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Argon plasma exposure enhanced intermixing in an undoped InGaAsP/InP quantum-well structure

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Intermixing in an undoped InGaAsP/InP quantum well structure enhanced by near-surface defects generated using inductively coupled argon plasma is temperature dependent. The group III sublattice interdiffusion can be four times as fast as that of the group V sublattice for the annealing temperature lower than 600 °C, and a maximum band gap redshift of 50 nm is obtained in experiment. Blueshift is obtained at 700 °C when the group V sublattice interdiffusion becomes appreciable. © 2006 American Institute of Physics. [DOI: 10.1063/1.2227267]

Quantum-well intermixing (QWI) has attracted considerable interest in recent decades as a postgrowth band gap engineering technique for monolithic integration of QW-based optoelectronic devices and performance improvement of discrete devices.¹ In addition, QWI also provides a unique opportunity to study the interdiffusion of semiconductor heterointerfaces and the role of defects in the interdiffusion.² QWI in InGaAs(P)/InP QWs is more complicated than that in GaAs/AlGaAs QWs, as interdiffusion can occur on both group III and V sublattices, which are characterized by their diffusion lengths $L_{d\text{III}}$ and $L_{d\text{V}}$, respectively. Not only a blueshift but also a redshift in the band gap may result from intermixing, depending on the diffusion length ratio, i.e., $k = L_{d\text{V}}/L_{d\text{III}}$.³ Experimentally, the value of k is subject to the nature of introduced defects, the method introducing defects, the annealing temperature, and the annealing time. A blueshift in InGaAs(P)/InP QWs is often observed as reported in a number of defect enhanced QWI techniques. Particularly, in experiments such as phosphor-doped silica cap enhanced QWI,⁴ phosphor ion implantation enhanced QWI,⁵ and low temperature grown-in defect enhanced QWI,⁶ the k values were deduced at around 1.4, 1.7, and 2, respectively, denoting dominant interdiffusion on the group V sublattice, which is enhanced by the phosphor interstitial via a kickout mechanism. In contrast, not many reports have presented results of dominant interdiffusion on the group III sublattice and the resulting redshift in InGaAs(P)/InP QWs. A redshift was observed in an InGaAsP/InP QW structure by Zn diffusion,⁷ and also in GaAs/InGaP multiple QWs by thermal annealing⁸ or fluorine implantation followed by annealing.⁹ However, the k parameter, under the case of redshift, has never been reported.

In this paper, we report intermixing of an undoped InGaAsP/InP QW structure using an inductively coupled ar-

gon plasma enhanced QWI technique.¹⁰ We show that, after argon plasma exposure, both the blueshift and the redshift of the band gap can be obtained by controlling the temperature of rapid thermal annealing (RTA), while without plasma exposure, only the band gap blueshift can be observed at all RTA temperatures. The k parameter is further estimated from the experimental result of the band gap redshift in association with theoretical calculations, and it is found that the interdiffusion on the group III sublattice can be four times as fast as that on the group V sublattice. The method to enhance intermixing is impurity-free in nature and capable of selective-area band gap modification incorporating both band gap blueshift and redshift.

Samples used in the experiment have a lattice-matched InGaAsP/InP QW structure grown by metal organic chemical vapor deposition on a (100)-oriented n -type sulfur-doped InP substrate. Four epilayers as shown in Table I were consecutively grown at a growth temperature of 620 °C without doping. Two sets of samples were prepared for experiments. The samples with the top InGaAs layer removed by wet etching are referred to as InP cap samples, whereas the samples keeping the as-grown structure are referred to as InGaAs cap samples. In experiment, samples were processed using argon plasma first. The RTA process was then performed in several steps with each duration fixed at 120 s and

TABLE I. The layer structure for the undoped InGaAsP/InP single quantum well.

No.	Composition	Thickness (Å)	Layer
4	In _{0.53} Ga _{0.47} As	5000	Buffer/cap
3	InP	5000	Barrier/cap
2	In _{0.71} Ga _{0.29} As _{0.61} P _{0.39}	35	Well
1	InP	3000	Barrier
(100) oriented n -type sulfur-doped InP substrate			

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FIG. 1. (Color online) (a) PL spectra for one InP cap sample before plasma exposure and after plasma exposure followed by annealing at (i) 580 °C, (ii) 600 °C, (iii) 620 °C, (iv) 650 °C, and (v) 700 °C. (b) PL peak wavelength shifts after each annealing step for the plasma-exposed (square) and the plasma-unexposed (circle) samples. The samples were with the InP cap layer throughout the experiment.

with temperature raised consecutively. In the RTA process, flowing nitrogen ambient was adopted, and each sample was sandwiched between two fresh pieces of InP or GaAs proximity caps to prevent out-diffusion of P and As for InP cap samples and InGaAs cap samples, respectively. After each RTA step, photoluminescence (PL) spectra were examined at 77 K using an argon ion laser ($\lambda=488$ nm) as excitation source to assess the bandgap modification.

Figure 1(a) shows the PL spectra of one InP cap sample before plasma exposure and after plasma exposure followed by several RTA processes. The argon plasma process was done for 1 min under the following parameters: 480 W rf power, 300 W inductively coupled plasma (ICP) power, 80 SCCM (SCCM denotes standard cubic centimeters per minute) argon flow rate, and 60 mTorr chamber pressure. The annealing was done in five steps with temperatures set at 580, 600, 620, 650, and 700 °C, consecutively. As a reference, one unexposed InP cap sample was also subjected to the above RTA processes. The PL peak wavelength shifts as a function of the RTA temperature for the plasma-exposed and -unexposed samples are presented in Fig. 1(b). It can be seen that the unexposed and annealed-only sample presents band gap blueshifts at all RTA steps, mainly due to the grown-in defects in the epilayers and substrates.² For the plasma-exposed sample, band gap redshifts were observed at several RTA steps for annealing temperatures below 650 °C, whereas a blueshift was obtained after the last RTA step at 700 °C. The PL peak intensity is extremely low as compared to that of the as-grown sample when there is a redshift, and starts to recover when a blueshift appears in the annealing

FIG. 2. (Color online) (a) The calculated wavelength shift of the ground state transition as a function of the group III diffusion length under different k parameters. (b) The calculated maximum redshift as a function of the k parameter. The group III diffusion lengths to obtain the maximum redshifts are labeled in the parentheses.

step at 700 °C. The reduction in PL peak intensity after the band gap redshift at low annealing temperature and its recovery after the band gap blueshift at high annealing temperature were also observed by other researchers in GaAs/InGaP QW samples.⁹

To interpret the above observations of band gap modification, the wavelength shift of the interdiffused QW structure was calculated using single band finite difference method, as was done in a previous publication.¹¹ Figure 2(a) shows the calculated PL peak wavelength shift as a function of group III diffusion length under different k parameters. It can be seen that, in this QW structure, an observable redshift can be obtained only when $k < 0.6$ roughly; i.e., the group III sublattice must interdiffuse about twice as fast as the group V sublattice. In addition, the maximum achievable redshift is subject to the k parameter rather than the diffusion length, as plotted in Fig. 2(b). Therefore, the observed band gap redshift of 34 nm after plasma exposure and annealing at 600 °C, as shown in Fig. 1(b), reveals a minimum k of less than 0.35, as a result of dominant group III sublattice interdiffusion. However, for the unexposed annealed-only sample, the band gap blueshift at all RTA steps indicates that the k parameter is larger than 0.6.

The obvious difference in intermixing behaviors of the plasma-exposed and -unexposed samples implies different intermixing mechanisms. For the unexposed sample, blueshifts at various temperatures denote that there are no sufficient group III grown-in defects to cause appreciable interdiffusion on the group III sublattice that exceeds interdiffusion on the group V sublattice. However, during plasma exposure, both group III and V defects are generated at the near-surface region due to the physical bombardment by high-density energetic argon ions. These defects can diffuse down towards the QW regions during the subsequent annealing to enhance interdiffusion on both group III and V sublattices. It has been determined that the group V sublattice diffusion is characterized by higher activation energy than that of the corresponding group III sublattice diffusion, and the diffusion of each atomic species proceeds through its own sublattice.¹² The diffusion of group V defects may require more energy than the diffusion of group III defects, since the former involves the removal of five electrons from the bond system while the latter involves the removal of only three electrons. Therefore, for annealing at low temperature

FIG. 3. (Color online) PL peak wavelength shifts after each annealing step. Plasma exposure was done on the InGaAs cap. In the curve with triangle symbols, the samples kept the InGaAs cap layer in all annealing steps, whereas in the curve with square symbols, the InGaAs cap layer was removed after the first annealing step thereafter, the InP layer was on top.

after plasma exposure, the group III defect diffusion is first activated to enhance intermixing primarily on the group III sublattice, resulting in a group III dominant intermixing process and a band gap redshift. The activation of interdiffusion on the group III sublattice at lower temperature compared to that for the group V sublattice is also supported by the reported intermixing results on the GaAs-based material with a GaAs/InGaP QW (Ref. 9) and the InP-based material with an InGaAs/InP QW.¹³ With the increase in the annealing temperature, the group V defect diffusion is activated to enhance intermixing primarily on the group V sublattice, increasing the k value and shifting the band gap redshift towards a blueshift.

For this undoped InGaAsP/InP QW structure, the different behavior of intermixing in the plasma-exposed sample from that in the as-grown sample is due to the introduction of near-surface defects in both sublattices, which is simply a result of physical ion bombardment. This nature should not be affected by the composition of the cap layer. For this regard, similar experiments were conducted using InGaAs cap samples. The results are shown in Fig. 3. The argon plasma exposure process was performed for 2 min under the following parameters: 480 W rf power, 500 W ICP power, 100 SCCM argon flow rate, and 60 mTorr chamber pressure. The annealing was done in four steps at temperatures of 560, 600, 650, and 700 °C, consecutively. For the curve with square symbols, the InGaAs cap layer was removed by wet chemical etching after the first annealing step at 560 °C, such that in the subsequent annealing steps the sample had InP as its cap layer without existence of near-surface defects. For the curve with triangular symbols, the samples were annealed with the InGaAs cap that contained the plasma-induced defects through all annealing steps. Four samples were used to obtain this curve because one had to be taken out after each annealing step to remove the thick InGaAs layer by wet chemical etching for PL signal sampling. The two curves show a similar trend as that seen in the plasma-exposed sample in Fig. 1(b), denoting that the defect introduction into both sublattices by plasma exposure and thus the temperature dependence of the resulting band gap shift are

not much affected by the composition of the cap layer. Redshift was seen in the beginning since the dominant group III sublattice interdiffusion was activated at low temperature. The maximum band gap redshift of ~ 50 nm reveals that a minimum k parameter of less than 0.25 was achieved in the history of annealing. In other words, the group III sublattice interdiffusion that is approximately four times as fast as that on the group V sublattice was remarkably induced by the argon-plasma-exposure-introduced defects. However, by removing the InGaAs cap layer and thus the plasma-introduced near-surface defects after the first annealing step at 560 °C, the intermixing process slowed down, resulting in a slower change from redshift to blueshift. This observation further confirms the role of plasma generated surface defects in enhancing intermixing and thus band gap blueshift at higher RTA temperatures.

In summary, both band gap blueshift and redshift can be achieved by controlling the RTA temperature in the inductively coupled argon plasma enhanced QWI process for the undoped InGaAsP/InP QW structure. After plasma exposure and annealing at temperatures below 650 °C, interdiffusion is dominant on the group III sublattice and a k parameter of 0.25 is reached, resulting in an appreciable band gap redshift as large as 50 nm in the experiment. The group V sublattice interdiffusion is activated at higher annealing temperature, and the band gap blueshift is obtained at 700 °C accompanied with recovery of PL intensity. The intermixing is implemented in an impurity-free style and is capable of selective-area band gap modification which is promising for photonic integration applications.

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