On the increased efficiency in InGaN-based multiple quantum wells emitting at 530 - 590 nm with AlGa_N interlayers

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Abstract

InGaN/AlGa_N/Ga_N-based multiple quantum wells (MQWs) with AlGa_N interlayers (ILs) are investigated, specifically to examine the fundamental mechanisms behind their increased radiative efficiency at wavelengths of 530 - 590 nm. The Al_zGa_{1-z}N ($z \sim 0.38$) IL is $\sim 1 - 2$ nm thick, and is grown after and at the same growth temperature as the ~ 3 nm thick InGa_N quantum well (QW). This is followed by an increase in temperature for the growth of a ~ 10 nm thick Ga_N barrier layer. The insertion of the AlGa_N IL within the MQW provides various benefits. First, the AlGa_N IL allows for growth of the In_xGa_{1-x}N QW well below typical growth temperatures to achieve higher x (up to ~ 0.25). Second, annealing the IL capped QW prior to the Ga_N barrier growth improves the AlGa_N IL smoothness as determined by atomic force microscopy, improves the InGa_N/AlGa_N/Ga_N interface quality as determined from scanning transmission electron microscope images and x-ray diffraction, and increases the radiative efficiency by reducing non-radiative defects as determined by time-resolved photoluminescence measurements. Finally, the AlGa_N IL increases the spontaneous and piezoelectric polarization induced electric fields acting on the InGa_N QW, providing an additional red-shift to the emission wavelength as determined by Schrodinger-Poisson modeling and fitting to the experimental data. The relative impact of increased indium concentration and polarization fields on the radiative efficiency of MQWs with AlGa_N ILs is explored along with implications to conventional longer wavelength emitters.

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Statement of Original Work:

This paper describes the fundamental mechanisms behind the increased PL intensity and smoother interfaces for InGa_N QW capped with an AlGa_N interlayer. This manuscript is the original work of the authors' and has not been published nor has it been submitted simultaneously elsewhere. All authors have checked the manuscript and have agreed to the submission.

1. Introduction

The efficiencies of InGaN based light-emitting diodes (LEDs) and laser diodes (LDs) have increased rapidly in the last decade,[1-4] with the highest efficiencies achieved at violet-blue wavelengths (400-465nm) with $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum wells (QWs) that contain modest indium concentrations ($x \sim 0.05 - 0.15$). Increasing the indium concentration beyond $x \sim 0.15$ can result in green to red wavelengths, but at the expense of efficiency [5], resulting in the well-known “green gap” for visible wavelength light emitters [2; 6]. This lack of efficiency at higher indium concentrations also impacts solar cells, where ideally, InGaN should span nearly the entire solar spectrum [7]. Yet, because of the poor material quality at longer wavelengths, InGaN-based solar cells exhibit lower power conversion efficiencies [8; 9] when compared to more conventional solar cell materials.

The exact reason for the decreasing InGaN efficiency is unknown; however several possible causes have been suggested. These include: 1) the higher lattice strain in the InGaN QWs which leads to increased defect formation [10] and surface roughening [11; 12], resulting in increased non-radiative recombination and reduced carrier confinement; 2) the lower growth temperatures required to incorporate indium, resulting in the incorporation of impurities[13; 14], point defects [15], and V-type defects[16], all of which have been proposed to act as non-radiative recombination centers [17; 18]; and 3) larger piezoelectric-polarization-induced electric fields which separate the QW electron and hole wavefunctions and decrease their overlap, resulting in a decreased spontaneous recombination rate [19].

These purported causes for reduced InGaN efficiency are relevant to the results presented here and to the recent ground-breaking improvements in longer-wavelength LEDs at Toshiba [20-23]. For their improvement the Toshiba group used AlGaIn interlayers (ILs) to cap the InGaIn QWs to achieve external quantum efficiencies (EQEs) of ~20% for yellow (560 nm) LEDs [22] and ~3% for red (629 nm) LEDs [23]. For the yellow emitting LEDs, this efficiency

is approximately two times greater than that of the standard planar InGaN/GaN MQW LEDs [22]. In addition to the Toshiba work, prior work by Lin *et al.* showed that internal quantum efficiencies (IQEs) of green wavelength lasers on semipolar substrates could be improved using AlGaIn barriers compared to GaN or InGaIn barriers [24]. The Toshiba group proposed possible causes for the improved efficiency with AlGaIn ILs, including improved heterointerfaces, higher InGaIn crystalline quality with fewer non-radiative defects, and a polarization field shift of electron and hole wavefunctions. However the exact contribution and validity of each of these contributions to the improved emission is uncertain.

In this paper, metalorganic vapor phase epitaxy (MOVPE) grown InGaIn-based MQWs capped with similar AlGaIn ILs are investigated, specifically to explore and comment on the relative contributions to the increased efficiency for green-gap wavelengths (530-590 nm).

2. Experimental Details

The QW structures were grown in a Veeco D125 short-jar MOVPE system. Growth temperatures were controlled using mid-IR pyrometers with direct optical access to the growth surface and confirmed with an emissivity-corrected UV ($\sim 405\text{nm}$) pyrometer [25]. GaIn templates were grown on c-plane sapphire at 500 torr (66.7 kPa) and 1050 °C using trimethylgallium (TMGa) and NH_3 in H_2 and N_2 using the two-step approach of Nakamura [26]. The first $\sim 2\text{ }\mu\text{m}$ thick GaIn templates were undoped followed by $\sim 2\text{ }\mu\text{m}$ Si doped GaIn using SiH_4 to a carrier concentration of $5 \times 10^{18}\text{ cm}^{-3}$ as measured by Hall Effect. The GaIn templates have total threading-dislocation densities averaging $\sim 8 \times 10^8\text{ cm}^{-2}$ as determined by x-ray diffraction analysis [27]. The QW active regions were grown at 300 torr (40.0 kPa) using 15 standard liters per minute (SLM) of NH_3 and 10 SLM of N_2 [28]. Prior to the growth of the QW structures, an $\text{In}_y\text{Ga}_{1-y}\text{N}$ underlayer (UL) ($y = 0.025\text{-}0.035$) was grown at 850 °C for 30 min to a thickness of $\sim 150\text{-}170\text{ nm}$ using 97 $\mu\text{mole/min}$ trimethylindium (TMIn) and 43 $\mu\text{mole/min}$ of

TMGa. The InGaN UL was capped with 8 nm Si-doped GaN barrier layer, prior to the growth of the first QW.

The five period InGaN/AlGaIn/GaN MQWs were grown in the following way. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ QWs and $\text{Al}_z\text{Ga}_{1-z}\text{N}$ interlayers (IL) were grown at fixed growth temperatures ranging from 700 to 740 °C, while the GaN barrier layers were grown from 800 to 900 °C. The sequence consisted of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ QW growth, followed by turning off the TMIn and turning on the TMAI for the growth of the $\text{Al}_z\text{Ga}_{1-z}\text{N}$ IL, after which both the TMGa and TMAI were turned off. The $\text{Al}_z\text{Ga}_{1-z}\text{N}$ IL has $z = 0.38$ and a thickness that varies from 1.0 - 1.9 nm as quantified by x-ray diffraction (XRD). After the IL growth, the temperature was increased 800 to 900 °C for the GaN barrier growth. After the GaN barrier growth, the temperature was reduced for the next QW and IL growth sequence. After the last sequence, the film was capped with a GaN barrier. The precursor flows were 97 $\mu\text{mole/min}$ TMIn and 6.9-27.8 $\mu\text{mole/min}$ of TMGa for the QW, 18.4 $\mu\text{mole/min}$ TMAI and 13.9 $\mu\text{mole/min}$ of TMGa for the IL, and 13.9 $\mu\text{mole/min}$ of TMGa for the GaN barrier layer.

Following growth, XRD analysis was performed using $\omega/2\theta$ scans about the (0002) reflection of GaN using a Panalytical X'Pert MRD Pro X-ray diffractometer. The XRD scans were fit using X'Pert Epitaxy 4.0 dynamic diffraction software to deduce the indium and aluminum concentrations and layer thicknesses. For each structure the fits are made under the assumption of full coherency strain of the InGaIn and AlGaIn layers to the underlying GaN lattice, discrete changes in alloy concentrations, and no compositional grading of the interfaces. The influence of compositional grades at the top InGaIn/GaN interface has been described by Lee *et al.* and leads to diminishing peak intensity for higher order superlattice peaks [29]. The IL aluminum concentrations and thicknesses were determined separately using XRD analysis of the same MQW growth run without TMIn flowing during the MQW growth. Usually, the aluminum and indium concentrations can be obtained to within 1% and thicknesses of alloy layers to ~ 0.1 nm.

Scanning transmission electron microscopy (STEM) images were acquired with a FEI Company Titan G2 80-200 operated at 200kV and equipped with a spherical aberration corrector on the probe forming optics and four silicon-drift (SDD) energy-dispersive X-ray detectors (EDX). The X-ray detectors were used to verify the composition of the layers while high-resolution high-angle annular dark-field (HAADF) STEM images were used to verify layer thickness and interface quality. Samples for STEM were prepared by focused ion beam (FIB) milling with a FEI Company Helios-600 dual-beam FIB-scanning electron microscope with the final thinning using 2 kV Ga⁺.

Optical emission from these structures was measured by room temperature PL using a Nanometrics RPM2000 PL mapper equipped with a continuous wave, 5mW, 325 nm HeCd laser. Time-resolved PL (TRPL) data was measured separately using a Ti:Sapphire laser operating at 407 nm with a pulse width of 2 ps. PL decay times were measured using a Hamamatsu streak camera with an attached 0.5 m spectrometer resulting in lifetime data that were measured from a 20 nm spectral band at the center of the PL peak. The overall system temporal resolution was ~ 25 ps.

3. Modeling

The influence of the spontaneous and piezoelectric polarization on the QW emission was calculated using the nextnano3 Schrodinger-Poisson solver software [30]. The simulation uses band structure parameters and effective masses for the electrons and holes from Vurgaftman and coworkers [31]. These simulations provide the energy band diagram, emission wavelengths, and the overlap of electron and hole wavefunctions within the QWs.

Obviously, the AlGa_N IL changes the polarization induced fields within the InGa_N QW, producing changes to the electron and hole wavefunctions, and their resulting overlap and radiative recombination rate. For comparisons where only the AlGa_N IL thickness and the QW indium concentration change, most variables involved with the recombination rate, such as the carrier occupation probability and carrier mass, change only slightly and therefore are assumed constant. With this assumption and only considering the QW ground states, the radiative

recombination rate (R_{rad}) depends on the square of the electron and hole wavefunction overlap, (I), or, $R_{rad} \propto |I|^2$.

The AlGaIn and InGaIn growth conditions (specifically temperature) could also affect the number of non-radiative recombination centers in the QWs. Therefore it is necessary to determine not only R_{rad} , but also the radiative efficiency (η_{rad}) which includes the radiative and non-radiative recombination rate (R_{nr}), and can be expressed as:

$$\eta_{rad} = \frac{R_{rad}}{(R_{nr} + R_{rad})} \quad (1)$$

The value of R_{nr} is determined by comparing results from the simulation to the experimental data. R_{nr} includes both Shockley-Read-Hall (SRH) and Auger recombination, but at the low PL pump intensities used in this work SRH dominates R_{nr} and Auger can be ignored.

Lastly, in comparing the simulated η_{rad} to experimental PL intensity of the MQWs (P_{out}), the absorption (A) of the input pump power (P_{in}) and light extraction efficiency (η_{ext}) of the emitted light is assumed to be identical for every sample. The radiative efficiency excited by PL can be expressed as:

$$\eta_{rad} = \frac{P_{out}}{(P_{in} \cdot A \cdot \eta_{ext})} \quad (2)$$

If all samples are measured with the same input power, the dominator in Eqn. 2 is constant for all samples, making the experimental P_{out} proportional to η_{rad} .

4. Results

4.1 Increase in emission wavelength with indium composition with and without ILs.

In Fig. 1, PL intensities are plotted vs. the resulting wavelength for AlGaIn IL capped InGaIn MQWs (left axis, red circles). Also shown in Fig. 1 are similar InGaIn MQWs without AlGaIn ILs (left axis, blue squares). For this data, the MQW growth temperature is varied to change the emission wavelength. Note that without AlGaIn ILs (blue squares) the QWs decrease in PL intensity as the wavelength increases more rapidly than MQWs capped with AlGaIn ILs (red circles). For example, near ~ 545 nm MQWs with ILs are ~10x brighter than without the ILs,

similar to previous reports [32]. Also shown in Fig. 1 is the emission full width at half maximum (FWHM) for the IL capped MQWs (right axis, green diamonds). For the IL capped QWs, the PL FWHM gradually increases from ~35 nm at $\lambda = 501$ nm to 73 nm at $\lambda = 586$ nm. For the uncapped QWs, a larger increase in the FWHM occurs with a FWHM of 32 nm at $\lambda = 515$ nm up to FWHM of 77 nm at 545 nm.

4.2 Heterointerface crystal quality with and without ILs.

InGaN MQWs with and without AlGaIn ILs are imaged using STEM as shown in Fig. 2. The HAADF STEM images are collected using low electron current (<75 pA) to avoid imaging damage of the QWs [33]. In Fig. 2(a), an annular dark-field STEM image measured at the [11-20] zone is shown of a conventional, five period InGaIn/GaN MQW stack. The inset in Fig. 2(a) shows a magnified section of one of the QWs. For this MQW, the $\text{In}_x\text{Ga}_{1-x}\text{N}$ QW is grown at a temperature of 730 °C resulting in $x \sim 0.20$ and capped with ~1 nm of GaN prior to heating the sample to 800 °C to complete the GaN barrier growth. A more abrupt atomic contrast is observed at the bottom of the QW at the GaN/InGaIn interface compared to the top InGaIn/GaN interface which shows a more gradual change in vertical atomic contrast (3-6 atomic planes). From EDX measurements (not shown), the indium tails into the GaN barrier layer over a distance of 1.5 to 2.0 nm. The top interface roughness is likely the result of multiple step height formation [11] and/or increased indium compositional grading [29].

In contrast to the rougher top interface shown in Fig. 2(a), the InGaIn/AlGaIn(IL)/GaN top interface has improved interface abruptness as shown in Fig. 2(b). This STEM image measured at the [10-10] zone shows the InGaIn QW (light contrast) capped by the AlGaIn IL (dark contrast). As shown in Fig. 2(b), the extent of atomic mixing between the InGaIn QW and AlGaIn IL visually occurs over only 1 - 2 atomic planes or ~1 nm as measured from the EDX elemental compositions (not shown). These results indicate smoother and more abrupt heterointerfaces similar to Saito *et al.* [21].

X-ray diffraction (XRD) scans from the $\text{In}_x\text{Ga}_{1-x}\text{N}$ MQWs shown in Figs. 2(a) and 2(b) are shown in Figs. 3(a) and 3(b). Dynamic diffraction analysis of the MQWs from Fig. 3(a) yielded an $x \sim 0.20$ and a thickness of 2.8 nm. For this sample, the PL wavelength is 526 nm with a FWHM of 34 nm. This sample and others grown without the AlGaIn IL capped QWs had a yellowish appearance with a slight hint of gray, suggesting possible indium or gallium metal inclusions. However, no evidence of metal inclusions was observed in the XRD scan [34]. For InGaIn QW growth temperatures less than 725 °C, further graying of the structure is observed along with decreased MQW superlattice peak intensity and complete absence of peaks for angles $< 15^\circ$. All these observations suggest a loss of the top QW/barrier interface fidelity [11; 29].

The $\omega/2\theta$ scan for the AlGaIn IL capped QW from Fig. 2(b) is shown in Fig. 3(b). For this sample the AlGaIn IL capped InGaIn QWs were grown at 700 °C and the GaN barriers at 850 °C. The 700 °C temperature is well below typical QW growth temperatures ($\sim 730^\circ\text{C}$) required to prevent gray appearing QWs and these samples had a pale yellow appearance. Also notable in the XRD scan is the intensity of superlattice peaks out to 13.8° . Observing these higher order superlattice peaks confirms the more abrupt InGaIn/AlGaIn heterointerfaces observed in the STEM cross-section shown in Fig. 2(b). From the diffraction fits, the InGaIn QWs have an indium composition of $x = 0.235$ and are 3.0 nm thick. For this sample, the PL wavelength is 558 nm with a FWHM of 42 nm.

4.3 Influence of annealing on QW interface smoothness and photoluminescence intensity

To determine how the PL intensity is improved by using AlGaIn ILs, the growth cycle of a single QW was studied. For this sequence, four steps along this sequence were grown and quenched in temperature to “freeze in” the structure. The four steps examined were after the growth of the InGaIn QW at 700 °C, after the growth of the AlGaIn IL at 710 °C, after annealing the AlGaIn capped InGaIn QW to 850 °C, and after the growth of the GaN barrier at 850 °C. Of the four samples grown and studied in this sequence, the most dramatic change in PL intensity

and AFM surface structure occurred before and after annealing the AlGa_N IL capped InGa_N QW.

As shown in Fig. 4(a), the PL emission of the non-annealed sample shows two peaks; one near 380 nm which is from the InGa_N UL and one centered around 550 nm which is due to the single InGa_N QW. The PL linewidth for the QW emission is 87 nm and the PL intensity for the InGa_N UL and QW are almost equivalent. An AFM image of this non-annealed AlGa_N IL film is shown in Fig. 4(b). The image shows a mounded structure with an RMS roughness of 0.48 nm. The mounds are suggestive of discrete AlGa_N grains with a size around 15 to 30 nm, however since this size is close to the AFM tip radius, the image is likely a convolution of the AFM tip and surface morphology. In contrast, the PL emission for the annealed sample shown in Fig. 4(c) is dominated by the QW emission which is ~20 times more intense and has a substantially narrower linewidth of 38 nm. The AFM image of this annealed sample is shown in Fig. 4(d) and has a substantially smoother surface morphology with an RMS roughness of 0.18 nm. The increased smoothness after annealing the AlGa_N IL capped QW leads to the improved heterointerfaces observed in the STEM image shown in Fig. 2(b).

Time-resolved PL studies also indicate improvement in the radiative emission rates after annealing. Fig. 5 shows the normalized PL intensity as a function of time for both samples shown in Fig. 4 (solid lines) with single exponential fits (dashed lines) used to quantify the change in PL lifetime. The sample without annealing has a PL lifetime of 2.7 ns while the sample with annealing has a lifetime of 9.3 ns. Since the only difference between the two samples is the annealing, it is expected that the radiative recombination rate is similar for both samples. This implies that the difference in the observed in the PL decay time can be solely attributed to changes in the non-radiative recombination rate. This assumption is supported by noting that the PL decay time for the annealed sample has a decay time closer to a single exponential indicative of a QW more dominated by radiative recombination.

As suggested by Figs. 4 and 5, the choice of barrier growth temperature influences the extent to which the IL capped QW is annealed during growth. To explore this impact further, IL capped QWs samples were grown with barrier temperatures ranging from 800 to 900 °C. Fig. 6(a) shows the PL wavelength (red circles, left-axis) and intensity (blue-squares, right axis) plotted versus the GaN barrier growth temperature. All samples have QWs grown at 710 °C and $\text{Al}_z\text{Ga}_{1-z}\text{N}$ ILs with $z = 0.38$ that are 1.5 nm thick. As shown in Fig. 6(a) the PL wavelength decreases as the GaN barrier temperature increases while the PL intensity increases. The decrease in the PL wavelength is due to a decrease in the QW indium concentration, x , which is listed next to each data point in Fig. 6(a). The PL intensity increase is due to the commonly observed increase in PL intensity as the indium concentration decreases. The decrease in x as the GaN barrier temperature increases suggests during annealing that indium can be lost from the QW.

To get an indication of the heterointerface quality for the samples described in Fig. 6(a), the XRD superlattice FWHM were plotted as a function of angle. This approach for assessing the interface quality for InGaN/GaN MQWs was reported in Refs. [35; 36] based on a formula first derived by Pan *et al.* [37]. In Fig. 6(b), the FWHM of the superlattice peaks are plotted vs. angle (diffraction order) for the same films shown in Fig. 6(a). The main GaN peak ($\omega = 17.27^\circ$) is denoted by arrows and the diffraction order increases away from this value. In Fig. 6(b), the peakwidths for temperatures $> 800^\circ\text{C}$ are offset along the y-axis and a quadratic fit is plotted as solid lines to indicate the change in peakwidth vs. ω . As indicated by the solid lines, larger increases in peakwidth versus angle are observed for MQWs with 800 and 900 °C barrier temperatures, compared to the samples with 850 and 875 °C GaN barriers. This qualitative assessment of interface quality suggests that the 850 and 875 °C GaN barrier films have smoother InGaN/AlGaIn/GaN interfaces compared to the MQW films with 800 or 900 °C GaN barriers.

4.4 Spontaneous and piezoelectric polarization effect

Fig. 7 shows the experimental and theoretical data for MQWs with different IL thicknesses at three different QW growth temperatures. The simulated band diagram (black lines) and electron and hole wavefunctions (red lines) for a single $\text{In}_x\text{Ga}_{1-x}\text{N}$ ($x = 0.215$) QW and $\text{Al}_z\text{Ga}_{1-z}\text{N}$ ($z = 0.4$) ILs with thicknesses of 1 nm (solid lines) and 2 nm (dashed lines) are plotted in Fig. 7(a). The thicker AlGa_N interlayer increases the polarization induced electric fields within the QW increasing the energy gradient (tilt) that further separates the electron and hole states more spatially, but coincidentally brings the wavefunctions closer in energy resulting in longer wavelengths. This is similar what is observed with increased GaN barrier thickness in standard InGa_N/GaN MQWs [9].

The measured PL wavelengths are plotted in Fig. 7(b) as a function of AlGa_N IL thickness, for growth temperatures and nominal indium concentrations, x , of 730 °C and $x \sim 0.19$ (red squares), 710 °C and $x \sim 0.215$ (blue circles), and 700 °C and $x \sim 0.24$ (green diamond). As expected for fixed AlGa_N thickness, reducing the QW growth temperature increases the PL wavelength due to an increase in x . In addition, the wavelength is also influenced by the IL thickness; with a larger red-shift in wavelength observed as the IL thickness is increased. The solid lines in Fig. 7(b) denote the simulations of PL wavelength versus the AlGa_N IL thickness for three different indium concentrations. For these simulations, indium compositions in the QW ($x = 0.19, 0.215$, and 0.23) were chosen to approximately match the measured wavelength and x obtained from the XRD analysis. Clearly, as the IL thickness increases the polarization induced fields within the QWs also increase resulting in a red-shift in wavelength, which matches the experimental trend.

The simulated overlap squared is plotted vs. the IL thickness in Fig. 7(c) for the three different QW indium compositions ($x = 0.19, 0.215$, and 0.23). The decrease in the $(\text{Overlap})^2$ as the IL thickness increases is also observed in the measured PL intensities shown in Fig. 7(d), however,

the measured PL intensities appear offset in absolute R_{rad} . Therefore, polarization induced electric fields are not the only variable influencing the PL intensity with IL thickness. Instead, a change in the non-radiative recombination rate, R_{nr} , must also be contributing to the decreased R_{rad} . The value of R_{nr} is assumed to increase as the indium composition increases and are set to ~ 5 and ~ 10 times higher for the QWs with $x = 0.215$ (710 °C) and $x = 0.23$ (700 °C) indium compositions, respectively, compared to the QWs with 0.19 (730 °C) indium composition. Using these values in Eq. (1) results in the solid line fits to the experimental data shown in Fig. 7(d), and as expected the density of non-radiative recombination centers is heavily influenced by the growth temperature and resulting indium composition.

5. Discussion

5.1 AlGaIn IL increase indium incorporation

In Sections 4.1 and 4.2 it was shown that the AlGaIn IL enables increased indium composition in the InGaIn QWs resulting in longer wavelength emission. During InGaIn growth on the GaN (0001), the surface coverage of indium is limited to $\sim 22\%$ of a monolayer due to indium site blocking further adsorption [38]. Higher indium coverages of $\sim 26\%$ can be obtained if the temperature is lowered below 730 °C [38]. Indium incorporation is also limited due to coherency strain applied by the GaN lattice [39-41] so that the $\text{In}_x\text{Ga}_{1-x}\text{N}$ QW is limited to $x \sim 0.20$ [11] and $x \sim 0.22$ [42]. Indium incorporation above this level requires InGaIn strain relaxation [39-41] which is unlikely since InGaIn QWs are well under the critical thickness for relaxation [41; 43]. Furthermore, there no evidence of strain relaxation or dislocation generation in the STEM images shown in Fig. 2.

However, a slight but quantifiable increase in the indium concentrations up to $x \sim 0.24$ (as shown in Fig. 3(b)) is observed when InGaIn QWs are capped with the AlGaIn IL. For these higher indium concentrations, the QW growth temperature is 700 °C, which is consistent with the higher indium surface coverage ($x \sim 0.26$) observed at lower temperature by Jiang *et al.* [38]. Since the AlGaIn IL is grown at the same temperature as the QW, it is possible that residual surface indium is incorporated into the InGaIn QW and in the first few monolayers of the AlGaIn

IL. Evidence of a thin AlInGaN layer is observed in EDX measurements (not shown) at the InGaN/AlGaN interface, with no evidence of indium segregation throughout the AlGaN IL and GaN barrier layers. This implies that the AlGaN IL helps the QW capture a higher indium concentration which is distributed in the InGaN QW.

5.2 Defect elimination and interface smoothing through annealing

The concentration of non-radiative centers increases as the QW growth temperature decreases as modeled in Fig. 7(d). These non-radiative centers could be impurities such as hydrogen or carbon [13] or more likely point defects [44; 45] formed to partly alleviate lattice strain. Hydrogen present from the incomplete dissociation of the metalorganics is known to readily diffusive in GaN [46; 47] and might be liberated from the AlGaN surface during annealing similar to p-type GaN [48]. The removal of point defects through annealing is less certain [49].

Also notable is the restructuring that occurs to the top AlGaN surface layer after annealing as shown by comparing Figs. 4(b) and 4(d). The as-grown AlGaN IL shown in Fig. 4(b) has a mounded structure expected for low temperature group III nitride growth [12]. However, the smoother AlGaN surface after annealing is puzzling since the 850 °C temperature is too low to cause significant AlGaN decomposition and metal atom rearrangement within the IL.

Instead, the AlGaN surface smoothing might be a combination of strain relaxation and defect removal. Recent work by Ahl and coworkers shows that the surface roughness decreases and the indium incorporation increases as the aluminum concentration is increased in AlInGaN films [50]. Ahl and coworkers inferred that the decrease in surface roughness arises from a change in the growth mode from step flow to two dimensional, while the increase in indium incorporation compensates the increased tensile strain from the higher aluminum fraction in the AlInGaN [50]. For the unannealed and annealed film shown in Fig. 4, no active growth occurs; however annealing the AlGaN/InGaN layers could produce some degree of strain relief, through atomic

mixing near the AlGaIn/InGaIn interface (observed in the EDX scans). In addition there is a slight loss of indium from the QW depending on the annealing temperature, suggesting some degree of indium migration through the AlGaIn IL along with subsequent desorption from the AlGaIn surface. All these observations suggest restructuring the AlGaIn IL surface is possible.

5.3 Polarization field contribution to red-shift in wavelength

The role of polarization induced fields has been suggested [32], but the experiments and simulation presented in Fig. 7 assuredly quantify their role. For example, a MQW with an indium composition of $x = 0.215$ with 10 nm thick GaN barriers has a simulated emission wavelength of ~527 nm. Modeling this same QW with a 2 nm thick $\text{Al}_{0.5}\text{Ga}_{0.5}\text{In}$ IL produces an emission wavelength of ~552 nm verifying that the AlGaIn IL provides a redshift of 25 nm. For actual MQWs this redshift could be less, especially if the heterointerfaces are less abrupt or if carriers screen the polarization fields, as both would have a greater influence on MQWs with ILs compared to ones without.

The red shift achieved by the increased polarization fields the AlGaIn IL produce is attractive to achieve green-gap wavelengths since no additional indium is required in the QWs. Yet, a tradeoff exists between the degree of red-shift achievable and the resultant efficiency. As shown in Fig. 8(c), the $(\text{Overlap})^2$ decreases by a factor of 3 - 6 as the AlGaIn IL thickness increases from 1 to 2 nm depending on indium concentration, while the corresponding wavelength only increases by 4-5 %. As expected, increased red-shifts can be achieved by lowering the QW growth temperature as shown in Fig. 7(b), but growth induced non-radiative defects further lower the radiative efficiency as shown in Fig. 7(d) by decreased radiative efficiency at fixed aluminum concentration. While these non-radiative defects are partly removed during the annealing step, improving their removal will be essential for improving QW emission intensity at these green gap wavelengths. Nevertheless, Fig. 1 demonstrates that QWs with AlGaIn ILs have improved radiative efficiency compared to QW without them.

6. Conclusion

In this paper InGaN/AlGaIn/GaN-based multiple quantum wells (MQWs) with AlGaIn interlayers (ILs) are investigated to examine the origins of their increased radiative efficiency at wavelengths of 530 - 590 nm. The interlayer MQWs are formed by growing InGaIn QWs at temperatures lower than those typically used for green wavelength QWs, growing the AlGaIn IL at the QW growth temperature, annealing the AlGaIn IL capped InGaIn QW up to the GaN barrier growth temperature, and then growing a GaN barrier layer at elevated temperature. From the data presented, the AlGaIn IL allows for increased indium incorporation into the InGaIn QW and annealing the AlGaIn IL is essential to produce sharp heterointerfaces and remove non-radiative recombination centers in the as grown QW. Finally, the AlGaIn IL also increases the polarization induced electric fields in the InGaIn QW, producing an additional red-shift in the emission wavelengths. This additional polarization induced field, in conjunction with the increased indium concentration in the QW, allows MQWs and LEDs to be produced out to red wavelengths [23].

While substantially longer wavelength QWs can be produced using AlGaIn IL as presented here and in the Toshiba work [20-23], dramatic further improvements must occur before these green to red LEDs have the performance necessary for commercial applications. Although the AlGaIn IL capped QWs contain more indium, the as-grown InGaIn contains too many non-radiative defects to be fully removed by annealing. Independent of how these defects are generated, fully eliminating their impact will be paramount to solving the lack of bright green to red InGaIn-based emitters.

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Figure Captions

Fig. 1. PL intensity versus wavelength (left axis) for MQWs with AlGaN ILs (red circles) and without AlGaN ILs (blue squares). PL FWHM versus wavelength (right axis) for MQWs with AlGaN ILs (green diamonds). The solid lines are power law fits for the intensity vs. wavelength plot and a guide for the eyes for the FWHM versus wavelength.

Fig. 2. STEM images of 5 period MQWs (a) with the InGaN QWs grown at 730 °C and the GaN barriers grown at 800 °C, and (b) with the QWs capped with AlGaN ILs at 700 °C and the GaN barriers grown at 850 °C. The inset for each image shows the atomically resolved planes for a single MQW period.

Fig. 3. X-ray diffraction $\omega/2\theta$ scans for the same (a) and (b) MQWs shown in Fig. 2.

Fig. 4. PL Intensity (a) and AFM scan (b) of a single InGaN QW capped with an AlGaN IL after growth at 700 °C. PL Intensity (c) and AFM scan (d) of a single InGaN QW and AlGaN IL after annealing to 850 °C. The PL was measured using a HeCd 325 nm cw laser at a power of 1.1 mW. The AFM scan size is 500 nm x 500 nm.

Fig. 5. Time-resolved PL data measured for the samples described in Fig. 4, with the 850 °C anneal (red solid line) and without the anneal (black solid line). The dashed lines are single exponential fits.

Fig. 6. Influence of the GaN barrier growth temperature on the luminescence and structural properties for InGaN QWs grown at 710 °C capped with a 1.5 nm thick $\text{Al}_{0.38}\text{Ga}_{0.62}\text{N}$ IL. In (a), the PL wavelength (red-left) and intensity (blue-right) are plotted vs. the GaN barrier growth temperature. In (b), the XRD superlattice peak FWHM were measured from a $\omega/2\theta$ scan and are plotted vs. ω for each of the different GaN barrier growth temperatures. The XRD peak width is

offset for clearer viewing by the amount denoted, and a quadratic fit is shown to visualize the FWHM change vs. ω . The arrows denote ω for the GaN (0002) reflection.

Fig. 7. Comparison of measured and simulated wavelengths and intensities as a function of the AlGa_N IL thickness. (a) Simulation results of the band diagram and electron and hole wavefunctions for a single In_xGa_{1-x}N ($x = 0.215$) QW with Al_zGa_{1-z}N ($z = 0.4$) ILs thicknesses of 1 nm (solid lines) and 2 nm (dashed lines). (b) PL measured wavelengths for QWs grown at 700 (green diamond), 710 (blue circles) and 730 °C (red squares) compared to simulation results (solid lines) with In_xGa_{1-x}N QW indium compositions (x) listed in the figure. (c) Simulated electron and hole wavefunction overlap squared. (d) PL measured intensities for the same samples shown in (b) along with the modeled radiative efficiency (solid lines) calculated as described in the text.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.