UV laser-based process for quantum well intermixing of III-V heterostructures

Jonathan Genest, Jan J. Dubowski and Vincent Aimez

Le Regroupement québécois sur les matériaux de pointe (RQMP)
Department of Electrical and Computer Engineering, Université de Sherbrooke, Sherbrooke,
Québec J1K 2R1, Canada

ABSTRACT

The influence of surface irradiation of GaAs with a KrF excimer laser on the magnitude of a quantum well (QW) intermixing effect has been investigated in GaAs/AlGaAs QW heterostructures. The irradiation was carried out in an atmospheric environment with laser pulses of fluence between 60 and 90 mJ/cm^2. Following the irradiation, the samples were annealed in a rapid thermal annealing furnace at temperatures ranging from 850 to 925 ºC. Compared with non-irradiated samples, a strong suppression of the bandgap shift has been observed in all laser irradiated samples. The suppression increased from 5 to 22 nm for samples irradiated with 88 mJ/cm^2 pulses and annealed at 850 and 900 ºC, respectively. This increased thermal stability of excimer laser irradiated samples indicates the potential for developing a process for selective area bandgap engineering of large area GaAs/AlGaAs QW wafers.

Keywords: quantum well microstructures, quantum well intermixing, photonic integrated circuits, laser processing

1. INTRODUCTION

When compared with Si-based electronic integrated-circuit Complementary Metal-Oxide Semiconductor (CMOS) technology, the fabrication of photonic devices has no available single-platform integration technology that would be capable of providing global manufacturing solutions. Integrated photonic and optoelectronic circuits, which require different bandgap materials, have been fabricated using various hybrid manufacturing schemes. However, the fabrication of monolithically integrated photonic circuits (MIPCs), due to the requirement of different bandgap materials within the same semiconductor wafer, has been even less successful and only limited examples of such structures have been demonstrated to date. Thus far, none of the investigated technologies for manufacturing MIPCs have provided the 'winning solution' and extensive research is still required in this area. Among the various methods of manufacturing MIPCs, quantum well intermixing (QWI) has been investigated as the leading approach for post-growth bandgap tuning of QW microstructures [1].

The most frequently investigated methods of QWI include impurity induced intermixing [2], impurity-free vacancy diffusion [3] and QWI induced by ion implantation [4]. In the latter case,

Integrated Optics and Photonic Integrated Circuits, edited by Giancarlo C. Righini, Seppo Honkanen,
Proc. of SPIE Vol. 5451 (SPIE, Bellingham, WA, 2004) · 0277-786X/04/$15 · doi: 10.1117/12.547948

the implantation leads to the formation of a point defect rich region. The point defects are responsible for locally enhancing the intermixing process in the subsequent high temperature annealing. QWI has also been achieved by selective area coating of QW wafers with different oxides, nitrides and fluorides fabricated by conventional thin film deposition techniques [5]. Both enhanced [6] and reduced [7] intermixing has been observed depending on the physical and chemical properties of coating layers. A thin layer of a heterogeneous material could also be fabricated at the surface of a QW microstructure irradiated with ultraviolet (UV) pulses of an excimer laser. Such an approach should allow control of the chemical properties of the surface layer by choosing different gas environments, while offering relatively large area processing capability.

In this paper, we investigate the influence of excimer laser generated layer of altered material at the surface of GaAs on the QWI process in GaAs/$Al_xGa_{1-x}As$ QW microstructures.

2. EXPERIMENTAL DETAILS

The investigated microstructure was grown by molecular beam epitaxy on a GaAs substrate. It consisted of a buffer layer of GaAs (0.1 µm thick), a lower confining layer of $Al_{.76}Ga_{.24}As$ (50 nm), lower $Al_{.30}Ga_{.70}As$ (147.9 nm), middle $Al_{.23}Ga_{.77}As$ (10.3 nm) and upper $Al_{.23}Ga_{.77}As$ (54.4 nm) barriers, which separated two quantum wells of GaAs (7.5 nm each). The microstructure was topped with a cladding layer of $Al_{.43}Ga_{.57}As$ (0.84 µm) and a contact layer of GaAs (0.1µm). The composition and width of the QWs was chosen such that a laser diode fabricated from this material would emit IR light at 852 nm at room temperature. Table 1 shows other details concerning the sample structure.

Table 1. Parameters of the QW microstructure investigated in this work.

Composition	Width (nm)	Doping (cm^{-3})	Dopant
GaAs-n	100	$7x10^{18}$	Zn
$Al_{.43}Ga_{.57}As$-n	740	$1.8x10^{18}$	C
$Al_{.43}Ga_{.57}As$	100		UD
$Al_{.23}Ga_{.77}As$	54.4		UD
GaAs (QW)	7.5		UD
$Al_{.23}Ga_{.77}As$	10.3		UD
GaAs (QW)	7.5		UD
$Al_{.30}Ga_{.70}As$	147.9		UD
$Al_{.76}Ga_{.24}As$	50		UD
$Al_{.73}Ga_{.27}As$-p	45	$1.7x10^{18}$	Se
GaAs-n	100	$1.7x10^{18}$	Se
GaAs-n	substrate		Se

The UV irradiation was carried out with a KrF excimer laser (Lambda Physik LPM 300i) operating at a wavelength of 248 nm. The laser delivered 22 ns long pulses. A 7 mm x 7 mm area of a sample was irradiated in an atmospheric environment with a laser beam that was shaped using beam homogenizing optics. A variable attenuator was used to control laser fluence at the sample surface. Positioning of the sample and low-magnification inspection of its surface was facilitated by a CCD camera.

Excimer laser induced photoluminescence (PL) was carried out using a 0.5 GHz oscilloscope, computer-controlled 30-cm spectrometer and a photomultiplier. The temporal characteristics of laser pulses were monitored using a fast Si photodiode. To reduce the effect of laser pulse-to-pulse fluctuations, the PL signal was normalized relative to the intensity of the laser pulse that induced the PL signal. The PL signal is a sensitive measure of the presence of surface states that act as non-radiative recombination centers. Thus, we were able to monitor in-situ the laser-induced formation of such centers. PL spectra were collected in the wavelength range of 850 to 1100 nm at a 5 nm step. For each wavelength, the results were averaged over 3 laser pulses. The experimental setup is schematically illustrated in Figure 1.

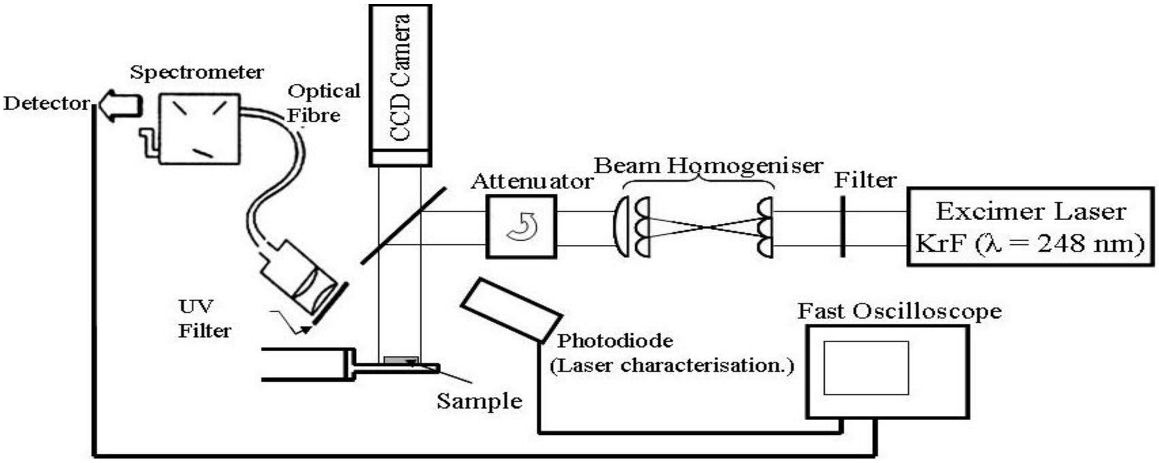

Fig. 1. Experimental setup for excimer laser irradiation and simultaneous collection of the photoluminescence signal.

Rapid thermal annealing (RTA) was carried out between 850°C and 925°C. The RTA treatment consisted of a 15-sec ramping from room temperature to the annealing temperature and a 30-sec anneal at a set-point temperature. The annealing and cooling was carried out at hydrogen and nitrogen atmospheres, respectively.

Low-temperature (20 K) PL measurements were carried out ex-situ using a setup equipped with a 1/4 m spectrometer, a 50 mW laser diode operating at 683 nm, a closed-cycle cryostat and a Ge photodiode.

3. RESULTS AND DISCUSSION

3.1. Excimer laser induced photoluminescence

Figure 2 shows an in-situ PL spectrum that was obtained for the sample irradiated with an excimer laser at 60 mJ/cm^2. The spectrum is dominated by a peak that is associated with the QW signal. A long-wavelength shoulder, which can be distinguished near 940 nm originates from GaAs. Fitting the spectrum with two Gaussian curves indicates that the QW and GaAs peaks are located at 891and 932 nm, respectively. The room temperature position of the GaAs peak is expected at 871 nm [8]. Thus, the long-wavelength shift observed in this experiment indicates that the measurements were taken at a temperature elevated by the excimer laser irradiation. By using an empirical relation [8]:

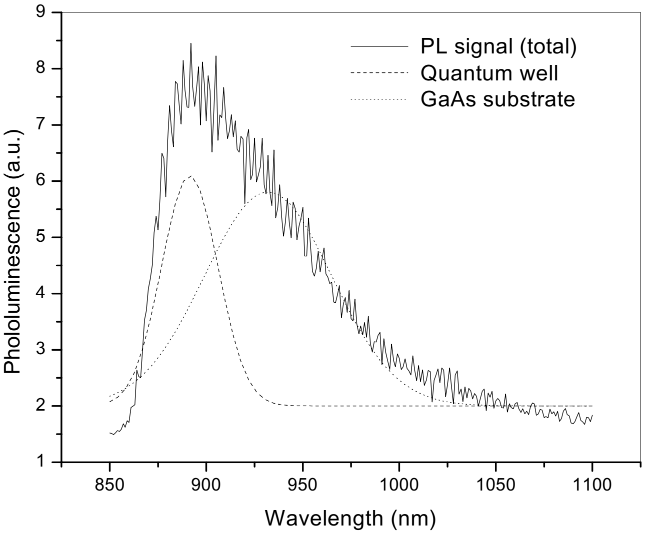

Fig. 2. In-situ photoluminescence spectrum (continuous line) of the irradiated structure. The dashed and doted lines represent the best fit with two Gaussian peaks.

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta} \quad (1),$$

we estimated that this temperature was about 200°C. The moderate temperature increase of the excimer laser irradiated sample is considered important for avoiding excessive or uncontrolled decomposition of the irradiated III-V material.

Figure 3 shows a series of PL signals measured as a function of the number of laser pulses, N, at the QW PL peak position. For the sample irradiated at 61 mJ/cm^2, the signal increased for the first 200 pulses and, subsequently, it showed a tendency towards weakening its intensity. The irradiation at 71 mJ/cm^2 resulted in the initial increase of the signal and for N > 50, the signal began to decrease. In contrast, a rapid decrease of the PL signal was observed for the sample irradiated at 88 mJ/cm^2. The exact nature of the excimer laser induced changes of the PL signal is not clear. It seems plausible that the intensity of the PL signal could increase following the laser-induced annealing of the surface defects and/or removal of such defects. Extended irradiation with a large number of laser pulses, as well as the irradiation at relatively high laser fluence could lead to chemical decomposition of the surface due to the preferential removal of As atoms. Generally, the formation of point defects at the surface could be responsible for the reduced PL signal observed in Fig. 3. It also remains to be determined if the laser irradiation could directly modify the investigated microstructure, e.g., by the formation of point defects in the QW region.

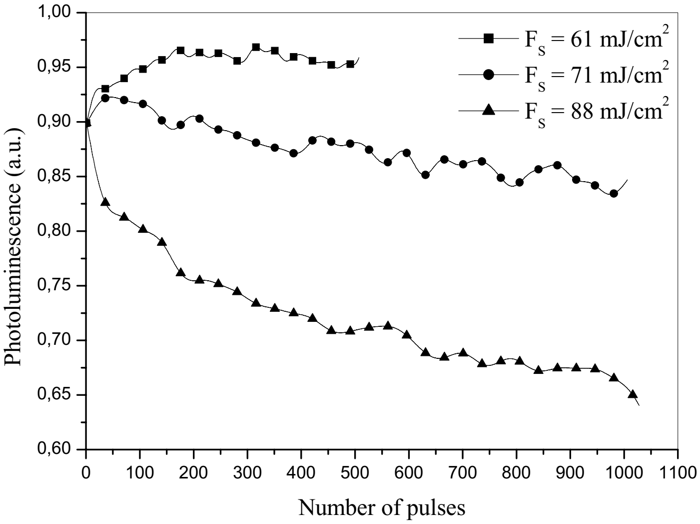

Fig. 3. Dependence of the QW photoluminescence signal on the number of excimer laser pulses delivered to the surface of the GaAs/AlGaAs microstructure. The results for 61, 71 and 88 mJ/cm^2 have been indicated with squares, circles and triangles, respectively.

3.2. Low temperature PL results

The investigated GaAs/AlGaAs microstructure exhibited a relatively strong QWI effect at all RTA temperatures applied in this work. Figure 4 shows a series of 20-K PL spectra of as-grown material and of the materials annealed at 850°C, 875°C and 925°C. It can be seen that after RTA, the QW peaks have all been shifted to a shorter wavelength and that this blueshift increased from 3 to almost 20 nm as the annealing temperature increased from 850 to 925 ºC. We note some variations in the QWs PL signal intensity that most likely are due to the wafer lateral inhomogeneity.

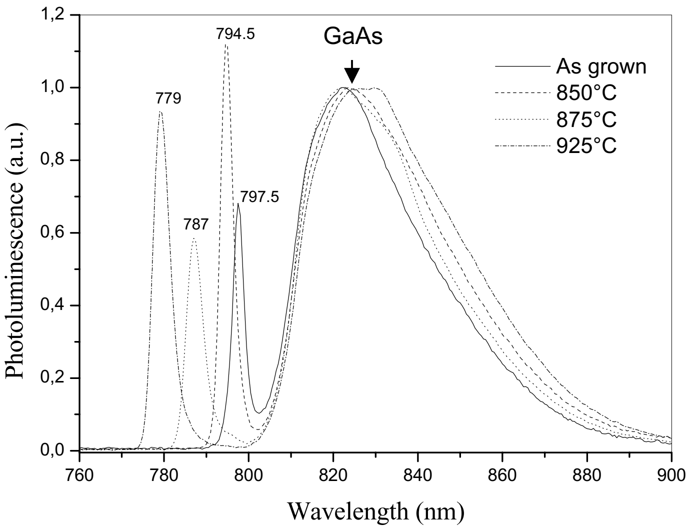

Fig. 4. Low temperature PL spectra of as-grown and RTA materials.

Figure 5 shows QW peaks in the PL spectra of a group of samples that were irradiated with N = 1000 pulses at different laser fluences and, consequently, annealed at 850 and 900 ºC. For both annealing temperatures the laser irradiation has strongly influenced the blue shift. Clearly, the shift was progressively suppressed with increasing laser fluence. For samples annealed at 850°C, the position of the QW peak changed from 793 nm for the non-irradiated material to 795, 796.4 and 798.5 nm for samples irradiated at 61, 71 and 88 mJ/cm^2, respectively. For samples annealed at 900°C, the peak shifted from 772.6 nm for the non-irradiated material to 793.3, 794 and 795 nm for samples irradiated at 61, 71 and 88 mJ/cm^2, respectively. Thus, the maximum blue shift suppression achieved in this experiment was about 5 and 22 nm for samples irradiated at 88 mJ/cm^2 and annealed at 850 and 900 ºC, respectively.

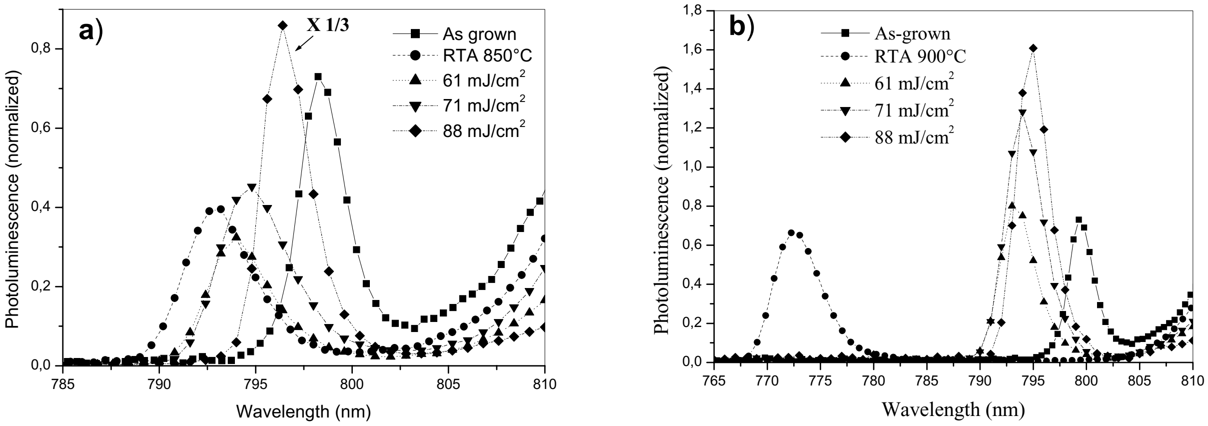

Fig. 5. Low temperature photoluminescence spectra after UV laser irradition and annealing at a) 850°C and b) 900°C.

Thermal stability of GaAs/AlGaAs QW microstructures investigated in this work indicates that this effect is strongly related to the properties of the surface of such microstructures. It is feasible to expect that the intermixing is mediated by point defects diffusing from the surface to the QW region. Enhanced photoluminescence that has been observed in excimer laser irradiated InGaAs/InGaAsP QW microstructures [9] indicated that the laser processed surface could become depleted of the PL intensity reducing non-radiative recombination centers. In this work, the evidence of the PL enhancement is also clearly visible for samples irradiated at 88 mJ/cm^2 (see Fig. 5). This appears to confirm that a less-defective surface has been fabricated following the irradiation with a UV laser. It remains to be determined if such surface could play the role of a defect migration inhibitor. We expect that it has some form of Ga-rich oxide and/or nitride formed during the irradiation in an atmospheric environment. Earlier work has shown that for fluences from 50 to 80 mJ/cm^2, UV laser pulses ($\lambda = 355$ nm) induce the evaporation of arsenic from the GaAs surface and lead to the growth of a Ga rich metallic structure [10]. Suppression of QWI has also been observed in GaAs/AlGaAs heterostructures covered with a thin layer of Ga_xO_y [11]. In that case, the suppression was explained by reduced diffusion of detects in the stressed Ga_xO_y/GaAs system.

4. CONCLUSIONS

We have investigated the influence of an excimer laser generated layer of altered material at the surface of GaAs on the quantum well intermixing process in GaAs/$Al_{.23}Ga_{.77}As$ QW microstructures. The formation of the layer was achieved with a KrF excimer laser ($\lambda = 248$ nm) delivering pulses at 61 to 88 mJ/cm^2 to the studied microstructures located in an atmospheric environment. Following the irradiation, the samples were annealed at 800 – 900 ºC in an RTA furnace. In comparison with non-irradiated samples, the excimer laser fabricated surface layer has drastically increased the thermal stability of the QW microstructures. For the most evident case of the sample irradiated with 1000 pulses at 88 mJ/cm^2, the annealing at 900 ºC resulted in only a slight shift of the QW bandgap energy from 798 to 795 nm. This compared with almost 27 nm blue shift in the non-irradiated sample (from 799.2 to 772.6 nm).

This new process has the potential to be applied for the fabrication of multi-bandgap QW wafers processed with an excimer laser in an similar manner as the excimer-based photolithography is used for wafer microstructuring. Alternatively, the ability to suppress the thermal shift using the excimer laser irradiation can be used in conjunction with other QWI approaches, such as ion implantation, to create zones of materials with increased bandgap contrast.

ACKNOWLEDGEMENTS

We are greatly indebted to Dr. Mike Post for enabling us to carry out the UV laser irradiation experiments in his laboratory at NRC Canada. This research was undertaken, in part, thanks to funding from the Canada Research Chairs Program.

REFERENCES

[1] E. Herbert Li, editor, "Selected papers on quantum well intermixing", SPIE milestones series, Vol. **MS 145** (1998).

[2] L. J. Guido, G. S. Jackson, W. E. Plano, K. C. Hsieh, N. Holonyak Jr., R. D. Burnham, J.E. Epler, R. L. Thornton and T. L. Paoli, *Index-guided* Al_x*-*Ga_{1-x}*As-GaAs quantum well heterostructure lasers fabricated by vacancy-enhanced impurity-induced layer disordering from an internal* $(Si_2)_y(GaAs)_{1-y}$ *source*, Appl. Phys. Lett. **50** (10), 609-611 (1987).

[3] J.H. Teng, J.R. Dong, S.J. Chua, D.A. Thompson, B.J. Robinson, A.S.W. Lee, J. Hazell and I. Sproule, *Impurity-free intermixing in compressively strained InGaAsP multiple quantum well structures*, Mat. Sci. in Semicond. Processing **4**, 621–624 (2001).

[4] V. Aimez, J. Beauvais, J. Beerens, D. Morris, H. S. Lim and B. S. Ooi, *Low-Energy Ion-Implantation-Induced Quantum-Well Intermixing*, IEEE J. Sel.Top. Quantum Electron. **8(4),** 870-879 (2002).

[5] J. S. Y., J. D. Song, Y. T. Lee and H. Lim, *Influence of dielectric deposition parameters on the* $In_{0.2}Ga_{0.8}As$*/GaAs quantum well intermixing by impurity-free vacancy disordering*, J. Appl. Phys., **92(3)**, 1386-1390 (2002).

[6] N. Shimada, Y. Fukumoto, M. Uemukai, T. Suhara, H. Nishihara and A. Larsson, lectronics-and-Communications-in-Japan,-Part-2-Electronics, *Monolithic integration of lasers and passive elements using selective QW disordering by rapid thermal annealing with* SiO_2 *caps of different thickness*, **87**(1), 34-42 (2001)

[7] J. Beauvais, J.H. Marsh, A.H. Kean, A. C. Bryce and C. Button, *Suppression of bandgap shifts in GaAs/AlGaAs quantum wells using strontium fluoride caps*, Electron Lett. **28**(17), 1670–1672 (1992).

[8] J. I. Pankove, "Optical Processes in semiconductors", Prentice Hall, Englewood Cliffs, N.J, 1971.

[9] J.J. Dubowski, P. J. Poole, G. I. Sproule, G. Marshall, S. Moisa, C. Lacelle and M. Buchanan, *Enhanced quantum-well photoluminescence in InGaAs/InGaAsP heterostructures following excimer-laser-assisted surface processing*, Appl. Phy. **A69** (Suppl.), S299-S303 (1999).

[10] L. Vivet, B. Dubreuil, T. Legrand, M. Schneider and C. Vieu, *Laser irradiation of GaAs-GaAlAs multi-quantum well structure*, Appl. Surf. Sci. **119,** 117-126 (1997).

[11] L. Fu, J. Wong-Leung, P. N. K. Deenapanray, H. H. Tan, C. Jagadish, B. Gong, R. N. Lamb, R. M. Cohen, W. Reichert, L. V. Dao and M. Gal, *Suppression of interdiffusion in GaAs/AlGaAs quantum-well structure capped with dielectric films by deposition of gallium oxide*, J. Appl. Phys., **92**(7), 3579-3583 (2002).