Multi-wavelength lasers fabricated by an Al layer controlled quantum well intermixing technology

J. H. Teng and S. J. Chua[a)]
Center for Optoelectronics, Department of Electrical Engineering, National University of Singapore, Singapore 119260

Y. H. Huang, G. Li, and Z. H. Zhang
Institute of Material Research and Engineering, 3 Research Link, Singapore 117602

A. Saher Helmy and J. H. Marsh
Department of Electronics and Electrical Engineering, University of Glasgow, G12 8QQ, United Kingdom

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We report that the shift in the band gap of $Al_{0.3}Ga_{0.7}As/GaAs$ quantum well structures can be precisely controlled by an Al layer buried between a spin-on silica film and a wet-oxidized GaAs surface. The blueshift in wavelength of the $Al_{0.3}Ga_{0.7}As/GaAs$ quantum well photoluminescence (PL) depends linearly on the thickness of the buried Al layer. By changing the Al layer thickness, the PL peak wavelength can be tuned from 7870 Å for the as-grown sample to 7300 and 7050 Å after 20 and 45 s rapid thermal annealing at 850 °C, respectively. Applying this technology, Al layers with different thickness, i.e., no Al, 200 and 300 Å thick, were applied to the oxidized GaAs surface in three adjacent regions with 200 μm spacing on a quantum well laser structure sample. Three wavelength lasers were successfully fabricated in a single chip by a one step rapid thermal annealing. All the lasers have similar threshold current and slope efficiency. © *2000 American Institute of Physics.* [S0021-8979(00)00819-7]

I. INTRODUCTION

The tremendous need for high data transfer rate in this information age demands the use of optical communication systems. This is also one of the driving forces for the development of the photonic integrated circuit (PIC) and the optoelectronic integrated circuit. The development of PIC, which requires the integration of both the active and passive devices, such as semiconductor lasers, switches, modulators, functional waveguides, photodetectors, etc., will produce breakthroughs in the areas of information processing and transfer. One key technology to implement monolithic integration of optoelectronic and photonic devices is the spatially selective modification of the band gap energy of quantum well (QW) across a wafer. The band gap energy of the QW structure determines the operating wavelength of photonic devices, such as semiconductor lasers and modulators. Other optoelectronic components, such as passive waveguides and optical interconnects, require the band gap energy to be larger than that of the operating photon energy to avoid absorption.

There are several methods to realize the monolithic integrated photonic circuit. One method involves the growth-etch-regrowth technique[1,2] and the other is selective epitaxy growth.[3,4] Both of them require critical growth and etch conditions. An alternative method is the postgrowth quantum well intermixing, QWI, which has attracted much interest in the past decade. In this technique, the band gap of a QW structure is modified selectively by intermixing the group III/or group V atoms in the well and barrier to form an alloy. In addition, the refractive index is also modified due to the increase in band gap energy. Most GaAs based semiconductor heterostructures are thermally stable at elevated temperatures. For example, the diffusion coefficient of Al in an undoped AlAs–GaAs heterostructure is on the order of 10^{-19} cm^2/s at 850 °C.[5] However, the intermixing process can be greatly enhanced due to the existence of point defects, either vacancies or interstitials, in the vicinity of the interface of the QWs. Several methods have, therefore, been developed to enhance interdiffusion through controlling the point defect concentration at QWs.[6,7] Methods to enhance QWI can be differentiated by the means of introducing point defects such as dopant diffusion,[8] ion implantation,[9] physical surface damage,[10,11] and interfacial reactions.[12–14] Localized QW intermixing is capable of blueshifting the QW band gap energy by several tenths of meV in pre-defined regions on the wafer. Previous work has demonstrated that the impurity-free vacancy disordering (IFVD) has minimum effects on the electrical properties, crystal quality, and optical propagation losses.[7] It is an especially advantageous technique if the intermixed QWs are to be used as active device regions.

For IFVD, the degree of QW intermixing could be spatially controlled across a wafer if one were capable of laterally controlling the number of generated vacancies, which subsequently redistribute within a heterostructure.[6] IFVD is usually implemented by coating the semiconductor with a dielectric encapsulant layer followed by thermal annealing. Although the exact mechanism by which Ga out-diffuses from the semiconductor surface (usually GaAs) into the dielectric layer (usually SiO_2) is not yet fully understood,

a)Electronic mail: elecsj@nus.edu.sg

group III vacancies are generated at the interface as a result of the Ga out-diffusion. Diffusion of these vacancies through a heterostructure substantially enhances QWI. Recently, Yuan *et al.* reported that the anodic GaAs oxide can enhance the quantum well intermixing,[15] and Cohen *et al.* reported that the interdiffusion could be greatly reduced by applying a 275 Å Al layer on the oxidized GaAs surface.[13] In this work, the Al layer was buried between a SiO_2 dielectric encapsulation film and the oxidized GaAs surface of $Al_{0.3}Ga_{0.7}As$/GaAs QW structures. We will show that the band gap shifts can be precisely controlled by varying the thickness of the buried Al layer. Applying this technology, a three-wavelength laser was successfully fabricated in a single wafer. This technique has the potential of being an effective means of fabricating integrated opto-electronic and photonic devices.

II. SAMPLES AND EXPERIMENTS

An $Al_{0.3}Ga_{0.7}As$/GaAs three QW sample was used in the QW intermixing experiment and a GRIN-SCH $Al_{0.3}Ga_{0.7}As$/GaAs laser sample which has exactly the same active region structure as the three QW sample was used in the multi-wavelength laser fabrication. They were all grown by metalorganic vaporphase epitaxy (MOVPE). For the sample with QW intermixing, a 200-nm-thick GaAs layer was first grown on a GaAs substrate followed by a 20-nm-thick $Al_{0.3}Ga_{0.7}As$ layer. After growth of three 7-nm-thick GaAs QWs separated by 25-nm-thick $Al_{0.3}Ga_{0.7}As$ barriers, a further 300-nm-thick $Al_{0.3}Ga_{0.7}As$ layer was grown and finally the sample was capped with 30 nm of GaAs. All the epitaxial layers were undoped. For the laser sample, first a 200-nm-thick GaAs doped with Si to $2\times10^{18}\,cm^{-3}$ was grown on a *n*-type GaAs substrate. Then a 100-nm-thick graded layer changing from GaAs to $Al_{0.7}Ga_{0.3}As$ and a further 800-nm-thick $Al_{0.7}Ga_{0.3}As$ layer were grown both doped with Si to $2\times10^{18}\,cm^{-3}$ to form the lower cladding layer. The graded index confinement layer was a 100-nm-thick undoped layer gradually changing from $Al_{0.7}Ga_{0.3}As$ to $Al_{0.3}Ga_{0.7}As$. The active region of the laser structure consisted of three 7 nm GaAs QWs separated by 25 nm $Al_{0.3}Ga_{0.7}As$ barriers. The upper confinement layer was a 100-nm-thick layer gradually changing in composition from $Al_{0.3}Ga_{0.7}As$ to $Al_{0.7}Ga_{0.3}As$. The confinement layers and the laser active region were all undoped. The upper cladding layer was a 900-nm-thick $Al_{0.7}Ga_{0.3}As$ layer doped with C to $5\times10^{17}\,cm^{-3}$ and a 100-nm-thick layer C doped to $2\times10^{19}\,cm^{-3}$ with composition changing from $Al_{0.3}Ga_{0.7}As$ to GaAs. The C dopant comes from the trimethylgallium (TMGa) during the MOVPE growth. The sample was finally capped with a 100-nm-thick GaAs contact layer doped with C to $2\times10^{19}\,cm^{-3}$. The QW intermixing experiments were carried out with the $Al_{0.3}Ga_{0.7}As$/GaAs three QW structure. Samples were oxidized at 450 °C for 2 h in wet O_2 ambient. The wet O_2 was obtained by bubbling O_2 through the deionized water held in a bath at 90 °C. An Al layer was then deposited on the oxidized GaAs surface using e-beam evaporation. For the QW intermixing experiment, the Al layer thickness was varied from 0 to 50 nm for different samples.

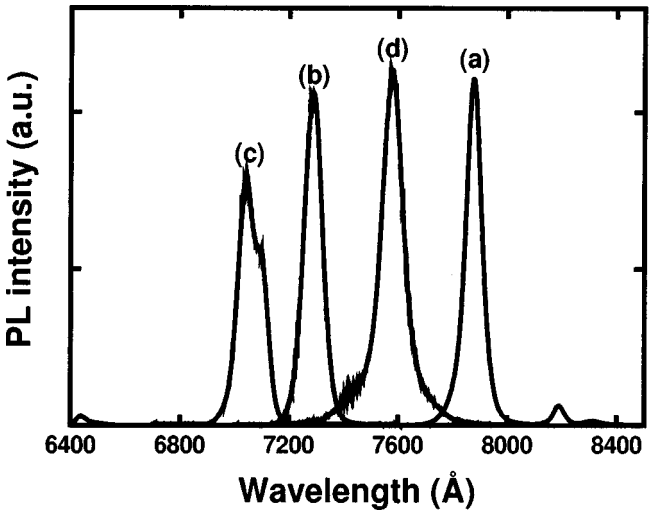

FIG. 1. Low temperature photoluminescence (7 K) spectra of $Al_{0.3}Ga_{0.7}As$/GaAs QW structures. (a) As-grown sample. (b) After 20 s of thermal annealing with a silica layer coated on an oxidized surface. (c) After 45 s of thermal annealing with a silica layer coated on an oxidized surface. (d) After 20 s of thermal annealing with a 20-nm-thick Al layer buried between a coated silica layer and an oxidized surface. The annealing temperature was 850 °C.

After the Al layer was evaporated, all the samples were immediately coated with a spin-on silica layer with a thickness of 150nm. Previous studies have shown that the spin-on silica is an effective dielectric encapsulant layer for IFVD.[12] Thermal annealing was conducted in a rapid thermal processor with the temperature controlled by a pyrometer. The samples were proximity capped and placed in a quartz chamber in N_2 ambient. Photoluminescence (PL) measurements were performed at 8 K. Samples were mounted on the same cold finger in a cryostat. The excitation source was an Ar^+ laser tuned to the wavelength of 488 nm. The PL signals were dispersed by a 0.75 m monochromator and detected by a GaAs photomultiplier.

III. QW INTERMIXNG RESULTS

For the impurity free vacancy enhanced interdiffusion (IFVD) in GaAs systems induced by a deposited SiO_2 layer, it is believed that an increased Ga vacancy concentration generated by the chemical reaction between GaAs and SiO_2 at an elevated temperature is responsible for the enhanced interdiffusion. The properties of SiO_2 may have a great effect on enhancing QW intermixing.[16] The spin-on silica film can reduce the threshold temperature at which significant QW intermixing takes place. From previous studies, it is clear that, compared to a bare surface, the oxidation of GaAs surface can enhance the QW intermixing.[13,15] Even though the exact reason is not clear, it is assumed that Ga vacancies were generated by the chemical reaction during oxidation. The spin-on silica coated on the GaAs native oxide surface strongly enhances the quantum well intermixing, as shown in Fig. 1 [see curves (a), (b), and (c)]. It can be seen that for the sample with the spin-on silica and oxidized GaAs surface, the blueshift of $Al_{0.3}Ga_{0.7}As$/GaAs QW was about 59 and 82 nm after 20 and 45 s of thermal annealing at 850 °C, respec-

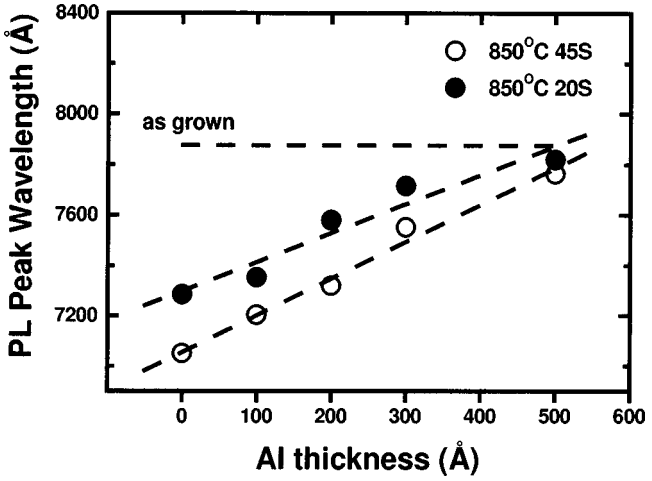

FIG. 2. Low temperature photoluminescence peak wavelength as a function of the thickness of the Al layer buried between the spin-on silica layer and the oxidized GaAs surface of an $Al_{0.3}Ga_{0.7}As/GaAs$ QW structure. Thermal annealing was conducted at 850 °C for 20 s (solid circles) and 45 s (open circles). Dashed lines are the guides to the eyes.

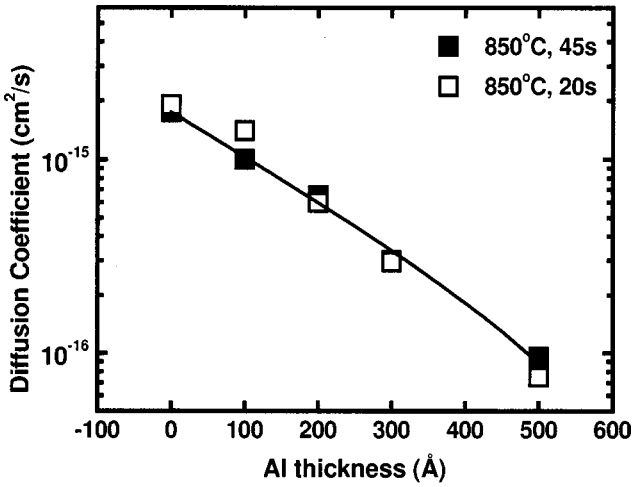

FIG. 3. Interdiffusion coefficient at 850 °C as a function of the thickness of the Al layer buried between the spin-on silica layer and the oxidized GaAs surface of $Al_{0.3}Ga_{0.7}As/GaAs$ QW structure. Thermal annealing time was 20 s (open squares) and 45 s (solid squares). The solid line is an exponential fitting curve.

tively. This is consistent with our previous report.[12] If we assume the intermixing process to be independent of Al concentration, the diffused Al composition profile $W(z)$ across the QW structure is given by the double error function[17]

$$W(z)=W_0\left[1+\frac{1}{2}\mathrm{erf}\left(\frac{z-\frac{l}{2}}{2L_D}\right)-\frac{1}{2}\mathrm{erf}\left(\frac{z+\frac{l}{2}}{2L_D}\right)\right], \quad (1)$$

where W_0 is the initial Al concentration in the barrier, l is the width of the as-grown quantum well, z is the growth direction, L_D is the diffusion length defined as $L_D=\sqrt{Dt}$, where D is the Al–Ga interdiffusion coefficient and t is the annealing time. By using Eq. (1) and the measured PL peak energy blueshift, the calculated interdiffusion coefficient was found to be $\sim 1.7\times 10^{-15}\,\mathrm{cm}^2/\mathrm{s}$. The same interdiffusion coefficient was obtained for both annealing times, implying that the vacancy concentration at the QW remains constant over this period of time. To a first approximation, this implies that the rate of Ga out-diffusion from the oxidized GaAs surface into the spin-on silica cap remains unchanged within the annealing period. The concentration gradient of Ga vacancies present in the region adjacent to the surface, resulting from the Ga out-diffusion, drives a constant flux of Ga vacancies through the structure. As a result, QW intermixing progresses with a constant interdiffusion coefficient, as the thermal annealing time increases.

One sample with a 20-nm-thick Al layer buried between the spin-on silica layer and the oxidized GaAs surface was subjected to the same 20 s thermal annealing process as that without a buried Al layer. It can be seen in Fig. 1 when comparing to the PL peak wavelength of the as-grown sample [curve (a)], the Al layer suppresses the blueshift from 59 nm [see curve (b)] to 30 nm [see curve (d)]. The amount by which blueshift is suppressed depends on the thickness of the Al layer. As can be seen in Fig. 2, for the two annealing times used (20 and 45 s), the blueshift decreases almost linearly with an increase of the Al layer thickness. Using a 50-nm-thick Al layer, the QW intermixing is almost totally suppressed. The interdiffusion coefficient was calculated and plotted as a function of the Al layer thickness in Fig. 3. As can be seen, the inter-diffusion coefficient can be changed by more than one order of magnitude simply by changing the Al layer thickness. The dependence of interdiffusion coefficients on the Al layer thickness is well fitted by an exponential function.

Previous reports have shown that a thin Al layer (27.5 nm) on the oxidized surface can substantially reduce the interdiffusion coefficient from $3\times 10^{-17}\,\mathrm{cm}^2/\mathrm{s}$ to less than $2\times 10^{-19}\,\mathrm{cm}^2/\mathrm{s}$ at 950 °C.[13] The QW intermixing is therefore almost totally suppressed. This clearly indicates that the interfacial reactions between the oxidized GaAs surface and the Al layer modifies the generation of Ga vacancies at an elevated annealing temperature. With a spin-on silica layer, a considerable blueshift still occurs even with a 30-nm-thick Al layer on the oxidized GaAs surface when annealed at 850 °C (see Fig. 2). The interdiffusion coefficient in this case is of the order of $10^{-16}\,\mathrm{cm}^2/\mathrm{s}$ (see Fig. 3). As postulated in Ref. 13, the chemical potential still drives diffusion of atomic Ga out of the GaAs beneath the oxidized surface into the spin-on silica at an elevated temperature.

In our structures, the wet-oxidized GaAs surface forms a thin mixture of amorphous GaO_x and AsO_x. At an elevated annealing temperature, AsO_x usually decomposes and GaO_x transfers into crystalline Ga_2O_3. The buried Al layer can react with SiO_2 or GaO_x during thermal annealing. Reactions of SiO_2 with Al produce Al_2O_3 and Si. The diffusion of atomic Si into the structure would lead to impurity-induced QW intermixing.[7] This does not appear to be happening here since QW intermixing is suppressed with increasing Al layer thickness. Reactions of the buried Al layer with GaO_x would reduce the oxide to produce atomic Ga and AlO_x. Partial annihilation of Ga vacancies by the atomic Ga would reduce the interdiffusion coefficient and consequently the degree of QW intermixing. The reaction of the Al layer with SiO_2 will

also change the property of the silica film which will in turn change the solubility of Ga. Also the dense and thermally stable AlO_x layer formed after Al evaporation may act as a diffusion barrier to limit the mass transport of atomic Ga from GaAs to the spin-on silica layer. All these effects will consequently limit the number of out-diffusion of Ga atoms and hence the number of vacancies available in the heterostructure for enhancing the Al–Ga interdiffusion. Using appropriate masking and lift-off technology, the deposition of Al layers with varying thickness on different regions on the oxidized GaAs surface can result in different degrees of QW intermixing across a wafer. This technology is a very promising means for lateral band gap control. Below we will demonstrate the laser device fabricated by applying this technology.

IV. MULTI-WAVELENGTH LASER

The wafer used in fabricating the multi-wavelength laser is a three quantum well GRIN-SCH structure grown by low pressure metal organic chemical vapor deposition as described above. It has as the same active region, the three QWs as used in the samples for the QW intermixing experiment. The wafer was first cleaned by diluted HCl solution and then oxidized at the same condition as described above. After the wet thermal oxidation, Al layers with different thickness, i.e., no Al, 200 Å Al, and 300 Å Al, respectively, were deposited on the GaAs native oxidized surface by a two step photolithography and lift-off in the three adjacent regions with 200 μm spacing. Then silica was spun on the whole wafer and baked at 120 °C for 1 h. Rapid thermal processing (RTP) was conducted in N_2 ambient at 875 °C for 45 s. The temperature selected here was higher than that used in the QW intermixing experiment. This is because the laser structure has a thicker and highly *p*-type doped upper-cladding and top-capping layer. A previous report and our study showed that the high concentration *p*-type doping would suppress the band gap blueshift due to the negatively charged Ga vacancies.[8,18] After RTP the GaAs oxide/Al/SiO_2 layers were all removed with buffered HF and a new 200 nm SiO_2 was deposited on the GaAs surface. Oxide stripe lasers with 6 μm width were formed at the center of each intermixed region with a space of 200 μm by lithography and etching. *P*-type contact of Cr(200 Å)/Au (2000 Å) was formed using lift-off technology. *N*-type metal of AuGe (800 Å)/Ni (100 Å)/Au(1500 Å) was deposited on the backside of the substrate after thinning the wafer to 100 μm. After alloying, lasers with 500 μm length were cleaved from the wafer and mounted *p* side up on a copper heat sink for laser characteristic measurement.

The lasers were tested under pulse conditions at room temperature. The current pulse width was 400 ns and repetition rate was 5 KHz. Figure 4 shows the spectra of the lasers emitting with different lasing wavelengths. Lasers operating at three different wavelengths of 8307, 8430, and 8536 Å, which correspond to no Al, 200 and 300-Å-thick Al layer buried between the GaAs oxide and the silica film, were integrated in one chip with a size of 600 μm×500 μm. The integrated laser can emit either three wavelengths simultaneously or each wavelength separately. The upper part of Fig. 4 shows the three light spot pattern captured by a charge coupled device camera when the three lasers were pumped simultaneously. The distance between the light spots is 200 μm. The spectrum of lasers fabricated from the as-grown sample were also illustrated in Fig. 4 as a reference, which showed a lasing wavelength of 8616 Å. Multi-mode spectra were observed since they were gain-guided Fabry-Pérot lasers without any special mode-selection design.

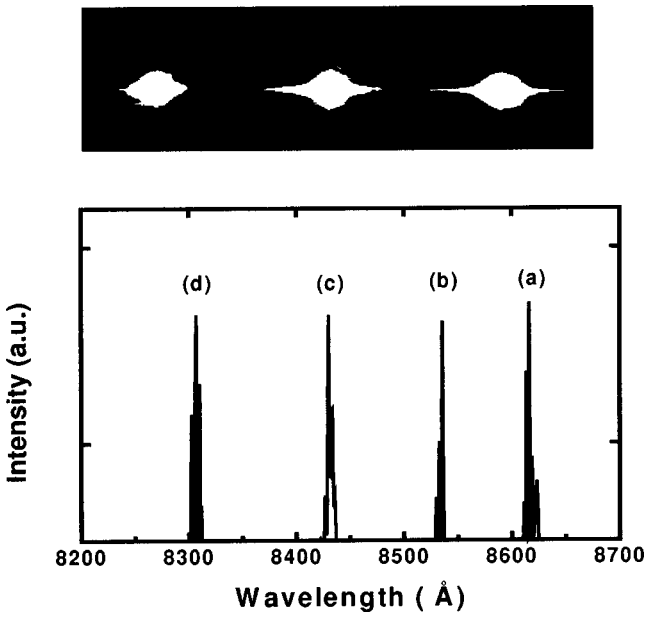

FIG. 4. Laser spectra with different blueshift by controlling the degree of quantum well intermixing with an Al layer buried between the native oxide of GaAs and the silica film. (a) As-grown laser as reference, (b) with 300 Å Al layer, (c) with 200 Å Al layer, (d) without any Al layer, and with silica on top of the oxidized GaAs surface. The RTP was conducted at 875 °C for 45 s. The upper picture is the light spot pattern at the facet of the three-wavelength laser.

Maintaining device performance is very important for the integration of different optoelectronic components on a single wafer. Any serious degradation in the performance of the Al covered and band gap tuned laser will negate the advantages of this technique. Figure 5 illustrates the light-

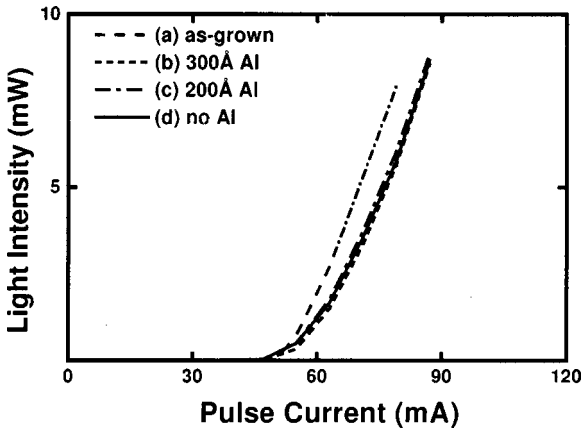

FIG. 5. Light-current characteristics for the oxide stripe lasers with band gap tuned by Al controlled QW intermixing operating at room temperature.

current characteristics for the lasers fabricated with the material (i) as grown, (ii) SiO_2 capped and intermixed, (iii) with 200-Å-thick and, (iv) with 300-Å-thick Al covered plus SiO_2 capping and intermixed. The lasers fabricated from the as-grown sample had a threshold current of 52 mA and an external differential quantum efficiency of 22% facet. The wavelength tuned lasers from either silica covered only region or from Al covered region all showed a similar threshold current of about 57 mA and with external differential quantum efficiency of 20% facet. There is a 5 mA increase in threshold current and a slight decrease in differential quantum efficiency compared to the as-grown sample. This small difference means that the quality of the material remains good with this Al controlled band gap tuning technology.

V. CONCLUSIONS

In conclusion, an Al layer located between the wet-oxidized GaAs surface and a spin-on silica cap was used to control the band gap shift of QW structures during QW intermixing. The blueshift of $Al_{0.3}Ga_{0.7}As/GaAs$ QW decreases linearly as the Al layer thickness increases. Using this process, the interdiffusion coefficient could be changed from 1.5×10^{-15} cm^2/s to 7.5×10^{-17} cm^2/s at 850 °C. Lasers operated at three different wavelengths were successfully integrated on one chip by applying different thickness of Al coverage during quantum well intermixing. No significant increase in threshold current and differential quantum efficiency was observed in band gap tuned lasers by a buried Al layer compared to the lasers fabricated from the as-grown material. This process has the potential of being an effective means to achieve spatially localized selective QW intermixing across a wafer, an essential technology for fabricating integrated optoelectronic and photonic devices.

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