Effect of Graded-Indium-Content Superlattice on the Optical and Structural Properties of Yellow-Emitting InGaN/GaN Quantum Wells

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Abstract: We have improved the material quality of the high indium composition InGaN/GaN multiple quantum wells (MQWs) grown on free-standing GaN substrates using the graded-indium-content superlattice. We found that by adopting a graded-indium-content superlattice structure, the spectral FWHM of the yellow emitting InGaN/GaN MQW was reduced from 181 meV to 160 meV, and the non-radiative recombination lifetime increased from 13 ns to 44 ns. Besides, the graded-indium-content superlattice can mitigate strain relaxation in high indium composition MQWs as shown by the TEM diffraction patterns.

Keywords: GaN; superlattice; InGaN; multiple quantum wells

1. Introduction

GaN-based emitters such as light-emitting diodes (LED) and laser diodes (LD) have made great success in the past decades, especially in the blue spectrum range [1–5]. However, when the wavelength extends to a longer range, corresponding to the maximum sensitivity of human eyes, the emitting efficiency of multi-quantum wells (MQWs) drops sharply which is known as the “green gap” [6–8]. The reason for the green gap can be attributed to the increasing non-radiative recombination rates caused by deteriorative material quality [9,10], a more severe Quantum Confinement Stark Effect (QCSE) [11,12], and the Auger effect. To overcome the gap, considerable approaches have been proposed by researchers. For example, nonpolar or semipolar substrates were used to control QCSE [13–16]. Blue MQWs were introduced as strain modulation layers to improve material quality and reduce strain in yellow MQWs as reported by Zhang et al. [17]. AlGaN interlayer (IL) was used as band engineering and strain compensation of active layers to enhance IQE [18–21]. Some literature reported the application of an InGaN underlayer to reduce potential point defects in the underlayer, and therefore, boost MQWs efficiency [22–24]. Specifically, Jiang’s team [25–28] came up with a pre-strained superlattice (SL) structure to solve the phase separation problem and improve the crystalline quality in high indium MQWs, assisting in realizing high performances light-emitting diodes in longer wavelength. However, for laser diodes, GaN free-standing substrates rather than foreign substrates are applied to decrease threading dislocations and improve material quality. There are few studies about the influence of pre-strained SL on homoepitaxial long-wavelength MQWs performances. The effect of the pre-strained superlattice structure on the homoepitaxial growth remains to be studied.
2. Experimental

In this experiment, the epitaxial growth of the samples was performed on a commercial Aixtron 6 × 2 inch Closed Coupled Shower Head (CCS) metal-organic chemical vapor deposition (MOCVD) reactor. Trimethylindium (TMIn) and ammonia (NH₃) were used as precursors for In and N, respectively. Trimethylgallium (TMGa) was used as a precursor for Ga when growing the GaN layer while triethylgallium (TEGa) was used as a precursor for Ga when growing the InGaN layer. Nitrogen and hydrogen were used as carrier gases. Monosilane (SiH₄) was used as n-type dopants. Sample A and B were grown on c-plane free-standing GaN substrates as shown in Figure 1a,b, respectively. Sample A was a traditional InGaN/GaN MQWs and sample B was an InGaN/GaN MQW with a graded-indium-content InGaN/GaN superlattice (GSLs) as the pre-strained structure. The growth conditions of MQWs of sample A and sample B were completely the same. The growth pressure was 400 mbar. The specific growth parameters are shown in Table 1. The growth temperature was thermocouple temperatures. The thickness of QWs and QBs were 2.5 nm and 17 nm, and the thickness of InGaN and GaN of SGLs were 5.5 nm and 1.5 nm, respectively.

![Cross-sectional schematic diagram of quantum well’s structure: (a) 4 MQWs without GSLs (b) 4 MQWs with GSLs.](image)

**Figure 1.** Cross-sectional schematic diagram of quantum well’s structure: (a) 4 MQWs without GSLs (b) 4 MQWs with GSLs.

| Scheme | $T_{\text{set}}$ (°C) | Growth Rate (nm/s) |
|--------|----------------------|-------------------|
| QW     | 830                  | 0.033             |
| QB     | 1005                 | 0.063             |
| GSL (16% InGaN) | 903                  | 0.022             |
| GSL (8% InGaN) | 903                  | 0.018             |
| GSL (4% InGaN) | 903                  | 0.017             |

Room-temperature photoluminescence (PL) measurement was performed with a 325 nm semiconductor laser diode with an excitation density of 1.6 W cm⁻². A digital modulated (10 kHz, 50% duty cycle) 405 nm CW semiconductor laser diode was used as the excitation source in the time-resolved photoluminescence (TRPL) experiment and the injected power density was kept around 5.7 W cm⁻². Transmission electron microscopy (TEM), scanning electron microscope (SEM), and atomic force microscopy (AFM) were used to observe and analyze dislocations in MQWs. AFM was the Dimension ICON produced by Bruker in the United States. SEM was S-4800 produced by HITACHI in Japan. TEM was Talos F200X and Themis Z produced by FEI in the United States.

3. Results and Discussion

The room temperature PL spectra of samples A and B are shown in Figure 2. The PL peak energy and the full width at half maximum (FWHM) of each spectrum were determined by peak fitting. The black and the blue curves represent the room temperature PL spectrum of samples A and B, respectively. It could be found that the peak emission energy
of sample A and sample B was the same, 2.214 eV. On the other hand, the FWHM of PL peak of sample A and sample B was 181 meV and 160 meV, respectively.

![Figure 2. (a) PL spectra of samples A and B recorded at room temperature; (b) Normalized spectra of samples A and B with the energy-scale horizontal axis.](image)

To figure out the reason for improved material quality, time resolve photoluminescence (TRPL) measurements were conducted. We used a novel method to determine both the radiative and non-radiation lifetime of excess carriers at room temperature. The related theoretical explanation could be found in References [29,30]. A modulated quasi-CW laser was used as the excitation source in the TRPL experiment. From the moment when the excitation was turned off until the photoluminescence intensity dropped to 1/e of the steady-state intensity, we used the formula $I_{PL,decay} \propto e^{-t/\tau_{eff}}$ to fit the curve of the decay of the photoluminescence intensity with time to a single exponential function as the effective lifetime of the carrier under steady-state excitation. The $\tau_{eff}$ is the effective lifetime of excess carriers and is given by:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{Auger}}$$

where $\tau_{rad}$, $\tau_{SRH}$, and $\tau_{Auger}$ are the lifetimes of radiative, SRH, and Auger recombination, respectively. Under low excitation, the SRH lifetime is the main factor affecting the effective lifetime because the radiative recombination and Auger recombination process are slow. Therefore, it can be considered that non-radiative recombination is equivalent to SRH recombination.

The curve of TRPL at room temperature in this experiment is shown in Figure 3. The black and the red curves represent PL decay curves of samples A and B, respectively. The non-radiative recombination lifetime of sample A and sample B was 13 ns and 44 ns, respectively. The lifetime of non-radiative recombination was closely related to the density defects. It was reasonable to believe sample B had fewer non-radiative recombination centers, and therefore, had a better material quality. This result agreed well with the PL measurement results. The reason was that native defects such as VN were trapped by the indium atom in the pre-strained well to form the In-VN with lower energy [31–33]; therefore, reducing the number of defects in the subsequently grown quantum well layer. Thus, the FWHM of the PL spectrum was reduced and the non-radiative recombination lifetime was increased.

AFM and SEM images are shown in Figures 4 and 5, respectively. The scan size of AFM images was 5 um × 5 um. We can see through the AFM and SEM images that there were many V-pits on the surface of two samples and most of the V-pits appear in pairs. The dislocations density of free-standing GaN substrates was less than $3 \times 10^6$/cm². However, it can be seen that the dislocations density of sample A and sample B on the surface are $10^7$/cm² through the AFM images. We think the reason was a large lattice mismatch between the InGaN and GaN in the high indium composition MQWs, which results in misfit dislocations.
To verify this conclusion, the formation of dislocations and the strain in MQWs was studied. Figure 6 shows bright-field scanning transmission electron microscope (STEM) images of samples A and B. As shown in Figure 6a,b, cross-sectional STEM of sample A and sample B show that the interface between the high indium composition yellow-emitting InGaN QWs and the GaN QBs is clear. Figure 6c,d show that the thickness of QWs and QBs is 2.5 nm and 17 nm, respectively. Dislocations also appeared from the first or second QW layer in both samples from the cross-sectional STEM as shown in Figure 6e,f. Figure 7a is a plan-view atomic resolution high-angle annular dark-field (HAADF) STEM image of a...
V-pit. The dark contrast was caused by the smaller thickness within the V-pit. Figure 7b was obtained by inverse Fourier transform after filtering out the (0000) from the reciprocal lattice obtained by Fourier transformation of Figure 7a. It showed a dislocation was formed within the red lines with Burgers vector of $\frac{1}{2}[11\overline{2}0]$. 

![Figure 6](image1.jpg)

**Figure 6.** Cross-sectional bright-field STEM images of yellow MQWs on freestanding GaN substrate (a) sample A, and (b) sample B, (c) the thickness of QW, (d) the thickness of QB, (e) a dislocation in sample A (f) a dislocation in sample B.

![Figure 7](image2.jpg)

**Figure 7.** (a) Plan-view atomic resolution high-angle annular dark-field STEM images of a V-pit. (b) was obtained by inverse Fourier transform after filtering out the (0000) from the diffraction pattern obtained by Fourier transformation of (a).

Next, we used selected area electron diffraction (SAED) to characterize the strain in the MQWs. Figure 8a is a cross-sectional view image of sample A. Figure 8b is a SAED pattern of the circled area of Figure 8a taken under zone axis (ZA) [\(\overline{2}110\)]. Figure 8c is a cross-sectional view image of sample B. Figure 8d is a diffraction pattern of the circled area of Figure 8c also under ZA [\(\overline{2}110\)]. The circled areas in both Figure 8a,c contain MQWs and n-GaN layer. The inset images of Figure 8b,d are enlarged views of the diffraction spots of 0004 of sample A and sample B, respectively. In Figure 8b, we can see that the diffraction
spots of 0004 of sample A are two spots, which means that the lattice constants of InGaN and GaN are different. It shows that relaxation has occurred in sample A. In Figure 8d, the diffraction spots of 0004 of sample B are a slightly elongated dot. Combined with the AFM image of sample B, it can be seen that relaxation also occurred in sample B, but the resolution of the diffraction pattern was not enough to distinguish them. According to the comparison of the diffraction patterns of 0004 of the two samples, it could be concluded that the relaxation of sample B was smaller than that of sample A. Therefore, the GSLs can play a key role to mitigate the strain in InGaN QWs.

4. Conclusions

We studied the effect of the graded-indium-content superlattice structure on the optical and structural properties of high indium composition yellow-emitting InGaN/GaN MQWs grown on free-standing GaN substrates. It is found that by adopting a graded-indium-content superlattice structure, the spectral FWHM of the yellow emitting InGaN/GaN MQW is reduced from 181 meV to 160 meV, and the non-radiative recombination lifetime is increased from 13 ns to 44 ns. The TEM diffraction patterns prove that the GSLs can mitigate strain relaxation in high indium composition MQWs.

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