Phase separations in graded-indium content InGaN/GaN multiple quantum wells and its function to high quantum efficiency*

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Abstract: Phase separations have been studied for graded-indium content $In_xGa_{1-x}N$/GaN multiple quantum wells (MQWs) with different indium contents by means of photoluminescence (PL), cathodeluminescence (CL) and time-resolved PL (TRPL) techniques. Besides the main emission peaks, all samples show another 2 peaks at the high and low energy parts of the main peaks in PL when excited at 10 K. CL images show a clear contrast for 3 samples, which indicates an increasing phase separation with increasing indium content. TRPL spectra at 15 K of the main emissions show an increasing delay of rising time with indium content, which means a carrier transferring from low indium content structures to high indium content structures.

Key words: carrier transfer; phase separation; graded-indium content; multiple quantum wells
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1. Introduction

Research interest in GaN-based materials has been driven by the significant technological importance of these materials. Indeed, InGaN materials are commonly used in the fabrication of a range of electronic and photonic devices[1]. The bandgap of $In_xGa_{1-x}N$ can be varied over nearly the whole spectral range from the ultraviolet (3.47 eV for GaN[2]) to red emission (1.97 eV for InN[3], recently infrared emission at 0.76 eV[4] has been reported). Due to such technical importance, a great deal of effort has been afforded to this promising material. To achieve long-wavelength LEDs by adopting InGaN as well layers, higher indium composition $In_xGa_{1-x}N$/GaN multiple quantum well (MQW) structures must be used as active layers. However, phase separation or composition fluctuation is always observed in an InGaN alloy because of the large atomic discrepancy between indium and gallium, and the large lattice mismatch between InN and GaN, which lead to the low efficiency of long-wavelength emitting InGaN structures (with more indium content) as compared to blue ones. It also has been reported that indium content, strain, quantum well (QW) structure, and composition fluctuation influence the optical and electrical properties greatly, and that strong carrier localization enhances the luminescence efficiency of blue/violet-light-emitting InGaN-based light emitting devices by hindering the movement of carriers to nonradiative recombination centers[5]. An effective formation of the quantum dot (QD)-like structure was observed by adjusting the profile of the nominal indium content profile during the low-indium-content InGaN well growth procedure[6], resulting in an improved characteristics of the blue-light-emitting InGaN QW LED structures. In this paper, we report the phase separation and its function to high quantum efficiency in InGaN/GaN multiple quantum well (MQW) LED structures. A clear phase separation was found and its effects on the optical properties were studied, in which the sample with more phase separation shows high quantum efficiency. The effective carrier transfer between delocalized and localized states caused by strong phase separation plays an important role in the high efficiency and brightness of InGaN MQWs.

2. Experiment

The graded-indium-content InGaN/GaN MQW samples were grown on c-plane sapphire substrates by horizontal MOCVD with trimethylgallium (TMGa), trimethylindium (TMIn), ammonia, and silane as the precursors of Ga, In, N, and Si, respectively. Nitrogen was used as a carrier gas for the sources. After thermal cleaning of the substrate in hydrogen ambient for 10 min at 1100 ℃, a 25-nm-thick GaN nucleation layer was grown on c-plane sapphire substrates at 560 ℃ and followed by a 1-μm Si-doped GaN layer at 1130 ℃. Five periods of InGaN/GaN QWs were grown at 795 ℃ and then a 100-nm-thick GaN capping layer was grown at 1050 ℃. The thickness of the barrier and well layers was about 8 and 3 nm, respectively. The graded-indium-content of InGaN MQW structures were formed by controlling the indium composition with time during the well growth. The average indium content

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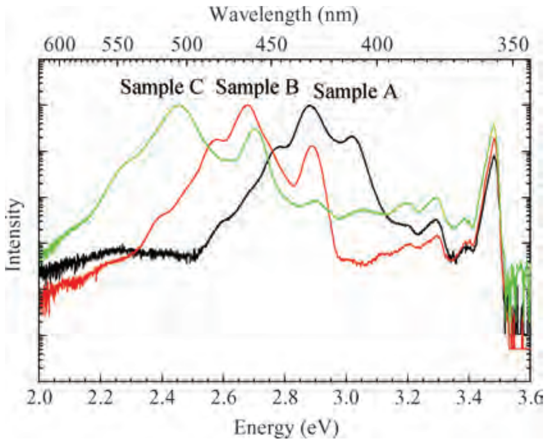

Fig. 1. Normalized PL spectra of the samples A, B, and C at 10 K excited by a 325 nm He–Cd laser.

in the well layers estimated from the flux of TMIn are $x_{\text{In}} < 0.2$, $0.2 < x_{\text{In}} < 0.3$, and $x_{\text{In}} > 0.3$ for the samples A, B and C, respectively. Temperature-dependent photoluminescence (T-PL) measurements were performed by using a He–Cd laser at the excitation wavelength of 325 nm and a He-cooling stage operating from 10 to 300 K. Cathodoluminescence (CL) images were acquired by using a commercial MonoCL2$^{\text{TM}}$ system on a high-resolution scanning electron microscope at room temperature (RT). Time-resolved PL (TRPL) measurement was carried out using a second harmonic pulsed Ti:sapphire laser at the wavelength of 390 nm and a time-correlated single photon counting detection system with a pulse width of approximate 100 ps.

3. Results and discussion

To study the optical properties of the graded-In-content InGaN/GaN samples, T-PL experiments were conducted with temperature varying from 10 to 300 K. The normalized PL spectra (to its main emission peak) at 10 K are shown in Fig. 1. Three peaks can be clearly distinguished for all samples with a main emission peak in the center and two other weaker shoulders located at the higher and lower energy part of the main peaks. The main peaks at 10 K are at 430, 463 and 505 nm for samples A, B, and C, respectively. The other two peaks are not the results of light interference and are attributed to structures with different indium content as a result of phase separation[7].

The temperature-dependent peak-shift of main emission for 3 samples is shown in Fig. 2 by comparing with the peak energy at 10 K for each sample. All the emission energy of the main peak shows a fluctuated temperature-dependent characteristic as the temperature increases from 10 to 300 K, which is attributed to the potential inhomogeneity and localized characteristic of the radiative electron–hole recombination[8]. The total red-shift with temperature from 10 to 300 K is 10.7, 15.5 and 27.8 meV for samples A, B, and C, respectively, which increase with indium content and indicate the high content of phase separation in sample with high indium content. In addition, the energy difference between the main and higher (lower) energy peaks is 139 (93), 208 (103) and 245 (116) meV for samples A, B, and C, respectively, which also increases with

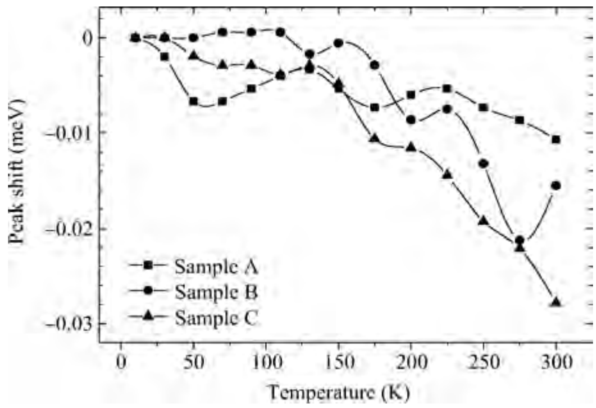

Fig. 2. Peak-shift of main emission peaks as a function of temperature for the samples A, B and C.

increasing indium content and indicates a high content of indium aggregation clusters with high indium content.

The main InGaN-related peaks show a very bright light emission even at 300 K, and the integrated intensity of the main emission is reduced by only a factor of about 13.2, 12.8 and 6.8 for samples A, B and C, respectively, around one order of magnitude, with increasing temperature from 10 to 300 K, indicating high quantum efficiency and good device performance of graded-In-content InGaN MQWs. Sample C in particular, which has a high indium content ($x > 0.3$) and shows severe phase separation, has its integrated PL intensity of the main peak decreased by only 6.8 times when the temperature increased from 10 to 300 K, less than 1 order, showing very excellent quantum efficiency with higher indium content. So the phase separation in trapezoidal InGaN samples seems to enable high quantum efficiency.

To investigate the luminescence quenching behavior of photon-emission from InGaN MQW structures, an Arrhenius plot is generally used to analyze the integrated intensity of emissions. The general luminescence quenching of an ideal quantum well is caused by the thermal escape of carriers from the well to the barrier, which the activation energy equals to the total QW binding energy of the electrons and holes[9]. In fact, there are always some non-radiative recombination centers in QWs with the active energy smaller than the total QW binding energy of electrons and holes[10]. If there are several kinds of non-radiative channels in the materials, the integrated PL intensity can be fitted by fitted the following multi-channel Arrhenius plot formula:

$$I = I_0 \Big/ \left[1 + \sum_{i=1} C_i \exp(-E_{\text{A}i}/k_{\text{B}}T) \right], \tag{1}$$

where $E_{\text{A}i}$ are the activation energy of the corresponding non-radiative recombination center and C_i are the constants related to the density of these centers.

Figure 3 shows the two channel (i.e., $i = 2$) Arrhenius plot of the integrated main PL emission from the InGaN structures of the samples A, B, and C, which gives the best fitting of the data. Together we show the fitted activation energies of each sample. The curves have been shifted vertically for more clarity. The solid lines are the least square fit of data with the above equation. The activation energies extracted for each sample

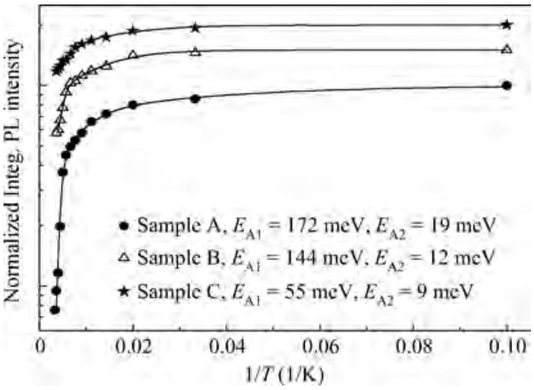

Fig. 3. Two-channel Arrhenius plots of the integrated main PL emissions and the best fitting of experimental data. The curves have been shifted vertically for clarity.

from the Arrhenius plot can be divided into 2 groups: one is larger, 172, 144, and 55 meV for the samples A, B and C respectively; and the other is relatively smaller, about 19, 12, and 9 meV for the samples A, B, and C respectively, as shown in Fig. 3. The larger activation energies (for the samples A and B) may be related to the dislocations or other nonradiative centers in the sample[11], which will decrease the radiative recombination; the smaller ones correspond to the energy of the carriers needed to escape from shallow localized state to deeper one, which will help the radiative recombination and enhance the radiative recombination. However, this effect will also increase the temperature-dependent red-shift of the main emissions, as indicated in Fig. 2.

CL is also a powerful method to investigate the sample inhomogeneity of III-nitride structures, which can provide a direct information at the sub-micron scale[12]. CL measurements have also been conducted on all samples at main emission peaks at room temperature and the data is shown in Fig. 4. As indicated from the contrast comparisons, the phase separations are more severe for samples with a high indium content, which means a universal potential fluctuation throughout the high indium content samples. This means that the carriers can move easily from normal QWs (with low indium content) to high indium content part because of the small energy difference among different indium content parts, which will decrease the probability of the dislocation traps on carriers (reduce the nonradiative recombination) and increase quantum efficiency.

Temperature-dependent TRPL have also been conducted and the decay curve at 15 K for main emission peak of three samples investigated. As we have shown before[7], the decay behavior of the main emission peak is slower than the side peak and the rising time of the main peak is also longer than side peaks, which can be interpreted as that the carriers generated in an indium-poor region will transfer to an indium-rich part and prolong the rise and decay time of the main emission peaks. In Fig. 5, we show the decay curves of the main emission peaks for 3 samples. The rising and decay times increase with indium content, which means a long lifetime of carriers in the high indium content sample. Once the carriers are excited by a pulse to a relatively low localization state (with low indium content), they will be transferred to another high localization state and prolong the rising time in curves. In addition, deep

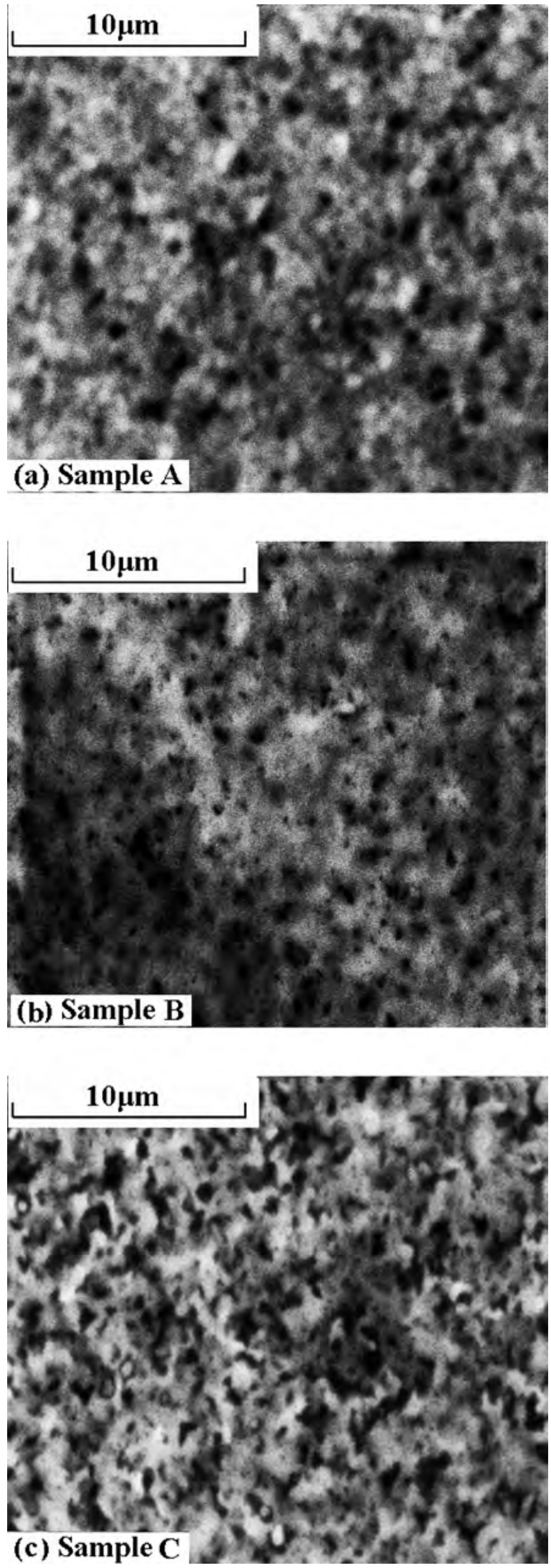

Fig. 4. CL images for the main emission peak at room temperature. (a) Sample A. (b) Sample B. (c) Sample C.

localization will make the carriers relatively difficult to recombine and delay the decay time. If we combine this phenomenon with phase separation, another explanation is possible: photon-induced carriers will be transferred to another deeper localized

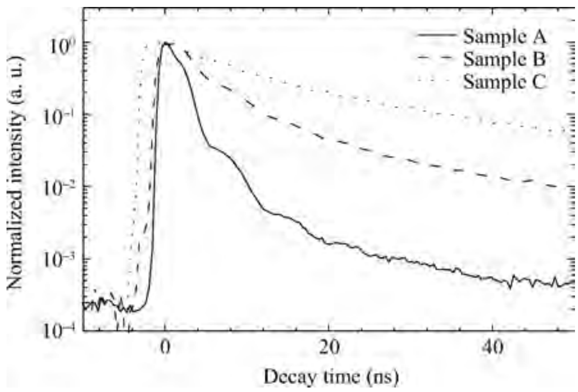

Fig. 5. TRPL decay curves measured at the main emission peaks of samples A, B and C at 10 K.

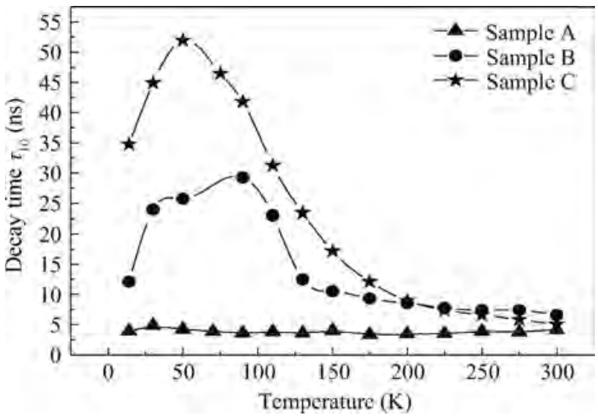

Fig. 6. Decay time τ_{10} as a function of temperature for the main peaks of the samples A, B and C.

state and delay the decay.

Figure 6 shows the decay time of main peaks with temperature. Due to the non-exponential decay behaviors of time evolution curves, the time when intensity decreases from the maximum to its 1/10, τ_{10}, is used to characterize the luminescence decay[13]. As we can see in Fig. 6 that the carrier decay time increases with increasing temperature up to a certain temperature, T_c (30 K for sample A, 90 K for sample B and 50 K for sample C), and then decreases as temperature increases further. This fact indicates that the radiative recombination process is more dominant in the temperature range below about T_c, and then the nonradiative recombination became dominant. However, it should be noted that the decay time of sample A does not change much as the temperature varies and it keeps almost constant for all the temperature range we examined, which means a small localization effect in the low-indium content samples. The decay time at 15 K is about 4, 12, and 35 ns for samples A, B, and C, respectively, which increase with indium content in the well layers. This agrees well with our explanations for the decay delay by carrier transfer, which will enhance the radiative recombination and increase the quantum efficiency.

4. Conclusion

Phase separation and its function in radiative recombination and high quantum efficiency have been systematically studied on graded-indium content $In_xGa_{1-x}N$/GaN MQWs with different indium content. The main emission peak together with two other peaks at the higher and lower energy parts in PL shows a clear phase separation phenomenon and is verified by CL images with a clear contrast. The activation energy decreases with increasing indium content to make it easier for carriers to transfer between different localized states, which increase the quantum efficiency. TRPL measurement also indicates carrier transfer from low indium content structures to high indium content structures, and leads to the high quantum efficiency.

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