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Evaluation of the In desorption during the capping process of diluted nitride In(Ga)As quantum dots

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Abstract. Diluted nitride self-assembled In(Ga)AsN quantum dots (QDs) grown on GaAs substrates are potential candidates to emit in the windows of maximum transmittance for optical fibres (1.3-1.55 μm). In this paper, we analyse the effect of nitrogen addition on the indium desorption occurring during the capping process of $In_xGa_{1-x}As$ QDs (x=1 and 0.7). The samples have been grown by molecular beam epitaxy and studied through transmission electron microscopy (TEM) and photoluminescence techniques. The composition distribution inside the dots was determined by statistical moiré analysis and measured by energy dispersive X-ray spectroscopy. First, the addition of nitrogen in In(Ga)As QDs gave rise to a strong redshift in the emission peak, together with a large loss of intensity and monochromaticity. Moreover, these samples showed changes in the QDs morphology as well as an increase in the density of defects. The statistical compositional analysis displayed a normal distribution in InAs QDs with an average In content of 0.7. Nevertheless, the addition of Ga and/or N leads to a bimodal distribution of the Indium content with two separated QD populations. We suggest that the nitrogen incorporation enhances the indium fixation inside the QDs where the indium/gallium ratio plays an important role in this process. The strong redshift observed in the PL should be explained not only by the N incorporation but also by the higher In content inside the QDs.

1. Introduction

In the past two decades, alloys based on diluted nitrogen III-V semiconductors have aroused great interest, especially, since Kondow proposed them as substitutes for GaInAsP alloys for use in telecommunications devices [1]. The smaller size and bigger electronegativity of N compared to other V-elements should produce simultaneously a reduction of lattice constant and bandgap in III-V alloys. In this sense, the incorporation of small amounts of N in In(Ga)As Stranski-Krastanov QDs grown on GaAs substrate by Molecular Beam Epitaxy (MBE) has deserved more attention, due to the fact that it allows to extend the emission wavelength to the windows of maximum transmittance for optical fibres

(1.3-1.55µm) [1-4]. However, obtaining the desired emission with the addition of N faces some difficulties, mainly due to two effects: (i) the appearance of defects that degrade the optical properties of the material and (ii) interdiffusion phenomena produced during the QDs capping process, which is necessary for any application. During the coating process, an exchange between the In/Ga is produced, causing morphological and compositional changes in QDs, making a controlled tuning to the desired wavelength difficult [5]. In this work, the influence of nitrogen on the In/Ga exchange and the effect of incorporation of Ga during growth of InAsN QDs is characterized by different TEM techniques.

2. Experimental details

Four samples of In(Ga)As(N) QDs have been grown by MBE with different Ga and N contents, as shown in Table 1. The structure of samples consists of 200 nm GaAs buffer layer grown on a (001) GaAs substrate at 590 ºC, 4 or 6 (Ga)InAs(N) monolayers (ML) at 440 ºC, a 200 nm GaAs capping layer, the firsts 27 nm being grown at the same temperature as QDs (to reduce segregation) and the rest of the layer at 590 ºC. Finally, a surface layer of (Ga)InAs(N) QDs is grown under the same conditions as the buried one. For the cases of samples AN and BN, N was supplied by an Oxford Applied Research radio frequency (RF) plasma source using 0.1 sccm flow of pure N_2 (6N) and 100W power, which corresponds to a nominal N incorporation of ~1%. Further details of the growth and photoluminescence (PL) of these samples can be found in Ref.[6]. The samples were studied using a JEOL JEM 2011 working at 200 kV in conventional transmission electron microscopy (CTEM) mode.

Table 1. Nominal composition (atomic %) and number of deposited monolayers in the active layer (QDs) of studied samples.

Sample	Ga%	In%	N%	ML
A	0	100	0	4
AN	0	100	1	4
B	30	70	0	6
BN	30	70	1	6

3. Results and discussions

Moiré fringe patterns are registered inside the QDs of every sample when imaging in diffraction contrast bright field mode using $\boldsymbol{g}$=(022) (**Figure 1**.a). These moiré fringes come from the interference pattern between two diffracted beams $\boldsymbol{g}_1$ and $\boldsymbol{g}_2$ when transmitted through the superposition of two lattices. In this case, it corresponds to the interference produced when the electron beam passes through the GaAs capping layer and the QD, the last being plastically relaxed. As a result, fringe distance in moiré patterns depends on the lattice mismatch between the (220) planes of the substrate and the relaxed QD structure, and therefore, on the QDs composition and the degree of plastic relaxation. In this framework, a statistical study of the composition of In and Ga within the QDs is carried out [4, 7].

The average distance between fringes was measured at QDs half height (**Figure 1**.b), allowing the calculation of (220) planes distance of QDs (details of this study can be found in Ref. [7]). No correlation between QD height and distance between fringes are observed in any of the studied cases. This result suggests that the lattice parameter of the plastically relaxed QDs does not depend on their size, indicating the same degree of plastic relaxation for all QDs. Therefore, the interplanar spacing mainly depends on the QDs composition. If totally relaxed QDs are assumed for all samples, the average composition inside QDs can be estimated from the interplanar spacings. Accordingly, **Figure 2** shows the histograms of In content of all the samples. The QDs of sample A present a normal distribution with a median of 0.73±0.03 of In content, while the sample AN show a bimodal distribution centred around 0.78±0.01 and 0.93±0.01, having higher In content than QDs in sample A.

These results suggest a stronger retention of In during the capping process of InAsN QDs compared to InAs ones, reaching a virtually total blocking of In/Ga intermixing in some of the analyzed QDs. On the other hand, the histograms of samples B and BN present a bimodal distribution of the In content, centred around 0.52±0.03 and 0.64±0.05 for both samples. However, population inversion is found in both samples. The integrated area of the second (higher In content) peak is 1.76 times larger than the first peak of the BN sample, while for sample B the integrated area of the second peak is 0.44 times the area of the first peak, thereby producing a larger number of QDs with higher In content by the addition of N. It should be noted that we have disregarded the nitrogen content in the lattice parameter calculation. Even though the nitrogen reduces the lattice constant, a consideration of nitrogen at percentage levels would imply an even higher amount of estimated In-content in the InAsN QDs.

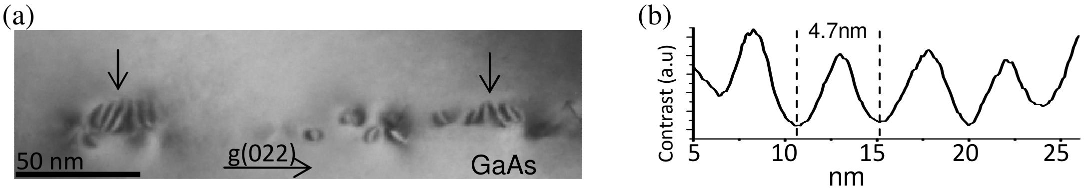

Figure 1. (a) BF (220) CTEM image taken in the [110] zone axis showing buried QDs. Arrows point to moiré fringe patterns found at QDs sites. (b) Typical image intensity contrast profile acquired at QDs half height used to measure fringe distances.

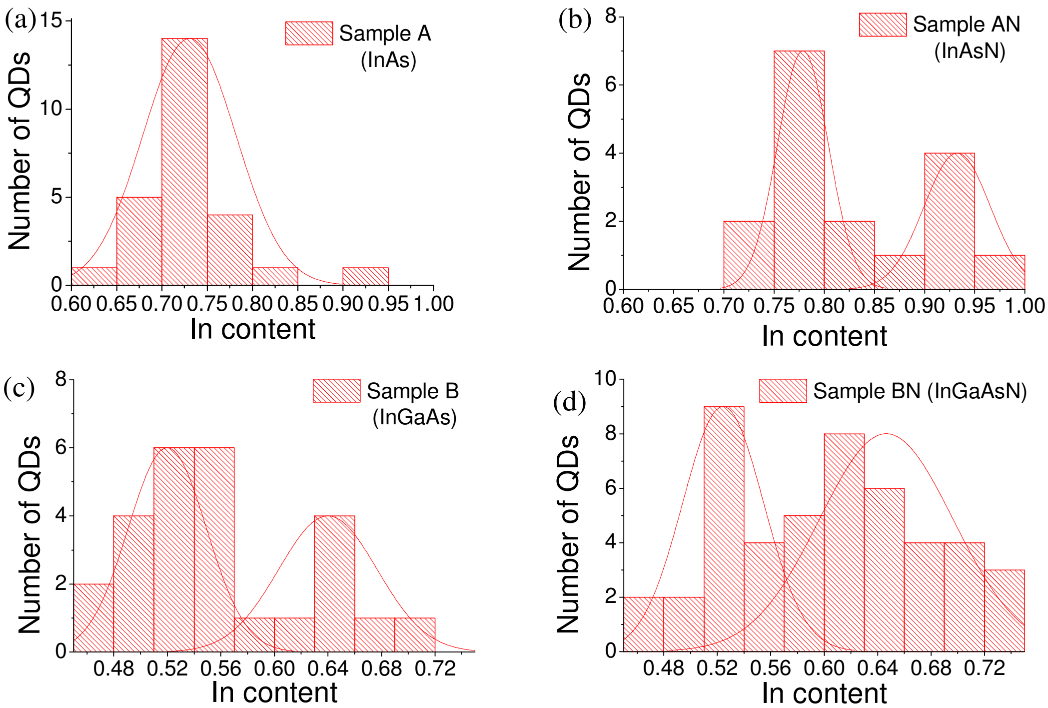

Figure 2. Histograms of determined In content of A (a), AN (b), B (c) and BN (d) QD samples respectively.

These results are in agreement with PL data (not shown in this article), where it is appreciated that a small incorporation of N produces a strong redshift in the emission peak, together with a large loss of intensity and monochromaticity compared to the PL emission of samples grown without N. Thus, the redshift in the sample AN (from 1076 nm to 1301 nm), and BN (from 1046 nm to 1550 nm) is explained both by the addition of N together with the higher In content observed within the QDs.

However, the largest displacement is observed in the BN sample, despite of having a lower content of In, which could be due to an increased content of N, as well as to the greater height of QDs. Previous report regarding the dependence of N incorporation on the Ga content into GaInAsN QDs demonstrated that the maximum N incorporation into GaInAsN QDs occurred at 30% Ga content [6]. Such behaviour was attributed to the competition between different mechanisms, such as the strong stability of the Ga-N bonds and the surface strain during the QDs growth. The increase of the number of gallium atoms bonded to nitrogen in the as-grown condition would explain the huge redshift in the bandgap of BN sample [8]. Further experiments are being performed to clarify the effects of the nitrogen in the atomic distribution of III atoms during the QDs growth and capping processes.

4. Conclusions

All the QDs studied showed moiré patterns due to a full plastic relaxation, allowing the statistical calculation of the composition within the QDs. A small amount of nitrogen diluted in InAs quantum dots during growth leads to an increased In content, as well as a bimodal distribution. As a consequence, there is a higher In content (up to 20%) in QDs of InAsN compared to InAs ones. Otherwise, the addition of Ga or Ga and N simultaneously during the growth of InAs QDs produces a bimodal distribution with two populations centred at the same positions in both samples (B and BN). In this case, the retention of In content is smaller, increasing only the number of QDs with a higher In content. The main retention of indium inside quantum dots suggests that nitrogen gives rise to a blockage of the exchange processes In/Ga during the capping step of the QDs, obtaining a enrichment of indium inside quantum dots and contributing to the redshift observed in the PL. The strong redshift of InGaAsN can be explained by an increase of Ga-N bonds compared to In-N ones in the as-grown condition.

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