Size control of InAs/InP(001) quantum wires by tailoring P/As exchange

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The size and emission wavelength of self-assembled InAs/InP(001) quantum wires (QWr) is affected by the P/As exchange process. In this work, we demonstrate by *in situ* stress measurements that P/As exchange at the InAs/InP interface depends on the surface reconstruction of the InAs starting surface and its immediate evolution when the arsenic cell is closed. Accordingly, the amount of InP grown on InAs by P/As exchange increases with substrate temperature in a steplike way. These results allow us to engineer the size of the QWr for emission at 1.3 and 1.55 μm at room temperature by selecting the range of substrate temperatures in which the InP cap layer is grown. © 2004 American Institute of Physics. [DOI: 10.1063/1.1787155]

InAs/InP quantum wires (QWr) or quantum dots (QDs) are very promising for optoelectronic devices operating in the 1.30–1.55 μm wavelength range employed in fiber optical telecommunications systems.^{1–3} However, these nanostructures have not been as extensively exploited as InAs/GaAs QD partly due to the intrinsic peculiarities of the interface between III–V_A/III–V_B compounds: On one hand, an asymmetric stress appears at the InAs/InP interface;⁴ on the other hand, complicated V_A/V_B exchange processes take place during epitaxial growth. Although P/As exchange has been widely studied,^{5–15} a deeper understanding of this process is still needed since it determines the size of the nanostructures, governing their emission wavelength.

In this work, we have carried out *in situ* and in real-time stress measurements on an InAs(001) surface exposed to a P₂ flux at different substrate temperatures T_s in order to quantify the P/As exchange effect. We have observed a strong dependence on T_s of the amount of InP formed (that is, grown without In delivering) during P₂ exposure in the 330–515 °C range. We prove that this behavior is directly related to the InAs surface reconstruction, which depends on temperature for a fixed arsenic pressure. Finally, we show that such InAs/InP surface dynamics can be used to engineer the size distribution of the nanostructures ensemble. To demonstrate this capability, we have studied the optical properties of the InAs QWr as a function of the growth temperature of the InP cap layer, T_C . A redshift of the photoluminescence (PL) spectrum is observed as the T_C decreases. The size reduction responsible for the observed change in emission energy has been directly demonstrated by transmission electron microscopy (TEM).

The P/As exchange process has been assessed by *in situ* and in real-time measurements of the stress evolution during P₂ exposure of an InAs (001) surface through the optical monitorization of the substrate curvature. This *in situ* technique provides a direct measurement of the film accumulated stress, $\Sigma\sigma$ (stress integrated along the layer thickness).⁴ We

have used thinned (175 μm) InAs substrates, elongated along the [110] axis to detect stress variations in this direction, in which the whole amount of incorporated InP can be quantified.⁵ The phosphorous and arsenic beam equivalent pressures (BEPs) used in these experiments were $\text{BEP}(\text{P}_2) = 2.37 \times 10^{-5}$ mbar and $\text{BEP}(\text{As}_4) = 0.53 \times 10^{-5}$ mbar. Simultaneous reflectance difference measurements and reflection high-energy electron diffraction (RHEED) observations at different T_s have also been carried out to determine the reconstructions of the InAs surface¹⁶ and its evolution when arsenic cell is closed.

For PL and TEM studies, two series of samples were grown by solid-source molecular beam epitaxy on InP (001) substrates. The series for PL consists of five samples of InAs QWr covered by a 20 nm thick InP cap layer grown at different temperatures inside three ranges: $330 < T_C < 450$ °C [low temperature (LT)], $450 < T_C < 500$ °C [medium temperature (MT)], and $T_C \geq 500$ °C, [high temperature (HT)]. We deposited ~ 1.7 ML of InAs, the critical thickness to form the QWr as detected by RHEED, at 0.1 monolayer per second (ML/s) and 515 °C. For TEM studies, we have grown two samples with six stacked layers of InAs QWr. A 20 nm thick InP spacer layer, was grown on top of each QWr layer at temperatures $T_C = 380$ °C (LT stack) and 515 °C (HT stack).

Figure 1 shows the accumulated stress $\Sigma\sigma$ evolution experimented by an InAs surface exposed to a P₂ flux for 15 s (0–15 s segment in the x axis) at three representative substrate temperatures: 380, 470, and 515 °C (corresponding to the growth temperatures of the InP cap layer in the LT, MT, and HT ranges, respectively). The arsenic cell was opened before and after the phosphorus exposure. When phosphorous flux was switched on, we observed, in the $\Sigma\sigma$ signal, the development of a tensile stress associated with the formation of InP at the expense of InAs due to As/P exchange processes (InP/InAs lattice mismatch $\approx -3.1\%$). The noise introduced in the stress measurements by the switch between V cells is apparent at $t=0$ and $t=15$ s, and can be used as a guideline of shutters sequence.

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FIG. 1. Accumulated stress evolution in an InAs surface exposed to a P_2 flux during 15 s at three temperatures: 515 °C (HT), 470 °C (MT), 380 °C (LT). The arrows mark the switch between As and P cells.

For all temperatures under study, we observe an initial quick jump of $\Sigma\sigma$ in coincident with the onset of phosphorous exposure, followed by a slower evolution with time. The first quick transient corresponds to the fast incorporation of the incoming P atoms that find an In-enriched InAs surface due to As desorption when As cell is closed, while the second one is related to the formation of InP at the expense of displacement of As by P atoms. Similar behavior also occurs when exposing InP to an As flux (reverse case of this work).^{5,14} At $T_s=380$ °C, the smallest change in the $\Sigma\sigma$ evolution when the P_2 cell is opened takes place. This means that at 380 °C, the As atoms hardly desorb from InAs surface when the As_4 flux is closed, and P atoms are not easily incorporated. Furthermore, no displacement of arsenic by phosphorous atoms is taking place during P_2 exposure because the value of $\Sigma\sigma$ remains constant with time. At $T_s=515$ °C, the first $\Sigma\sigma$ quick jump (partially hindered by the shutters switching noise) corresponds to the formation of ~ 0.9 InP ML, and after 15 s of P_2 exposure $\Sigma\sigma$ reaches a value of 2 Nm^{-1} , that corresponds to 2.2 ML of InP on InAs. When the P_2 flux is interrupted and the As_4 flux re-established, $\Sigma\sigma$ does not recover the initial value remaining a residual stress of 1.2 Nm^{-1} . This indicates that the reverse As/P exchange process leaves buried 1.3 ML of InP. Note that the amount of material produced by these exchange processes is only approximate because: (1) the elastic constants used to calculate the stress induced by 1 ML of InP on InAs are bulk values that could be no longer valid for 1 or 2 ML, and (2) the surface stress variations due to the different surface reconstructions at each temperature during the V element flux exposure should be considered (although this would not account for more than 0.2 Nm^{-1}).¹⁷

The stress measurements plotted in Fig. 1 show a dependence on temperature of the amount of InP formed on InAs by P/As exchange. In the following, we will show that this behavior can be correlated with the surface reconstruction of

FIG. 2. 12 K (continuous line) and room-temperature (dotted lines) PL spectra of the InAs QWrs capped with 20 nm thick InP layer grown at different temperature ranges (LT, MT, and HT).

the InAs starting surface¹⁶ at a given temperature. In fact, not only is surface reconstruction of the starting surface important, but also its evolution during the first 0.1 s after the As cell is closed (the time scale relevant for As/P cells switch operation). Accordingly, we have determined temperature ranges where the P/As process is practically identical (same surface reconstruction evolution), and so far the same amount of InP formed by P/As exchange is obtained: (1) A LT range (330–450 °C) where the InAs surface reconstruction with the As cell opened is $\gamma(2 \times 4)$ [As rich] and remains $\gamma(2 \times 4)$ after 0.1 s with the As cell closed. In this case, we measure a negligible formation of InP (LT curve in Fig. 1); (2) A MT range (450–500 °C) where the InAs starting surface is $\gamma(2 \times 4)$ and immediately (<0.1 s) evolves to a $\alpha(2 \times 4)$ [In surface coverage of 0.5] when the As cell is closed (MT curve in Fig. 1), easily allowing P incorporation; and (3) a temperature range ($T \geq 500$ °C) where the InAs starting surface is at $\alpha(2 \times 4)$ and quickly (<0.1 s) changes to (4×2) [In rich] when the As cell is closed, thus providing a larger InP formation due to exchange (HT curve in Fig. 1).

For InAs QWr capped with InP grown at temperatures where the P/As exchange is relevant ($T_c > 450$ °C), some amount of InP will be formed at the expense of the InAs nanostructures, reducing their size. In this case, the amount of InP formed will be even larger than that obtained in plain InAs surfaces, as the P/As exchange will be enhanced by the strain.^{6,7}

The effects produced by the P/As exchange can be beneficial to adjust the QWr size for a predetermined emission wavelength. Figure 2 shows the 12 K PL (continuous line) and 300 K (dotted lines) spectra of the first series of samples studied (one layer of QWr capped by InP grown at LT, MT, and HT regions). We observe a strong energy blueshift of the PL band from LT to HT samples, i.e., when T_c increases. This blueshift evolves in a discontinuous way with T_c , showing abrupt variations in coincidence with the change of T_c range (LT, MT, and HT). An increase in T_c would imply a size reduction of the nanostructures, and consequently an

FIG. 3. TEM images, in the left, and HRTEM images, in the right, of the HT and LT stack samples of InAs QWRs.

increase of the average PL energy, as shown in Fig. 2. The multipeak structure of the PL band is due to the emission of QWR families with a height difference of 1 ML.² Technologically, the HT ($T_C=515^\circ\text{C}$) and LT ($T_C=380^\circ\text{C}$) samples are the most attractive because of their maximum emission wavelengths: 1.30 and 1.55 μm at room temperature (see dotted plot in Fig. 2).

For a further confirmation of the size reduction of QWRs due to P/As exchange, we have studied by TEM and high-resolution TEM (HRTEM) (see Fig. 3) the second series of samples (LT and HT stack). The average width w and height h (in nm) obtained over all stacked layers are $w=12.9$ and $h=1.2$ for HT stack sample, and $w=10.3$ and $h=3.2$ for LT stack sample. So, we have QWRs of smaller height in the HT sample than in the LT sample (nearly a factor of 3), as clearly determined from the HRTEM images registered at Scherzer defocus.

Suggestions about the role of P/As exchange in InAs/InP systems to modify the shape and size of nanostructures, and consequently the emission wavelength, have been previously advanced. In this way, different growth processes and structures have been designed to take advantage of the As/P exchange.^{9–14} The results obtained in this work clearly demonstrate the role of P/As exchange in the resulting InAs/InP nanostructures at a given temperature, and establish a correlation between the InAs starting surface reconstruction and the amount of InP formed during the switching operation of the As/P cells.

In summary, we have measured *in situ* and in real time the amount of InP formed by the P/As exchange when exposing to phosphorous an InAs flat surface at different temperatures, and this has been correlated with InAs surface reconstruction evolution in a short time interval after the arsenic cell is closed (≈ 0.1 s, the time scale of the switching operation for As–P cells). Under these conditions, we have found three ranges of substrate temperatures (for a fixed As_4 pressure) that are relevant for the P/As exchange process. These results allow us to control the size of self-assembled InAs QWRs, and consequently their optical emission, by selecting the substrate temperature during the growth of the InP cap layer. As a final result, we have designed InAs QWR samples for emission wavelengths centered at 1.3 and 1.55 μm at room temperature.

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- ¹L. González, J. M. García, R. García, F. Briones, J. Martínez-Pastor, and C. Ballesteros, *Appl. Phys. Lett.* **76**, 1104 (2000).
- ²B. Alén, J. Martínez-Pastor, A. García-Cristóbal, L. González, and J. M. García, *Appl. Phys. Lett.* **78**, 4025 (2001).
- ³R. Schwerberger, D. Gold, J. P. Reithmaier, and A. Forchel, *J. Cryst. Growth* **251**, 248 (2003).
- ⁴M. U. González, L. González, J. M. García, Y. González, J. P. Silveira, and F. Briones, *Microelectron. J.* **35**, 13 (2004).
- ⁵M. U. González, J. M. García, L. González, J. P. Silveira, Y. González, J. D. Gómez, and F. Briones, *Appl. Surf. Sci.* **188**, 188 (2002).
- ⁶Y. Kobayashi and N. Kobayashi, *Jpn. J. Appl. Phys., Part 1* **31**, 3988 (1992).
- ⁷D. Fuster, M. U. González, L. González, Y. González, T. Ben, A. Ponce, and S. I. Molina, *Appl. Phys. Lett.* **84**, 4723 (2004).
- ⁸B. Wang, F. Zhao, Y. Peng, Z. Jin, Y. Li, and S. Liu, *Appl. Phys. Lett.* **72**, 2433 (1998).
- ⁹S. Yoon, Y. Moon, T.-W. Lee, E. Yoon, and Y. D. Kim, *Appl. Phys. Lett.* **74**, 2029 (1999).
- ¹⁰H. R. Gutiérrez, M. A. Cotta, J. R. R. Bortoleto, and M. M. G. de Carvalho, *J. Appl. Phys.* **92**, 7523 (2002).
- ¹¹P. J. Poole, R. L. Williams, J. Lefebvre, and S. Moisa, *J. Cryst. Growth* **257**, 89 (2003).
- ¹²S. Frechengués, N. Bertru, V. Drouot, B. Lambert, S. Robinet, S. Loualiche, D. Lacombe, and A. Ponchet, *Appl. Phys. Lett.* **74**, 3356 (1999).
- ¹³C. Paranthoen, N. Bertru, O. Dehaese, A. Le Corre, S. Loualiche, B. Lambert, and G. Patriarche, *Appl. Phys. Lett.* **78**, 1751 (2001).
- ¹⁴Q. Gong, R. Nötzel, P. J. van Veldhoven, T. J. Eijkemans, and J. H. Wolter, *Appl. Phys. Lett.* **84**, 275 (2004).
- ¹⁵K. Y. Suh, H. H. Lee, and E. Yoon, *J. Appl. Phys.* **85**, 233 (1998).
- ¹⁶K. B. Ozanyan, P. J. Parbrook, M. Hopkinson, and C. R. Whitehouse, *Thin Solid Films* **364**, 6 (2000).
- ¹⁷D. Fuster, M. U. González, Y. González, and L. González (unpublished).