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# $SiN_x$-induced intermixing in AlInGaAs/InP quantum well through interdiffusion of group III atoms

Ko-Hsin Lee,[1] Kevin Thomas,[1] Agnieszka Gocalinska,[1] Marina Manganaro,[1] Emanuele Pelucchi,[1,2] Frank H. Peters,[1,2] and Brian Corbett[1]
[1]*Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland*
[2]*Department of Physics, University College Cork, Cork, Ireland*

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We analyze the composition profiles within intermixed and non-intermixed AlInGaAs-based multiple quantum wells structures by secondary ion mass spectrometry and observe that the band gap blue shift is mainly attributed to the interdiffusion of In and Ga atoms between the quantum wells and the barriers. Based on these results, several AlInGaAs-based single quantum well (SQW) structures with various compressive strain (CS) levels were grown and their photoluminescence spectra were investigated after the intermixing process involving the encapsulation of thin $SiN_x$ dielectric films on the surface followed by rapid thermal annealing. In addition to the annealing temperature, we report that the band gap shift can be also enhanced by increasing the CS level in the SQW. For instance, at an annealing temperature of 850 °C, the photoluminescence blue shift is found to reach more than 110 nm for the sample with 1.2%-CS SQW, but only 35 nm with 0.4%-CS SQW. We expect that this relatively larger atomic compositional gradient of In (and Ga) between the compressively strained quantum well and the barrier can facilitate the atomic interdiffusion and it thus leads to the larger band gap shift. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4764856]

## I. INTRODUCTION

AlInGaAs-based multiple quantum well (MQW) structures have a larger conduction band offset compared to the conventional InGaAsP MQW structures and have been investigated intensively in recent years as the active layers of lasers and modulators for high-speed and high temperature operation.[1] The ability to transmit and modulate high-speed data in an un-cooled temperature environment makes AlInGaAs MQW structures very appealing as the base material for the realization of photonic integrated circuits (PICs).

As a means to achieve monolithic integration of different optoelectronic functions, the quantum well intermixing (QWI) technique is a potential post-growth approach to engineer the bandgap on selected areas through the interdiffusion of certain atoms between the quantum wells and the barriers.[2,3] The process steps associated with the QWI are generally simple in comparison with the asymmetric twin-waveguide (ATG)[4] approach to PICs, where delicate taper designs are required to transfer light in the vertical plane or with the epitaxial regrowth approach where regrowth[5] with Al containing materials is difficult. Among the various intermixing methods, the top surface being encapsulated with a dielectric film prior to thermal annealing[6–12] is advantageous since it does not require sacrificial layers or external atoms and thus potential additional damage to the quantum well (QW) structure can be minimized. In this intermixing scenario, the creation and diffusion of vacancies created at the interface of the dielectric film and semiconductor top layer[6] are a prerequisite and those point defects may in turn cause the inbuilt strain within QW to be relaxed through the atomic interdiffusion. It is then possible to control the extent of the bandgap shift by properly choosing the dielectric capping layers and the annealing conditions including temperature and duration.[7–9] Different dielectric films such as $SiO_2$, $SiN_x$, $SrF_2$, and $TiO_2$ have been demonstrated to induce or prevent the intermixing in diverse quantum well structures. Besides, the intermixing mechanism on different material systems has been investigated and can be ascribed to the disordering of different atoms. It has been shown that the intermixing of group V atoms (As and P) is responsible for the bandgap shift in InGaAsP-based QW structures;[10] while the interdiffusion of In and Ga atoms can be found in intermixed GaInNAs/GaAs QW structures.[11]

We have previously reported promoted and inhibited intermixing in AlInGaAs-based MQW laser structures by depositing $SiN_x$ and $SiO_2$ dielectric capping layers, respectively, followed by rapid thermal annealing (RTA), where the differential emission wavelength was measured to be more than 100 nm.[12] In this paper, we analyze the composition information in intermixed AlInGaAs-based MQW structures by secondary ion mass spectrometry (SIMS) and demonstrate that the bandgap shift is mainly attributed to the interdiffusion of In and Ga between quantum wells and barriers. Based on this result, we suggest that the bandgap shift can be more pronounced if the In/Ga composition ratio is higher in the QW compared to that in barrier. The correlation of In-Ga compositional variation on bandgap blue shift is then demonstrated here as an additional degree of freedom leading to intermixing in an AlInGaAs single quantum well (SQW) structure. Hence, by intentionally increasing the level of compressive strain (CS) in a quantum well, a controlled bandgap shift can be achieved at a lower annealing temperature. In this case, the degradation in performance of devices due to back diffusion of dopants (especially Zn) and/or grown-in defects is expected to be reduced.

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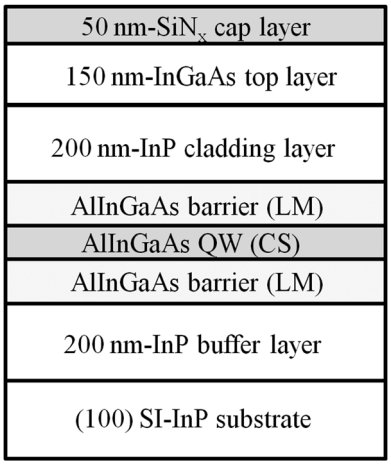


FIG. 1. Schematic of the undoped AlInGaAs SQW layer structure and the $SiN_x$ cap layer.

## II. EXPERIMENT

### A. SIMS analysis of AlInGaAs-MQW laser structure

The SIMS analysis of an AlInGaAs-based MQW laser structure with epitaxial layers grown by metal organic vapor phase epitaxy (MOVPE) on a (100) Si-doped InP substrate was performed. The active region consists of five 1.2%–$Al_{0.07}In_{0.71}Ga_{0.22}As$ compressively strained wells with a thickness of 6 nm separated by 10 nm-thick tensile-strained $Al_{0.22}In_{0.49}Ga_{0.29}As$ barriers. The as-grown photoluminescence (PL) peak was measured to be 1521 nm. The MQW was sandwiched between AlInGaAs separate confinement heterostructure (SCH) layers and with a p-type (Zn) InP upper cladding layer and a p-type InGaAs contact layer doped with Zn. The detailed layer structure can be found in Ref. 12. Samples to be intermixed were deposited with a 50-nm-thick $SiN_x$ dielectric film by plasma-enhanced chemical vapor deposition (PECVD) on the InGaAs contact layer and were then annealed in a nitrogen ambient at 720 °C for 120 s. A thin (50 nm) film is used as we found that thicker layers are cracked following RTA. This suggests that the differential expansion may play a role in the generation of vacancies. After this intermixing process, the measured PL peak was blue shifted to 1410 nm. Under the same annealing condition, the thermal-induced bandgap blue shift was limited for a sample without any capping layer where the PL peak was shifted to 1512 nm. The composition variation within quantum wells and barriers of intermixed and non-intermixed samples was measured using SIMS with $Cs^+$ as the primary ion beam and the results were compared to the as-grown MQW.

### B. AlInGaAs structure with compressively strained single quantum well

The correlation of the In/Ga ratio between quantum well and barrier on the bandgap blue shift was studied in a series of undoped AlInGaAs SQW structures grown on (100) semi-insulating InP substrates by MOVPE.[13] Figure 1 shows the schematic of the layer stacking, where the thickness of quantum well was designed to be 6-7 nm. The atomic compositional ratios of Al, In, and Ga in the AlInGaAs SQW structures were adjusted to give a variation in In composition ratio from 53% to 71% corresponding to an increase of the CS from 0% to 1.2%. The PL emission peak was maintained around 1530 nm when altering the proportions of Al and Ga atoms, as summarized in Table I. The CS-AlInGaAs SQW was embedded within two lattice-matched (LM) AlInGaAs barriers (PL = 1240 nm) with a thickness of 10 nm after which a 200 nm-thick InP cladding layer and a 150 nm-thick InGaAs top layer were grown. A 50 nm-thick $SiN_x$ dielectric layer was then deposited on the sample surfaces using PECVD. The samples were then annealed by RTA in a nitrogen ambient at temperatures between 700 °C and 850 °C for 120 s. After annealing, both the $SiN_x$ dielectric layer and the InGaAs top layer were removed by selective wet etching. The bandgap shift was determined by PL measurements carried out using a 1042 nm-wavelength pump source.

## III. SIMS ANALYSIS IN INTERMIXED ALINGAAS-MQW LASER STRUCTURE

Figures 2(a) and 2(b) present the relative composition profiles of In and Ga atoms in the intermixed AlInGaAs-MQW region (PL peak ~ 1410 nm) and in the reference sample (PL peak ~ 1521 nm) before and after the intermixing process. The compositional variations in the five wells and six barriers can be clearly resolved by the SIMS analysis. The composition ratio of In atoms in the quantum wells is found to be reduced in the intermixed sample and those In atoms appear to diffuse into the barrier layers (Figure 2(a)). In contrast, the Ga atoms move from the barriers into the wells and this leads to an increase in the Ga composition ratio in the quantum wells after the QWI process (Figure 2(b)). However, the same compositional variations are not seen in the non-intermixed sample (PL peak ~ 1512 nm), which also experienced the high temperature

TABLE I. The atomic compositional ratios of the designed compressively strained quantum wells (0%, 0.4%, 0.8%, and 1.2%) and LM barrier.

| | | | Atomic compositional ratio | | | | |
|---|---|---|---|---|---|---|---|
| Layer | Thickness (nm) | Strain | A1 | Ga | In | As | Designed PL peak (nm) |
| QW | 6 | 0%-CS | 0 | 0.47 | 0.53 | 1 | 1530 |
| QW | 7 | 0.4%-CS | 0.05 | 0.36 | 0.59 | 1 | 1530 |
| QW | 7 | 0.8%-CS | 0.09 | 0.26 | 0.65 | 1 | 1530 |
| QW | 7 | 1.2%-CS | 0.12 | 0.17 | 0.71 | 1 | 1530 |
| Barrier | 10 | LM | 0.19 | 0.28 | 0.53 | I | 1240 |

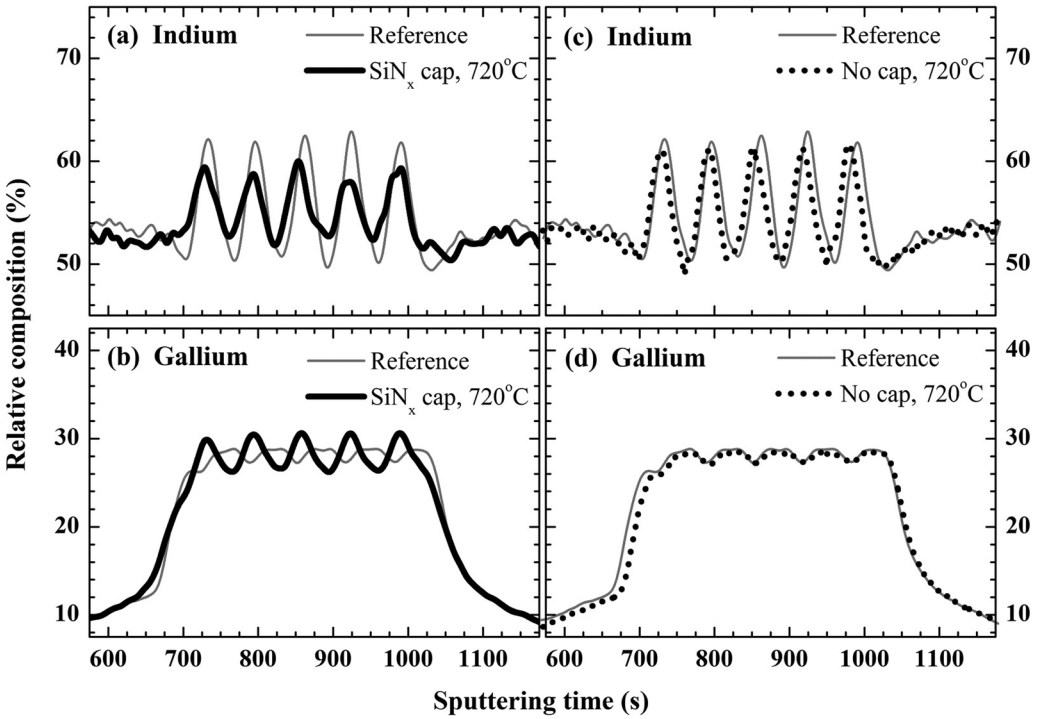


FIG. 2. Profile of the relative atomic compositions through the AlInGaAs multiple quantum wells and barriers measured by SIMS for (a) In and (b) Ga atoms in the intermixed sample and for (c) In and (d) Ga atoms in the non-intermixed sample. Both samples were annealed at 720 °C for 120 s and only the intermixed one was with a $SiN_x$ dielectric film capping layer. The data are compared to a reference (no annealing) sample.

annealing step but was not capped with a $SiN_x$ layer. As shown in Figures 2(c) and 2(d), the composition ratios of In and Ga atoms in quantum wells and barriers of non-intermixed sample have similar levels to those of the reference (no heat treatment) sample. Therefore, we can mainly attribute the bandgap blue shift by the applied QWI technique to the interdiffusion of In-Ga atoms between QWs and barriers. This observation is consistent as the atomic disordering found in the intermixed GaInNAs/GaAs MQW material system.[11]

The relative composition ratio of Al atoms is found to be unchanged within MQW region (Figure 3(a)), but Al seems to outdiffuse close to the top of SCH guiding layer. Moreover, after the high temperature annealing process, the SIMS profile shows that the Zn dopants have back-diffused into the SCH guiding layer and have accumulated in the MQW region in the sample where the intermixing has been promoted (Figure 3(b)). This will increase the optical waveguide loss due to intervalence band absorption as well as causing sub-bandgap absorption and may degrade the device performance.

## IV. QWI ON UNDOPED ALINGAAS-SQW STRUCTURES WITH VARIOUS COMPRESSIVE STRAINS

Figure 4 shows the photoluminescence spectra of the 1.2%-CS AlInGaAs SQW structure (as-grown PL peak ~1543 nm) with PECVD $SiN_x$ cap layer, which have been annealed at different temperatures for 120 s. When the intermixing was performed at higher annealing temperatures, the PL emission peaks generally blue shifted and thus increased the bandgap in the SQW. At an annealing temperature of 850 °C, the measured PL peak was 1430 nm, which results in a differential wavelength of 113 nm (~63 meV

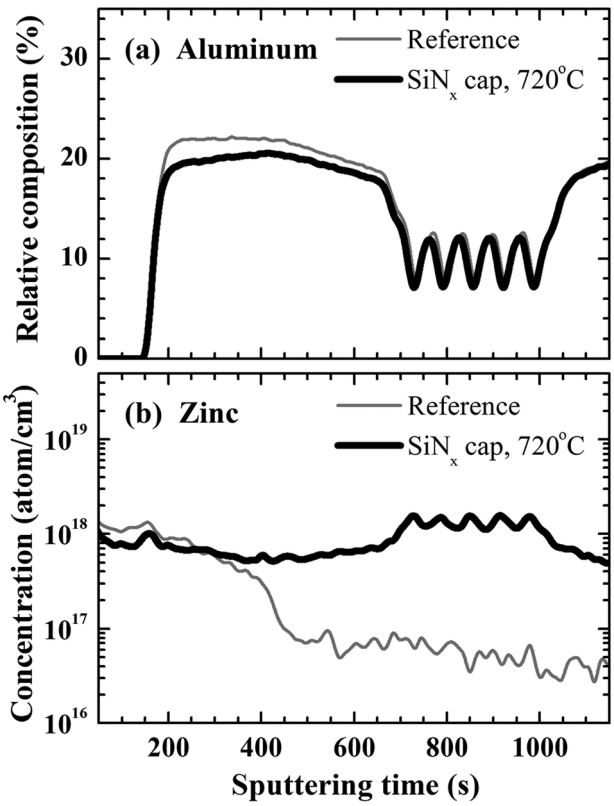


FIG. 3. (a) Profile of the relative atomic composition measured by SIMS for Al atom in intermixed AlInGaAs multiple quantum wells and barriers as well as in top AlInGaAs SCH guiding layer. (b) Variation of Zn concentration after the intermixing process. The intermixed sample was annealed at 720 °C for 120 s with a $SiN_x$ dielectric film capping layer. The data are compared to a reference (no annealing) sample.

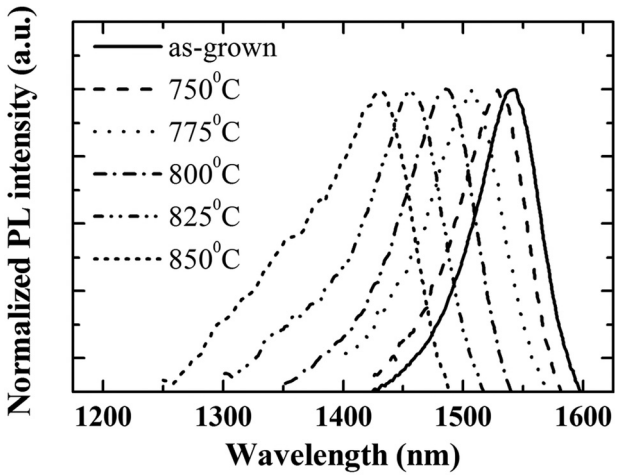


FIG. 4. PL spectra of undoped AlInGaAs SQW (1.2%-CS) structures capped with PECVD SiNx dielectric films followed by rapid thermal annealing at various annealing temperatures for 120 s.

bandgap difference). Note that a higher annealing temperature is required to achieve a significant blue shift of the bandgap in these undoped samples thus demonstrating the contributing role of Zn doping in the earlier samples. In addition to the annealing temperature, the level of compressive strain in the SQW can also be a factor to enhance the magnitude of the bandgap shift. As presented in Figure 5, the intermixing is promoted at a large compressive strain level in the SQW within the range of annealing temperatures investigated. For instance, the PL blue shift can reach more than 110 nm for the sample with 1.2%-CS SQW at an annealing temperature of 850 °C, but it is only 35 nm with 0.4%-CS SQW. As described in Sec. II B, the composition ratios of In atom in the lattice-matched AlInGaAs barrier and the 0%-CS (i.e., lattice-matched) quantum well were both designed to be 0.53 (see Table I). Therefore, there was no distinct compositional gradient of In atoms between barrier and well thus reducing the driving force provided through the diffusion of defects under high temperature annealing. In contrast, for 1.2%-CS quantum well, the indium composition ratio was 0.71 and this relatively larger indium compositional gradient

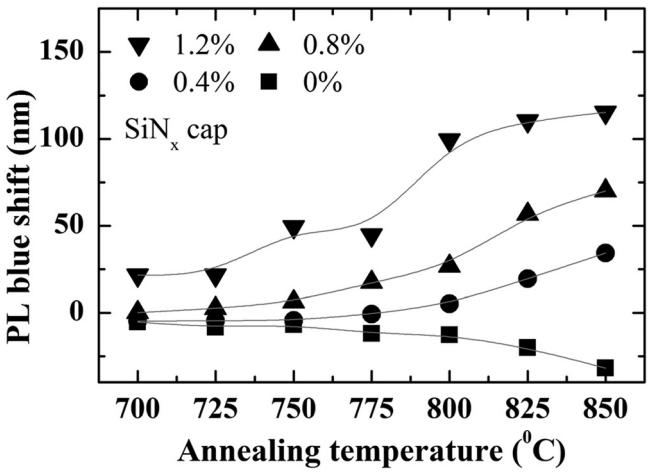


FIG. 5. PL blue shifts at various annealing temperatures for undoped AlInGaAs SQW structures with 0%, 0.4%, 0.8%, and 1.2%-CS in the quantum well.

between the barrier and the quantum well is expected to facilitate atomic interdiffusion. Thus, the correlation between the strain in SQW and the bandgap shift indicates that the interdiffusion of group III atoms between QW and barriers can be further promoted through the design of an increased differential in the In to Ga composition ratio in the SQW, which can thus lead to a more pronounced bandgap shift. Hence, in order to obtain the same amount of bandgap shift, the annealing temperature can be lowered when a highly compressively strained quantum well is employed which, in turn, can reduce the diffusion of dopants such as Zn.

## V. CONCLUSIONS

We have analyzed the composition profiles in intermixed and non-intermixed AlInGaAs-based MQW structures by SIMS and have shown that the bandgap blue shift is strongly dependent on the interdiffusion of In and Ga atoms between the QWs and the barriers, while the composition ratio of Al atom within the MQW region is unchanged. We speculated that a larger initial indium compositional gradient between QW and barrier should facilitate the atomic interdiffusion at a given annealing temperature. Several AlInGaAs SQW structures with various CSs were grown using MOVPE by modifying mainly the In composition ratios within the quantum well. We measured an enhancement of the bandgap shift by increasing the level of the compressive strain in the QW.

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