Optical and structural properties of InAsP ternary self-assembled quantum dots embedded in GaAs

E. Ribeiro, R. L. Maltez, W. Carvalho Jr., D. Ugarte, and G. Medeiros-Ribeiro

Citation: Applied Physics Letters **81**, 2953 (2002); doi: 10.1063/1.1513215
View online: http://dx.doi.org/10.1063/1.1513215
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/81/16?ver=pdfcov
Published by the AIP Publishing

Optical and structural properties of InAsP ternary self-assembled quantum dots embedded in GaAs

E. Ribeiro,[a] R. L. Maltez,[b] W. Carvalho, Jr., D. Ugarte, and G. Medeiros-Ribeiro
Laboratório Nacional de Luz Síncrotron, CP 6192, 13084-971 Campinas-SP, Brazil

(Received 14 June 2002; accepted 19 August 2002)

We report on the growth of self-assembled ternary InAsP quantum dots embedded into GaAs. A comparison between average sizes and recombination energies for different dot species (InAs, InAsP, and InP) confirms the formation of the ternary alloy islands. By carefully changing the growth conditions, we determined a global growth map for InAs, InAsP, and InP dots, showing that it is possible to tailor the optical characteristics of the InAsP species, thus covering the energy range between InAs and InP quantum dot emission. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1513215]

The development of the fabrication techniques for defect-free self-assembled quantum dots (QDs)[1–3] has opened the possibility of using their unique properties for device applications.[4] QD lasers,[5,6] optical memories,[7,8] and normal-incidence midinfrared photodetectors,[9,10] among others, are some examples of how one can explore the particularities offered by incorporating zero-dimensional systems into devices.

The ability to tune the luminescence wavelength is of particular interest for optoelectronic applications. That can be achieved by either controlling the growth kinetics[3,11] and/or the chemical composition. $III_xIII_{1-x}V$-type QDs, such as InGaAs/GaAs[11,12] or InAlAs/AlGaAs,[11,13–15] are already well established. However, the stoichiometry of $III-V_xV_{1-x}$ compounds is hard to control and, in fact, there are limited reports on QD growth of these materials.[16,17] An early attempt by Vinokurov and collaborators[16] consisted of growing InAsP QDs on InGaP and they found no appreciable shift in energy, all samples emitting around the InP/InGaP QD luminescence. In the present work, we investigate the nucleation of high optical quality InAsP QDs embedded in GaAs, allowing us to cover the full energy range from InAs to InP QD emissions. By using different growth rates and phosphine (PH_3) flux, we were able to change the relative rate of incorporation for the V materials (P and As), leading to a variation of the InAsP alloy composition and thus different QD recombination energies.

The samples were grown by low-pressure metalorganic vapor phase epitaxy (reactor pressure of 70 Torr, H_2 flow of 12 l/min) on GaAs:Cr nominally flat (001) substrates. The precursors were trimethylindium, trimethylgallium, PH_3, and arsine (AsH_3). A 3000 Å thick GaAs buffer layer was grown on the substrate, followed by the deposition of the QD layer (InAs, InAsP, or InP). The dots were annealed under a H_2 flux for 60 s (except for the InP samples) and then covered by a 500 Å GaAs capping layer. The growth temperature T_g was 640 °C for the GaAs buffer and 550 °C for the remaining layers. The amount of deposited material was 2.1 monolayers (MLs) for InAs, near the coherence/incoherence transition, and 4 ML for the remaining samples. The AsH_3 flux was kept constant at 0.8 sccm; InAsP QDs of different compositions were obtained by varying the growth rate and the PH_3 flux.

Photoluminescence (PL) experiments were performed at 77 K (liquid-nitrogen immersion cryostat) using the 5145 Å line of an Ar^+ laser as excitation source. Power density varied from 1.5 to 400 W/cm^2. The PL emission was dispersed by a 0.75 m single spectrometer and detected by a cooled Ge photodiode. Cross-sectional and plan-view transmission electron microscopy (TEM) micrographs were taken using an atomic resolution JEOL JEM-3010 microscope operating at 300 kV of acceleration voltage. Specimens were prepared by mechanical polishing and dimpling, followed by ion milling using a nitrogen-cooled stage.

Figure 1 shows normalized PL spectra of samples with different QD compositions: InAs (A), InAsP (B and C), and InP (D), all grown at the same nominal growth rate g_r

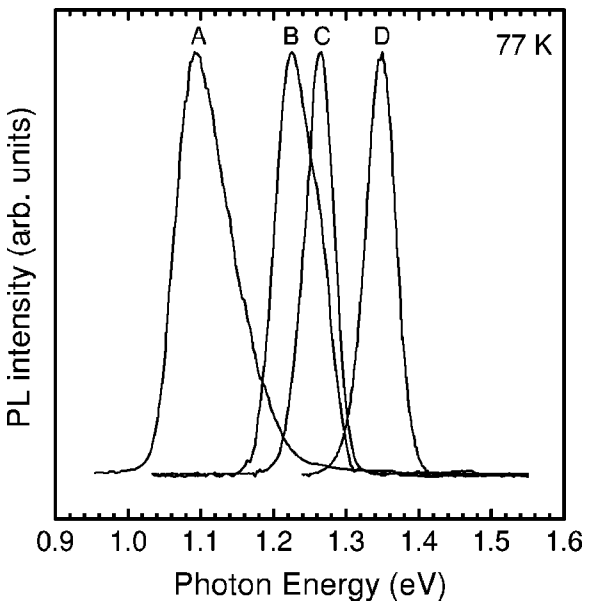

FIG. 1. Normalized PL spectra of samples A (InAs), B and C (InAsP), and D (InP), for an excitation of 77.5 W/cm^2. State filling occurs only for sample A at this excitation conditions. All spectra were taken at 77 K.

[a]Electronic mail: evaldo@lnls.br
[b]Present address: Instituto de Física, UFRGS, C.P. 15051, 91501-970, Porto Alegre, RS, Brazil.

TABLE I. Sample identification, QD material, PH_3 flux, average dot densities and dimensions (from TEM), and island aspect ratio for selected samples of the present work.

Sample	Material	PH_3 flux (sccm)	Dot density (10^{10} dots/cm^2)	Dot diameter/dot high (nm)	Aspect ratio
A	InAs	···	(2.1 ± 0.5)	$(13\pm2)/(3.6\pm0.6)$	3.6
B	InAsP	5	(3.9 ± 0.3)	$(15\pm3)/(2.6\pm0.5)$	5.8
C	InAsP	10	(4.2 ± 0.3)	$(20\pm5)/(2.9\pm0.7)$	6.9
D	InP	10	(3.0 ± 0.3)	$(32\pm6)/(4\pm1)$	8.0

$=0.2$ ML/s (see Table I). First, sample A exhibits typical InAs QD PL line shape: A single peak at $E_A=1.094$ eV and a small tail for higher energies (excited states are beginning to be populated). The addition of a PH_3 flux during the InAs QD growth allows one to form InAsP QDs, for example, samples B and C (5 and 10 sccm of PH_3), that present PL recombination at energies which are intermediate between InAs and InP QDs ($E_B=1.224$ eV and $E_C=1.264$ eV). Finally, sample D spectrum (pure InP QDs) sets an upper limit for recombination energies ($E_D=1.350$ eV) within the growth parameters used in this work. The PL linewidths were 87, 70, 49, and 39 meV for samples A through D, following a monotonic trend. For the laser excitation range used, no excited states were found for InAsP and InP samples. However, sample D presents a noticeable blueshift with increasing optical excitation (23 meV). This is consistent with recently reported results where a similar energy blueshift was associated with the type-II band alignment of InP on GaAs.[18] In this light, the absence of a blueshift for samples A to C may indicate that InAsP QDs still keep the type-I band alignment of InAs/GaAs. This suggestion requires further detailed studies of the InAsP QD electronic properties since, to the best of our knowledge, there is no report on the band alignment of InAsP/GaAs (even for two dimensional films) so far.

Despite the consistent picture drawn from PL measurements for the growth of the InAsP ternary alloy, it is very important to assess two key points: (1) the existence of islands, and (2) their morphology. The later is crucial because smaller, pure-InAs QDs would also result in a blueshifted PL spectrum. Figure 2 shows dark-field 002 (DF 002) cross section TEM micrographs of samples A through D. The formation of InAsP islands is evident from Figs. 2(b) and 2(c) (white regions). The dot densities ρ_{dot} (extracted from plan-view TEM, not shown) are $(2.1\pm0.5)\times10^{10}$ cm^{-2}, $(3.9\pm0.3)\times10^{10}$ cm^{-2}, $(4.2\pm0.3)\times10^{10}$ cm^{-2}, and $(3.0\pm0.3)\times10^{10}$ cm^{-2} for samples A through D. TEM also shows the presence of few defective islands in samples A, B, and C (about one order of magnitude lower in density). Regarding the QD morphology, the average height of the islands is about the same for all samples within the experimental error (see Table I). However, the most relevant result observed in Fig. 2 is the monotonic trend found for the dot average diameter: It increases from (13 ± 2) nm for InAs QDs to (32 ± 6) nm for InP QDs, while the InAsP QDs present an intermediary size [(15 ± 3) and (20 ± 5) nm for samples B and C]. Since the island equilibrium size L depends inversely on the strain ε squared ($L\propto\varepsilon^{-2}$),[19] the observed continuous shape change, as inferred by the island aspect ratios (see Table I) is consistent with the formation of the ternary InAsP QDs. This trend also accounts for the progressive reduction of the PL linewidths discussed herein. In a QD, the confined energies depend inversely on L^2 ($E\propto L^{-2}$); thus, the energy dispersion (broadening of the PL linewidth) will be given by $\Delta E\propto\Delta L/L^3$, which decreases drastically as L increases (for

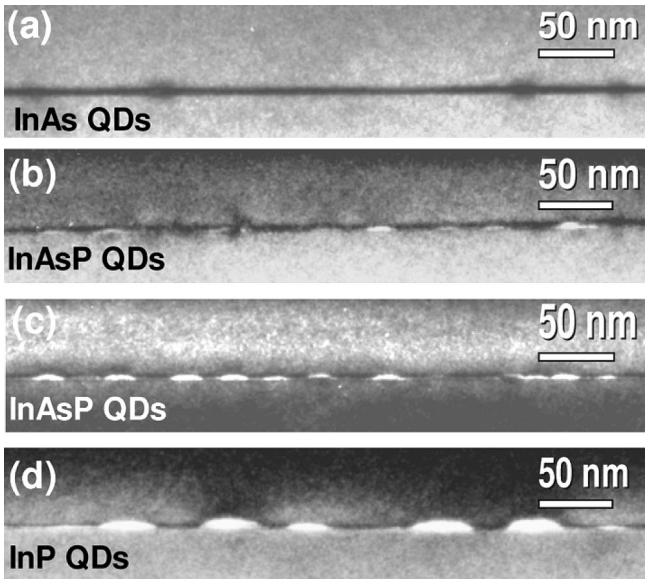

FIG. 2. (a)–(d) Cross section TEM DF 002 micrographs of samples A (InAs), B and C (InAsP), and D (InP), respectively. Dot densities are $(2.1\pm0.5)\times10^{10}$ cm^{-2}, $(3.9\pm0.3)\times10^{10}$ cm^{-2}, $(4.2\pm0.3)\times10^{10}$ cm^{-2}, and $(3.0\pm0.3)\times10^{10}$ cm^{-2}, as measured via plan-view images.

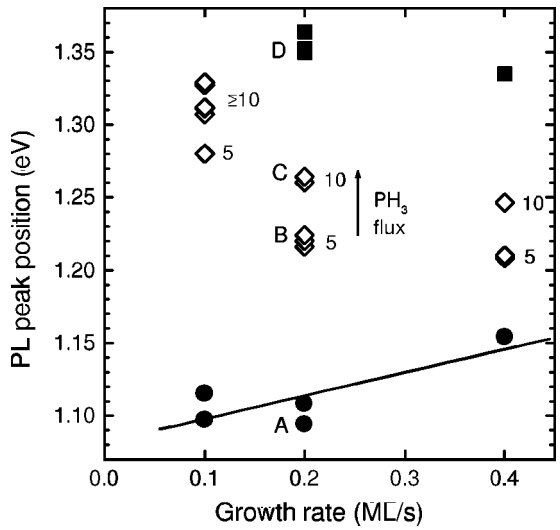

FIG. 3. PL peak position as a function of the growth rate for the QD samples grown for the present study: InAs (solid circles), InAsP (open diamonds), and InP (solid squares). Labels indicate the samples presented in Figs. 1 and 2, and the PH_3 flux (sccm) for the InAsP samples. The line is a guide for the eye.

a fixed ΔL). On the other hand, it is expected that the formation of an InAsP alloy will lead to an additional broadening of the emission spectra. However, this effect is not observed for samples B and C because the dominant contribution for the PL linewidths comes from the size dispersion of the islands.

Figure 3 presents a global map of the samples grown for the present study, by plotting their PL peak position as a function of g_r. Samples A through D are indicated by labels, as well as the PH_3 flux (in sccm) used for each growth. First, one can infer that the InAs QDs (solid circles) decrease their volume (leading to an energy blueshift of their PL peak) with increasing g_r. Second, for all growth conditions used, InAsP QDs (open diamonds) are obtained with PL energies always intermediate between InAs and InP island emission. For $g_r = 0.1$ ML/s, it was impossible to grow InAsP QDs with recombination energies below 1.28 eV because the incorporation of P seemed to prevail over As, even for the lowest measurable PH_3 flux. For higher growth rates (0.2 and 0.4 ML/s), the incorporation of As into the InAsP alloy was favored, allowing us to reach energies as low as 1.208 eV. For all the experiments described herein, the AsH_3 flux was kept constant. Alternatively, in attempting to improve As incorporation by increasing the AsH_3 partial pressure at low g_r, a severely degraded PL emission was obtained.

TEM analysis performed on InAsP samples grown under different g_r (not shown) indicates that InAsP QDs require low g_r for growing defect free, similar to what has been determined for InAs.[3] However, there is an additional and important mechanism that is inherent to this ternary alloy: By increasing g_r, one also increases the incorporation of As, which leads to a larger mismatch (between QD and host materials) and, thus, to a higher probability of defect nucleation. The same physical reasoning (lower mismatch) accounts for the observation of defect-free InP QDs, even for $g_r = 0.4$ ML/s (TEM not shown). In this light, in order to achieve InAsP QD growth with the best optical quality and the lowest defect density, one should limit the growth rate to values in the range $0.1 < g_r < 0.4$ ML/s (see Fig. 3), for thickness of about 2 ML.

In summary, we report on the growth of good optical and structural quality InAsP QDs embedded in GaAs. The formation of QDs with different InAsP alloys is consistent with PL and TEM results. By carefully changing the growth conditions, we determined a global growth map that explores most of the possible growth conditions for InAsP QDs on GaAs. Based on this map, it is possible to tailor the optical characteristics of the InAsP dots, leading to the possibility of covering the full energy range between InAs and InP QD emissions.

The authors wish to thank H. Gazetta Filho for technical support on crystal growth and gratefully acknowledge financial support from FAPESP, CAPES, and CNPq-MCT.

[1] D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. Denbaars, and P. M. Petroff, Appl. Phys. Lett. **63**, 3203 (1993).
[2] J. M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André, and O. Vatel, Appl. Phys. Lett. **64**, 196 (1994).
[3] D. Leonard, K. Pond, and P. M. Petroff, Phys. Rev. B **50**, 11687 (1994).
[4] H. Sakaki, Surf. Sci. **267**, 623 (1992).
[5] H. Saito, K. Nishi, I. Ogura, S. Sugou, and Y. Sugimoto, Appl. Phys. Lett. **69**, 3140 (1996).
[6] S. Fafard, K. Hinzer, S. Raymond, M. Dion, J. McCaffrey, Y. Feng, and S. Charbonneau, Science **274**, 1350 (1996).
[7] K. Imamura, Y. Sugiyama, Y. Nakata, S. Muto, and N. Yokoyama, Jpn. J. Appl. Phys., Part 2 **34**, L1445 (1995).
[8] J. J. Finley, M. Skalitz, M. Arzberger, A. Zrenner, G. Böhm, and G. Abstreiter, Appl. Phys. Lett. **73**, 2618 (1998).
[9] A. D. Stiff, S. Krishna, P. Bhattacharya, and S. Kennerly, Appl. Phys. Lett. **79**, 421 (2001).
[10] A. D. Stiff-Roberts, S. Chakrabarti, S. Pradhan, B. Kochman, and P. Bhattacharya, Appl. Phys. Lett. **80**, 3265 (2002).
[11] R. Leon, C. Lobo, A. Clark, R. Bozek, A. Wysmolek, A. Kurpiewski, and M. Kaminska, J. Appl. Phys. **84**, 248 (1998).
[12] S. Fafard, D. Leonard, J. L. Merz, and P. M. Petroff, Appl. Phys. Lett. **65**, 1388 (1994).
[13] R Leon, S Fafard, D Leonard, J. L Merz, and P. M Petroff, Appl. Phys. Lett. **67**, 521 (1995).
[14] S. Fafard, R. Leon, D. Leonard, J. L. Merz, and P. M. Petroff, Phys. Rev. B **50**, 8086 (1994).
[15] W. Zhou, Z. M. Zhu, F. Q. Liu, B. Xu, H. Z. Xu, and Z. G. Wang, J. Cryst. Growth **200**, 608 (1999).
[16] D. A. Vinokurov, V. A. Kapitonov, O. V. Kovalenkov, D. A. Livshits, and I. S. Tarasov, Tech. Phys. Lett. **24**, 623 (1998).
[17] K. Suzuki and Y. Arakawa, Phys. Status Solidi B **224**, 139 (2001).
[18] B. Wang and S.-J. Chua, Appl. Phys. Lett. **78**, 628 (2001).
[19] V. A. Shchukin, N. N. Ledenstov, P. S. Kop'ev, and D. Bimberg, Phys. Rev. Lett. **75**, 2968 (1995).