Persistence of In/Ga intermixing beyond the emission energy blueshift saturation of proton-implanted InAs/GaAs quantum dots

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Low temperature photoluminescence (PL) measurements are carried out to investigate the influence of the high extent of intermixing induced by proton implantation and subsequent annealing on the optical and electronic properties of the InAs/GaAs quantum dots (QDs). Several QDs structures were proton implanted at various doses (5 × 10^{11}–1 × 10^{15} ions cm^{-2}) with an acceleration energy of 18 keV and then annealed at 700 °C for 30 s. A saturation of the emission energy blueshift is found to occur for implantation doses higher than 5 × 10^{13} ions cm^{-2} accompanied with a continual decrease in the intersublevel spacing energy suggesting that the intermixing process persists beyond the emission energy blueshift saturation. An additional emission peak was found to appear in PL spectra for proton doses higher than 1 × 10^{14} ions cm^{-2} and attributed to the coalescence of closely spaced QDs. Strain assisted predominant lateral intermixing is proposed as the main factor responsible for the observed behavior. © 2010 American Institute of Physics. [doi:10.1063/1.3436594]

I. INTRODUCTION

Self-assembled quantum dots (QDs), have evoked an increasing fundamental and technological interest owing to their three-dimensional (3D) carriers confinement. Indeed, QDs based optoelectronic devices have shown improved performance. For monolithic integration of optoelectronic devices, a selective postgrowth energy band gap tuning is necessary. This can be ensured by highly spatial selective intermixing across the same sample surface. Examples of spatially selective intermixing techniques include laser irradiation, dielectric capping, grown-in defects, and ion implantation. This latter technique has successfully been used for the band gap tuning of quantum wells structures. This intermixing process has been widely and successively used to study the evolution of the QDs properties as a function of the ion implantation dose. The huge energy shift in InAs/InP QDs system has been accompanied by a loss of information concerning the carriers’ confinement nature especially for relatively high implantation doses. While, less controllable energy shift has been reported for InAs/GaAs QDs system, the well separated and resolved excited states emission peaks allow the depiction of a complete picture concerning the evolution the QDs properties as a function of the intermixing degree. The previous works involved in this context have so far been limited to ion implantation doses up to the emission energy blueshift saturation. More works are clearly required to understand the evolution of the intermixing process for higher implantation doses beyond the emission energy blueshift saturation.

In this paper, we study the evolution of the PL properties of InAs/GaAs QDs subjected to proton implantation at different doses and subsequent annealing with a special emphasis on the impact of the intermixing process on the evolution of the QDs properties beyond the emission energy blueshift saturation.

II. EXPERIMENTAL DETAILS

InAs QDs were grown on semi-insulating (100) GaAs substrates by solid-source molecular beam epitaxy. After the deposition of a 0.5 μm thick GaAs buffer layer at 580 °C, the growth temperature was ramped down to 500 °C. The InAs QD layer, with a nominal thickness of 2.4 monolayers (MLs), was then deposited at a rate of 0.026 ML s^{-1}. After a 30 s interruption to allow the redistribution of QDs, 50 nm GaAs cap layer was grown at the same temperature to avoid In segregation. Atomic force microscopy observation on similar uncapped sample revealed a surface density of approximately 2 × 10^{10} cm^{-2}. Proton implantation was performed at room temperature with doses varying from 5 × 10^{11} to 1 × 10^{15} ions cm^{-2}. The implantation energy was chosen to be 18 keV so that the damage peak is located in the buffer layer allowing a relatively uniform displacement profile across the QD layer. All implantations were done at 7° off the (100) direction to minimize the channeling effect. To initiate intermixing and to remove the damage caused by the implantation, the implanted samples are annealed at 700 °C for 30 s in high pure nitrogen ambient. To protect the samples from the excessive loss of group V atoms during annealing, the samples are proximity capped with a semi-insulating GaAs wafer.

Low temperature (10 K) photoluminescence (PL) measurements were carried out under the excitation of 514.5 nm...
excited levels be related to optical transitions between the QD’s electron from the state filling effect. These bands can unambiguously the increase in the proton implantation doses up to 5
implantation dose’s range. As shown in the Fig. 2, and a decrease in the intersublevel spacing energy. These
system is achieved after a proton implantation dose of 5
annealing. The emission energy blueshift saturation for this
samples subjected to proton implantation and subsequent an-
sequence of the thermally induced intermixing due to the
reference sample with respect to the as-grown one, is a con-
factor responsible for the predominant lateral interdiffusion
change in the growth direction. The reduction in the
implantation induced In–Ga intermixing and consequent
changes in the QDs strain, size, and composition.16–18
However, for higher doses (≥5 × 10^{13} ions cm^{−2}), the
QDs ground state emission energy remains insensitive to the
increase in the implantation dose. In the meanwhile, the,
ter sublevel spacing energy shows a continual decrease. This
latter behavior is accompanied with the appearance of a new
emission peak, denoted by P_{0}, at about 1.37 eV for implan-
tation doses higher than 1 × 10^{14} ions cm^{−2} as indicated in
Fig. 1.

The emission energy blueshift saturation was commonly interpreted in terms of a prohibited interdiffusion due to the accumulation of high point defects density and consequent formation of complex defects that are hard to be restored after annealing.5,19 However, in our case, the continual decrease in the intersublevel spacing energy indicates that the intermixing process persists beyond the emission energy blueshift saturation.

Since the height of QDs is much smaller than their lateral size, the blueshift in the emission energy, and the variation in the PL linewidth are the consequence of In/Ga exchange in the growth direction. The reduction in the intersublevel spacing energy of the InAs/GaAs QDs has been theoretically attributed to the variation in the QDs aspect ratio.20–22 Therefore, for samples implanted at higher doses (beyond the emission energy blueshift saturation), the base length of InAs dots becomes larger due to the lateral interdiffusion but the variation in the dot height can be ignored. The possible explanation may reside in the anisotropic distribution of strain at the interface. The strain distribution around the dots is always concentrated at the base boundary for buried dots.23 It is, therefore, expected that the accumulation of point defects at the contour of the QD base leads, upon annealing, to a predominant In–Ga intermixing in the lateral direction. As a consequence, an enlargement of the QD base length is favored under these conditions. It has to be noted that some previous reports confirm that the main factor responsible for the predominant lateral interdiffusion of the QDs and saturation of blueshift in interdiffused QDs, is the non-Fickian strain-enhanced interdiffusion. This phe-

![FIG. 1. 10 K PL normalized spectra taken at high power excitation density (100 W cm^{−2}) of the as-grown sample, the reference sample (annealed-only), and samples implanted at various proton doses (5 × 10^{11} – 1 × 10^{15} ions cm^{−2}) followed by RTA at 700 °C for 30 s.](image)

**FIG. 1.** 10 K PL normalized spectra taken at high power excitation density (100 W cm^{−2}) of the as-grown sample, the reference sample (annealed-only), and samples implanted at various proton doses (5 × 10^{11} – 1 × 10^{15} ions cm^{−2}) followed by RTA at 700 °C for 30 s.

![FIG. 2. Low excitation density (1 W cm^{−2}) PL peak blueshift (empty square) and high excitation density (100 W cm^{−2}) intersublevel spacing energy (between “p” and “s” shell levels emission energy) (ΔE) (filled square) as a function of the proton implantation doses.](image)

**FIG. 2.** Low excitation density (1 W cm^{−2}) PL peak blueshift (empty square) and high excitation density (100 W cm^{−2}) intersublevel spacing energy (between “p” and “s” shell levels emission energy) (ΔE) (filled square) as a function of the proton implantation doses.
This excludes the possibility that P₀ originates from the previously be detected at the lowest excitation power density QDs electronically coupled and can be attributed to the isolated modified wetting layer. Furthermore, the inset of the Fig. 3 integrated PL intensity ratio of peak P₀ and that of the I-QDs shows the evolution of the integrated PL intensity measure-
tions of samples implanted at higher doses together with the integrated PL intensity at higher doses is accompanied with a broadening of the intermixing degree leading to the appearance of additional peak at higher proton doses.

The excitation power density dependent 10 K-PL spectra of samples implanted at $1 \times 10^{14} - 1 \times 10^{15}$ ions cm$^{-2}$, depicted by the Fig. 3, show two PL features. They are not electronically coupled and can be attributed to the isolated QDs (I-QDs) and coalescent QDs. Indeed, P₀ can unambiguously be detected at the lowest excitation power density where the QDs excited states feature cannot be observed. This excludes the possibility that P₀ originates from the modified wetting layer. Furthermore, the inset of the Fig. 3 shows the evolution of the integrated PL intensity measure-
tions of samples implanted at higher doses together with the integrated PL intensity ratio of peak P₀ and that of the I-QDs as a function of the proton implantation doses. An increase in the integrated PL intensity from P₀ occurs in detriment of a decrease in the I-QDs intensity. This behavior suggests that a prominent quasi-two-dimensional layer is formed by the coalescence of closely spaced QDs as the proton implantation dose increases. The decrease in the I-QDs integrated PL intensity at higher doses is accompanied with a broadening of the PL line width. Previous investigation of the thermal induced QDs intermixing, showed that the strong intermixing that occur at high annealing temperature or high phosphorous implantation doses destroy the QDs and the material quality through the generation of high dislocations density. Analogously, high proton implantation dose and consequent large damage accumulation might induce extended defects once clustering. Therefore, our interpretation goes toward a predominant formation of high dislocation density and/or complex defects that are hard to be restored after annealing.

The evolution of the InAs/GaAs QDs intermixing as a function of the proton implantation dose is schematically summarized in the Fig. 4. Indeed, in the lower doses range ($5 \times 10^{10} - 5 \times 10^{13}$ ions cm$^{-2}$), In/Ga intermixing is governed by both point defects and strain assisted intermixing. The intermixing affects both the height and the base length of the QDs, resulting in a blueshift in the emission energy and a decrease in the intersublevel spacing energy. However, at higher doses the accumulation of point defects leads to the formation of complex and relatively stable defects once clustering. This may reduces the contribution of the point defects to the intermixing in favor of the strain assisted one. In such a case, the intermixing evolves predominantly in the lateral direction leading to the continual decrease in the intersublevel energy beyond the band gap blueshift saturation. Accordingly, as a consequence of the QDs self-organizing nature, the coalescence of closely spaced QDs may arise for higher intermixing degree leading to the appearance of additional PL peak.

**IV. CONCLUSION**

In conclusion, the effects of InAs/GaAs QDs intermixing, induced by higher proton implantation doses ($5 \times 10^{11} - 1 \times 10^{15}$ ions cm$^{-2}$) and subsequent RTA have been studied by using PL measurements. The blueshift saturation has been achieved at proton dose of $5 \times 10^{13}$ ions cm$^{-2}$. For higher proton doses the QDs ground state emission energy remains insensitive to the increase in the implantation dose while, the intersublevel spacing energy shows a continual decrease. A distinct additional PL emission peak; stem from the dissolution of closely spaced QDs into surrounding wet-
ttering layer has been depicted for proton doses higher than $1 \times 10^{14}$ ions cm$^{-2}$ suggesting that In/Ga interdiffusion persists even beyond the emission energy blueshift saturation. The strain-enhanced predominant lateral In/Ga intermixing is suggested as a possible explanation of the partial dissolution of closely spaced InAs QDs at higher proton doses.