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Large bandgap blueshifts in the InGaP/InAlGaP laser structure using novel strain-induced quantum well intermixing

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We report on a novel quantum well intermixing (QWI) technique that induces a large degree of bandgap blueshift in the InGaP/InAlGaP laser structure. In this technique, high external compressive strain induced by a thick layer of SiO2 cap with a thickness $\geq 1 \mu$m was used to enhance QWI in the tensile-strained InGaP/InAlGaP quantum well layer. A bandgap blueshift as large as 200 meV was observed in samples capped with 1-$\mu$m SiO2 and annealed at 1000 °C for 120 s. To further enhance the degree of QWI, cycles of annealing steps were applied to the SiO2 cap. Using this method, wavelength tunability over the range of 640 nm to 565 nm (~250 meV) was demonstrated. Light-emitting diodes emitting at red (628 nm), orange (602 nm), and yellow (585 nm) wavelengths were successfully fabricated on the intermixed samples. Our results show that this new QWI method technique may pave the way for the realization of high-efficiency orange and yellow light-emitting devices based on the InGaP/InAlGaP material system. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Recently, there has been strong interest in visible laser diodes (LDs), which have several important applications in solid-state lighting,1 photodynamic therapy (PDT),2 medicine, and visible light communication.3 The available high-efficiency visible LDs are primarily made of III-V and III-N material systems. These light-emitting devices are either InGaN/GaN-based, covering the violet to green wavelengths (405–530 nm), or InGaP/InAlGaP-based, covering the red (632–690 nm) wavelengths. High-efficiency LDs in the green-yellow-orange (GYO) (550–620 nm) wavelengths are still not available. Large strain and indium segregations in InGaN/GaN prevent the growth of high-quality LDs with emission beyond 540 nm.4 For the InGaP/InAlGaP material system, more Al incorporation in the active layer shortens the emission wavelength; however, oxygen-related defects severely reduce their efficiency.5 In addition, the small band offset between the quantum well (QW) and barriers leads to low carrier confinement and large carrier leakage current.6

The research community has performed a substantial amount of work in an effort to produce LDs in the GYO range. For example, in 1992, room temperature (RT) orange emission at approximately 625 nm with 6 pairs of multi-quantum barriers was reported, but with a low-output power per facet of approximately 1 mW.7 Although the devices were lasing at RT, the growth process was complicated and costly. In 2002, devices emitting in the range of 560–590 nm based on strained InGaP quantum wells were grown on a transparent, compositionally graded InAlGaP buffer. The devices emitted spontaneous emission at a relatively low optical power of 0.18 $\mu$W per facet.8 Although InGaP/InAlGaP LDs emitting approximately 650 nm can achieve a high differential quantum efficiency of 85%,9 the device quality degrades and the threshold current increases as the constituent atoms are tuned to reduce the lasing wavelength.10 Only by applying high pressure and low temperature was yellow lasing demonstrated at 574 nm from red InGaP/InAlGaP LDs; however, this process is not practical in terms of real applications.11,12

The other route explored by researchers was to utilize post-growth quantum well intermixing (QWI) on InGaP/InAlGaP laser structures. Two approaches were considered that resulted in bandgap blueshifts, namely, impurity-induced disordering (IID) and impurity-free vacancy disordering (IFVD). In the IID intermixing process, a thin impurity film, for example, Zn, is deposited, followed by annealing below the growth temperature to allow the impurity atoms to diffuse into the structure. Because the impurities subsequently degrade the quality of the laser structure, no active devices have been fabricated using this method.13,14

The IFVD technique involves the deposition of a dielectric (impurity free), such as silicon dioxide (SiO2), on the sample surface. In this technique, defects with a lower density than that obtained using the IID technique are created. After the deposition of the dielectric, group-III atoms, i.e., Al and Ga, interdiffusion between the QW and the barrier interfaces occurs, thereby blueshifting the bandgap of the material without introducing severe damage to the QWs.10,15 Because this process is essentially impurity free, the degradation of the optical and electrical properties is minimized.

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In addition, this technique was used to selectively intermix different areas of QW lasers to achieve bandgap-tuned devices in the monolithic integration of photonic elements.\textsuperscript{16–18} Beernink \textit{et al.} were first to apply this technique on the InGaP/InAlGaP material system using plasma-enhanced chemical vapor deposition (PECVD) to deposit a SiO\textsubscript{2} capping layer and reported a negligible bandgap blueshift.\textsuperscript{18} Another group annealed bare (uncapped) and SiO\textsubscript{2}-capped samples of InGaP/InAlGaP QWs at 900 °C for 4 h and showed only a slight bandgap blueshift of 10 nm.\textsuperscript{19} Kowalski \textit{et al.} reported a differential shift of 100 meV using 200-nm sputter-deposited SiO\textsubscript{2}, whereas no wavelength shift was observed for devices capped with PECVD-deposited SiO\textsubscript{2}. Hamilton \textit{et al.}, from the same group, reported an intermixed InGaP/InAlGaP laser emitting at approximately 670 nm. The device intermixed with this method was blueshifted (29 nm, 91 meV) and demonstrated lasing at 640 nm.\textsuperscript{20} Recently, hafnium oxide (HfO\textsubscript{2}) was also used to induce IFVD, and a bandgap shift of 18 nm was reported for the InGaP/InAlGaP material system emitting at 670 nm.\textsuperscript{21} There are no reports of IFVD at the short wavelength of 640 nm or with a large degree of intermixing in this material system.

As discussed, SiO\textsubscript{2} film is reported to inhibit intermixing process for dielectric film thicknesses of 200 nm to 500 nm. In this work, we introduce a novel, strain-induced QWI technique utilizing a relatively thick, 1-μm, PECVD-deposited SiO\textsubscript{2} layer that induces a high compressive strain on the InGaP/InAlGaP laser structure with an as-grown wavelength of ~640 nm. The high compressive strain interacts with the internal tensile strain during the annealing process, creating point defects at the interface between the QW and the barrier, thus enabling Al/Ga interdiffusion. This interdiffusion affects the material composition, strain, QW size, and material ordering/disordering, thereby causing blueshifting of the bandgap. Furthermore, cyclic annealing is reported to enhance the degree of intermixing.\textsuperscript{22} In this technique, cyclic annealing and impurity-free capping promoted the intermixing process with no extended defects that can degrade the material quality. A maximum blueshift of ~75 nm (250 meV) is achieved, which is the highest ever reported in this material system. Bandgap-tuned, light-emitting devices are shown to emit in the red, orange, and yellow range at RT; these results are evidence of the superiority of this technique to shift the bandgap without deteriorating the material quality. This technique may pave the way for high-efficiency emitters in the orange and yellow wavelength range in the InGaP/InAlGaP material system.

II. EXPERIMENTS

A single QW (SQW) InGaP/InAlGaP laser structure was grown on a 10°-offcut GaAs substrate using metal-organic chemical vapor deposition (MOCVD), as shown in Fig. 1(a). The structure consisted of a 200-nm thick, Si-doped, GaAs buffer layer with a carrier concentration of 1–2 × 10\textsuperscript{18} cm\textsuperscript{-3}, a 1-μm thick n-In\textsubscript{0.5}Al\textsubscript{0.5}P with a carrier concentration of 1 × 10\textsuperscript{18} cm\textsuperscript{-3} lattice-matched lower cladding layer, a 6-nm thick InGaP SQW sandwiched between two 80-nm undoped In\textsubscript{0.5}Al\textsubscript{0.5}P/GaAs waveguide layers, a 1-μm thick Zn-doped In\textsubscript{0.5}Al\textsubscript{0.5}P with a carrier concentration of 1 × 10\textsuperscript{18} cm\textsuperscript{-3} lattice-matched upper cladding, a 75-nm lattice-matched p-In\textsubscript{0.5}Ga\textsubscript{0.5}P with a carrier concentration of 3 × 10\textsuperscript{18} cm\textsuperscript{-3} barrier reduction layer, and a 200-nm thick highly doped p-GaAs with a carrier concentration of 2–3 × 10\textsuperscript{19} cm\textsuperscript{-3} contact layer. The laser was designed to have peak emission at 635 ± 3 nm. Fig. 1(b) shows the photoluminescence (PL) spectrum at RT.

A set of samples were cleaved to approximately 2 × 2 mm, and then a 1-μm thick film of SiO\textsubscript{2} was deposited. The samples were annealed using rapid thermal process (RTP) at temperatures between 700 °C and 1000 °C, with annealing durations between 30 s and 240 s, along with bare (uncapped) as-grown samples. The blueshifts induced by the above procedure were measured at RT using a PL spectroscopy apparatus equipped with a 473 nm cobalt laser as the excitation source. The PL of all the samples was measured after the processing. Samples blueshifted to the red, orange, and yellow regions were chosen for electrical characterization, which involves the application of back and front contacts only. Electroluminescence (EL) emissions were measured using a fiber placed very close to the sample.

III. RESULTS

A. Intermixing process optimization

In this study, a relatively thick film of SiO\textsubscript{2} and a higher annealing temperature were utilized to induce high strain and enhance QWI. The optimum process conditions are obtained by the QWI process that provides a high degree of
intermixing while maintaining strong PL intensity, narrow full wave at half maximum (FWHM), and good surface morphology in the QW sample. Maintaining these parameters ensures the high quality of the laser structure after the intermixing process for further laser fabrication. These parameters are analyzed in Secs. III A 1–III A 3.

1. Optimization of the annealing temperature

We studied the effect of the annealing temperature on group III elemental intermixing to find the threshold temperature at which the intermixing process initiates. The annealing duration was set to 120 s, and the samples were annealed at different temperatures from 700°C to 1000°C. Fig. 2(a) shows the PL spectra for the InGaP/InAlGaP samples as a function of RTP temperature. The SiO2-capped samples exhibit negligible blueshifts for temperatures in the range of 700°C–900°C. Above 900°C, the wavelength blueshift increased rapidly with increasing annealing temperature. Fig. 2(b) presents the blueshift and FWHM obtained for SiO2-capped samples as a function of temperature. The blueshift started at temperatures of 900 and 925°C. Above these temperatures, the blueshift rapidly increased to over 60 nm (200 meV) at 1000°C. Up to 975°C, all the samples retained high PL intensity with a negligible increase in FWHM while maintaining good surface morphology. The uncapped samples were also annealed, and a negligible blueshift was obtained, as shown in Fig. 2(b). To further investigate the effect of annealing below the activation temperature, we annealed the SiO2-capped samples for several cycles and obtained a negligible blueshift (not shown). Therefore, the threshold temperature for initiating interdiffusion is 900°C.

To determine the optimum annealing temperature, we studied the blueshift as a function of annealing temperature above the threshold temperature of 900°C, as indicated in Fig. 3. For simplicity of analysis, we selected regions that showed a linear intermixing process. The slope of the linear fit provides the rate of intermixing, which is 1 meV/°C and 3 meV/°C for annealing temperatures of 900–950°C and 950–1000°C, respectively. This quantitative analysis confirms our earlier observation that the degree of intermixing rapidly increases above 925°C, in this case, by more than a factor of 3 for 950–1000°C. Based on the above analysis, 950°C is the critical temperature for enhanced intermixing in this material system.

2. Optimization of the annealing duration

We further investigated the effect of the annealing duration. We selected 950°C and varied the annealing duration from 30 s to 240 s. Fig. 4(a) shows the PL spectra of annealed samples for varied annealing durations from 30 s to 240 s. A progressive blueshift was observed as the annealing time increased. The increase of blueshift with annealing time was almost linear compared to the exponential increase of the bandgap shift against temperature in Sec. III A 1. In Fig. 4(b), the peak emission and the FWHM are extracted and plotted against the annealing time. The high crystal quality of the active layer after annealing below 180 s is indicated by the FWHM curve. As the annealing time was increased to 240 s, the PL intensity decreased, with subsequent broadening of the FWHM. A maximum bandgap shift in peak wavelength of up to 595 nm was obtained after 240 s of annealing, with an equivalent bandgap shift of 45 nm (~140 meV). A noticeable blueshift only occurred after an annealing duration of 90 s; therefore, the threshold time for 950°C is approximately 90 s.

To determine the optimum annealing duration, we studied the blueshift as a function of annealing duration at 950°C. The slope of the linear fit line provides the rate of intermixing, which is 0.67 meV/s for annealing durations of 30 s to 240 s. A critical duration of 45 s is extrapolated from the linear fit, as shown in Fig. 5.

3. Optimization of cyclic annealing

We achieved a large degree of blueshifting at 240 s, but the associated decrease in PL intensity and broadening of the FWHM
FWHM suggest the material quality deteriorated. As mentioned above, cyclic annealing was reported to enhance the material quality of the intermixed structure. In this section, the objective was to determine the optimum duration for cyclic annealing at 950 °C. For each sample, we fixed the annealing duration and repeated the process for up to three cycles. The annealing durations were 30 s, 60 s, 90 s, 120 s, 180 s, and 240 s. Fig. 6 shows the blueshift versus the number of cycles. Cycle 0 represents the peak wavelength before intermixing. As shown in Fig. 6, the same wavelength, yellow (580 nm), for example, can be achieved by several schemes, e.g., 2 cycles of 240 s or 3 cycles of 120 s. However, note that the PL intensity and the surface quality of the shorter durations are better. From the above study, we determined 950 °C and 30 s as the optimum annealing temperature and duration, respectively. With this process, we were able to blueshift the peak emission from red (640 nm) to yellow (565 nm) (~250 meV) with number of cycles of annealing, which is largest blueshift reported for this material system.

B. Intermixed emitters

The temperature, annealing duration, and dielectric thickness are relatively higher than that used in other material systems. The main concern is the top surfaces which tend to crack if capped with a dielectric film thicker than 1.5 μm. Therefore, the optimum annealing process at 950 °C for 30 s was chosen as described in the above. The samples were annealed for 2, 5, and 9 cycles to obtain the desired wavelengths of red (620 nm), orange (595 nm), and yellow (575 nm), respectively. Emitters were prepared by removing the capping dielectric and applying front and back contacts on the samples. Broad area pumping of current was applied on the samples. Fig. 7 shows the images of the as-grown laser and the intermixed emitters. Efficient emission was obtained, even for the yellow emitter, where the band offset is less than 150 meV. Fig. 8 shows the EL spectra of the spontaneous emission of the emitters with the as-grown red laser. The EL peak was approximately 5–10 nm redshifted from the PL peak due to heating induced by the broad-area pumping. Details of the characterization of these light-emitting diodes (LEDs) will be reported elsewhere.

Fig. 8(b) shows the turn-on voltages of the intermixed emitter. The yellow emitter has a turn-on voltage of 2.1 V, which is approximately the bandgap of the device emitting at the operating wavelength of 585 nm. The emitter also has a low series resistance (<5 Ω). These good electrical characteristics for the yellow emitter with the highest degree of intermixing are evidence of the superiority of our intermixing process. In addition, the result confirms that the dopant concentration in the top contact and the cladding layers remained at a similar level and did not diffuse into the active region of the laser structure, even after the successive annealing at elevated temperatures.
IV. DISCUSSION

As shown in Fig. 9, we believe the intermixing process in our work is due to the high strain applied and the elevated temperature. The deposited SiO$_2$ film has a thermal expansion coefficient ($\alpha = 0.5 \times 10^{-6}/\degree{C}$) that is lower than that of the p-GaAs cladding layer ($\alpha = 5.73 \times 10^{-6}/\degree{C}$). During annealing, the mismatch in expansion at the interface of the dielectric and semiconductor induces high compressive strain, whereas the QW is under tensile strain. The opposite strains applied on the barriers create point defects at (1) the interface of the dielectric and the laser structure and (2) the interface of the barrier and the QW, as shown in Fig. 9. These point defects, with energy given to the atoms by heat, facilitate the interdiffusion of (group III) atoms between the QW and the barrier.

To emphasize on the relationship between applied strain and the intermixing process, we intentionally increased the applied strain by increasing the thickness of the SiO$_2$ capping film. This is performed in separate runs, in which batch-to-batch process variation is expected. Fig. 10(a) shows the normalized spectra of samples annealed at slightly low temperature of 925 $\degree{C}$ for 120 s. The capping film thicknesses are 200 nm, 500 nm, 800 nm, 1000 nm, and 2000 nm. As the thickness of the capping film increases, the amount of blue-shift increases as expected. At a thickness of 2000 nm, the dielectric film started cracking, and some areas of the top surface were damaged. Fig. 10(b) shows the increase in bandgap blueshift as a function of dielectric film thickness up to 37 nm. This validated the effect of strain in enabling the intermixing process.

The effects of the intermixing process on the laser structure can be categorized into 1 bandgap effect and 2 propagation effects. Regarding the bandgap, the intermixing process causes a blueshift that is related to the change in material composition, the change in strain, and the change in QW shape. After interdiffusion of Ga and Al atoms from the barrier into the QW, the InGaP ternary material is transformed to InAlGaP. An increase in Al content increases the bandgap and causes a bandgap blueshift. In addition, the lattice constant of the new InAlGaP is greater than that of InGaP, causing a relaxation in the strain. The relaxation in strain also

FIG. 7. Images of the as-grown LD with peak PL emission of 638 nm (a), and the intermixed laser structures having the front and back contacts with peak PL emissions of 620 nm (b), 595 nm (c), and 575 nm (d). The EL peak wavelengths are indicated accordingly.

FIG. 8. Plot of: (a) the EL spectra for as-grown and intermixed devices emitting at 628 nm, 602 nm, and 585 nm and (b) the voltage versus current characteristics of the corresponding devices.

FIG. 9. Intermixing mechanism of the strain-induced QWI on the InGaP/InAlGaP material system. Opposite strains applied on the barriers cause point defects to be generated at the QW-barrier interface. As the point defects are created, and with sufficient energy given to the atoms, they started to interdiffuse between the QW and barrier. [The built-in strain is illustrated.]
causes a bandgap blueshift. Finally, the change in the QW shape changes the bandgap of the QW. As the thickness of the QW increases, a small redshift is expected due to the quantum effect. However, the cumulative effect is an increase in the bandgap, as shown in the PL spectra.

Regarding propagation effects, the point defects created during the QWI process increase the optical losses and the scattering points. Second, the guided mode will be affected by the change of the emission wavelength and the change in refractive indices due to the migration of Al atoms from the barriers to the QW. In addition, the GaAs absorption increases as the wavelength decreases toward yellow. These factors reduce the efficiency of the device. Finally, as mentioned before, high Al-content active layers grown by MOCVD or molecular beam epitaxy (MBE) have low efficiency due to the oxygen-related defects. Here, we demonstrated the increase in the Al content in the QW using a novel approach that may eliminate oxygen-related defects in the active layer.

V. CONCLUSION

We presented a novel strain-induced QWI technique on an InGaP/InAlGaP red laser structure that induces a large degree of bandgap blue shift. By optimizing the annealing temperature, the annealing duration, and the number of cycles of annealing, we made the first observation of a bandgap blueshift as large as 250 meV (75 nm) in this material system at the short wavelength of ~640 nm. The QWI samples were characterized by PL and EL measurements, the results of which indicated the high quality of the material and operational devices. The novel technique presented in this paper may represent the solution for producing high-efficiency AlGaInP devices at the shorter wavelengths of yellow and orange color and has potential application for producing passive sections, e.g., the non-absorbing window, in the InGaP/InAlGaP material system.

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