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Research Article

Using Pre-TMIn Treatment to Improve the Optical Properties of Green Light Emitting Diodes

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We investigated the effects of pre-TMIn treatment on the optical properties of green light emitting diodes (LEDs). Although pre-TMIn treatment did not affect the epitaxial structure of quantum wells, it significantly improved the quality of the surface morphology relative to that of the untreated sample. Indium cluster can be seen by high-resolution transmission electron microscopy (HR-TEM), which is the explanation for the red-shift of photoluminescence (PL). Time-resolved photoluminescence measurements indicated that the sample prepared with pre-TMIn treatment had a shorter radiative decay time. As a result, the light output power of the treated green LED was higher than that of the conventional untreated one. Thus, pre-TMIn treatment appears to be a simple and efficient means of improving the performance of green LEDs.

1. Introduction

Group III-nitride materials have attracted much interest for their use in optoelectronic applications because their emission spectra cover a wide range from the infrared to the deep ultraviolet [1–3]. Among them, indium gallium nitride (InGaN) is the most promising material for the preparation of high-efficiency, high-power light emitting diodes (LEDs), which are employed widely in backlighting, traffic lights, headlights, and general illumination [4]. Although InGaN-based blue LEDs are well established, the InGaN-based green LEDs continue to suffer from low efficiency, which limits their further applications in white lighting devices.

V-shaped defects [5–7] readily form at InGaN/GaN quantum wells (QWs) having high indium mole fractions, triggered by threading dislocations in the buffer layer. Several factors can lead to a low-quality InGaN layer, including lattice mismatch between InN and GaN [8], low miscibility of InN [9, 10], phase separation [11], indium surface segregation [12], and V-shaped defects [5–7]. A growth interruption technique [13, 14] can be used to improve the quality of InGaN layers and to enhance the luminescence intensity of LED devices. By applying growth interruption at a high growth temperature, the atoms in the InGaN layer can migrate to their minimum energy sites to approach thermal equilibrium and decomposition of In-rich regions, leading to a flat InGaN surface. Another growth method in which trimethylindium (TMIn) is employed during the growth interruption process is known as "TMIn treatment" [15]; it can suppress InGaN decomposition and indium aggregation to achieve a more homogeneous indium composition, a lower density of V-shaped defects, higher energy states, stronger photoluminescence intensity,

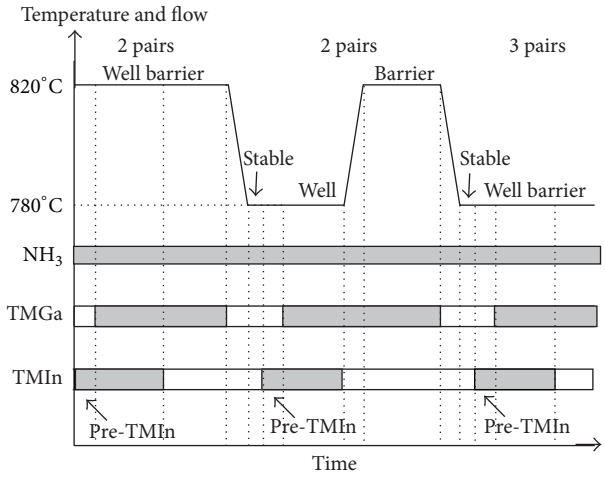


Figure 1: Growth conditions for pre-TMIn treatment in InGaN/GaN MQW.

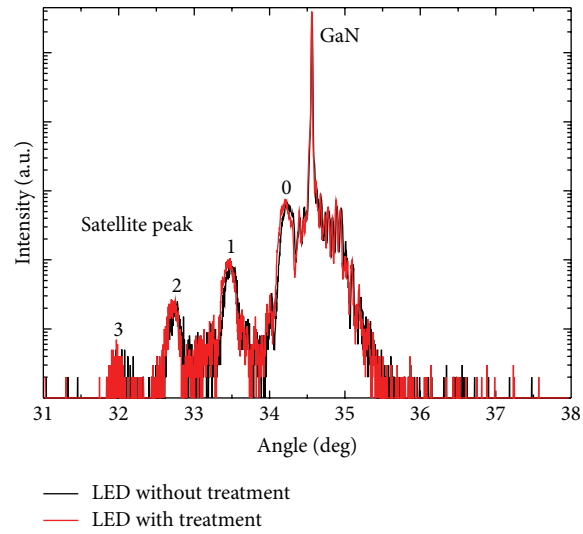


Figure 2: XRD spectra for the LEDs prepared with and without TMIn treatment.

and shorter decay times. In this study, we examined the effects of pre-TMIn treatment prior to QW growth on the output power of InGaN-based green LEDs. Our experimental results revealed that the light output intensity from a sample subjected to pre-TMIn treatment exceeded that of conventional LEDs at a quite high injection level, a result of stronger quantum confinement ability arising from indium-rich sites. Time-resolved photoluminescence (TRPL) revealed that the radiative recombination effect of the TMIn-treated sample was better than that of its untreated counterpart.

2. Experimental Methods

InGaN/GaN multiple quantum well (MQW) samples were grown on a (0001) sapphire substrate using an atmospheric pressure metal-organic chemical vapor deposition system. Trimethylgallium, trimethylindium, trimethylaluminum, and ammonia (NH_3) are used as precursors of the Ga, In, Al, and N atoms, respectively. Bicyclopentadienyl and silane are used as the p- and n-type dopant precursors. The substrates were first heated in H_2 ambient to remove any contaminants prior to performing the growth process. The LED structures comprised a 25 nm low-temperature GaN nucleation layer; a 1 μm unintentionally doped GaN buffer layer; a 3 μm n-GaN layer; seven periods of MQW layers featuring 2.7 nm InGaN well layers and 8 nm GaN barrier layers; a 10 nm AlGaN electron blocking layer; and a 100 nm p-GaN layer. There are two samples which are without and with pre-TMIn flow and each sample has three sets of MQW layers. The detail of pre-TMIn flow condition is (i) two pairs of InGaN QWs and GaN barriers grown at 820°C with a TMIn preflow temperature of 820°C; (ii) three pairs of InGaN QWs and GaN barriers grown at 780 and 820°C, respectively, with a TMIn preflow temperature of 780°C; and (iii) three pairs of InGaN QWs and GaN barriers grown at 780°C with a TMIn preflow temperature of 780°C. Before the deposition of the InGaN QW layers, only TMIn and NH_3 were flowed into the reactor. For easy understanding, the details are schematically represented in Figure 1. The final LEDs were fabricated, by means of standard LED process technology, to have an active area of $1 \times 1\,mm^2$.

The epitaxial wafers were subjected to analysis through high-resolution X-ray diffraction (HR-XRD), high-resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM), TRPL, and room-temperature photoluminescence; the light output power was measured to characterize the optical properties of the LED devices.

3. Results and Discussion

Figure 2 displays the HR-XRD spectra of the LEDs prepared with and without pre-TMIn treatment. The diffraction peak of GaN is identified and marked in the curve; it arose from the buffer and the n- and p-type contact layers. We used Vegard's law to calculate the indium composition from the lattice parameters determined through XRD. The XRD curves of the two samples are almost identical, implying that the structure of the MQWs did not change as a result of TMIn treatment, except for a slight increase in the indium content in the InGaN layer. The indium compositions are 24.5% and 25% for the samples without and with pre-TMIn treatment, respectively. The satellite peaks suggested good quality interfaces for the MQW structures. Our results confirm that indium diffusion into the barrier could be suppressed and that the indium composition became homogeneous after TMIn treatment [15].

We used AFM and SEM to observe the surface morphologies of the two samples (Figure 3). The surface morphology of the sample that had experienced pre-TMIn treatment was better than that of the untreated sample, with the root-mean-square (RMS) surface roughness observed decreasing from 0.819 to 0.708 nm. Figures 3(c) and 3(d) show the surface morphology of InGaN QWs layer etched by phosphoric acid (H_3PO_4) for 30 s at 220°C. The etch pits density is about 1.1 $\times$ 10^9 cm^{-2} and 7.3 $\times$ 10^8 cm^{-2} for the sample without and

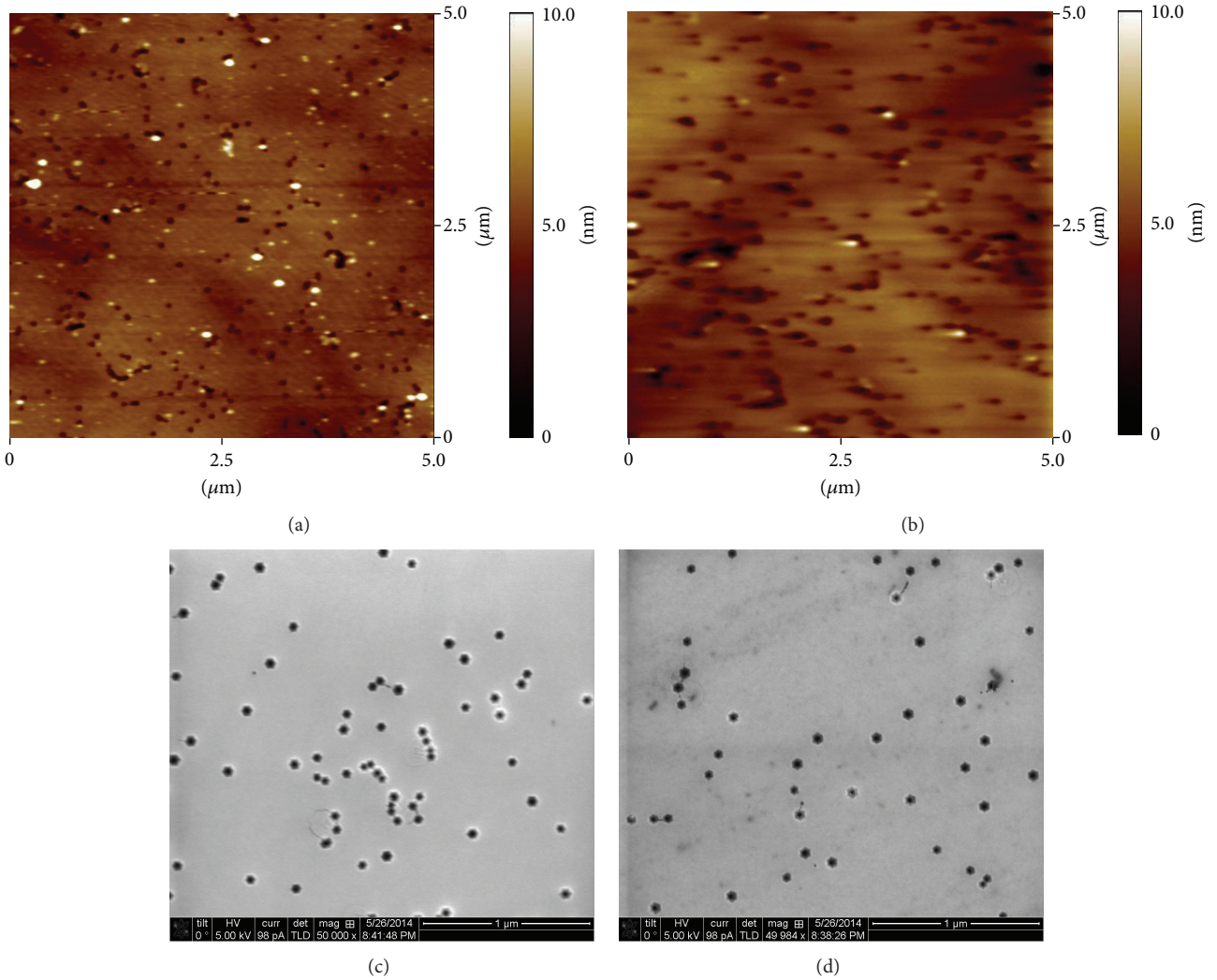


Figure 3: AFM and SEM images of the surface morphologies of the (a), (c) sample without TMIn treatment and (b), (d) sample with TMIn treatment.

with TMIn treatment, respectively. This finding suggested that TMIn treatment could improve the quality of the InGaN-GaN interface, thereby potentially improving the optical properties of green LEDs.

We used room-temperature photoluminescence to determine the center wavelengths of the two samples; Figure 4 displays their spectra. Photoluminescence peaks for the untreated and treated samples appeared at 520 and 535 nm, respectively; that is, a red-shift in the signal occurred after TMIn treatment. In general, such a red-shift occurs upon increasing the mole fraction of indium. Our XRD profiles in Figure 2 reveal, however, that the indium content increased only slightly. Considering the material properties of indium, we believe that the red-shift was related to aggregation of indium atoms in the QW during TMIn treatment [15, 16]. The action of TMIn and NH_3 could not form a continuous InN film, but rather InN islands, during the short treatment time and under the high growth temperature. In order to prove our thought, HR-TEM measurement was employed. Figure 5 presents the cross section HR-TEM images for two samples (a) without TMIn treatment, (b) with TMIn treatment. From Figures 5(a) and 5(b), the barriers and wells can be easily distinguished. As we can see, the dark dots in Figure 5(b) are much more than in Figure 5(a). These dark points are In-rich cluster and their formation can be explained by pre-TMIn flow treatment, which is the main reason for the red-shift of PL.

We employed TRPL to examine the recombination rate of green LEDs that had been prepared with pre-TMIn treatment. We fitted the PL decay profiles in Figure 6 with the following double-exponential equation to obtain the decay time:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_r}\right) + A_2 \exp\left(-\frac{t}{\tau_{nr}}\right), \quad (1)$$

where $I(t)$ is the PL intensity, A_1 and A_2 are the decay parameters, and τ_r and τ_{nr} are the decay times for radiative and nonradiative recombination [17]. For the treated sample, the values of τ_r and τ_{nr} were 6.2×10^{-12} and 3.6×10^{-9} s, respectively; for the untreated sample, they were 9.1×10^{-12}

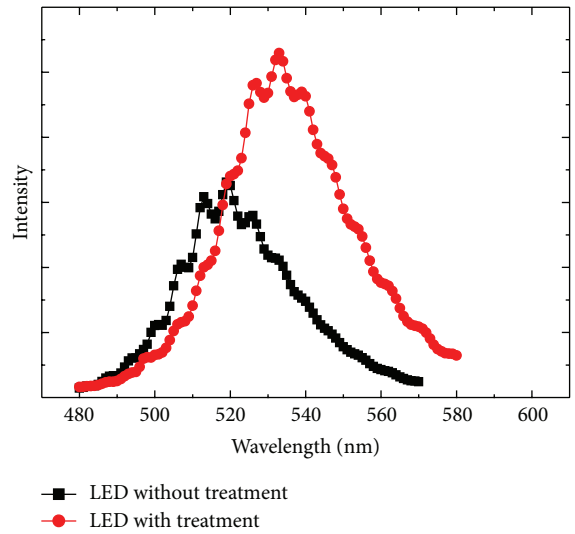
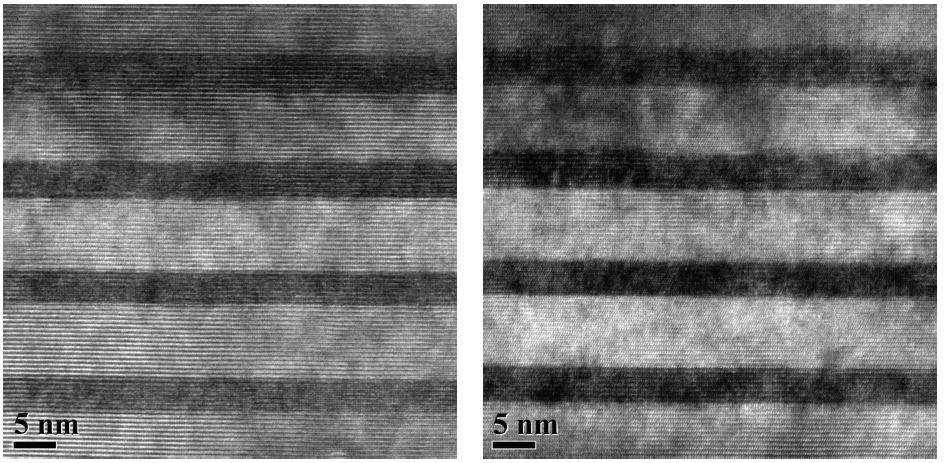


Figure 4: Room-temperature photoluminescence spectra for the LEDs prepared without and with TMIn treatment, with central peaks located at 520 and 535 nm, respectively.



(a) (b)

Figure 5: HR-TEM images of MQWs for two samples, (a) without TMIn treatment and (b) with TMIn treatment.

and 3.4×10^{-9} s, respectively. Thus, the radiative decay time decreased as a result of pre-TMIn treatment, leading to a greater radiative recombination effect. Because carrier transport into weakly localized states requires a certain energy to overcome a potential barrier, it is more difficult for carriers to transfer into weakly localized states [17, 18]. In the localized exciton model, trap centers are originated from a spatial disorder such as the fluctuation of indium within InGaN/GaN MQWs. Using TMIn treatment, the decay time becomes shorter, because treatment leads to more strongly localized stats due to the indium cluster [18].

Figure 7 plots the light output power (L) and the voltage (V) with respect to the injection current (I) for the pre-TMIn-treated and untreated LEDs. The treated sample exhibited higher output power throughout the whole injection current density. At an injection current of 350 mA, the light output power of the treated LED was 59% higher than that of the untreated LED and the forward voltages are 3.66 and 3.68 V for the samples without and with pre-TMIn treatment. We attribute this enhancement in light output power to the presence of In-rich clusters in the pre-TMIn-treated sample; these clusters could confine electrons and holes efficiently. As a result, indium treatment plays an important role in improving the luminescence of green LEDs.

4. Conclusion

Pre-TMIn treatment of the InGaN layer appears to be an efficient means of improving the luminescence performance of an InGaN green LED because it leads to a smoother surface and a shorter radiative decay time. XRD revealed that pre-TMIn treatment did not change the structure of the

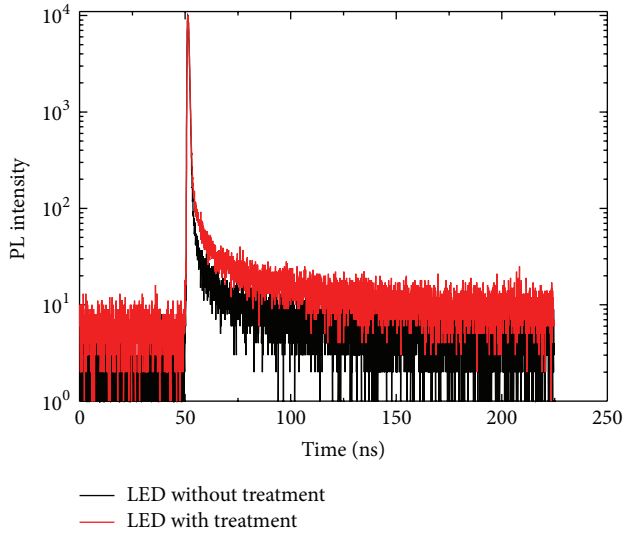


Figure 6: Time-resolved photoluminescence decay profiles of the LEDs prepared with and without TMIn treatment.

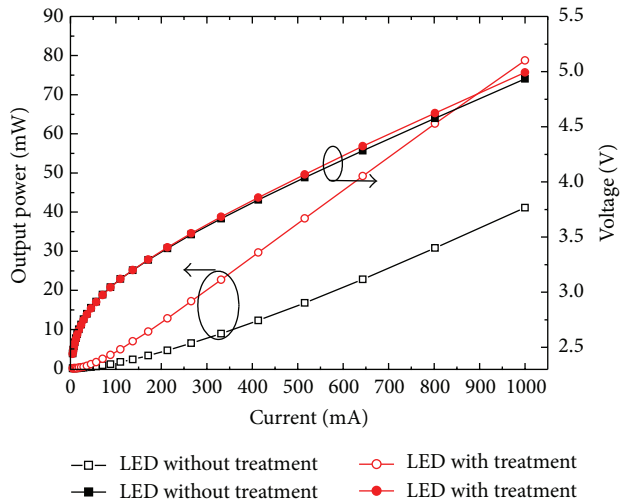


Figure 7: Plots of light output power and forward voltage with respect to injection current for the LEDs prepared with and without TMIn treatment.

MQWs and only slightly increased the indium concentration. Photoluminescence spectra of the treated sample featured a red-shifted peak wavelength, due to enhancement of the indium-cluster, which can be seen by HR-TEM. In addition, the light output power improved significantly when the LED was prepared with pre-TMIn treatment of the InGaN layer.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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