Improvement of InAs quantum dots optical properties in close proximity to GaAs(001) substrate surface

J. Martín-Sánchez*, Y.González, P. Alonso-González and L.González.

Instituto de Microelectrónica de Madrid (CNM-CSIC), Isaac Newton 8 (PTM), 28760-Tres Cantos
(Madrid), Spain.

* Corresponding author. Tel.: +34918060700; Fax: +34918060701.

E-mail address: javierms@imm.cnm.csic.es

ABSTRACT

In this work we demonstrate a growth process for obtaining high optical emission efficiency InAs/GaAs(001) quantum dots (QD) formed at short distance to the interface with the GaAs substrate. In particular, after an initial exposure of the substrate surface to long times of atomic hydrogen flux (t_H up to 45 min) followed by a posterior growth of a GaAs buffer layer by atomic layer molecular beam epitaxy, both steps at low substrate temperature ($T_S=450$ °C), an enhancement of InAs QD optical emission efficiency is obtained, even at close proximity (3.5 nm) to the substrate interface. This process fulfils the strict requirements in terms of substrate temperature and buffer layer thickness (distance from the QD to the substrate interface) for its possible use as an optimal regrowth protocol on previously patterned GaAs substrates.

Keywords: A1.Interfaces, A1.Nanostructures, A3.Molecular Beam Epitaxy, B2.Semiconducting III-V materials.

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INTRODUCTION

Semiconductor quantum dots (QD) have attracted much attention during the last decade due to their special opto-electronic properties. As a result, a variety of novel devices have been

developed and much more predicted. Moreover, their particular nature of fully quantized electronic states together with the possibility of manipulation as artificial atoms make them perfect candidates in order to study new phenomena predicted by theoretical quantum physics studies [1-3]. In order to obtain an actual advantage of their properties, it is mandatory to develop technological processes that allow fabricating QD with accurate control in their size, shape and spatial position. For that purpose, the use of pre-patterned substrates is a quite wide-spread strategy in order to obtain highly ordered arrays of QD using different lithographic approaches [4-11]. In this direction, the preparation of a patterned surface for a subsequent epitaxial growth that allows obtaining selective QD nucleation while keeping their optical emission efficiency just in one single layer of QD is a key factor for a successful application of this approach in devices where stacked layers of QD must be avoided. In particular, for single photon emitter devices, one of the most promising approaches is based on the fabrication of an optical microcavity containing a single QD. The total thickness of the microcavity d is limited to a hundred of nanometers and the QD should be situated at a specific location inside the optical microcavity. If a patterned substrate is used for the localization of the QD, a regrowth process step at an intermediate thickness of the optical microcavity is mandatory. Consequently, the device design seriously limits the thickness of the buffer layer that can be grown. In this context, optimization of the interface quality is an important issue, as photoluminescence (PL) emission properties of QD depend drastically on their proximity to non-radiative recombination channels [12,13].

Besides the restrictions imposed by devices design, the use of patterned substrates imposes even more severe limitations to the buffer layer thickness and substrate temperature (T_s) used in the whole process (oxide desorption and epitaxial growth). In particular, the buffer layer thickness is usually restricted to tens of atomic monolayers (ML) [4,5,7-10], depending on the initial size of the pattern features and on the kinetics of the growth mode employed. With respect to the substrate temperature, considering that atom surface migration for III–V compound

semiconductors is significant for $T_S \geq 500$ °C [4], it would be desirable to maintain the maximum T_S as close as possible to 500 °C, at least in the case of shallow pattern features (a few nanometers).

Thus, the development of a whole surface preparation process fully compatible with the use of patterned substrates has to be tackled to achieve clean, flat and defect free surfaces on which high optical quality QD in close proximity to the interface can be obtained.

In this work we have developed a growth process in order to obtain high optical emission efficiency site controlled QD grown by molecular beam epitaxy (MBE) on a surface that has been previously patterned by local oxidation nanolithography using an atomic force microscope (AFM) as a future application. The usual pattern motives obtained by this lithographic method are very shallow (around 10 nm as maximum) [14] and so far, the conditions for preservation of the pattern features after the different technological processes involved are rather strict.

With this aim we have studied the influence of several parameters on the PL emission of self-assembled QD in close proximity to the interface: type of initial substrate used, surface preparation before epitaxial growth and GaAs buffer layer thickness. Our results show that the atomic hydrogen exposure time on the substrate surface after the GaAs oxide has been removed is the most relevant parameter for interface quality improvement. The results shown in this work would allow the development of a process for achieving QD with high optical efficiency nucleated at specific sites provided by shallow features on patterned substrates.

EXPERIMENTAL

InAs self-assembled QD were grown by MBE on two different kind of GaAs (001) substrates: commercial epi-ready GaAs (001) substrates and 0.5 μm thick epitaxial layers grown by MBE GaAs(001) substrates (referred from now on as CS and ES respectively). The epitaxial substrates (ES) were obtained by growing a 0.5 μm thick GaAs layer by MBE at a growth rate of 1 ML/s at

$T_S=580$ °C under a V / III flux ratio of 8. This epitaxial layer was grown on epi-ready CS after the GaAs oxide was removed by a conventional thermal process: heating at $T_S= 600^\circ\text{C}$ during 5 min under As_4 flux. Under the used growth conditions flat surfaces at atomic level are obtained in a reproducible way.

In our experiments, previous to epitaxial growth, oxides and contaminants are removed from the surface on both kind of substrates by exposing the surface to an atomic hydrogen flux using a Ta H_2 thermal cracker at low substrate temperature ($T_S= 450$ °C), which is significantly lower than that required for conventional thermal oxide desorption process ($T_S= 600$ °C) [15-18]. A H_2 base pressure of 1×10^{-5} Torr was used during this process. Together with H beam, As_4 was simultaneously supplied to compensate arsenic losses from the surface. At $T_S=450$ °C and after 5 min of exposure to H and As_4 beams, a clear $c(4 \times 4)$ As rich surface reconstruction is observed on the reflection high energy electron diffraction (RHEED) pattern, indicating that the surface oxide has been removed.

With the aim of optimizing the interface, we have studied the influence of both the H exposure time and substrate temperature used at the oxide removal stage. We have used H exposure periods (t_H) of 10, 20, 30 and 45 min (from this point we will refer to this treatment as H process). For the study of the influence of substrate temperature, the former H treatment (always supplied with As_4) is followed by a thermal annealing step during 5 min at $T_S=600$ °C under As_4 flux. After this high T_S process (referred as H + T), a (2×4) surface reconstruction is observed on the RHEED pattern. The step at high substrate temperature is made to inform about the presence of possible contaminants that would require higher temperatures to be desorbed.

Previous to InAs deposition for QD growth, GaAs buffer layers with different thickness ($\theta_{th} = 3.5, 30, 70$ and 150 nm) were grown at $T_S = 450^\circ\text{C}$ by atomic layer molecular beam epitaxy (ALMBE). This growth mode allows growing atomically flat GaAs epitaxial layers at low substrate temperature without thickness limitation [19]. Once the GaAs buffer was grown at low substrate

temperature, T_s was increased to 510°C for growing the InAs QD: 1.7 ML of InAs were deposited by pulses of 0.1 ML of InAs at 0.05 ML/s followed by a pause of 2s under As_2 flux. Under these growth conditions, this amount of InAs deposited corresponds to the critical thickness for the 2D-3D transition as shown by the RHEED pattern [20].

In order to evaluate the GaAs interface quality dependence on the different parameters involved in the preparation process, capped and uncapped InAs QD samples were grown for their optical and morphological characterization by means of photoluminescence (PL) and atomic force microscopy (AFM) measurements respectively. For capped InAs QD samples, a 50 nm thick GaAs layer was grown by MBE at 0.5 ML/s in a two-step process: The first 20 nm at 510 °C under As_2 and the remaining 30 nm at $T_s=580$ °C under As_4 . The change of temperature between 510°C and 580°C was made dynamically without growth interruption.[20]

For PL measurements, a conventional low magnification setup with excitation at 532 nm (diode pumped solid laser) was used. The PL signal at 20K was detected by a Ge cooled photodetector attached to a 0.22 m focal length monochromator. For AFM characterization, a commercial Nanotec scanning probe microscopy (SPM) system was used in tapping mode under ambient conditions.

RESULTS

On Fig. 1 we show the PL spectra obtained from capped InAs QD samples grown on both ES and CS with GaAs buffer layer thickness, $\theta_{th} = 3.5$ nm. These samples have followed both H and H+T processes with $t_H=10$ min as surface preparation previously to the epitaxial growth. PL measurements were made at $T=20$ K with an excitation power of $P_{exc}=1$ mW. Given that no excited states are seen up to higher excitation powers, only ground state energy levels are populated in the QD under these experimental conditions. It is clearly observed that higher PL intensities are obtained for samples that have undergone a thermal annealing step at 600°C (H+T). This result implies that there are some contaminants that have not been removed from the

substrate surface by exposure to H during 10 min at a substrate temperature ($T_s = 450\text{ }^\circ\text{C}$) compatible with growth on patterned substrates. Furthermore, H+T samples grown on CS show the highest PL intensity and the lowest PL peak width. These results would indicate that cleaner interfaces could be obtained using conventional substrates (CS) than using epitaxial substrates (ES). However, we obtain quite the contrary if the exposure time to H is sufficiently increased. On Fig. 2 we show a) the PL spectra and b) the integrated PL intensity obtained as a function of the H exposure time ($t_H = 10, 20, 30$ and 45 min.) for samples with a GaAs buffer layer thickness of 3.5 nm. The results shown on Fig. 2a correspond to samples grown on ES. On Fig. 2b, empty symbols (full symbols) are used for samples grown on ES (CS). Integrated PL intensity obtained from samples shown on Fig. 1 is also included for comparison. We clearly observe that the integrated PL signal increases with t_H for the samples grown on both type of substrates, although with a higher slope for those grown on ES. In the case of ES samples, the integrated PL intensity obtained for $t_H = 45$ min increases up to values even higher than those obtained for samples with $t_H = 10$ min where an annealing process at high temperature ($T_s = 600\text{ }^\circ\text{C}$) was also performed (ES (H+T) and CS (H+T)). This can be interpreted considering the differences between the oxides in epi-ready commercial substrates (CS) and epitaxial layers used as substrates (ES). In ES the native oxide is formed by exposure to air after epitaxial growth and during heating for indium attaching and detaching from sample holder. This procedure gives rise to a non-stoichiometric native oxide in which additional carbon uptake from the ambient is incorporated during its formation process [21,22] and, accordingly, larger t_H is necessary to obtain clean surfaces. However, the higher PL signal measured for samples grown on ES for $t_H \geq 45$ min, as compared with samples grown on CS, could be ascribed to a better crystalline quality of MBE epitaxial substrates: as the distance of the QD to the interface is only of 3.5 nm (buffer layer thickness), the largest part of the GaAs matrix that supplies carriers to the QD is inside the substrate used in these samples.

On the other hand, results shown on Fig.1 and Fig. 2a show that a blue emission shift and PL peak width decrease are always associated with an integrated PL intensity improvement. This behaviour could be directly related with a decrease of the density of non radiative recombination centres at the interface which would reduce the spectral diffusion effects (leading to PL peak width enlargement and red shift of emission wavelength) on the PL emission of the QD. Similar qualitative PL behaviour has been reported in micro-PL experiments [23] by changing the QD distance, in this case, to the surface sample. The PL peak intensity change was related with the availability of non radiative recombination channels for QD in close proximity to the surface. In our case, as the QD are closer to the interface with the substrate ($d = 3.5$ nm) than to the free surface (50 nm), the observable variations will be related with the proximity to the interface that would be then, the main source of nonradiative centres [12,13]. In this way, the measured PL efficiency would be a direct measurement of the interface quality obtained for the different substrate preparation processes used. However, we want to notice that a similar phenomenology would have been observed if the different preparation processes had yield different QD size distributions. In fact, it is expected that changes in surface morphology affect the QD nucleation process and that important variations on characteristic parameters of the QD distribution (height, width and size uniformity) could take place. These variations would modify the PL emission properties [24,25] even in the absence of an interface or surface in its influence region. We want to remark that the QD under study have been formed on surfaces at only 3.5 nm from the interface and that the different H exposure times for each sample could give raise to surfaces with different flatness degree producing different QD distributions for an otherwise identical growth sequence. In order to discard a possible morphological influence on the optical performance of the samples, an AFM study of the QD distributions obtained as a function of the H exposure time of the substrate surface has been done on uncapped samples with the same GaAs buffer layer thickness, $\theta_{th} = 3.5$ nm. On Fig. 3 the values of diameters and heights of the QD

obtained after a statistical study of a $2\ \mu\text{m} \times 2\ \mu\text{m}$ surface area with their respective errors bars are shown. The AFM results indicate that, taking into account the dispersion ($\pm 7\%$) of the values, all samples are similar and there is not any clear tendency as the H exposure time increases that could explain the PL peak trends (emission energy and width) observed on Fig. 2a. In this way, the differences measured in the PL efficiency of the samples can be related with a reduction of the non radiative recombination centres as the H exposure time of the substrate surface increases.

Another relevant aspect for a successful development of a growth process fully compatible with regrowth processes on patterned substrates is the limitation of the GaAs buffer thickness. The integrated PL intensity values obtained for QD grown on different GaAs buffer layer thicknesses (3.5, 30, 70 and 150 nm) are shown on Fig. 4. Results obtained from samples grown on CS and ES substrates with H exposure time of 10 min. and 45 min. are plotted. For low H exposure times no significant differences between samples grown on CS and ES are observed. In these samples the PL efficiency increases as expected with the GaAs buffer layer thickness. When the H exposure time increases to 45 min, the samples grown on ES clearly show higher integrated PL intensity for all buffer layer thicknesses studied. Moreover, it is necessary the growth of a 30nm thick GaAs buffer layer on CS for obtaining the same integrated PL intensity than that measured on ES samples with a 3.5 nm thick buffer layer. On the other hand, longer H exposure times than those explored in this work, could result in better QD optical efficiencies because a saturation integrated PL intensity value is not observed on Fig. 2b. These results mean that the use of epitaxial substrates is a key point for obtaining better optical efficiencies in QD at close interface proximity, which is the usual situation when patterned substrates are used.

CONCLUSIONS

In conclusion, we have studied different approximations in order to improve the optical properties of InAs QD grown on GaAs (001) substrates taking into account the restrictions imposed by patterned substrates. We have demonstrated that the use of epitaxial substrates, instead of commercial ones, allows a reduction of the GaAs buffer thickness necessary to achieve optimal optical efficiencies in QD. The substrate surface exposure to long times of H and As₄ flux ($t_H=45$ min) followed by the growth of a very thin GaAs buffer layer ($\theta_{th}=3.5$ nm) by ALMBE, both steps at low temperature ($T_S=450$ °C), has been demonstrated as an excellent approach for obtaining high optical quality QD situated in close proximity to the interface with the substrate. This procedure is fully compatible with the use of patterned substrates, and therefore allows one to get over the difficulties associated with patterned substrates technologies.

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FIGURE CAPTIONS

Figure 1: Photoluminescence (PL) spectra ($T=20\text{K}$, $P_{\text{exc}}=1\text{mW}$) obtained from QD samples at 3.5 nm interface distance grown on both epitaxial substrates (ES) and commercial available epi-ready substrates (CS). H is used for samples whose substrate surface was exposed to atomic hydrogen (H) during 10 min. H+T is used for samples whose substrate surface was undergone a H step plus an annealing process consisting of heating at $600\text{ }^{\circ}\text{C}$ for 5 min.

Figure 2: a) Photoluminescence (PL) spectra and b) integrated PL intensity obtained as a function of the atomic H exposure time ($t_{\text{H}}= 10, 20, 30$ and 45 min.) for samples with a GaAs buffer layer thickness of 3.5 nm. The results shown on Fig. 2a correspond to samples grown on

ES. On Fig. 2 b) empty symbols (full symbols) are used for samples grown on epitaxial substrates ES (commercial substrates, CS). The integrated PL intensity from the samples shown on Fig. 1 is also included for comparison.

Figure 3: QD diameters (left) and heights (right) measured on samples with different substrate surface atomic H exposure time. The values were obtained by a statistical study (error bars) of a $2\ \mu\text{m} \times 2\ \mu\text{m}$ AFM surface image. The QD were grown at 3.5 nm substrate surface distance. Empty symbols are used for samples grown on epitaxial substrates (ES) and full symbols correspond to samples grown on commercially available epi-ready substrates (CS).

Figure 4: Integrated photoluminescence (PL) intensity values obtained for QD grown on different GaAs buffer layer thicknesses (3.5, 30, 70 and 150 nm). Empty symbols are used for samples grown on epitaxial substrates (ES) and full symbols correspond to samples grown on commercially available epi-ready substrates (CS). Results from samples grown on substrates with atomic H exposure time of 10 min. and 45 min. are plotted.

Fig.1

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