A novel wavelength-adjusting method in InGaN-based light-emitting diodes

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The pursuit of high internal quantum efficiency (IQE) for green emission spectral regime is referred as “green gap” challenge. Now researchers place their hope on the InGaN-based materials to develop high-brightness green light-emitting diodes. However, IQE drops fast when emission wavelength of InGaN LED increases by changing growth temperature or well thickness. In this paper, a new wavelength-adjusting method is proposed and the optical properties of LED are investigated. By additional process of indium pre-deposition before InGaN well layer growth, the indium distribution along growth direction becomes more uniform, which leads to the increase of average indium content in InGaN well layer and results in a redshift of peak-wavelength. We also find that the IQE of LED with indium pre-deposition increases with the wavelength redshift. Such dependence is opposite to the IQE-wavelength behavior in conventional InGaN LEDs. The relations among the IQE, wavelength and the indium pre-deposition process are discussed.

In recent years, both InGaN-based blue Light emitting diodes (LEDs) and AlGaInP LEDs have been developing rapidly and used widely in various applications1–7. The AlGaInP material system is the primary material system for high brightness LEDs emitting in the long-wavelength part of the visible spectrum from 570 nm to 680 nm8,9, while InGaN LEDs have been commercialized for short-wavelength applications below 530 nm10–13. Neither InGaN nor AlGaInP LEDs can emit light efficiently in the range of 530 nm, which makes it difficult to realize high efficiency InGaN LEDs at “green gap” as long as such IQE-wavelength dependence exists.

In the conventional growth process, both changing the InGaN well thickness and indium content can adjust the wavelength14,15. Since the LED efficiency is very sensitive to the InGaN well thickness, it is usually fixed at an optimum value of 2.5 nm in commercial LED products. Consequently reducing the growth temperature of InGaN quantum well layer is the main way to increase the wavelength by enhancing the indium corporation rate. Lower growth temperature leads to poor crystal quality and more impurities incorporated into InGaN well layer. Furthermore, when the indium content in the InGaN well layer increases, the polarization field will be enhanced16–21, which makes the band bending more aggravated. These two factors both lower the IQE at higher indium content when longer wavelength demanded. Motivated by these considerations, new methods are needed to push the major emission peak towards longer wavelength without reducing the IQE.

Atoms pre-deposition method before a certain layer growth is commonly used in semiconductor material growth22–24. In the Ge/Si or InGaAs/GaAs system grown by MBE, it has been demonstrated that the atoms pre-deposition can improve the atom content distribution. In this paper, we demonstrate a new way to adjust the emission wavelength without degrading IQE by indium pre-deposition in metal-organic chemical-vapor deposition technology.
Results

The normalized photoluminescence (PL) spectra are measured for all samples at room temperature (300 K). Figure 1 demonstrates that the major emission peak wavelengths for sample A, B, and C are 460.0, 470.0, and 475.0 nm, respectively. According to the variation of peak wavelength, it is observed that the peak wavelength red-shifts with the increase of the indium pre-deposition time for LED A, B, and C. This PL red-shift proved that the wavelength can be adjusted by the indium pre-deposition method.

High-resolution X-ray diffraction (HRXRD) measurements are carried out to study the relation between InGaN quantum well structure and indium pre-deposition process. Figure 2 shows (0002) plane scans along the growth direction for the three samples. The satellite peaks are clearly observed for all samples, indicating that the fine periodic multi-quantum wells (MQWs) structures are well formed. As shown in Fig. 2 (green line), compared to LED A, the InGaN diffraction peaks for LED B and C have a little shift outward the diffraction peak of GaN bulk material, which shows that the indium content varies slightly in the InGaN layer due to the indium pre-deposition, indicating that the pre-deposited indium is incorporated into InGaN/GaN MQWs. However, the spacing between the satellite peak positions, which determines the MQWs' period thickness, is exactly the same for these samples. The structure parameters obtained by the simulation fitting of the measured curves are presented in Table 1. The results present that the GaN barrier and InGaN well layers are all around 14 nm and 2.5 nm, respectively, indicating that the thickness is not affected by the pre-deposition. The average indium content of QWs increases along with the increase of the indium deposition time. The FWHM values of the InGaN "1st" diffraction peak for the LED B and C are much smaller than that of LED A, which suggests that the uniformity of indium content distribution is improved due to the indium pre-deposition. It is also noted that the high series satellite peaks of LED B, C is more distinct than that of LED A, which shows that the structure properties and the interface roughness between InGaN well layer and GaN barrier are significantly improved.

In order to study the mechanism of unusual IQE-wavelength behavior in InGaN LEDs with indium pre-deposition, the integrated PL intensity V.S. temperature curve is analyzed using Arrhenius fitting. Nonradiative recombination centers (NRCs) exist in InGaN QWs and the activation energy of these NRCs is always smaller than the total QW binding energy of electrons and holes. Therefore, the luminescence thermal quenching of the InGaN LEDs is dominated by the NRCs.

![Figure 1](image1.png) **Figure 1** | The normalized PL spectra for all samples at room temperature (300 K). The major emission peak wavelengths for LED (A), (B), and (C) are 460.0, 470.0, 475.0 nm, respectively. The redshift value is about 15 nm.

![Figure 2](image2.png) **Figure 2** | HRXRD θ/2θ scanning curves (black line) and simulations (red line) of LED A, B, and C. The green line shows the InGaN diffraction peaks for LED B and C have a little shift outward the diffraction peak of GaN bulk material.

| Sample | Indium pre-deposition Time (min) | Period Thickness (nm) | Well thickness (nm) | Barrier thickness (nm) | Indium content of InGaN layer % | FWHM of InGaN"1st" diffraction peak |
|--------|----------------------------------|-----------------------|--------------------|-----------------------|-------------------------------|------------------------------------|
| LED A  | 0                                | 16.51                 | 2.51               | 14                    | 13.02%                        | 267                                |
| LED B  | 1.5                              | 16.50                 | 2.50               | 14                    | 13.52%                        | 223                                |
| LED C  | 2                                | 16.52                 | 2.52               | 14                    | 13.76%                        | 201                                |

Table 1 | Structural parameters of InGaN/GaN MQWs of LED A, LED B, and LED C determined by HRXRD. (Chen)
by the nonradiative recombination process. If there are several kinds of NRCs, the integrated PL intensity can be fitted by the following expression\textsuperscript{30,31}:

\[
I(T) \propto \frac{1}{1 + \sum S_i \exp \left(-E_i/k_B T \right)}
\]

Where \(k_B\) is Boltzmann’s constant, \(E_i\) are the activation energies of the corresponding NRCs, and \(S_i\) are factors related to the density of these centers. Two kinds of NRCs are considered here to obtain good fitting. The fitted parameters are shown in Table 2. LED A, B, and C have almost the same values of \(E_1\) (~13 meV) and \(E_2\) (~67 meV), respectively. This suggests that the same types of NRCs are shown in three samples. However, \(S_1\) and \(S_2\) of LED B and LED C are much smaller than those of LED A, which means that the number of effective NRCs is reduced by indium pre-deposition before the InGaN well layer growth. Furthermore, it has been reported that in composition-nonuniform-distributed InGaN layers due to segregation, the defect density near the InGaN layer top is lower than that near the InGaN layer bottom\textsuperscript{14}. It is probably because the diffusion indium atoms from subsurface can leave sites for defect formation. This explains why \(S_1\) and \(S_2\) are smaller in LED B and LED C, where the indium atoms diffusion is suppressed by indium pre-deposition.

**Discussion**

In the light of the above, it is quite clear that the emission wavelength can be effectively adjusted by the indium pre-deposition method. It is noteworthy to mention here that the abnormal IQE-wavelength dependence observed in our experiment shows that the new method has competitive advantages over the conventional method in realizing high-efficiency long-wavelength InGaN-based LEDs. However, to push the emission wavelength of LEDs into “green gap” region, there are still lots of problems need to be solved. Compared to the blue InGaN LEDs, the green InGaN LEDs have higher indium content in MQWs, which requires lower growth temperature of InGaN well layer. As a result, decomposition of \(\text{NH}_3\) is insufficient and indium atoms are more difficult to incorporate into InGaN well layer during MQW growth of green LEDs. Moreover, the higher indium content results in much stronger polarization field and indium phase separation is easier to occur. Therefore, more efforts are required to introduce the pre-deposition method to InGaN-based green LEDs. For example, strain adjustment method may be combined with indium pre-deposition to solve the strain issues in green LEDs.

We have demonstrated the experimental realization of InGaN/GaN MQWs LED with indium pre-deposition for adjusting the emission wavelength. The structure with indium pre-deposition shows higher average indium content and more uniform indium distribution than that of the conventional LED. An abnormal dependence of IQE-wavelength is observed from LEDs with different indium pre-deposition time. The IQE increases while the wavelength red shifts due to the decrease of defect density in the QWs. Furthermore, the results of HRXRD indicate that the high quality InGaN well layer is obtained and the interface between InGaN well layer and GaN barrier is improved. This finding may provide a train of thought to realize high efficiency LEDs emitting light in the “green gap” region.

**Methods**

The InGaN/GaN MQW LED samples used in this study are grown on sapphire substrates by metal-organic chemical-vapor deposition. The precursors are trimethylgallium (TMGa), triethylgallium (TEGa), trimethylindium (TMIn), and ammonia (\(\text{NH}_3\)) respectively. The active region is grown on a 3 nm thick Si-doped GaN layer, followed by a 10 nm-GaN spacer layer and an 180 nm-thick Mg-doped GaN layer. For a comparative study, the LED A is a conventional one without indium pre-deposition. The InGaN/GaN MQW active region consists of five 2.5 nm thick InGaN well layers separated by 14 nm-thick GaN barrier layers. Samples LED B and LED C are distinguished by adopting indium pre-deposition time. In LED B, prior to the growth of each InGaN QW layer, indium atoms are deposited and the deposition time is 1.5 and 2 min, respectively. Then all the samples were characterized by HRXRD and temperature-dependent PL spectroscopy. HRXRD was performed using a Bede D1 double-axis diffractometer with a parabolic graded monolayer-Gutman mirror collimator, following by a four-bounce channel-cut Si (2 2 0) monochromator, delivering a Cu K\(\alpha\) line of wavelength \(\lambda = 0.154056\) nm. Temperature-dependent PL spectra from 20 to 300 K were recorded using a 325 nm He/Cd continuous wave laser at an emission power. The emitted light was dispersed by a triple grating monochromator and detected by a GaAs photomultiplier tube using conventional lock-in technique.

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CORRIGENDUM: A novel wavelength-adjusting method in InGaN-based light-emitting diodes

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