD systems, where InP QD's are embedded in a $Ga_xIn_{1-x}P$ matrix, an improved understanding of the interplay between dot and barrier and the processes involved in QD overgrowth is of great importance.

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[1] L. Landin, M.S. Miller, M.-E. Pistol, C.E. Pryor, and L. Samuelson, Science **280**, 262 (1998).

[2] J.-Y. Marzin, J.-M. Gérard, A. Izraël, D. Barrier, and G. Bastard, Phys. Rev. Lett. **73**, 716 (1994).

[3] D. Hessman, P. Castrillo, M.-E. Pistol, C. Pryor, and L. Samuelson, Appl. Phys. Lett. **69**, 749 (1996).

[4] D. Hessman, J. Persson, M.-E. Pistol, C. Pryor, and L. Samuelson, Phys. Rev. B **64**, 233308 (2001).

[5] M. Sugisaki, H.-W. Ren, S.V. Nair, K. Nishi, S. Sugou, T. Okuno, and Y. Masumoto, Phys. Rev. B **59**, R5300 (1999).

[6] Y.M. Manz, O.G. Schmidt, and K. Eberl, Appl. Phys. Lett. **76**, 3343 (2000).

[7] Y. Hsu, G.B. Stringfellow, C.E. Inglefield, M.C. DeLong, P.C. Taylor, J.H. Cho, and T.-Y. Seong, Appl. Phys. Lett. **73**, 3905 (1998).

[8] E. Greger, K.H. Gulden, P. Riel, H.P. Schweizer, M. Moser, G.

Schmiedel, P. Kiesel, and G.H. Döhler, Appl. Phys. Lett. **68**, 2383 (1996).
[9] L.C. Su, I.H. Ho, and G.B. Stringfellow, J. Appl. Phys. **75**, 5135 (1994).
[10] N. Liu, C.K. Shih, J. Geisz, A. Mascarenhas, and J.M. Olson, Appl. Phys. Lett. **73**, 1979 (1998).
[11] A. Zunger and S. Mahajan, in *Handbook on Semiconductors*, edited by S. Mahajan (Elsevier, Amsterdam, 1994), Vol. 3, Chap. 19.
[12] T. Saß, I. Pietzonka, and H. Schmidt, J. Appl. Phys. **85**, 3561 (1999).
[13] S. Smith, H.M. Cheong, B.D. Fluegel, J.F. Geisz, J.M. Olson, L.L. Kazmerski, and A. Mascarenhas, Appl. Phys. Lett. **74**, 706 (1999).
[14] L.C. Su, S.T. Pu, G.B. Stringfellow, J. Christen, H. Selber, and D. Bimberg, Appl. Phys. Lett. **62**, 3496 (1993).
[15] M.J. Gregor *et al.*, Appl. Phys. Lett. **67**, 3572 (1995).
[16] U. Kops, P.G. Blome, M. Wenderoth, R.G. Ulbrich, C. Geng, and F. Scholz, Phys. Rev. B **61**, 1992 (2000).
[17] B. Fluegel, S. Smith, Y. Zhang, A. Mascarenhas, J.F. Geisz, and J.M. Olson, Phys. Rev. B **65**, 115320 (2002).
[18] U. Håkanson, M.K.-J. Johansson, J. Persson, J. Johansson, M.-E. Pistol, L. Montelius, and L. Samuelson, Appl. Phys. Lett. **80**, 494 (2002).
[19] N. Carlsson, W. Seifert, A. Petersson, P. Castrillo, M.-E. Pistol, and L. Samuelson, Appl. Phys. Lett. **65**, 3093 (1994).
[20] N. Carlsson, K. Georgsson, L. Montelius, L. Samuelson, W. Seifert, and R. Wallenberg, J. Cryst. Growth **156**, 23 (1995).
[21] M. K.-J. Johansson (unpublished).
[22] K. Georgsson, N. Carlsson, L. Samuelson, W. Seifert, and L.R. Wallenberg, Appl. Phys. Lett. **67**, 2981 (1995).
[23] H. Murata, S.H. Lee, I.H. Ho, and G.B. Stringfellow, J. Vac. Sci. Technol. B **14**, 3013 (1996).
[24] M.-E. Pistol, N. Carlsson, C. Persson, W. Seifert, and L. Samuelson, Appl. Phys. Lett. **67**, 1438 (1995).
[25] P. Ernst, C. Geng, F. Scholz, H. Schweizer, Y. Zhang, and A. Mascarenhas, Appl. Phys. Lett. **67**, 2347 (1995).
[26] T. Mattila, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **83**, 2010 (1999).