Optical properties of InGaN/GaN multiple quantum wells with trimethylindium treatment during growth interruption

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A B S T R A C T

In this study, the effects of trimethylindium (TMIn) treatment on the optical properties of InGaN/GaN multiple quantum wells with green emission were investigated. With TMIn treatment, InGaN decomposition, indium aggregation, and indium diffusion into the barrier region were suppressed such that more homogeneous indium composition and lower defect density lead to stronger and more uniform luminescence. It benefits the fabrication process and device design that TMIn treatment only enhances the luminescence intensity while changing the luminescence peak position (CIE coordinate) only a little. The research results provide important information to optimize the performance of green LEDs.

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1. Introduction

Solid-state lighting through light emitting diodes (LEDs) is considered as the next generation lighting [1]. The quantum efficiency (QE) of InGaN LEDs at wavelengths between 365 and 450 nm has been greatly improved but the QE of InGaN green LEDs is still relatively poor [2]. Because the large lattice mismatch between InN and GaN leads to low miscibility [3], indium aggregation and phase separation usually occur through spinodal decomposition [4]. Spinodal decomposition produces quantum-dot-like structures, which form spatial potential fluctuations. With these clusters, carriers are localized in potential minima for effective radiative recombination [5–7]. It was claimed that the electroluminescence (EL) emission comes from the recombination of localized excitons in In-rich InGaN clusters [8,9].

The process of aggregation and the effect of carrier localization become stronger with increasing indium content [4,10]. InGaN alloys at a high indium mole fraction often lead to low crystalline quality because of indium aggregation and/or phase separation [4]. V-shaped defects are the most common defects of InGaN/GaN multiple quantum wells (MQWs). V-shaped defects are easily formed in high-indium MQWs and triggered by threading dislocations in the buffer layer. A threading dislocation or a stacking fault usually terminates on the sample surface with a V-shaped defect [11–13]. These defects are formed because of strain relaxation associated with stacking faults or indium segregation [14–16]. In our previous study, it was determined that the performance of green LEDs can be greatly improved by reducing the V-shaped defects through trimethylindium (TMIn) treatment and growth parameter optimization [17]. However, the mechanism of improvement due to TMIn treatment was not well studied.

In this study two samples, with and without TMIn treatment, were prepared to study the effects of TMIn treatment on InGaN/GaN MQWs. With TMIn treatment, the more homogeneous indium composition and lower defect density lead to stronger and more uniform luminescence.

This paper is organized as follows: In Section 2, sample preparation and experimental methods are described. In Section 3, experimental results are discussed. Finally, conclusions are drawn in Section 4.

2. Sample structures and experimental procedures

To study the effects of TMIn treatment during the growth interruption at each InGaN-well-to-GaN-barrier interface, InGaN/GaN MQWs were grown on c-sapphire by low-pressure metal organic vapor phase epitaxy (MOVPE). Ammonia(NH₃), trimethylgallium
(Ga(CH₃)₃), triethylgallium (Ga(C₂H₅)₃), TMIn, trimethylaluminum (Al(CH₃)₃), bicyclopentadienyl (Cp₂Mg), and disilane (Si₂H₆) were used as the dopants. The sample structures consist of a 30 nm GaN nucleation layer, a 1.5 μm GaN buffer layer, a 2.5 μm n-type GaN contact layer, and five GaN[15 nm]/InGaN[3 nm] MQWs. The substrate temperatures for the low-temperature GaN nucleation layer and high temperature GaN buffer layer were 530 and 1100 °C, respectively. The QWs and barriers were grown at 780 °C. At each InGaN-well-to-GaN-barrier interface during the growth interruption of QW an extra step, in which only TMIn and NH₃ were allowed to flow into the reactor, was introduced. This is called “TMIn treatment”. The details of growth procedures were described in the previous study [17]. With the same sample structures two samples, with and without TMIn treatment were prepared. Experiments were conducted on the two kinds of samples.

The structural properties of the TMIn-treated and -untreated samples were investigated by a high-resolution X-ray diffraction (XRD; Bede D1). The surface morphology was revealed by atomic force microscopy (AFM). Cathodoluminescence (CL) images were obtained using a Gatan monoCL3 spectrometer in a scanning electron microscope system (JEOL JSM 7000 F). The kinetic energies of electrons in CL measurements ranged from 5 to 20 kV with an electron beam current of 60 to 300 pA. Photoluminescence (PL) measurements were carried out with the 325 nm line of a 50 mW He–Cd laser for excitation. For time-resolved photoluminescence (TRPL) measurements, a picosecond diode laser (PicoQuant) generated optical pulses of 100 ps width with a 5 MHz repetition rate to excite the epilayers. The excitation energy was 3.324 eV (375 nm) for pumping the InGaN wells. Light emitted from the sample was detected by a photomultiplier (PMT) and a monochromator. The signal from the PMT was recorded by means of time-correlated single-photon-counting technology (Model TimeHarp 200, PicoQuant). The overall time resolution was 50 ps. The samples were placed in a cryostat for temperature-dependent measurements.

3. Results and discussion

3.1. Material characteristics: XRD and AFM measurements

Fig. 1 shows the X-ray diffraction patterns of the two samples. Diffraction peaks corresponding to GaN, InGaN, and InN were observed [4]. For the TMIn-untreated sample, the GaN diffraction peak is mainly from the contact and barrier layers. The side shoulder with a broad distribution below the GaN main peak (31.5°) was attributed to InGaN aggregation with various indium contents, sizes, and shapes in the quantum wells. The weak InN diffraction peak implies slight phase separation. For the TMIn-treated sample, the diffraction peak of GaN shows a narrower width and the broad side shoulder mostly disappears (except for the peak around 33.1°). Because indium diffusion into the barrier region was suppressed, a purer phase and more homogeneous indium composition were observed. The weak peak around 33.1° implies that 30–35% indium content is the major indium composition in the well region. The small InN diffraction peak implies less phase separation in the TMIn-treated sample.

Fig. 2 shows the surface morphologies of the two samples as revealed by AFM. With TMIn treatment, the surface roughness decreases from 5.016 to 2.094 nm. TMIn treatment suppresses InGaN decomposition and indium aggregation such that lower V-shaped defect densities and less surface roughness were obtained. Hence, the surface morphology of the TMIn-treated sample is more uniform than that of the TMIn-untreated sample.

3.2. Optical characteristics: CL, PL, and TRPL measurements

Fig. 3(a) and (b) shows spatially resolved CL images for the TMIn-untreated and -treated samples, respectively. An electron acceleration voltage excitation of 10 kV roughly corresponds to the penetration depth 600 nm. For the TMIn-untreated sample, the CL image shows light spots a few hundred nanometers in size and tiny glimmers in the background. The light spots a few hundred nanometers in size correspond to the indium-rich clusters [13]. The dark regions may represent the defects, which correspond to nonradiative recombination. For the TMIn-treated
sample, fewer and smaller light spots and a brighter background were observed. This directly indicates the advantages of the TMIn treatment for improving luminescence efficiency. A more uniform and brighter luminescence reveals the better sample quality and more homogeneous indium composition of the TMIn-treated sample. In addition, Fig. 4(a) and (b) shows the CL spectra of the TMIn-untreated and -treated samples, respectively. In the TMIn-untreated sample, the green emission is stronger than the UV emission (around 360 nm) from GaN in a shallow layer (with 5 and 10 kV probes). As the electron acceleration voltage increases to excite deep regions, the green emission reaches saturation and the UV emission increases. With the same excitation voltage, the stronger green emission of the TMIn-treated sample also shows the advantages of the TMIn treatment for improving luminescence efficiency.

Fig. 4(a) shows the normalized PL spectra at 10 K for the two samples. The spectra on the high-energy side for the two samples nearly coincide, while the spectrum on the low energy side of the TMIn-treated sample becomes slightly stronger. It was claimed that the electroluminescence emission comes from the recombination of localized excitons in In-rich InGaN clusters with various indium contents, sizes, and shapes in the quantum wells [8–12]. Because TMIn treatment suppresses indium diffusion into the barrier region, a higher indium composition and lower effective potential level in the well region are observed. The enhanced luminescence on the low energy side can be due to carrier recombination in the lower-energy localized states. In addition, Fig. 5(b) shows the PL peak position as a function of temperature for each of the two samples. The PL peak positions of the two samples are nearly the same. For both samples, the temperature-dependent PL peak positions show an S-shaped behavior. The S-shaped behavior has been attributed to the carrier dynamics associated with carrier localization in potential minimums [18,19]. Furthermore, Fig. 5(c) shows the temperature-dependent PL integral intensity for both samples. The PL integral intensities were normalized at low temperature (~10 K). At higher temperature(s), the enhanced nonradiative recombination decreased the PL integral intensity. The stronger PL intensity of green emission for the TMIn-treated samples is consistent with the CL results. It helps the fabrication process and device design.
that TMIn treatment enhances the luminescence intensity, and changes the luminescence peak position (CIE coordinate) only a little. To study the effect of TMIn treatment on the carrier dynamics, TRPL measurements were conducted. Fig. 6 shows the TRPL decay profiles at 10 K for (a) TMIn-untreated and (b) TMIn-treated samples. For both samples the curve corresponding to the high-energy side (the curve of 500 nm) shows bi-exponential decays, which are relatively faster in the early stage and slower in the extended range. Near the PL spectral peak in the early stage, there exist delayed slow rises for a few hundred ps. Similar temporal behaviors, attributed to exciton transfer between localized states, were observed in the InGaN/GaN system in our previous study [18,19]. In addition, compared with the untreated sample, the decay profiles corresponding to the same emission wavelength decay are faster for the TMIn-treated sample. It was noted that radiative recombination should be a dominant process at low temperature(s). Hence, the better sample quality of the TMIn-treated sample helps the recombination rate.

The multiple exponential curves could be fitted well with the bi-exponential model (except the delayed slow rise duration)

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + I_0 \]

where \( \tau_1 \) and \( \tau_2 \) are the early stages (fast) and extended (slow) decay times, respectively, and \( A_1 \) and \( A_2 \) are the contributions of the corresponding parts to the total PL intensity. \( I_0 \) is the background intensity. Because the amplitude fractions of \( A_1 \) for all PL decay profiles are over 80%, the discussion is focused on the early-stage decay times. Fig. 7 shows the early-stage decay times as a function of wavelength for the two samples. On the short-wavelength side, the early-stage decay time can be shorter than 1 ns. Besides carrier recombination, such a short decay time was attributed to the carrier transport process from the higher-energy localized states to lower-energy localized states. In addition, the decay time increases first and then decreases with increasing emission wavelength. The increasing trend left of the peak of the decay times is a typical characteristic of a localized exciton distribution within a semiconductor alloy [18–20]. Within the localization model, strongly localized (lower-energy) excitons decay primarily via radiative recombination while weakly localized (higher-energy) excitons exhibit a decreased decay time due to the additional channel of transfer to lower-energy sites. In addition, the shorter decay times at the long wavelength ends of the spectra can be explained by the fact that it may be more difficult for carriers to transfer to strongly localized states [18–20]. In addition, the decay times for the TMIn-treated sample are shorter than those of the untreated sample. Because TMIn treatment suppresses InGaN decomposition and indium aggregation, the more homogeneous indium composition, lower defect density, and better sample quality improve recombination efficiency and help increase the recombination rate.

4. Conclusions

In summary, we have studied the effects of TMIn treatment on the optical properties of InGaN/GaN MQWs. With TMIn treatment, more homogeneous indium composition and lower defect density lead to stronger and more uniform luminescence. It can benefit the fabrication process and device design that TMIn treatment enhances the luminescence intensity while changing the luminescence peak position (CIE coordinate) only a little. The research results provide important information to optimize the performance of green LEDs.

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