InAs nanostructures grown by droplet epitaxy directly on InP(001) substrates

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1. Introduction

The three dimensional (3D) confinement of electrons and holes in semiconductor quantum dots (QDs) gives rise to discrete electron hole states and sharp absorption and emission lines, analogous to those in atomic systems. These features of semiconductor nanostructures will allow addressing the production of quantum states of light (single photons and entangled photon pairs) in a chip. Semiconductor-based single photon and entangled photon pairs emission has been achieved by several groups [1]. For applications in quantum information technologies it would be beneficial that quantum light sources operating around 1.3 and 1.5 μm were available. In this respect, nanostructures based on the InAs/InP system would offer efficient single photons and entangled photon pairs sources for quantum communication.

Single photon emission has already been demonstrated in InAs/InP (001) QDs grown by low-pressure metal organic chemical vapor deposition (MOCVD) [3–5]. More recently, around 1.3 μm single photon source was demonstrated by growing InAs QD on InP (311) B substrates by molecular beam epitaxy (MBE) [6].

The realization of quantum light emitter devices requires a high degree of control of the materials structure and quality. The nanostructures have to fulfill several requisites, as low areal density, high optical yield and fine structure splitting comparable to the exciton homogeneous linewidth. MBE is the optimum epitaxial growth technique for achieving these features due to its capabilities for control the growth of epitaxial layers at atomic monolayer level. However, it has been demonstrated in the past that the growth of InAs on InP (001) substrates produces dashes or wires elongated along [1-10] direction [7,8]. This has been explained considering the intrinsic stress asymmetry along [1-10] and [110] directions at the InAs/InP(001) interface that is also common for any heteroepitaxial system where the compounds have different group V elements and growth is carried out under group V stabilized surface (typically standard MBE conditions) [9,10]. These elongated nanostructures exhibit electronic properties of quantum wires [11] and has been successfully used as active elements for ultra-low threshold lasers [12]. However, due to their
one dimensional density of states, the quantum wires do not show single photon emission properties.

In a previous work we demonstrated that, under restrictive experimental conditions, InAs QDs instead of quantum wires can also be obtained on InP (001) substrates by MBE [13]. The developed process was based in the formation of indium droplets and further crystallization into 3D InAs islands on an In-stabilized InP (001) surface. More recently, other approaches have been followed for obtaining InAs/InP QD by MBE circumventing the intrinsic constraints imposed by the InAs/InP(001) interface under usual MBE growth conditions. One approach consisted of changing the orientation of the InP substrate from (001) to (311) B surface [6]. The other approach is based on the use of droplet epitaxy technique [14,15] on (001) and on InP(111) A substrates [16,17].

In this work we have used droplet epitaxy technique in a solid source MBE system for the growth of InAs/InP(001) nanostructures looking for a robust technology to obtain nanostructures with 3D confinement, control in areal density, and single photon emission at 1.55 μm. We have used droplet epitaxy technique at different substrate temperature, $T_s \leq 300$ °C, to form indium droplets by depositing indium on InP layers grown on InP (001) substrates. The InAs nanostructures were formed after indium droplet crystallization with arsenic directly on InP, without any intermediate InGaAs or InAlAs layer, a material configuration more interesting for technological applications. We have studied the evolution of the density and shape of the nanostructures with substrate temperature and extracted values of relevant magnitudes that describe indium atoms diffusivity. The nanostructures evolve with $T_s$ from complete towards fragmented nanorings of different size, sometimes surrounded by disks with $T_s$ dependent size. The photoluminescence (PL) emission wavelength of the discrete nanostructures lays around 1.3–1.5 μm by applying in situ partial capping plus anneal and post-growth thermal annealing procedures. The proper combination of these processes shall allow in the future obtaining InAs nanostructures directly on InP (001) surfaces with improved single photon emission properties.

2. Experimental

Indium droplets were formed by depositing indium at substrate temperature in the range of $T_s = 50–300$ °C. Prior to the droplet epitaxy processes, a 118 nm thick InP buffer layer was grown by solid source MBE on InP(001) substrates after thermally oxide removal. Denoting the indium coverage, $\theta$, in monolayers (ML) and In flux, $F$, in equivalent ML per second (ML/s) of InP on InP(001), we have deposited $\theta = 3$ ML, at $F = 0.1$ ML/s, at $T_s = 50, 150, 180, 220, 260$ and 300 °C. After In deposition, arsenic was supplied for droplet crystallization during 5 min at a beam equivalent pressure BEP ($A_{sa}$) $\geq 10^{-8}$ Torr, corresponding to an equivalent flux of arsenic of 1.3 ML/s, as measured by monitoring the specular beam $I_{00}$ reflection high energy electron diffraction (RHEED) oscillations during GaAs (001) homoepitaxial growth limited by group V element incorporation [18] and corrected by the different surface atomic density between GaAs (001) and InP (001) surfaces. In the samples grown and crystallized at $T_s = 50$ °C, $T_s$ was further raised under arsenic flux from 50 °C up to 300 °C during 10 min.

The samples were characterized by atomic force microscopy (AFM) in a Veeco Dimension Icon scanning probe microscopy system, using Bruker silicon cantilevers ($K = 0.4$ N/m) under Bruker ScanasySTM mode. Those grown at $T_s = 50$ °C and 180 °C were covered by a 118 nm thick InP layer for photoluminescence characterization using the partial capping plus anneal process: $T_s$ remained at that used for droplet crystallization during the growth of the first 3 nm of InP cap layer (partial capping) [19]. Then sample temperature was raised up to 515 °C under $P_2$ flux and the remaining 115 nm of the InP cap layer was grown. A post-growth annealing of these samples at 600 °C during 10 min was made in order to improve their crystalline quality.

Standard PL characterization was performed at $T = 18$ K using as excitation source a frequency doubled Nd:YAG laser emitting at $\lambda = 532$ nm. Light was dispersed by a 0.3 m focal length monochromator and detected with an infrared photomultiplier connected to a lock-in amplifier. Spatially resolved μPL characterization was performed at 4 K using a diffraction limited confocal microscope inserted in a low vibration cryogen free cryostat. 980 nm and 785 nm continuous wave diode lasers were used to excite the photoluminescence which was dispersed by a 750 mm focal length spectrometer at a resolution of $\sim 30$ μeV and detected with a Peltier cooled InGaAs photodiode array. A piezo scanner was used to record raster scanning μPL maps.

3. Results and discussion

The density of nanostructures formed by droplet epitaxy is determined by the density of the metallic droplets, which in turn depends on the diffusion length of the adatoms on the surface leading to processes of coarsening and coalescence of the liquid clusters [20–23]. Accordingly, different parameters as substrate temperature, flux and time of deposition (coverage) of the group III element atoms are relevant for controlling droplet density and therefore nanostructures density.

We have studied the evolution of InAs nanostructures density by varying the substrate temperature (50–300 °C) during In deposition for droplet formation. On Fig. 1 we have plotted the density of nanostructures (squares) as a function of the inverse of temperature. We have also included some values of the density of In droplets that have not been exposed to arsenic flux (triangles). As expected from the one to one correspondence between droplets and nanostructures formed after droplet crystallization, all the experimental points follow the same behavior with $T_s$: the evolution with the inverse of $T_s$ is exponential, with an activation energy of 0.126 ± 0.010 eV, with a change of density between $5 \times 10^7$ and $4 \times 10^{10}$ cm$^{-2}$ in the substrate temperature range $T_s = 50–300$ °C. We observe that, in contrast to Ga droplet on GaAs (001) substrates [22], there is not any change of slope at a certain temperature. These data indicate that the same coarsening processes are active in the wide range of substrate temperatures under study. Our results show that following the growth

![Fig. 1. Density of InAs nanostructures (squares) grown by droplet epitaxy and In droplets without exposing to arsenic flux (triangles) as a function of the inverse of substrate temperature $T_s$. The straight line is an exponential fit of the experimental values.](image-url)
procedure described it is possible to control the nanostructures density in the interesting range for optical characterization of single nanostructures or for embedding a single nanostructure in a photonic microcavity as required for several quantum information applications.

It is expected that the size and shape of the InAs nanostructures resulting from droplet crystallization depend on $T_S$ during indium deposition and crystallization with arsenic. In fact, as the In coverage ($\theta$) is the same for all samples, the change in droplet density is linked to a change in the droplet size and so, the starting point before crystallization with arsenic will be different for the samples with different $T_S$ during indium deposition. Moreover, substrate temperature will also influence on the kinetics effects that take place during In droplets evolution under arsenic exposure, affecting the out-diffusion of In atoms from the droplets and their incorporation as InAs on flat areas between droplets and therefore the nanostructures shape.

In Fig. 2 we show AFM images of the nanostructures formed after the As crystallization for different substrate temperatures. We observe ring-like nanostructures in all the samples. They are surrounded by extended disks except in those that In was deposited at the highest ($300 \, ^\circ\text{C}$) and the lowest substrate temperature ($50 \, ^\circ\text{C}$) explored in this work (Fig. 2(a) and (f) respectively).

The inner nanostructures shape and size also depends on substrate temperature $T_S$ as shown in the insets on Fig. 2. At $T_S=50 \, ^\circ\text{C}$, AFM image (Fig. 2(a)) shows whole ring-like shape with four isolated dots situated on top of the ring that are equidistant along [100] and [010] crystal directions. These isolated quantum dots are as high as 12 nm but their height gradually decreases with $T_S$ until they become indistinguishable from the ring-like profile at $T_S=260 \, ^\circ\text{C}$ (Fig. 2(e)). The ring-like shape also evolves with $T_S$ from complete rings with a height of $\sim 6$ nm towards uncompleted rings (Fig. 2(d)-(f)) with a height below 2 nm (for sample grown at $T_S=300 \, ^\circ\text{C}$). The diameter of these nanostructures measured along [100] varies from 65 to 150 nm in the studied $T_S$ range. The disks surrounding the inner nanostructures are elongated along [110] direction with a height that varies with $T_S$ from 2.8 nm ($T_S=150 \, ^\circ\text{C}$) to 1.3 nm ($T_S=260 \, ^\circ\text{C}$).

The observed change of morphology with substrate temperature is very similar to that observed and modeled for other systems grown by droplet epitaxy: GaAs/GaAs [24–29], InAs/InGaAs [16], GaSb/GaAs [30]. In those systems, the metallic droplets exposed to group V element flux results in the formation of ring-like structures eventually surrounded by disks of different diameter and height. Extending those results to the InAs/InP(001) system, the inner structures would correspond to InAs formation at the In droplet edge, while the surrounding disks would correspond to InAs formation from indium atoms spreading out from the droplets and arsenic from the incident flux. Our results show (Fig. 3) that there is a close correspondence between the droplet diameter and the diameter of the inner ring formed after arsenization of the In droplets. The observed increase of the diameter of the inner rings and outer disks with $T_S$ is in correspondence with the increase with $T_S$ of In droplet size and enhanced In diffusion respectively.

In relation with the surrounding disks, we observe that in the InAs/InP system the process of formation of the disks is kinetically hindered at the lowest substrate temperature ($T_S=50 \, ^\circ\text{C}$), while at the highest substrate temperature ($T_S=300 \, ^\circ\text{C}$), the indium atoms are smeared out far enough so that the InAs islands around the droplet are not visible. The disks are not observable in both extreme cases (Fig. 2(a) and (f) respectively). Notice nevertheless (inset of Fig. 2(a)) that a small elongated structure close to the ring can be observed even when In has been deposited at $T_S=50 \, ^\circ\text{C}$, which could have been formed during annealing at $T_S=300 \, ^\circ\text{C}$ after arsenic crystallization.

As previously described, the disks are produced by InAs formation from In atoms coming from the In droplet. In this way, their radio is a direct measure of the diffusion length ($L$), the distance traveled by the In atoms until their incorporation into surface lattice. We have measured $L$ in the AFM images for substrate temperature between 150 $^\circ\text{C}$ and 260 $^\circ\text{C}$ obtaining that the diffusion length of In adatoms changes from 160 to 400 nm along [1-10] ($100$ to $300$ nm along [110]). On Fig. 3 we plot $L$ in both directions versus the inverse of the substrate temperature.

Diffusion length anisotropy on (001) surfaces has been observed in different systems by different experimental techniques and experimental conditions, as for example in In/InGaAs at $T_S$ between 200 $^\circ\text{C}$ and 300 $^\circ\text{C}$ [16] and Ga/InAs at $T_S$ around 500 $^\circ\text{C}$ [31,32]. In turn, we have not observed anisotropy in Ga/
GaAs at 350 °C (not shown) in agreement with previously reported data [29]. The measured diffusion length anisotropy has been analyzed following the same procedure as in Ref.[29], where the $L^2$ dependence on $T_s$ is expressed as:

$$L^2 = \frac{D_0 N_s}{J_{As}} \frac{1}{e^{E_a/k_B T_s}},$$

where $N_s$ is the number of surface sites, $J_{As}$ is the arsenic flux and $E_a$ is the activation energy for In atoms surface diffusion. The exponential pre-factor $D_0$ is related to the vibrational free energy of the atom and depends on its position at the surface [33]. $N_s/J_{As}$ is constant under our experimental conditions and equal to 0.8.

We have fitted the experimental $L$ values measured at different $T_s$ to that expression (straight lines on Fig. 3), and determined the values of the activation energy and exponential pre-factor. We have obtained $E_a=0.28 \pm 0.01$ eV and $0.25 \pm 0.02$ eV along [1-10] and [110], respectively. For the exponential pre-factor, we obtain $D_0=(1.5 \pm 0.4) \times 10^{-6}$ cm$^2$ s$^{-1}$ and $(0.40 \pm 0.14) \times 10^{-6}$ cm$^2$ s$^{-1}$ for [1-10] and [110], respectively. These results show that, within the resolution of our experimental data, the activation energies obtained are similar in both directions, while $D_0$ [1-10] is four times $D_0$ [110]. Accordingly, the anisotropy of In atoms migration observed by AFM (elongated disks shape on Fig. 2(b)–(e)) is confined to the exponential pre-factor $D_0$. The observed anisotropy in $D_0$ in <110> directions in InAs/InP (001) system should be ascribed to the intrinsic strain asymmetry of this interface [9,10], and to other contributions as the difference in the arsenic bonds configuration for In incorporation, which is dependent on the surface reconstruction.

Similar results were shown by Ohta et al. for Ga atoms migration on GaAs (001) surfaces using RHEED measurements [31], in spite of the differences in the heteroepitaxial systems and experimental conditions. As in our case, they observe anisotropy in Ga diffusion along...
<110> directions due to differences in the exponential pre-factors, while they do not observe any differences in the activation energies for the adatoms migration. It is remarkable the coincidence in the value of the ratio in $D_0^{110}/D_0^{110} = 4$.

Values of the activation energy of about 0.81 eV for In on InAs(001) were reported using micro RHEED measurements at substrate temperatures above 420 °C [34]. Given the huge dispersion of data related with surface diffusion reported in the literature using different experimental techniques (see Ref. [29] for a detailed discussion), the AFM measurements of the disks dimensions presented here stand out as a straightforward way to determine the diffusion lengths in the range under study (150–260 °C).

PL and μPL characterization at low temperature was performed in capped samples where 3 ML of In were deposited at $T_S = 50$ °C and 180 °C. A 3 nm thick InP partial capping + annealing and a total InP cap layer of 118 nm was used in both cases. Fig. 4 shows in log scale the ensemble PL spectra obtained at 18 K in these samples before and after the post-growth annealing treatment. Solid and hollow symbols correspond to the as-grown and post-growth annealed samples, respectively. The as-grown samples exhibit several emission bands covering the spectral range from 1000 to the detector cut-off at 1650 nm. We identify the high energy emission bands at 1142 nm (1.085 eV) with FWHM = 36 meV, in the sample grown at $T_S = 50$ °C, and at 1131 nm (1.007 eV) with FWHM = 168 meV in the sample grown at $T_S = 180$ °C, with small InAs/InP quantum dots [35], and/or with InAs quantum wells [36], formed during the As exposure in the flat In-terminated InP surface areas between droplets. The remaining low energy emission bands would be related to the nanostructures identified before by AFM. On the one hand, at these substrate temperatures there is no arsenic/phosphorous exchange [37] and the amount of deposited In is not enough for the formation of extended quantum wells with emission at long
wavelengths [38]. Moreover, the wavelength range and inhomogeneous broadening agrees with our own results found in InAs/InP QDs with similar sizes but grown by a different method [13]. These low emission bands peak at 1549.8 nm (0.800 eV) with FWHM = 104 meV in the sample grown at $T_S = 50 \, ^\circ C$ and at 1373 nm (0.903 eV, FWHM = 157 meV) in the sample grown at $T_S = 180 \, ^\circ C$. An energy shift by $\sim 100$ meV is consistent with the shrinking of the nanostructure height caused by the larger In diffusion observed by AFM while increasing the substrate temperature (see Fig. 2 and related discussion).

The integrated intensity of the low energy bands is 3.7 times larger in the sample grown at $T_S = 50 \, ^\circ C$. In this sample the substrate temperature was raised under arsenic flux up to 300 $^\circ C$ before capping and after droplet crystallization. This annealing step at $T_S = 300 \, ^\circ C$ would explain the actual improvement in terms of emission intensity of the 50 $^\circ C$ sample.

Despite these differences, the emission intensity of the as-grown samples was rather poor if compared with InAs/InP self-assembled quantum wires and dashes grown in the past in the same reactor and could not be explained by the small areal densities of the droplets [36]. The post-growth annealing treatment at 600 $^\circ C$ during 10 min alleviated this situation as shown in Fig. 5. In both samples an energy blue shift and a huge increase (up to three decades) of the PL intensity can be observed as expected after rapid thermal annealing processes [39]. The dramatic improvement in PL signal strongly suggests that the crystalline quality of the nanostructures and surroundings was seriously affected by the low crystallization temperatures used here. In fact, the low crystallization temperatures and relatively high As over-pressure could leave a metal core behind that can then be annealed out, as suggest previous simulations on GaAs system [40].

Thanks to the low areal density attainable by droplet epitaxy, scanning confocal micro-spectroscopy at 4 K can be used to investigate further the optical properties of these nanostructures. Fig. 6 shows typical µPL spectra obtained in the four samples. In each case, the ensemble PL spectrum has been plotted and normalized to the maximum of the µPL signal in the region of interest. The poor efficiency observed in the ensemble characterization of the as-grown samples is consistent with their low µPL intensity as depicted by gray lines in Fig. 6(a) and (c). Their µPL spectra consist of broad and featureless bands extending between 1300 and 1600 nm. We have also recorded µPL images scanning 8 x 8 μm² (confocal spot size $\sim$ 950 nm) in each sample while integrating the intensity in different spectral regions. The results are shown in the insets of Fig. 6. For the as-grown samples, we find that the emission is spatially localized and conclude that the nanostructures survived to the capping process although their emission is low and broad due to non-radiative capture and spectral diffusion caused by nearby defects.

The analysis of the µPL signal give us also information about the different effect produced by the post-growth thermal annealing depending on the temperature used for the In droplet deposition. The emission of the sample deposited at 50 $^\circ C$ exhibits two bands after thermal annealing as observed in Fig. 6(b). The band at 1033 nm looks very similar (apart of the absolute intensity) both in ensemble and µPL and must be related to the blue-shifted emission of an InAs quantum well already present in the as-grown sample at 1170 nm. The remaining material was emitting before in featureless bands around 1500 nm, but after the thermal treatment gives rise to much narrower peaks between 1120 and 1250 nm as detailed in Fig. 7. These emissions are spatially localized in the sample surface and thus must be related to the annealed and blue-shifted QDs. The typical observed linewidth $\sim 3$ meV is not limited by our spectral resolution and is very far from being transform limited so we must conclude that spectral diffusion effects have been mitigated but are still important in this sample.

The results in the sample deposited at 180 $^\circ C$ are very different after thermal annealing as observed in Fig. 6(d). Again two emission bands can be detected but they are characteristic of two quantum wells since, on the one hand, the ensemble and µPL spectra look very similar, and furthermore, the emission is homogeneous in large areas of the sample surface as shown in the inset image. We must conclude that after annealing this sample, the 3D inner nanostructures and the 2D surrounding disks observed by AFM do not maintain their shape and eventually merge into a 2D extended layer. The 3D and localized 2D nanostructures are smoothed out as a consequence of the change in the composition and size of these small height nanostructures resulting from the intermixing of the interfaces observed after thermal annealing processes [39].

Our attempts to fabricate InAs nanostructures directly on InP(001) by droplet assisted epitaxial techniques reveal clearly the major advantages and difficulties of kinetically limited growth of nanostructures at low temperatures. The nucleation density, size and shape can be controlled with great accuracy at the expense of the crystalline quality of the material. Although we can apply post growth thermal annealing processes to mitigate this situation, this kind of treatment also modifies the nanostructure morphology and might produce unexpected effects. Overall, our study reveals that, by increasing the size of the nanostructures, using crystallization processes that preserve the 3D confinement and a suitable partial capping thickness, a strategy could be defined to match the intended spectral range and optical properties for a given application.

4. Conclusion

In short, this work explores a realistic path for obtaining high optical quality InAs/InP(001) 3D nanostructures at 1.5 μm relying on solid source MBE droplet epitaxy. We have developed growth processes based on droplet epitaxy in a solid source MBE system to obtain InAs/InP(001) nanostructures with 3D confinement. We have demonstrated that the areal density of these nanostructures can be controlled in the range of interest for quantum information devices. For a fixed In coverage, the shape and size of the nanostructures depend on substrate temperature, and their evolution with this parameter has been used to extract values of diffusion lengths, activation energies and exponential prefactors for In atoms diffusivity on InP(001) substrates that have not ever been reported in the literature. The poor optical quality of the nanostructures, intrinsically linked to low substrate temperatures growth, can be improved by applying in situ and post-growth thermal annealing processes.
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References


