APPLIED PHYSICS LETTERS **89**, 131905 (2006)

Tuning of the electronic properties of self-assembled InAs/InP(001) quantum dots using grown-in defect mediated intermixing

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(Received 6 June 2006; accepted 5 August 2006; published online 25 September 2006)

This paper examines the influence of rapid thermal annealing on the photoluminescence spectra of self-assembled InAs/InP(001) quantum dots capped with 760 nm InP deposited at a reduced temperature. The capping layer contained a large concentration of point defects that can promote interdiffusion upon annealing. The onset temperature for measurable blueshift in the emission spectra was found to be ~600 °C whereas shifts of 270 meV were obtained after annealing at 750 °C for 300 s. Gradual etching of the InP capping layer enabled to progressively quench energy shifts upon annealing, a promising result for spatially selective emission tuning. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357162]

Broadband light sources operating in the 1.5 μm range are acknowledged as being key components for future generations of optically based communication networks[1] and biological imaging systems.[2] Because of their intrinsic distribution in size and composition, self-assembled InAs quantum dots (QDs) grown on InP are characterized by a naturally broad emission around 1.5 μm, therefore making this materials system very promising for such applications. In this respect, InAs/InP QDs could be either used as the active element in tunable lasers[3] or as the superluminescent diode materials in optical coherence tomography.[4] Despite the prospective characteristics of InAs/InP QDs, the achievement of wider laser tuning range and higher imaging resolution still requires further broadening of the QD emission. This can be realized through spatially selective band gap tuning where different regions of the QD-based device emit at different wavelengths.

Band gap tuning can be achieved after epitaxial growth through atomic interdiffusion, or intermixing, at the QD/barrier interface. This modifies the confinement profile and alters the QD energy levels, thereby inducing a shift of the emission spectra. Thermally induced intermixing has proven to be a generic approach for the adjustment of the electronic properties of QD structures.[5] Furthermore, spatial selectivity can be achieved through the localized creation or inclusion in the structure of point defects, which enhance intermixing during subsequent rapid thermal annealing (RTA). Examples of such defect mediated intermixing techniques include dielectric capping (or impurity-free vacancy disordering),[6] ion implantation,[7,8] and grown-in defects (GIDs).[9–12] In the GID mediated intermixing, nonequilibrium concentrations of point defects are introduced into epitaxial layers during growth at reduced temperatures. While this technique has so far been limited to the band gap engineering of InGaAs/InP and InGaAsP/InP quantum wells (QWs),[10–12] we examine in this letter its potential in lower-dimensionality systems. More specifically, we investigate the influence of rapid thermal annealing on the photoluminescence (PL) spectra of self-assembled InAs QDs grown on InP(001) and capped with a thick InP layer deposited at low temperature (LT-InP). We demonstrate that the GID mediated intermixing technique is a very promising approach for the spatially selective adjustment of the electronic properties of InAs/InP QDs by providing large and controllable blueshifts in the PL emission spectra.

The samples were grown on semi-insulating Fe-doped InP(001) substrates by chemical beam epitaxy from trimethylindium, arsine, and phosphine. The sample structure consisted of a 120-nm-thick InP buffer layer, 2.2 ML of InAs followed by a 35 s growth interruption to allow QD formation, and a 40-nm-thick InP capping layer, all grown at 505 °C. The temperature was then ramped down to 450 °C for the growth of a LT-InP layer with a thickness of 760 nm. Optimal conditions were then reestablished for the growth of a 33-nm-thick InGaAs cap. From cross-sectional transmission electron microscopy, this procedure resulted in 1–3-nm-high QD structures on a 0.3-nm-thick wetting layer (WL). Plan-view analysis on similar samples revealed a mean in-plane QD diameter of 30 nm with a rms deviation of 12 nm and a QD density of approximately 10^{10} QDs cm^{-2}. A reference sample, which consisted in the same 2.2 ML InAs QD layer but this time capped with 120 nm InP grown at the standard temperature (ST) of 515 °C, was also prepared. RTA was carried out in a VLSI grade N_2 atmosphere using an A.G. Associates Heatpulse 410 system with thermocouple temperature control. During RTA, GID and reference samples were, respectively, surrounded with sacrificial GaAs and InP pieces to minimize As and P desorptions. PL measurements were performed on each as-grown sample and fol-

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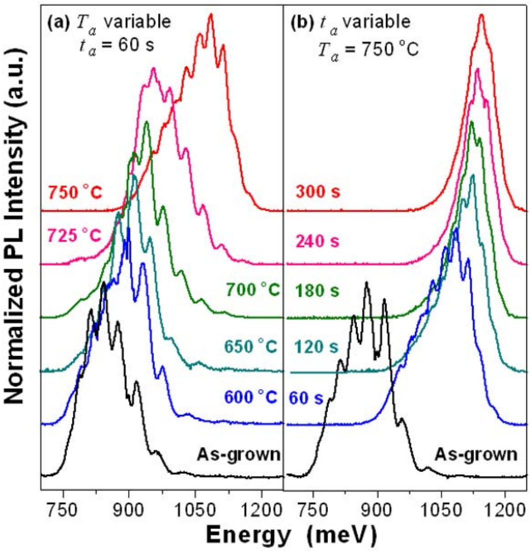

FIG. 1. (Color online) PL spectra from as-grown and annealed GID samples (a) as a function of annealing temperature T_a for an annealing time t_a=60 s and (b) as a function of t_a for T_a=750 °C.

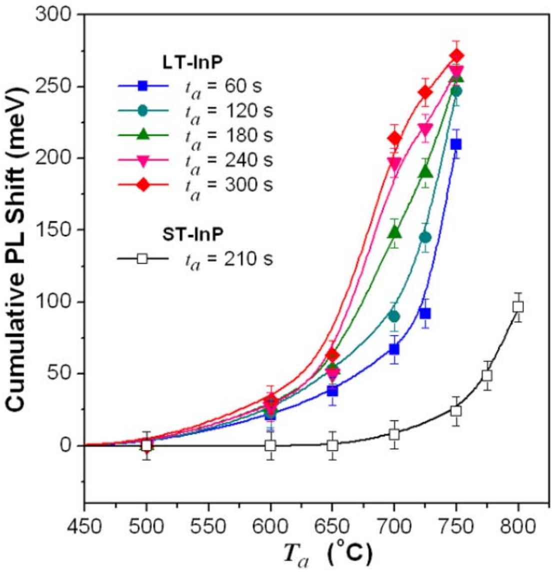

FIG. 2. (Color online) Cumulative PL shift as a function of T_a for LT-InP (solid symbols) and reference ST-InP (open squares) samples.

lowing each anneal using the 760 nm line of a Ti-sapphire laser as the excitation source. Spectra were acquired using a double grating spectrometer and a cooled Ge detector, the sample temperature being maintained at 77 K. The incident light power density was kept at 200 W cm^{-2} over a 50-μm-diameter spot. This proved to be sufficiently low to prevent any distortion of the spectra by excess carrier population in the QDs.

Spatially selective emission tuning experiments were also carried out in GID samples by removing fractions of the LT-InP layer in specific areas defined by photolithography. For these experiments, the upper InGaAs cap layer was first removed in the unmasked region by selective wet chemical etching using $C_6H_8O_7:H_20_2$ (3:1). The samples were then dipped in a $HCl:H_3PO_4$ (1:9) solution for various times to progressively etch the InP layer. The resulting LT-InP layer thickness was measured to a precision of ±10 nm using stylus profilometry.

Figure 1 shows the normalized PL spectra from as-grown and annealed GID samples as a function of the annealing temperature T_a for an annealing time t_a=60 s [Fig. 1(a)] and as a function of t_a for T_a=750 °C [Fig. 1(b)]. The as-grown spectra are characterized by a broad 145-meV-wide emission peak centered near 875 meV, the WL emission being undetected. The distinctive peaks in the PL spectra can be attributed to the ground state emission of QD families having the same thickness in terms of an integer number of monolayers.[13] Upon annealing, Figs. 1(a) and 1(b) reveal that the overall QD emission spectra exhibit a blueshift whose magnitude increases with t_a and T_a. In Fig. 1(a), a progressive blueshift of the emission spectra up to 210 meV can be observed. Individual QD family peaks remain visible after annealing whereas no significant PL broadening is apparent. One thus concludes that all QD families are shifting at comparable rates as in InAs/InP QDs subjected to RTA alone.[5] However, as the degree of intermixing intensifies with increasing t_a at T_a=750 °C, Fig. 1(b) reveals a significant departure from this behavior. Indeed, when the emission energy approaches that predicted for the WL (~1100 meV in the InAs/InP system[14]), the blueshift tends to saturate and the PL spectra become much narrower with less resolvable QD family peaks. This suggests that the smaller QD families progressively dissolve into the WL to form a thin highly disordered QW. Although not explicitly shown in Fig. 1, we note that the PL emission intensity from annealed samples is typically 50% higher than for as-grown materials. This points out that GID meditated intermixing did not cause any degradation of the optical quality of the samples even for the largest shifts observed and indicates that GIDs in as-grown samples act as nonradiative recombination centers.

Figure 2 presents the cumulative PL shifts as a function of the T_a for annealed In/As QDs capped with LT-InP. For comparison, the results obtained using a ST-InP capping layer are also shown. The shifts were obtained by comparing the peak position of the overall emission band with that of the as-grown material. For LT-InP, the *cumulative* PL shifts increase monotonically with T_a. However, the *incremental* PL shift is largest during the first 60 s anneal and decreases thereafter. Figure 2 further shows that PL emission from the reference sample remains stable up to ~725 °C whereas measurable PL shifts are obtained in the LT-InP samples at T_a as low as 600 °C. From an application standpoint, this result suggests the possibility of achieving spatially selective emission tuning using LT-InP layers. For example, at T_a=725 °C, one obtains PL shifts of 250 meV for LT-InP but only 20 meV for ST-InP.

In order to demonstrate the potential of GID-induded intermixing for spatially selective emission tuning, we present in Fig. 3 the cumulative PL shifts obtained as a function of the remaining thickness of the LT-InP capping layer ($d_{\text{LT-InP}}$) following the etching procedure described above. For instance, a large difference in PL shift, 220 meV, is measured between an unetched sample and one with the LT-InP layer completely removed after annealing under the same conditions (T_a=725 °C, t_a=120 s). We also note that while a 60 s anneal on a sample with $d_{\text{LT-InP}}$=180 nm leads to a shift of 100 meV, further annealing has no measurable effect. In samples with thicker LT-InP capping layers, the PL shift increases systematically with $d_{\text{LT-InP}}$, this effect being largest

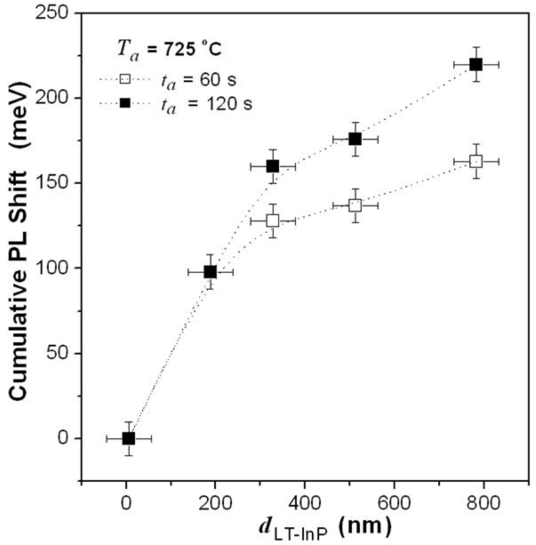

FIG. 3. Cumulative PL shift as a function of the thickness of the LT-InP capping layer following anneals at T_a=725 °C for t_a=60 s (open squares) and t_a=120 s (solid squares).

during the first 60 s anneal. These results therefore provide strong evidence that an excellent control of the magnitude of the blueshifts in InAs/InP QD structures can be achieved by selecting the appropriate LT-InP layer thickness.

Our overall set of results clearly demonstrates that the introduction of a LT-InP layer leads to an enhancement of the PL blueshift and a reduction of the T_a threshold for intermixing down to ~600 °C in InAs/InP QD structures. These results are qualitatively similar to those reported for InGaAs/InP and InGaAsP/InP QW systems and can be attributed to the presence of a nonequilibrium concentration of point defects in the LT-InP capping layer.[10,12] Indeed, these previous studies have indicated that LT-InP contains excess P atoms occupying antisite defects. Upon annealing, these defects dissociate to form P interstitials and In vacancies. The highly mobile interstitials subsequently diffuse to the active region to enhance the intermixing process at the QD/barrier interface. As intermixing proceeds, these defects become annihilated or trapped at various sinks such as the free surface, interfaces, and the substrate. As a consequence, their effect on promoting intermixing gradually decreases, thereby explaining the reduction of the incremental PL shift observed in Figs. 2 and 3. Although not explicitly shown here, our experiments revealed that the PL shifts from samples in which the InGaAs cap was etched off before annealing were systematically larger (by about 70 meV) than those with the InGaAs cap left intact. We attribute this behavior to the fact that InP is less stable than InGaAs towards degradation during the RTA treatment. This can result in the generation of additional defects at the free InP surface which can move towards the active region upon annealing and promote intermixing. It is therefore of prime importance to account for all sources of defects when exploiting intermixing for spatially selective emission tuning.

In summary, we have investigated the influence of rapid thermal annealing on the PL properties from InAs/InP QD structures containing a LT-InP capping layer. While no significant PL shift was obtained below T_a=725 °C in the ST-InP based structure, the temperature threshold for observable PL shift in LT-InP samples is ~600 °C. Shifts of 270 meV were obtained after annealing at 750 °C for 300 s. This enhancement of intermixing in GID samples can be attributed to the presence of a nonequilibrium concentration of point defects in the LT-InP capping layer. This interpretation was further confirmed by the progressive etching of the LT-InP cap, which led to the gradual quenching of the PL shift. This clearly demonstrates the strong potential of the GID mediated intermixing technique for the spatially selective band gap tuning of InAs/InP QDs for the fabrication of broadband light sources.

The authors acknowledge the National Science and Engineering Research Council of Canada, the National Research Council of Canada, and the Canada Research Chair program for financial support. The authors would also like to thank Andrew Bezinger for his help with the etching and Dr. Geof Aers for useful discussions.

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