Fabrication of Deep Green Light Emitting Diode on Bulk Gallium Nitride Substrate

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ABSTRACT. The indium composition in InₓGa₁₋ₓN/GaN multi-quantum well structure (MQW) is crucial because lower indium composition will shift the wavelength towards ultraviolet region. Nevertheless, at certain indium content in MQW, it will out diffuse from the MQW resulting in the wavelength shift from green to much shorter wavelength, after the annealing process for p-type activation. In this study, we had grown a full Light Emitting Diode device with the MQW layer at a relative high temperature for green LED with indium pre-flow at the top of n-type layer just beneath the MQW using Metal Organic Chemical Vapor Deposition (MOCVD). Transmission Electron Microscopy (TEM) image of the MQW prior and post the activation of p-type had been observed, which resulted in good contrast, showing the abruptness of the MQW layer of the device. Homogenous layers of InₓGa₁₋ₓN/GaN has been observed. We also managed to reduce the wavelength shift of the device significantly. The optical, crystal properties of grown devices had been studied.

1. Introduction
Green Light Emitting Diode has been one of the main focus of solid state lighting research. Green LED has good lumens per watt efficacy which by itself can be an incandescent light source with low current consumption. This makes green LED’s perfect for illumination and lighting. Green LED also improved color rendering index in the process of making white light LED, however it needed to reach the deep green region around 530-570nm [1] in order to that. Light in this range also causes maximum luminous sensation in the human eye and is therefore advantageous for many potential uses.

The green LED had been researched and fabricated for several times [2-4]. InₓGa₁₋ₓN has a direct bandgap span from the infrared (0.69 eV) for InN to the ultraviolet (3.4 eV) of GaN. This property made the InₓGa₁₋ₓN compound crucial for green light which requires band gap around 2.17eV – 2.43eV. Early studies use double hetero structure (DH) as the active layers but resulted with a very wide spectrum emitted with 2 peaks due to deep band recombination. This phenomena is believed resulted by the crystal defect caused by the dislocation in InₓGa₁₋ₓN from the presence of a lot of indium [5]. The quantum well (QW) was introduced to counter this problem, and it tackled the double peak problem [2, 6]. Contrary, the very thin InₓGa₁₋ₓN layer in the QW causes the indium content escaped from the layer...
when heated. This low melting point of InN create a new problem, since we need high content of indium in the In$_x$Ga$_{1-x}$N layer to achieve bandgap energy around 2.17eV – 2.43eV mentioned above. For full LED device, the LED need to be annealed to activate the p-type layer [7-8] to remove the hydrogen atom can bind with Mg atom which acted as dopant. The annealing process causes the indium within the QW out diffused thus making the band gap energy of the In$_x$Ga$_{1-x}$N shifting to the ultraviolet region.

In order to fabricate an LED with narrow spectrum and have longer wavelength it is crucial to have a LED structure that have sufficiently a lot of indium in its active layers and at the same time high percentage of singular crystalline. Multi Quantum Well (MQW) was introduced to increase the indium content in the active layers but the problem of wavelength blue shift still has not been tackled. The problem of out diffused indium can be controlled if high concentration indium is introduced to the layers adjacent to the MQW. Deng et al [9] had approached pre-flow technique for blue region LED, although it has very little MQW indium dissipation problem.

In this paper, we fabricated deep green LED’s and did some alteration to the structure to reduce the indium lost from the MQW’s so that the wavelength shift towards the blue region can be reduced. A layer with rich indium content was introduced right under the MQW. While the indium replace the gallium as the host to the crystal structure, the whole layer remains it n-type properties. To maintain high crystal quality, we controlled the growth temperature for MQW layer at 700°C and the G:In flow at MQW at 1:6. We used C-plane GaN for the substrate.

2. Methodology

![Figure 1](image). The full LED structure of (a) Sample A and (b) sample B.

Figure 1 shows the basic deep green LED structure. The full LED epitaxy growth was done in Metal Organic Vapor Chemical Deposition (MOCVD). The reactor pressure in the MOCVD was 0.5 Torr and the temperature of the MQW growth was 700°C. C-plane GaN (0 0 1) was used as substrate. Trimethylgallium (TMG), NH$_3$ and CP$_2$MG were respectively used as precursor for gallium, nitrogen and magnesium in the p type layer. Trimethylgallium(TMG), trimethylaluminum (TMA), disilane (Si$_2$H$_6$) and NH$_3$ were respectively used as precursor for gallium, aluminum and nitrogen in the n-type layer. Trimethylgallium(TMG), trimethylaluminum(TMA) and NH$_3$ were used respectively as the precursor for gallium, aluminum and nitrogen in the cap layers. Triethylgallium(TEG), trimethylindium(TMI) and NH$_3$ was used respectively as the precursor for gallium, indium and nitrogen for the MQW layer of the structure. The ratio of Ga:In for the InGaN layers were set as 1:6. The flow rate, growth rate and other parameters were set so that the final structure to be as follows: a p type layer of 140nm, the AlGaN cap layer of 70nm, 6 pairs of 12nm GaN and 3nm InGaN, total 90nm of MQW was grown on 5000nm n type layer. These are steps of growing one sample, which is shown in Figure
1 (a) and this called as Sample A. While as shown in Figure 1(b), an alteration was introduced where a layer of rich indium content (In$_x$Ga$_{1-x}$N, n type) layer was included between n type GaN and the MQW by flowing TMI while growing the n-type layer with thickness around 30nm. This was done to reduced or prevent the wavelength shift towards the blue region and will be discussed in the result section.

3. Result and Discussion

3.1 Photoluminescence Spectrum

![Figure 2](image.png)

**Figure 2.** The Photoluminescence result of (a) Sample A and (b) Sample B.

Figure 2 are the photoluminescence (PL) spectrums for sample A and Sample B. The black lines are the PL spectrum before annealing in order to activate the p-type and the red line are the spectrum after the annealing. Sample A has the peak wavelength of 567nm before annealing and 523nm after annealing. It was found that the wavelength shifted 44nm to the blue region due to indium loss from MQW. This was supported by the XRD analysis which will be discussed later. Sample B has the peak wavelength of 500nm before annealing and 473nm after the annealing. The blue-shift was 27nm. It can be distressed from these PL spectrum results, the wavelength shift can be reduced by introducing the indium rich layer right beneath the MQW.

3.2 TEM Cross sectional Image

![Figure 3](image.png)

**Figure 3.** TEM image of (a) Sample A and (b) Sample B.
Figure 3 demonstrate the cross sectional TEM image of Sample A and Sample B. These are the image taken after the samples were annealed. The images shows that the MQWs of both samples have the abruptness between the layers and maintain it homogenous properties. Indium loss from the annealing process did not interrupt the MQW structure and properties, which is the most important part in producing light as well as determine the monochromatic quality of the light emitted. It can be said that the annealing process even though change the content of the MQW, it does not affect the main structure of the MQW itself.

3.3 XRD Analysis

![XRD Omega-2-theta results of (a) Sample A and (b) Sample B.](image)

Figure 4. XRD Omega-2-theta results of (a) Sample A and (b) Sample B.

Figure 4 exhibits the omega2theta scan of sample A and Sample B. The red line is the actual measurement of the omega2theta and the blue line is the calculation plot. Both graph gave peak at 17.25° which the peak of (0,0,2) GaN. It can clearly be observed 6 sequences of peak and slope which represent the 6 pairs of GaN/AlGaN layer of the MQW, which confirmed the existence of relatively thin paired layers in the MQW. From the calculation plot the GaN/AlGaN thickness was obtained was 17.1nm and 3.3nm respectively. These results emphasized the consistence with the result from the TEM image. It also proved that p-type the activation, even though changed the indium content within the MQW, it didn’t change the crystal structure.

3.4 FESEM Morphology Image

![FESEM image for (a) Sample A and (b) Sample B.](image)

Figure 5. FESEM image for (a) Sample A and (b) Sample B.
Figure 5 shows the FESEM image of sample A(left) and sample B(right) at 50 000 times magnification. Both samples give smooth surface. For sample B, we can observe a number of black spots which might be the “V” pits, since Sample A had more indium loss compared to Sample A. But related articles [10-11] stated that the normal v-pits size would have been much bigger than appeared on the surface of Sample A. For that reason, we can say that the surface is smooth, as these small dots were neither v-pits nor impurities.

3.5 AFM Morphology Image

![AFM Images](a) Sample A and (b) Sample B.

Figure 6 shows the AFM 2D image of Sample A and sample B after annealing. Both samples demonstrate very low contrast which explain low surface roughness with no notable holes or valley This condition reflected on the calculated surface roughness RMS value, which is 0.00133 µm for sample A before activation and 0.0167µm for Sample B. Even though the difference is nearly 10 times, it is still small and very smooth. The peak to valley value for Sample A is 0.0036 µm and µm 0.0022 µm for Sample B. These values prove even more the surface of these samples are very smooth, and the lost of indium from the MQW didn’t affect the surface morphology.

4. Conclusion
We had grown full LED structure on GaN substrate to compare the effect of Indium pre-flow effect on green LED. We proposed the pre-flow technique to decrease the wavelength shift towards the blue region due to indium dissipation from the MQW. We had concluded that:

- The pre-flow of indium does reduce the blue-shift of the emitted wave length of the LED. This is evident by the PL result of 44nm shift prior to the pre-flow to 27nm shift after the pre-flow.
- The MQW remains its abruptness and homogenous properties after annealing.
- The cross sectional TEM image proved despite the change of composition within the crystal structure.
- The XRD Omega2Theta result clarify that crystal quality of the samples remains high despite the indium composition change.
- The indium loss from the MQW’s didn’t affect the surface morphology of the samples from the AFM and FESEM images.
The knowledge gain from this paper will be applied in the future projects regarding high indium content MQWs LED.

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