Enhancement of quantum well intermixing on InP/InGaAs/InGaAsP heterostructures using titanium oxide surface stressors to induce forced point defect diffusion

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Quantum well intermixing was studied on InP/InGaAs/InGaAsP heterostructures under stress induced by a TiO_x surface stressor. Results provide a comparison of thermal emission wavelength shift and effective emission wavelength shift for samples intermixed with and without applied stress. It is shown that TiO_x decreases the measured thermal shift depending on the amplitude of the induced stress. It is also shown that the diffusion of point defects created during ion implantation prior to TiO_x stressor deposition is significantly enhanced. This results in an increase of the effective wavelength shift by up to 300%. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2364058]

Quantum well intermixing (QWI) is a postgrowth technique that enables local modification of quantum well emission wavelength. It relies on the diffusion of point defects that will induce modifications of the well composition and therefore the band structure. The main consequence of QWI is a blueshift of the luminescence wavelength. Essentially, there are two different contributions to the total wavelength shift, a thermal shift, and an effective shift. The thermal shift is induced by the diffusion of intrinsic point defects at high temperature and occurs over the entire wafer. The effective shift is induced by extrinsic point defects that can be locally introduced in the heterostructure by different methods such as ion implantation[1] or dielectric capping.[2] Point defect creation is followed by rapid thermal annealing in order to enhance the diffusion of point defects throughout the heterostructure. For the purpose of photonic device integration, a large wavelength contrast between intermixed and nonintermixed regions of the wafer is required. Therefore, the thermal shift should be reduced whereas the effective shift should be increased.

Defect diffusion is described by Fick's first and second laws [Eqs. (1) and (2)] where J_D is the flux of diffusing particles, D the diffusion coefficient, and c the diffusing particle concentration. In this case, the diffusion is driven by the concentration gradient of diffusing particles. However, other interactions may change the diffusion profile.[3,4] Equation (3) describes the flux of particles caused by stress, where η is the particle mobility and F the force acting on the particle.

$$J_D = -D\nabla c, \tag{1}$$

$$\frac{\partial c}{\partial t} = -\nabla J, \tag{2}$$

$$J_F = \eta c F. \tag{3}$$

Eshelby[5] has first considered point defects as elastic inclusions with a different volume V to that of the surrounding matrix of volume V_0. The difference of volume between the point defects and the surrounding matrix can be expressed as a function of a mismatch parameter α [Eq. (4)]. For a vacancy, α is negative whereas α is positive for an interstitial.[3] Eshelby[5] has also described the force acting on a point defect [Eq. (5)], where r_0 is the radius of the defect and $\mathrm{Tr}(\sigma)$ is the trace of the stress tensor.

$$V = V_0(1+\alpha), \tag{4}$$

$$F = \alpha\frac{4}{3}\pi r_0^3 \nabla \ \mathrm{Tr}(\sigma). \tag{5}$$

From Eq. (5), it is clear that stress will induce diffusion of a vacancy and an interstitial in opposite directions. Furthermore, the diffusion of point defects under stress depends on the stress gradient and not on the magnitude of the stress. Only tensile or compressive components of the stress tensor may induce forced diffusion.

Surface stressors are thin films deposited on the top of the quantum well heterostructure in order to induce stress, which results from the difference in linear expansion coefficients of the stressor and the substrate during thermal processing.[6] Among the different materials used as a stressor, TiO_x has proven to be effective when deposited on InP based heterostructures[7] and it has been shown that a TiO_x surface stressor reduces the thermal shift on GaAs based quantum dots heterostructure[8] and GaAs based quantum well heterostructure[9] using impurity free vacancy diffusion. However, there are no previous reports showing that stress induced by a TiO_x surface stressor or any other stressor material modifies ion implantation induced quantum well intermixing process. In the following, results obtained from quantum well intermixing in the presence of a TiO_x surface stressor are presented. Two different InP based quantum well heterostructures are used to study the effects of this surface stressor on thermal shift and effective shift.

The influence of titanium oxide on the thermal stability has been studied on a single quantum well InGaAsP/InGaAs/InGaAsP lattice matched quantum well

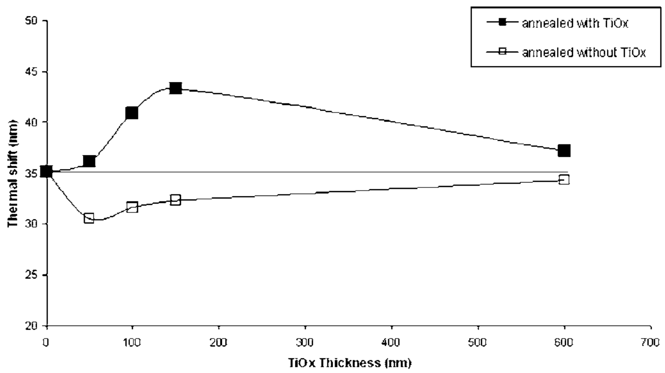

FIG. 1. Wavelength shift as function of the TiO_x thickness for samples annealed with TiO_x layer and samples annealed without the TiO_x layer.

heterostructure, grown by molecular beam epitaxy on an InP substrate (n type). An InP buffer layer of 1 μm was first grown on the substrate, followed by an InGaAsP barrier (q=1.28 μm, 20 nm), single InGaAs quantum well (5 nm), InGaAsP barrier (q=1.28μm, 20 nm), InP (80 nm), InGaAsP (q=1.28 μm, 10 nm), InP [1 μm, p(Be)10^{18} at./cm^2], and InGaAs (150 nm, p(Be)10^{19} at./cm^2), where q is the emission wavelength.

Different layers of titanium oxide with thickness ranging from 50 to 600 nm have been deposited by electron gun evaporation and all samples were subsequently characterized by photoluminescence (PL) at 20 K. During the cooling of the samples, compressive stress is induced by the difference of linear thermal expansion coefficient between the heterostructure and the TiO_x layer [$\alpha_{TiO_2}=8.2\times10^{-6}$ °C^{-1},[10] $\alpha_{InP}=4\times10^{-6}$ °C^{-1} (Ref. 11)]. It has been shown that the compressive stress induced by the TiO_x stressor exceeds the elastic limit resulting in plastic deformation during cooling of such samples.[7] After the PL measurements, the TiO_x layer is removed by wet etching on half of the samples. Annealing was performed at 700 °C for 120 s in a forming gas atmosphere and PL measurements were repeated on all samples. During the annealing, tensile stress is induced on samples covered by TiO_x stressor, whereas the stress on samples annealed without the stressor layer remains compressive.

For this annealing process, the as-grown sample exhibits a thermal shift of 35 nm. The wavelength shift for samples covered with a TiO_x layer during the annealing as well as samples annealed without the TiO_x layers are shown in Fig. 1 as a function of TiO_x thickness. It can be seen that samples annealed with a TiO_x layer exhibit a greater thermal shift than samples annealed without the TiO_x layer. The difference between samples annealed with the stressor and the samples annealed without the stressor can be explained by the different stress patterns induced by the thermal cycling and the nature of intrinsic point defects in InP.

The nature of the predominant point defects in InP is not a simple question as it depends on heterostructure growth technique and conditions, and few results have been discussed in the literature. However, Jansen[12] have concluded from calculations of the defect free energy of formation that In interstitials and P antisites might be the predominant intrinsic point defects in p-type InP, whereas In vacancies and In antisites might be predominant in n-type InP. Similar calculations including the effect of charge defects and relaxation of stress around the defects point out similar results.[13]

TABLE I. Effective wavelength shifts for samples implanted at 100 keV, 5×10^{13} P$^+$/cm^2, 200 °C, and annealed for 120 s. Sample A: reference sample implanted, sample B: TiO_x 85 nm, sample C: TiO_x 85 nm etched before annealing, sample D: TiO_x 531 nm, and sample E: TiO_x 530 nm etched before annealing.

	Sample A (nm)	Sample B (nm)	Sample C (nm)	Sample D (nm)	Sample E (nm)
Annealed at 700 °C	9	21	16	13	20
Annealed at 725 °C	10	35	26	32	35

For samples annealed with the TiO_x layer, the stress gradient is positive (tensile strain) and decreasing from the interface between the stressor and the heterostructure to the quantum well. Therefore, interstitials diffuse faster through the heterostructure due to the forced diffusion phenomenon. For samples annealed without the TiO_x layer, the stress gradient is negative (compressive strain), decreasing from the interface between the TiO_x layer and the heterostructure to the quantum well, which slows In interstitial diffusion through the heterostructure. Thus, when compressive stress is applied, the thermal shift is reduced whereas it is increased when tensile stress occurs.

In order to study the influence of stress on the effective wavelength shift, phosphorus ion implantation was carried out at an energy of 100 keV with the substrate held at 200 °C, and using a dose of 5×10^{13} P$^+$/cm^2. After implantation, two different values of TiO_x stressor layer thickness were deposited, 85 and 530 nm. All samples were processed with the same thermal treatment, as described previously. Afterwards, all samples were annealed for 120 s in a forming gas atmosphere at 700 and 725 °C. Table I gives the effective wavelength shift as a function of temperature of annealing.

The effective wavelength shift of the implanted reference sample (A) is limited to 10 nm because the energy of implantation and dose are too low. However, the effective wavelength shifts of samples covered with TiO_x are higher, independently of the stress pattern (compressive or tensile). Multiple defect types are created during ion implantation and it can be assumed that comparable numbers of interstitials and vacancies are created in this manner. Therefore, interstitial diffusion is increased when the TiO_x layer is etched before annealing and vacancy diffusion is increased when the TiO_x layer is not removed before annealing, resulting in similar improvements of the effective wavelength shift in both cases. It can also be noticed that the improvement of the effective shift with samples covered with TiO_x is highly dependent on the annealing temperature.

Similar experiments have been reproduced on a second InGaAsP/InGaAs/InGaAsP lattice matched quantum well heterostructure in order to confirm our results. The second heterostructure, initially designed for laser fabrication, contains five quantum wells and has been grown by metal-organic chemical vapor deposition on an InP substrate (n type). An InP buffer layer of 1.4 μm (2×10^{18} Si/cm^2) was first grown on the substrate, followed by a series of five quantum wells (InGaAs, 5 nm) and barriers (InGaAsP, q=1.25 μm, 12 nm) surrounded by InGaAsP layer (Q=1.2 μm,50 nm) and InGaAsP layer (q=1.05 μm,80 nm). The growth was terminated by an InP layer (200 nm,

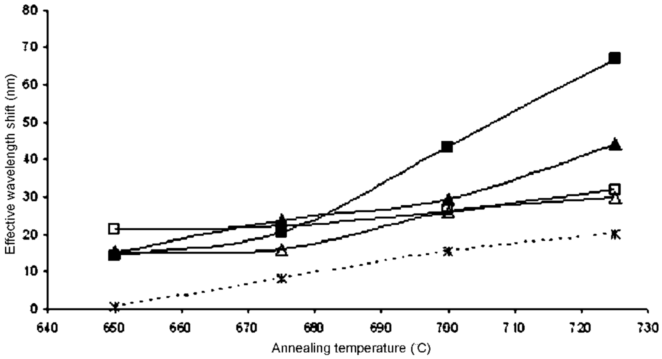

FIG. 2. Effective wavelength shift as function of the TiO_x thickness and annealing temperature. (×): implanted reference sample, (▲): TiO_x 100 nm, (△): TiO_x 100 nm etched before annealing, (■): TiO_x 600 nm, and (□): TiO_x 600 nm etched before annealing.

p type, 6×10^{17} Zn/cm^2), InGaAsP (q=1.3 μm, 10 nm, 6×10^{17} Zn/cm^2), InP (1.2 μm, p type, 6×10^{17} Zn/cm^2) and InGaAsP (q=1.2 μm, 50 nm, 2×10^{18} Zn/cm^2), InGaAs (100 nm, 8×10^{18} Zn/cm^2), and an InP sacrificial layer (200 nm). This laser heterostructure exhibits a small thermal shift at 725 °C ($\Delta\lambda_{th}<5$ nm), which may indicate that the intrinsic point defect concentration is very low. Ion implantation was performed as described previously (E =100 keV, 5×10^{13} P$^+$/cm^2, 200 °C), followed by TiO_x deposition (100 and 600 nm). Samples were annealed at temperatures ranging from 650 to 725 °C for 120 s. Figure 2 represents the effective wavelength shift as a function of annealing temperature, stressor thickness, and stress pattern. It can be seen that the effective wavelength shift is greatly increased when the sample is covered with a TiO_x stressor during the annealing. Samples with the TiO_x stressor etched before annealing also show a limited increase of the effective wavelength shift.

Table II gives a comparison between regular QWI induced by ion implantation and enhanced QWI forced diffusion by TiO_x stressor. The maximum effective wavelength shift that has been obtained on the second heterostructure without TiO_x stressor is 53 nm for an ion implantation performed at 360 keV with a dose of 5×10^{14} P^{++}/cm^2. For samples covered with TiO_x after implantation, the effective wavelength shift can reach 67 nm while the implantation is performed at 100 KeV with a dose of 5×10^{13} P$^+$/cm^2. The damage quantity created by the implantation at 100 keV is almost two orders of magnitude lower than damage quantity induced by the implantation at 360 keV. However, the effective wavelength shift is higher, which confirms that the diffusion of point defects under stress is more efficient than diffusion without stress.

TABLE II. Comparison of quantum well intermixing with forced diffusion phenomenon induced by TiO_x stressor (E=100 keV) and without TiO_x (E =360 keV), annealed at 725 °C for 120 s ($\Delta\lambda_{th}<5$ nm for both samples).

Implantation energy	100 keV Without stressor	100 keV With stressor	360 keV Without stressor
Dose	5×10^{13} P$^+$/cm^2	5×10^{13} P$^+$/cm^2	5×10^{14} P^{++}/cm^2
Defects created calculated with TRIM	4×10^{16} Å^{-1}	4×10^{16} Å^{-1}	1×10^{18} Å^{-2}
Effective wavelength shift	20 nm	67 nm	53 nm

It has been shown that a TiO_x surface stressor can be used in order to improve the thermal stability of InP based quantum well heterostructures. Moreover, it can be used to improve the diffusion of point defects created during ion implantation due to a forced diffusion phenomenon, depending on the type of stress induced (compressive or tensile). The improvement of the effective wavelength shift can be as high as 300% depending on the stress induced by the TiO_x surface stressor. Consequently, it is possible to obtain higher effective wavelength shifts with lower defect concentration, which should result in improving the quality of devices fabricated using this process.

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[1] S. Charbonneau, E. S. Koteles, P. J. Poole, J. J. He, G. C. Aers, J. Haysom, M. Buchanan, Y. Feng, A. Delage, F. Yang, M. Davies, R. D. Goldberg, P. G. Piva, and I. V. Mitchell, IEEE J. Sel. Top. Quantum Electron. **4**, 772 (1998).
[2] I. Gontijo, T. Krauss, J. H. Marsh, and R. M. De La Rue, IEEE J. Quantum Electron. **30**, 1189 (1994).
[3] D. T. Britton and M. Härting, Adv. Eng. Mater. **4**, 629 (2002).
[4] M. Aziz, Appl. Phys. Lett. **70**, 2810 (1997).
[5] J. D. Eshelby, Philos. Trans. R. Soc. London, Ser. A **244**, 87 (1952).
[6] S. C. Jain, M. Willander, and H. Maes, Semicond. Sci. Technol. **11**, 641 (1996).
[7] A. François, V. Aimez, J. Beauvais, and D. Barba, J. Vac. Sci. Technol. A **24**, 797 (2006).
[8] L. Fu, P. Lever, H. H. Tan, C. Jagadish, P. Reece, and M. Gal, Appl. Phys. Lett. **82**, 2613 (2003).
[9] P. L. Gareso, M. Buda, L. Fu, H. H. Tan, and C. Jagadish, Appl. Phys. Lett. **85**, 5583 (2004).
[10] L. Fu, P. Lever, H. H. Tan, C. Jagadish, P. Reece, and M. Gal, Appl. Phys. Lett. **82**, 2613 (2003).
[11] S. Greek, R. Gupta, and K. Hjort, J. Microelectromech. Syst. **8**, 328 (1999).
[12] R. W. Jansen, Phys. Rev. B **41**, 7666 (1990).
[13] C. W. M. Castleton, A. Höglund, and S. Mirbt, Phys. Rev. B **73**, 035215 (2006).