

## Large blueshift in InGaAs/InGaAsP laser structure using inductively coupled argon plasma-enhanced quantum well intermixing

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An inductively coupled plasma-enhanced quantum well intermixing technique has been developed to induce a shift in the band gap in quantum well structures using argon plasma. The emission of the InGaAs/InGaAsP laser structure was blueshifted as much as 104 nm with linewidth broadening of only 10.6 nm using 5 min plasma exposure and subsequent rapid thermal annealing. This large shift is attributed to inductively coupled plasma at high ion current density (with 100's of eV ion impact energy) that promotes desirable point defects near the surface of the samples. The result has demonstrated an effective approach for large band gap tuning of InGaAs/InGaAsP laser structures.

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### I. INTRODUCTION

There has been a strong motivation to develop an effective quantum well intermixing (QWI) technology to tune quantum well (QW) properties at the postgrowth level for optoelectronic and photonic integrated circuit (PIC) applications. Monolithic InP-based ternary or quaternary PICs play an important role in optical fiber telecommunications because their operating wavelengths can match very low loss and dispersion windows at 1.3 and 1.55  $\mu\text{m}$ . The ability to modify the band gap energy across a single substrate is a key requirement for monolithic integration of multiple photonic devices. The specifications of individual components such as gain, absorption or transmission at the operating wavelength can be posttuned by modifying the band gap across an InP-based semiconductor wafer. The QWI technique has generated considerable interest due to its simplicity and effectiveness. The emergence in the past few decades of QWI technology,<sup>1</sup> such as impurity-induced disordering (IID),<sup>2</sup> impurity-free vacancy disordering (IFVD),<sup>3</sup> and laser-induced disordering (LID),<sup>4</sup> has been utilized in wide application for PICs. Among the techniques, plasma-induced QWI is relatively new and attractive. In this technique, high ion dose current at low energy that can be created using high-density plasma sources that can be used to promote a type of impurity-induced QWI with little damage. Thereby, it will be useful for high-quality photonic devices for PIC application. Initial work has been done using H<sub>2</sub> plasma generated by an reactive ion etcher (RIE) on GaAs/AlGaAs QW structures and a maximum wavelength blueshift of 24 nm was obtained using up to nine cycles of exposure and annealing.<sup>5</sup> In this article, we investigate both the QWI effect of high-density inductively coupled argon plasma on InGaAs/InGaAsP QW

structures generated in an inductively coupled plasma (ICP) system, and the shift in wavelength after intermixing using photoluminescence (PL) spectroscopy.

### II. EXPERIMENT

The lattice-matched InGaAs/InGaAsP QW samples used in the present investigation were grown by metalorganic vapor phase epitaxy on (100) oriented  $n^+$ -type S-doped InP substrates with less than 1000  $\text{cm}^{-2}$  etch-pit density. The laser structure consisted of five periods of 55 Å In<sub>0.53</sub>Ga<sub>0.47</sub>As QWs with 120 Å InGaAsP barriers. The active region was sandwiched by a step-graded index waveguide core consisting of InGaAsP confining layers. The thicknesses of these confining layers were 500 and 800 Å, respectively. The structure was completed by an upper InP cladding layer of 1.4  $\mu\text{m}$  with Zn doping of  $5 \times 10^{17} \text{cm}^{-3}$ . The contact layers consisted of 500 Å InGaAsP (Zn doping of  $2 \times 10^{18} \text{cm}^{-3}$ ) and 1000 Å InGaAs (Zn doping of  $2 \times 10^{19} \text{cm}^{-3}$ ), respectively. The samples produced a PL peak at  $1.51 \pm 0.02 \mu\text{m}$  at room temperature (RT) and one at  $1.43 \pm 0.02 \mu\text{m}$  at 77 K.

The plasma source generator, ICP180, used in this experiment was built by Plasmalab System100. The system used an inductive coil to generate a high-density "remote" plasma. A 13.56 MHz radio frequency (rf) chuck power and an ICP power supply can provide independent control on the ion bombardment energy and ion current density with powers up to 500 and 3000 W, respectively. The ICP parameter settings for the experiments were optimized by the Taguchi method,<sup>6</sup> i.e., 100 sccm Ar flow rate and 80 mTorr chamber pressure. After Ar plasma exposure, the samples were annealed using single step annealing at a thermally stable temperature of 600 °C for 120 s in flowing nitrogen ambient. Two fresh pieces of GaAs proximity caps were used to provide an As overpressure environment during the annealing process and also to prevent the sample surface from outdiffusion. The

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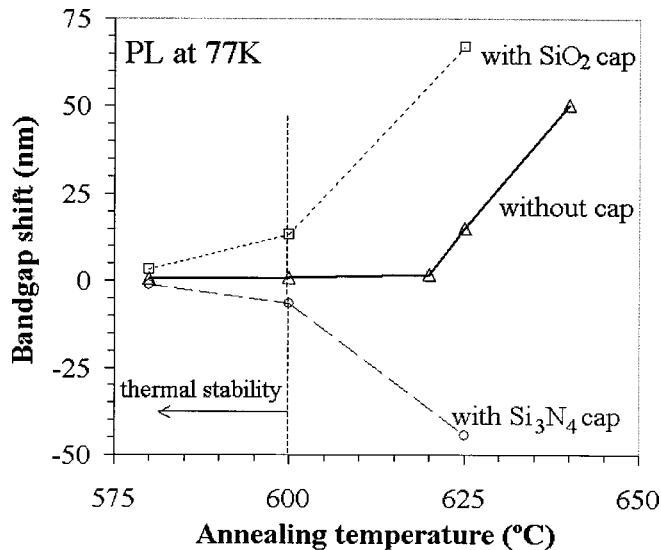


FIG. 1. PL peak shift at 77 K vs the annealing temperature to achieve thermal stability for the intermixing study of InGaAs/InGaAsP QW samples without a cap ( $\Delta$ ), with 250 nm thickness of the SiO<sub>2</sub> cap ( $\square$ ), and with 250 nm thickness of the Si<sub>3</sub>N<sub>4</sub> cap ( $\circ$ ). The annealing time was fixed at 120 s in flowing nitrogen ambient.

annealing conditions were determined from a thermal stability test performed on as-grown samples with and without dielectric cap layers. A control sample was annealed to determine the thermal shift without plasma exposure. PL was then performed to assess the degree of band gap shifting and linewidth broadening. The PL measurements were carried out at 77 K and at RT using a Nd:YAG laser (1.064  $\mu\text{m}$ ) for excitation, a monochromator and a thermo electrically (TE) cooled InGaAs photodetector in conjunction with a SR-830 lock-in amplifier.

### III. RESULTS AND DISCUSSION

The annealing process significantly affects the band gap energy of QWs with regard to the interdiffusion of QW constituent atoms and material properties. Hence in order to understand the influence of the annealing process, a thermal stability study from 500 to 650 °C was carried out for the as-grown sample. The annealing time was fixed at 120 s, which is short enough to minimize surface decomposition while promoting QWI. An optimal shift in the band gap mainly due to Ar exposure, was obtained by annealing below a critical temperature, beyond which the as-grown sample started to experience appreciable band gap shifting due to other effects. Figure 1 shows the band gap shifts due to annealing the uncapped, SiO<sub>2</sub> capped, and Si<sub>3</sub>N<sub>4</sub> capped as-grown samples. The uncapped sample annealed at 600 °C had a small blueshift of 0.8 nm with minimal linewidth broadening, whereas the SiO<sub>2</sub>-capped and Si<sub>3</sub>N<sub>4</sub>-capped samples were shifted 13.4 and 6.4 nm, respectively. A further increase in the annealing temperature caused rapid changes in thermal shifts in the capped samples whereas in the uncapped samples this trend occurred beyond 620 °C. Larger band gap shifts were observed in the dielectric capped

samples because the dielectric caps affect the QWI results through IFVD effects<sup>3</sup> due to vacancies generated at the dielectric-sample interface under a stress gradient caused by the difference in thermal expansion coefficients. The band gap shift due to the thermal diffusion effect is insignificant in the uncapped sample annealed below 620 °C and the very small linewidth broadening implies that the material had no significant degradation. This is in good agreement with the annealing study reported for the influence of the defect density in S-doped InP substrates<sup>7</sup> and the effect of thermal stability on QWs.<sup>8</sup> Larger band gap shifts in samples annealed at higher temperatures indicate that the thermal damage is possibly due to thermally induced material decomposition. From the experimental results, it can be concluded that the annealing process at 600 °C can promote QWI with plasma exposure while avoiding thermal damage as well as large thermal shifting in the masked area.

The effect of an inductively coupled Ar plasma exposure is the primary part of this work to produce a shift in the band gap. In order to study this effect, a set of QW samples from the same wafer with no dielectric cap were exposed under Ar plasma in the ICP chamber with 480 W rf power only. The ICP power was turned off during plasma exposure. After plasma exposure, there was no shift in the PL spectra compared to the as-grown sample. This indicates that near-surface point defects were created during low Ar ion energy (100's of eV) exposure, thus avoiding direct damage to the QW region which is located more than 1.6  $\mu\text{m}$  below the sample surface. Upon annealing, the near-surface point defects propagated into the QW region via diffusion. When the defects reached the QW region, the interdiffusion between the atoms of the QW and the barrier layer widened the band gap and resulted in a blueshift. The PL spectra at 77 K from the exposed samples after annealing versus exposure times are plotted in Fig. 2. Large blueshifts in the PL spectra are observed and the degree of intermixing increases with the exposure time. The shift in band gap extracted from the PL spectra was saturated after 10 min exposure at about 70 nm. This shift is comparable to similar work on Ar plasma-induced QWI using a conventional parallel plate RIE machine in InGaAs/InGaAsP QW structures.<sup>9</sup> Since no direct damage is created in the QW region during exposure, there is little small linewidth broadening in the PL spectra of the intermixed samples compared to in the as-grown samples. The subsequent annealing not only promotes intermixing between the QWs and the barriers but also recovers the crystal damage caused by plasma exposure.

With the absence of ICP power, the ionic species in the plasma sheath region are accelerated at normal incidence by the electric field and obtain kinetic energy relative to the samples. Under this condition, ion bombardment with a high potential difference between the plasma and the sample results in near-surface point defects in the sample. Hence from Fig. 2, we can conclude that the band gap shift in QWs is mainly attributable to the relatively high energetic (100's of eV depending on the rf bias voltage) ion bombardment effect.

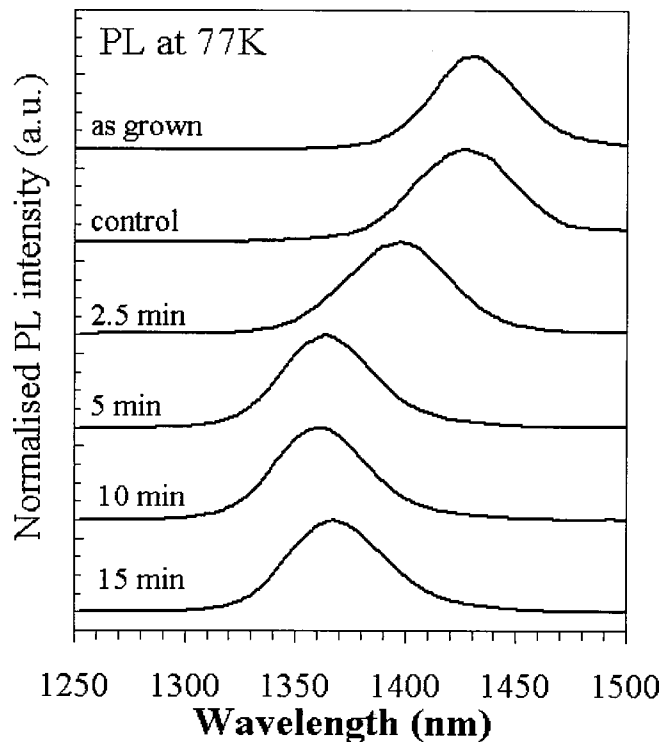


FIG. 2. Plot of normalized 77 K PL spectra at various Ar plasma exposure times. The samples were exposed under 480 W rf power only and subsequently annealed at 600 °C for 120 s.

Here in Sec. III, we have investigated the effects of QWI in the presence of inductively coupled Ar plasma during exposure. In our previous paper,<sup>6</sup> both high rf power and low ICP power were required for high band gap shifts with little linewidth broadening. Figure 3 shows the optimal shift of PL at RT and linewidth broadening versus ICP power with rf power at 480 W. At 0 W ICP power, the PL peak at RT was

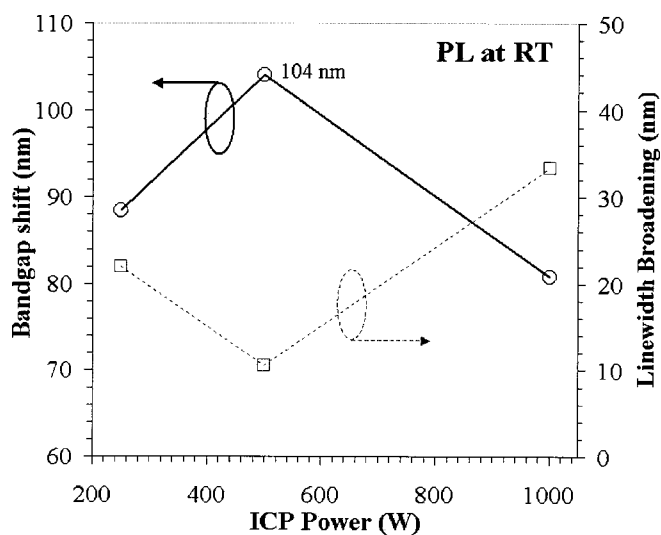


FIG. 3. Optimal band gap shift (○) and linewidth broadening (□) vs the ICP power. The condition was taken at fixed rf power of 480 W for up to a 15 min exposure time. Annealing was carried out at the optimum condition below the critical temperature (600 °C for 120 s).

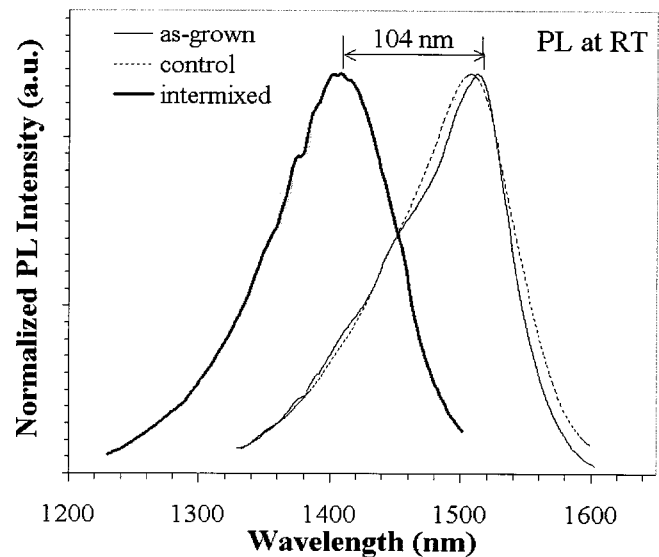


FIG. 4. Normalized PL spectra for as-grown, control and intermixed samples with 5 min Ar exposure at ICP power of 500 W. The PL peak shifted as much as 104 nm with linewidth broadening of 10.6 nm after exposure and subsequent annealing at 600 °C for 120 s.

blueshifted as much as 79.8 nm with  $-840$  V rf-induced dc bias. The application of ICP power from 250 to 1000 W promotes a much higher degree of QWI ( $>80$  nm) along with a linear decrease in rf-induced dc bias with ICP power. The rf-induced dc bias reduction leads to less energetic ion bombardment-induced damage with high ion current density. This implies that the presence of high plasma density from inductively coupled Ar plasma plays an important role in enhancing QWI. The application of ICP power enhances fast damage diffusion due to radiation on the samples such as that observed and reported elsewhere.<sup>10</sup> An optimal band gap shift using ICP power with minimum linewidth broadening was obtained at an ICP power of 500 W and a rf-induced dc bias of  $-730$  V. The further increase in ICP power led to a reduction of blueshifting with an increase in linewidth broadening. The reduction in blueshifting might be attributed to the accumulation of damage clusters and extended point defects due to high-density ion dose exposure, which also account for significant broadening of the PL spectra after annealing. Figure 4 exhibits PL spectra at RT of the intermixed QW sample at an optimal band gap shift. The band gap shift of the control sample was 6.2 nm with linewidth broadening of 5.2 nm. The band gap of the QW was blueshifted by as much as 104 nm with linewidth broadening of 10.6 nm after plasma exposure for 5 min at 500 W ICP power.

Low energy Ar plasma-induced QWI can achieve relatively high or comparable band gap shifts of 104 nm compared to implantation-induced QWI using a 360 keV arsenic ion,<sup>11</sup> a 30 keV argon ion,<sup>12</sup> and a 20 keV plasma immersion argon ion<sup>13</sup> in InGaAs/InP QWs. The defects that formed near the sample surface lead to minimal crystal damage in the QW region during the QWI process as evidenced by the minimal linewidth broadening in PL. Further work on good

preservation of the crystalline quality of QW samples by Ar plasma QWI is under investigation.

#### IV. CONCLUSION

In summary, we have developed an efficient QWI technique to shift the band gap using an ICP system. The presence of high ion plasma density from inductively coupled Ar plasma plays an important role in enhancing QWI. A shift in the band gap as large as 104 nm was achieved in the InGaAs/InGaAsP laser structure with small linewidth broadening of 10.6 nm. Hence this ICP-QWI technique paves the way for active photonic devices being integrated into monolithic chips, where high crystalline quality after postprocessing is required.

<sup>1</sup>A. C. Bryce, F. Camacho, P. Cusumano, and J. H. Marsh, *IEEE J. Sel. Top. Quantum Electron.* **3**, 885 (1997).

<sup>2</sup>D. G. Deppe and N. Holonyak, Jr., *J. Appl. Phys.* **64**, R93 (1998).

<sup>3</sup>A. S. Saher Helmy, S. K. Murad, A. C. Bryce, J. S. Aitchison, J. H.

Marsh, S. E. Hicks, and C. D. W. Wilkinson, *Appl. Phys. Lett.* **74**, 732 (1999).

<sup>4</sup>T. K. Ong, Y. C. Chan, Y. L. Lam, and B. S. Ooi, *Appl. Phys. Lett.* **78**, 2637 (2001).

<sup>5</sup>B. S. Ooi, A. C. Bryce, and J. H. Marsh, *Electron. Lett.* **31**, 449 (1995).

<sup>6</sup>D. Leong, H. S. Djie, and P. Dowd, *Proceedings of the 14th International IEEE Conference on Indium Phosphide and Related Materials*, 2002, p. 319.

<sup>7</sup>H. S. Lim, T. K. Ong, B. S. Ooi, Y. L. Lam, Y. C. Chan, and Y. Zhou, *Proc. SPIE* **3896**, 207 (1999).

<sup>8</sup>J. E. Haysom, G. C. Aers, S. Raymond, and P. J. Poole, *J. Appl. Phys.* **88**, 616 (2000).

<sup>9</sup>D. Leong, H. S. Djie, and L. K. Ang, *Proceedings International Conference for the IEEE/LEOS Workshop on Fibre and Optical Passive Components*, 2002, p. 148.

<sup>10</sup>M. Rahman, L. G. Deng, J. van den Berg, and C. D. W. Wilkinson, *J. Phys. D* **34**, 2792 (2001).

<sup>11</sup>S. L. Ng, H. S. Lim, Y. L. Lam, Y. C. Chan, B. S. Ooi, V. Aimez, J. Beauvais, and J. Beerens, *Jpn. J. Appl. Phys., Part 1* **41**, 1080 (2002).

<sup>12</sup>J. Oshinowo, J. Dreybrodt, A. Forchel, N. Mestres, J. M. Calleja, I. Gyuro, P. Speier, and E. Zielinski, *J. Appl. Phys.* **74**, 1983 (1993).

<sup>13</sup>L. M. Lam, C. W. Kwong, H. P. Ho, E. Y. B. Pun, K. S. Chan, Z. N. Fan, and P. K. Chu, *Electron. Lett.* **34**, 817 (1998).