Proton irradiation-induced intermixing in $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ quantum wells—the effect of In composition

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Abstract

We have investigated atomic intermixing in $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ quantum well (QW) structures induced by proton irradiation using photoluminescence (PL) and time-resolved photoluminescence. Photoluminescence results revealed that energy shift was systematically decreased as irradiation temperature was increased, followed by a broadening of the PL linewidth and reduction of the PL intensity. Time-resolved photoluminescence results at room temperature showed that the capture time of carriers in the quantum well region which reflects in the rise time of PL intensity is different for various quantum well structures with different strain and the carrier collection efficiency enhanced in the intermixed QWs. The time evolution of PL intensity also indicates that intermixing changes the strain profile of three QWs.

1. Introduction

$\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ quantum well (QW) structures have been extensively studied for many years due to their application in lasers that operate in the wavelength range of 1.3 to 1.55 μm , which is suitable for long haul optical-fibre communications [1, 2]. For future optoelectronic device integration, it is desirable to produce lasers, modulators and waveguides on the same wafer. One technique that can be used to achieve integration is the post-growth quantum well intermixing (QWI) technique where the band gap is selectively modified by intermixing of the group III/V atoms between the quantum well and barrier region [3–5]. There are several methods commonly used to generate the well-barrier intermixing such as impurity-induced disordering [6], impurity-free vacancy disordering (IFVD) [7, 8] and ion irradiation-induced intermixing [9–11]. Among these various techniques, intermixing by ion irradiation with subsequent thermal annealing has been shown to be very effective due

to its advantage of precise control of defects generation to induce intermixing by varying the irradiation conditions. Several studies on ion irradiation-enhanced interdiffusion in an InGaAs/InP system using heavy ions have been reported [10, 11], but considerably fewer studies using light ions such as protons. Compared to heavier ions, proton irradiation is expected to be able to generate dilute damage cascades with high concentration of point defects (and minimal formation of extended defects) which are available during annealing, leading to a higher degree of intermixing.

In this present study, we investigate the atomic intermixing between the barrier and quantum well region in $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ induced by proton irradiation using photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements. The time-integrated and time-resolved techniques were used to study the degree of intermixing and carrier dynamics, respectively. The mechanism of group V and group III interdiffusion in InGaAs/InP QWs will also be discussed.

2. Experimental details

Three samples of single InGaAs/InP QW structures were grown on semi-insulating (1 0 0) InP substrates by low pressure metalorganic chemical vapour deposition (MOCVD) at 650 °C. The indium composition was nominally 0.38, 0.53 and 0.68 corresponding to tensile-strained (TS), lattice-matched (LM) and compressively-strained (CS) QWs, respectively. Each of the samples was comprised of (from bottom) 600 nm InP, 5 nm thick $\text{In}_x\text{Ga}_{1-x}\text{As}$ QW and 400 nm InP. Proton irradiation was carried out using 50 keV ions with doses ranging from $5 \times 10^{14} \text{ H cm}^{-2}$ to $1 \times 10^{16} \text{ H cm}^{-2}$. Based on TRIM [12] simulation at 50 keV, the peak of the damage profile lies in the quantum well region. The irradiation temperature was varied from room temperature to 300 °C. During implantation, half of each of the sample was masked so as to provide a reference. Subsequent thermal annealing was performed under Ar flow in a rapid thermal annealer (RTA) at 750 °C for 60 s. This temperature was chosen after our study of thermal interdiffusion which showed that at this temperature, the diffusion caused by thermal component could be kept low. Thus, by annealing the implanted samples at this temperature, any measured peak energy shift could be assigned solely to the effect caused by implantation. Low temperature PL (77 K) was performed to characterize the energy shift in the quantum well region using a diode-pumped solid-state frequency-doubled green laser at 532 nm for excitation and a cooled InGaAs photodetector at the output slit of a 0.5 m monochromator. The TRPL measurements based on the up-conversion technique [13] with a temporal resolution of about 200 fs was carried out to investigate the time evolution of QW and barrier luminescence at room temperature. The samples were excited with 100 fs pulses at 800 nm which is well above the band gap of the barriers (InP) where the photoexcited carriers were generated mostly in the barriers. The energy of the excitation laser pulse is 1.24 eV (1 μm wavelength) with a photon density of about $10^{14} \text{ photons cm}^{-2}$.

3. Results and discussion

3.1. Thermal stability of the quantum wells

The InGaAs/InP system has poor thermal stability compared to the InGaAs/GaAs or AlGaAs/GaAs system; therefore, it is important to first evaluate their thermal stability before intermixing studies because an annealing step is required after implantation to initiate the intermixing process. For this purpose, all the samples were annealed for 60 s at various temperatures from 700 °C to 800 °C in a rapid thermal annealer.

Figure 1 shows the PL energy shift of the LM, CS and TS QWs annealed for 60 s at different temperatures with respect to the as-grown samples. As the annealing temperature was increased, the PL energy shift also increased. For implantation-induced intermixing, higher annealing temperatures are much preferred not only to initiate the intermixing process but also to remove the implantation-induced defects. However, too high an annealing temperature will result in a large energy shift due to thermal effects alone. Therefore, based on this study of the temperature dependence of interdiffusion, annealing the samples for 60 s at 750 °C was chosen for subsequent experiments involving implantation, so

Figure 1. The PL energy shift of lattice-matched (LM), compressively-strained (CS) and tensile-strained (TS) $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ QWs annealed at various temperatures from 700 °C to 800 °C for 60 s.

Figure 2. Low temperature PL spectra of as-grown tensile-strained (TS), lattice-matched (LM) and compressively-strained (CS) $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ QWs.

that any measurement of the peak energy shift can be attributed to implantation-induced interdiffusion, and yet the recovery of the crystal quality can be maintained.

3.2. Photoluminescence

Figure 2 shows the PL spectra at 77 K of the three as-grown samples. For LM and CS QWs, each of the peak corresponds to the excitonic recombination between electrons and heavy holes from the $n = 1$ subband levels (C-HH), while for TS QWs, the peak is related to the excitonic recombination of electrons and light holes from the $n = 1$ subband levels (C-LH) of InGaAs QWs. As can be seen from figure 2, the peak position of a TS QW was at 1280 nm. This peak position was shifted to a higher wavelength of 1393 nm for LM structures and 1555 nm for CS structures, respectively, as the indium composition in InGaAs QWs was increased. These changes in the peak position of the quantum wells are due to changes in indium composition and strain. Also, it is worth noting that the high PL peak intensity, and narrow, small and symmetrical linewidth of the peak emission of the samples were relatively similar for LM, TS and CS indicating the smoothness of interfaces and homogeneous thickness of each of the InGaAs QW after growth.

Figure 3 displays the 77 K PL spectra for implanted TS, LM and CS QW samples annealed at 750 °C for 60 s for doses

Figure 3. The PL spectra of lattice-matched (LM), compressively-strained (CS) and tensile-strained (TS) $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ QWs after implantation and annealing at 750 °C for 60 s for (a) reference unimplanted and annealed, (b) $5 \times 10^{14} \text{ H cm}^{-2}$, (c) $1 \times 10^{15} \text{ H cm}^{-2}$, (d) $5 \times 10^{15} \text{ H cm}^{-2}$ and (e) $1 \times 10^{16} \text{ H cm}^{-2}$.

ranging from $5 \times 10^{14} \text{ H cm}^{-2}$ to $1 \times 10^{16} \text{ H cm}^{-2}$. It can be clearly seen from this figure that after implantation, blue shift was observed for all implanted and annealed samples in comparison to the reference samples (unimplanted and annealed). However, the magnitude of the energy shift became saturated at high implantation doses, followed by a reduction of the PL intensity and the broadening of the PL linewidth. It is worth mentioning that prior to annealing, PL emission was not observed due to defects that formed after irradiation which act as non-radiative recombination centres. After annealing, the PL emission was recovered, but the PL intensities were still lower than unirradiated samples indicating that defects were still present and not sufficiently removed after annealing at this temperature.

A plot of the energy shift for TS, LM and CS samples after annealing at 750 °C for 60 s as a function of dose is shown in figure 4. In all cases, the energy shift initially increased as the dose was increased and it reached a maximum at $5 \times 10^{15} \text{ H cm}^{-2}$. As the dose was further increased to $1 \times 10^{16} \text{ H cm}^{-2}$, a saturation in the energy shift was observed. These results are in contrast to the previous studies of $\text{InGaAs}/\text{AlGaAs}$ and $\text{AlGaAs}/\text{GaAs}$ QWs using proton irradiation in which the energy shift was not saturated even at the highest doses ($5 \times 10^{16} \text{ H cm}^{-2}$) [9, 14]. This may be due to differences in the types of defects formed in various material systems. In addition to this, it is well known that in $\text{AlGaAs}/\text{GaAs}$ and $\text{InGaAs}/\text{AlGaAs}$ systems, the well-barrier interdiffusion during the annealing occurs only on the group III sublattice (In, Ga, Al). However, in the InGaAs/InP system both the group III and group V sublattices may contribute to interdiffusion. Blue shift is observed when the diffusion

Figure 4. The PL energy shift of lattice-matched (LM), compressively-strained (CS) and tensile-strained (TS) $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ QWs as a function of implantation dose after annealing at 750 °C for 60 s.

rate of group V sublattice is larger than the diffusion rate of group III sublattice, while a red shift is observed if the group III sublattice diffusion is more dominant. At low doses, the results show that group V diffusion is dominant. At high doses, it is possible that the group III diffusion rate is enhanced (or the reduction in the group V diffusion rate), thereby leading to saturation in the blue shift. However, it is more likely that at high doses, extended defects such as large clusters are formed and these defects are thermally more stable than the simple point defects. Since only point defects (vacancies, interstitials) contribute to the well-barrier intermixing, these clusters would result in lowering the concentration of available point defects to promote intermixing during annealing. Our results also consistently show that at high doses the recovery of the PL intensity is much worse which strongly support this argument.

Protons create only point defects and dilute damage clusters whereas in contrast, heavier ions create denser and larger damage clusters [15, 16]. The denser and larger clusters result in the trapping of the available point defects to induce intermixing, particularly at higher doses. Hence, a saturation effect of the energy shift is observed with an increasing dose and followed by a reduction in the energy shift. Indeed, this was reported in several studies where heavier ions were used [17–19]. In addition, these results show that the concentration of residual defects after annealing is higher in samples implanted with heavier ions, resulting in poorer recovery of the optical properties.

The effect of implantation temperature on intermixing was also studied. The implantation was carried out using two doses at $1 \times 10^{15} \text{ H cm}^{-2}$ and $5 \times 10^{15} \text{ H cm}^{-2}$ in the temperature range of 20–300 °C. The plots of the energy shift as a function of irradiation temperature for the two different doses are shown in figure 5. For all samples, there was a decrease in the amount of the PL energy shift as the irradiation temperature was increased. It has been previously reported that the magnitude of the energy shift in $\text{AlGaAs}/\text{GaAs}$ QWs decreased as the irradiation temperature increased [15, 16], which agrees with our results for the InGaAs/InP system. The reduction in the degree of energy shift and PL intensities as the irradiation temperature increased can be explained by the following: at elevated implantation temperature, dynamic annealing and the mobility of the defects play an important

Figure 5. The PL energy shift of lattice-matched (LM), compressively-strained (CS) and tensile-strained (TS) $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ QWs as a function of implantation temperature for two implantation doses of $1 \times 10^{15} \text{ H cm}^{-2}$ and $5 \times 10^{15} \text{ H cm}^{-2}$.

role in the type and concentration of residual defects. Since proton irradiation creates dilute damage cascades, there could be significant annihilation of vacancies and interstitials at elevated temperature which lead to lowering the concentration of residual point defects. Also, at elevated temperature the increased mobility of the point defects may result in the agglomeration of large clusters or the formation of extended defects. Since interdiffusion relies on the availability of points defects during the annealing, both of these result in less interdiffusion at elevated temperature. However, it is more likely that the latter scenario occurs at elevated irradiation temperature based on observed lower PL intensities.

It is interesting to note from figures 4 and 5 that at the same dose the blue shift in the CS QW was the largest, followed by LM while the smallest blue shift was observed in the TS case. It is expected that the group III sublattice diffusion rate will be the highest for TS samples since it has the highest In–Ga concentration gradient, followed by LM and CS samples. Assuming that the group V sublattice diffusion rate is the same for all the samples, the higher group III diffusion rate of the TS samples would counter the effect of blue shift caused by the group V diffusion more efficiently than the other two samples. Hence, the lower degree of energy shift. However, this simplistic argument does not take into account the effect of the strain during the interdiffusion. It is known that compressive strain may enhance the interdiffusion during annealing whereas tensile strain suppresses it [20].

3.3. Time resolved photoluminescence

Figures 6 (a)–(c) display the time evolution of PL emission from the lattice-matched, compressively-strained and tensile-strained QWs, respectively, for unimplanted (reference) and implanted samples with two different doses. The time

Figure 6. Time evolution of photoluminescence of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ quantum wells at room temperature for reference samples and for samples implanted with $1 \times 10^{15} \text{ H cm}^{-2}$ and $5 \times 10^{15} \text{ H cm}^{-2}$: (a) lattice-matched (LM), (b) compressively-strained (CS) and (c) tensile-strained (TS) samples. The symbols are the experimental data and lines are the fitting curves using equation (1).

Table 1. PL effective capture times (τ_c) and lifetimes (τ_{lw}) in the quantum well region for reference samples and intermixed samples.

Indium composition	Reference as-grown + RTA		Intermixed $1 \times 10^{15} \text{ H cm}^{-2}$		Intermixed $5 \times 10^{15} \text{ H cm}^{-2}$	
	τ_c (ps)	τ_{lw} (ps)	τ_c (ps)	τ_{lw} (ps)	τ_c (ps)	τ_{lw} (ps)
0.38 (TS)	85	750	70	350	60	270
0.53 (LM)	60	700	45	290	55	280
0.68 (CS)	80	420	60	270	60	220

evolution of the PL intensity $I_{PL}(t)$ can be fitted with the equation

$$I_{PL}(t) = a_0 \exp(-t/\tau_{lw}) - a_1 \exp(-t/\tau_c), \quad (1)$$

where τ_{lw} is the effective lifetime of carriers in QWs, τ_c is the effective capture time of carriers in QWs, a_0 and a_1 are the fitting parameters for the lifetime and effective capture time, respectively, which are shown in table 1. As can be seen from table 1, the effective lifetime decreased as the implantation dose was increased. In the case of TS samples, the PL lifetime of intermixed samples ($5 \times 10^{15} \text{ H cm}^{-2}$) was significantly decreased in comparison to the reference samples. A smaller reduction of the effective lifetime (420 ps for reference samples and 220 ps for the sample implanted with $5 \times 10^{15} \text{ H cm}^{-2}$) was measured for the CS sample. Reduction of the effective lifetime in an intermixed QW can be explained by the residual non-radiative defects in the quantum well or in the barrier layers after implantation and annealing. These defects act as non-radiative centres thereby reducing the effective lifetime of the photoexcited carriers which has been reported in previous

studies [21]. These results are reflected in the reduction of the CW-PL intensity and the broadening of the PL emission linewidth for intermixed samples.

At room temperature where the origin of light emission in the quantum well region is due to the recombination of free electrons and holes, the PL rise time (the time required for PL to reach its maximum) is determined by the rate of carriers capture into QW. The effective carrier capture from the barrier into the quantum well consists of two processes, the fast quantum capture (~ 1 ps) that involves the carrier–carrier or carrier–phonon scattering and the other longer process related to the carrier diffusion across the barrier into the well. Although all samples have the same barrier thickness, for reference samples the capture times of compressively-strained (80 ps) and tensile-strained (85 ps) samples are longer than those of the lattice-matched (60 ps) samples (see table 1). Since the thickness of the InP barriers is the same in all cases, the difference in the effective capture times for the CS, TS and LM samples suggests the presence of a ‘potential barrier’ at the heterointerfaces due to strain and/or internal electric fields (i.e. concentration gradients). Previous studies have shown that carrier capture time in the quantum well is reduced in intermixed samples as a result of the change in the quantum well potential caused by intermixing [22]. For samples implanted with $5 \times 10^{15} \text{ H cm}^{-2}$, the effective capture times are similar for all the samples (55–60 ps). The reduction in capture times after irradiation is due to the modification of the strain and the internal field profile. It is unlikely that the carrier diffusion/transport component of the effective carrier capture time is reduced since irradiation creates defects which will actually increase this transport component. This is further supported by the results when the irradiation dose (i.e. more defects) is increased and yet the effective carrier capture time is further reduced. At higher irradiation doses, this ‘potential barrier’ is reduced and hence the faster effective carrier captures times.

The influence of the additional potential energy barriers at the quantum well–barrier interface on the carrier capture can be studied from the time evolution of barrier PL. Figure 7 shows the time evolution of the luminescence signal at 930 nm corresponding to the recombination of electrons and holes from InP barrier layers for the reference and intermixed samples (LM, CS, TS) at room temperature. Since the photoexcited carriers were generated in the barrier layer directly, a very short rise time is observed at room temperature. Equation (2) can be used for fitting the decay time of PL intensity:

$$I_{\text{PL}}(t) = A \exp(-t/\tau_{\text{lb}}), \quad (2)$$

where τ_{lb} is the effective lifetime of carriers localized in the barrier layer and A can reflect the contribution of localized states in the barrier which is dependent on the strain. The results of fitting for reference and $5 \times 10^{15} \text{ H cm}^{-2}$ implanted samples are summarized in table 2. The lifetimes of the localized carriers in the barrier were < 100 ps for intermixed samples which were much shorter than those in the reference samples. The ion-induced damage to lattice can lead to a drastic reduction of its optical quality but with thermal annealing the heterostructures usually recovered most of their optical properties, although some defects are still left in the

Figure 7. Time evolution of the photoluminescence of InP barriers at room temperature for reference samples and for samples implanted with $5 \times 10^{15} \text{ H cm}^{-2}$ for lattice-matched (LM), compressively-strained (CS) and tensile-strained (TS). The symbols are the experimental data and the lines are the fitting curves using equation (2).

Table 2. PL effective lifetime of carriers localized in the barrier layer for reference samples and intermixed samples.

Indium composition	Reference as-grown + RTA		Intermixed $5 \times 10^{15} \text{ H cm}^{-2}$	
	A	τ_{lb} (ps)	A	τ_{lb} (ps)
0.38 (TS)	0.35	450	2.5	100
0.53 (LM)	1.2	410	0.4	110
0.68 (CS)	0.3	350	0	60

samples. Increasing the concentration of non-radiative defects leads to a shorter decay time of the barrier PL. This observation supports the additional potential energy barrier at the QW interfaces which can be reduced by intermixing. Atomic diffusion by intermixing leads to the reduction of the internal electric field at the interface.

In summary, we have studied the atomic intermixing of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}$ quantum wells induced by proton irradiation using photoluminescence and time-resolved photoluminescence. Photoluminescence results show that the energy shift saturates at high doses indicating that the concentration of available point defects is reduced at high doses due to the formation of extended defects. The time-resolved photoluminescence shows a variation of carrier capture times and lifetimes for intermixed QWs.

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