Enhanced localisation effect and reduced quantum-confined Stark effect of carriers in InGaN/GaN multiple quantum wells embedded in nanopillars

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A conventional planar InGaN/GaN multiple quantum well (MQW)-based light emitting diode (LED) producing a blue-green dual-wavelength spectrum, due to phase separation in the InGaN well layers, is grown, and fabricated into a nanopillar (NP) LED array structure with an etching depth penetrating through the MQW region using a top-down dry etching process. Excitation power and temperature dependences of the photoluminescence (PL) spectra of the planar and NP samples have shown that the fabrication of the nanotexture not only decreases the quantum-confined Stark effect (QCSE), but also enhances the carrier localisation effect, both in the InGaN matrix region and in the In-rich quasi-quantum dot (QD) region, due to the reduction of the strain relaxation-induced piezoelectric field in the MQWs embedded in the nanopillars. Moreover, the fabrication of the nanotexture also improves the light extraction efficiency (LEE), due to the increased light-extracting surface area and light-guiding effect. These results are also consistent with the measured quantum efficiencies of the two samples.

\section{1. Introduction}

InGaN/GaN multiple quantum well (MQW) structures, as active layers, have been widely used in light emitting diodes (LEDs) due to the tenability of the emitted light from UV through visible spectral range [1–3]; however, due to the large discrepancy in atomic size between indium and gallium, and a large lattice mismatch of 11\% between InN and GaN, either a phase separation or a slight composition fluctuation always occurs in the InGaN well layers [4–7]. In such a structure, on one hand, these In-rich regions (i.e., so-called quasi-quantum dots (QDs)) act as carrier localisation centres, providing deep potential levels to suppress the outflow of carriers toward surrounding non-radiative centres [5,7–9], on the other hand, it also results in generation of structural defects that act as non-radiative recombination centres which is detrimental to the radiative recombination efficiency [5,7,10,11]. Also, due to a large lattice and thermal mismatch between the InGaN well layer and the GaN barrier layer, a large strain is induced in the MQWs, which can generate a large piezoelectric field in the MQW region. This induces a quantum-confined Stark effect (QCSE) therein, and therefore reduces the radiative recombination efficiency of the carriers in the MQWs [5,10,12]. Besides, as most commercial LEDs are fabricated on the basis of a conventional structure with a planar light-extracting surface, their light extraction efficiency (LEE) is limited by an internal reflection effect due to the large difference in the refractive index between the GaN (n = 2.5) and air (n = 1) [13,14]. Therefore, to obtain a high-quantum efficiency, the conventional c-plane InGaN/GaN MQW-based LED structures, especially for green LED structures with higher indium concentrations, should be optimised to improve the radiative recombination efficiency (i.e., internal quantum efficiency IQE) and the LEE.

Recently, it has been reported that InGaN/GaN MQW-based nanopillar (NP) or nanowire (NW) LED array structures can effectively alleviate the aforementioned problems associated with conventional planar LEDs [15,16]: this is because the fabrication of the nanotextures penetrating through the MQW region can increase the free surface areas and surface/volume ratios which not only results in the reduction of the QCSE due to the relaxation of the strain in the MQWs regions embedded in these NPs or NWs, but also improves the probability of escape of photons inside the LED and light-guiding effect [17–22]. Therefore, the IQE and LEE can be significantly improved after the etching process
However, it is noted that most of the related studies are mainly concerned with the effect of this nanotexture on the QCSE in the InGaN matrix and LEE of InGaNGaN MQW LEDs with single wavelength emission arising from the InGaN matrix. In contrast, research into the effect of such nanotextures on the localisation effect of the carriers in the InGaN/GaN MQW LEDs producing a dual-wavelength emissions arising from the InGaN matrix and In-rich QDs due to a phase separation, is rarely reported, although it is important to obtain high-performance LEDs that emit different wavelengths with the appropriate power ratio.

In this study, a conventional planar InGaN/GaN MQW LED producing a blue-green dual-wavelength spectrum, due to phase separation in the InGaN well layers, was first grown on a (0001)-oriented sapphire using metal organic chemical vapour deposition (MOCVD). Then, based on the planar LED, an NP LED array structure with an etching depth penetrating through the MQW region was fabricated by using electron beam lithography (EBL) and inductively coupled plasma reactive ion etching (ICP-RIE). Microstructure properties of the planar sample were analyzed by high-resolution transmission electron microscopy (HRTEM), and the NP sample was structurally characterised using a scanning electron microscope (SEM). Finally, the excitation power and temperature dependences of the photoluminescence (PL) spectra from the two MQW structures are measured to clarify the underlying physics of carrier transfer and distribution as well as recombination therein.

2. Experiments

2.1. Planar LED fabrication

The InGaN/GaN MQWs-based planar LED (denoted as planar sample) was grown on a c-plane sapphire substrate using MOCVD. The precursors of Ga, In, N, and Si were trimethylgallium (TMGa), trimethylindium (TMIn), ammonia (NH3), and silane (SiH4), respectively. The epitaxial structure consisted of a 40-nm-thick low-temperature GaN nucleation layer, a 2-μm-thick unintentionally doped GaN buffer layer, a 2-μm-thick Si-doped n-GaN layer, and followed by 10 periods of InGaN(3 nm)/GaN(8 nm) MQWs as the active region, a 65-nm-thick low temperature p-GaN layer, a 28-nm-thick p-AlGaN layer, and a 200-nm-thick p-GaN layer. The structural sketch of the planar sample is shown in Fig. 1(a). The nominal indium content of the active region was approximately 32%.

![Flowchart showing processing steps for the fabrication of InGaNGaN MQW-based NP LED array structure using the top-down method.](image)

![Flowchart for the fabrication of the NP sample using a top-down etching method.](image)

2.2. Nanopillar array LED fabrication

An NP LED array structure (denoted as NP sample) was obtained starting from the aforementioned planar sample. Fig. 1 shows the process flowchart for the fabrication of the NP sample using a top-down etching method. First, a 60 nm-thick SiO2 layer was deposited on the surface of the planar sample by plasma enhanced chemical vapour deposition (PECVD), then, a 200 nm-thick polymethyl methacrylate (PMMA) resist was spin-coated onto the sample (see Fig. 1(b)). The PMMA resist was then exposed by electron beam lithography (EBL; JBX-6300FS). The exposed PMMA resist was developed by methyl isobutyl ketone (MIBK): isopropyl alcohol (IPA) (1:3) at room temperature for 40 s, rinsed in IPA for 30 s and blown dry by pure nitrogen gas, and a uniformly distributed array of circular holes with a diameter of approximately 110 nm and pitch of approximately 150 nm was obtained (Fig. 1(c)). After developing, a 60 nm-thick Cr layer was deposited by e-beam evaporation (Peva-600E) (Fig. 1(d)). After lift-off in acetone, the patterned Cr nano-disk structure used as a mask for etching the SiO2 layer by ICP-RIE (Oxford Instruments PLS100 ICP180), was formed on its surface. ICP-RIE operating at pressure of 10 mT with a C6F5/Ar flow of 10/40 sccm was used to etch the SiO2 layer at a substrate temperature of 15 °C. ICP and RF powers were 300 and 30 W, respectively. The etching time was set to 30 s, corresponding to an etch depth of about 60 nm. As a result, the Cr/SiO2 nano-disk structure, which was subsequently used as a mask for fabricating InGaN/GaN MQW NP arrays of the desired dimensions using ICP-RIE, was formed (Fig. 1(e)). For the ICP-RIE of InGaN/GaN active region, the flows of Cl2, Ar, and BCl3 were 18, 15, and 25 sccm respectively with an ICP/RF power of 300/50 W, an operating pressure of 10 mT, and at a constant temperature of 25 °C. The etching time was set to 4 min, corresponding to an etching depth of about 400 nm at which the etching depth is sufficient to penetrate through the entire active region (i.e., reaching the Si-doped n-GaN layer, Fig. 1(f)). Subsequently, a Cr etchant ((NH4)2Ce(NO3)6/CH3COOH/H2O) solution were used to remove the Cr and SiO2 mask, respectively. At this point, the obtained NP LEDs are cone structures with oblique sidewalls. Finally, the InGaN/GaN MQW-based NP LEDs with smooth facet surfaces and vertical facet sidewalls were achieved by further etching in KOH-based etchant (AZ400K photoresist developer), as shown in Fig. 1(g).
2.3. Other details

Microstructure properties of the planar sample were analyzed by HRTEM (JEM-2100), and the NP sample was structurally characterised by SEM (FEI Helios600i). For excitation power-, and temperature-dependent PL measurements, the samples were mounted on a Cu cold-stage in a temperature-variable closed-cycle He cryostat to allow variation of the sample temperature between 6 and 300 K. A 405 nm cw semiconductor laser was used as an excitation light source with a spot size of approximately 170 µm, and the excitation power was varied from 0.5 µW to 50 mW. The PL signal from the sample was dispersed by a Jobin-Yvon iHR320 monochromator and detected by a thermo-electrical cooled Synapse CCD detector.

3. Results and discussion

3.1. Structural characterization

Fig. 2(a) illustrates a typical cross-section HRTEM picture of the planar sample. The barriers and wells in the MQW can easily be distinguished by the fluctuations in the indium composition. Also, these samples exhibit a uniform distribution of areas with a strong black/white contrast inside the wells, implying strong strain, which may result from coherent interfaces between the In-rich QDs and the surrounding InGaN matrix. The strain relaxation can be explained by the fact that the fabrication of the nanopillar LED array structure penetrating through the MQW region increases the surface-to-volume ratio of the MQW region embedded in these nanopillars.

Fig. 2(b) shows a typical SEM image of the resulting NP sample with cylindrical shapes and smooth sidewalls. From the SEM image, the heights, diameters, and pitches of the nanopillar LEDs are seen to almost be uniform, and were estimated to be approximately 400, 100, and 150 nm, respectively. These parameters were consistent with those envisaged at the design stage.

3.2. Optical characterization

Fig. 3 presents the PL spectra of the planar and NP samples measured at 20 µW and 6 K. As can be seen from Fig. 3, the PL spectra of both the samples exhibit two InGaN-related emission peaks at around 2.305 eV (537.74 nm) and 2.635 eV (470.39 nm), due to the strong phase separation in the InGaN well layers, as evinced by the HRTEM image in Fig. 2(a). The higher energy peak corresponds to the InGaN matrix-related near-band-edge transition (denoted by \( P_M \)) and the lower energy peak (green) is assigned to the In-rich QDs-related transition (denoted by \( P_D \)) [26,27]. Moreover, Fig. 3 also shows that both the emissions \( P_M \) and \( P_D \) of NP sample exhibit a pronounced peak blue-shift and a significant enhancement in PL intensity, relative to that of the counterpart planar sample. The behaviour for NP sample may be attributed to reduction of QCSE originating from the relaxation of the strain in the MQWs embedded in the nanopillars. To elucidate the transfer and recombination process of the carriers inside these two phase-separated structures, the excitation power and temperature dependences of the PL spectra for both samples will be investigated and discussed in the following sections.

Fig. 4(a) and (b) show the excitation power dependences of the \( P_M \) and \( P_D \) peak energies of the two samples measured at 6 K, respectively. As shown in Fig. 4, when increasing the excitation power from 0.5 µW to 50 mW, the \( P_M \) peak blue-shift (\( \Delta E_{P_M} \)) and the \( P_D \) peak blue-shift (\( \Delta E_{P_D} \)) are 38.7 and 47.2 meV for the planar sample, and 21.3 and 34.3 meV for the NP sample, respectively, indicating that both the emissions \( P_M \) and \( P_D \) of NP sample exhibit a smaller peak blue-shift than that of the counterpart planar sample. The behaviour of the NP sample can be attributed to reduction of the QCSE, due to the relaxation of the strain in the MQWs embedded in the nanopillars including the InGaN matrix and the In-rich QDs. The strain relaxation can be explained by the fact that the fabrication of the nanopillar LED array structure penetrating through the MQW region increases the surface-to-volume ratio of the MQW region embedded in these nanopillars [17,28,29].

Fig. 5(a) and (b) show the temperature dependences of the \( P_M \) and \( P_D \) peak energies of the two samples measured at 20 µW, respectively. As can be seen in Fig. 5, the anomalous temperature behaviours of both the \( P_M \) and \( P_D \) peak energies for the two samples are seen to be “S-shaped” (decrease-increase-decrease), which are attributed to the potential inhomogeneity, and localised nature, of carrier recombination due to compositional fluctuations in the InGaN matrix and In-rich QDs [30–32]. Moreover, it is also found from Fig. 5 that both the \( P_M \) and \( P_D \) peak energies of the NP sample show stronger “S-shaped” temperature dependences, compare with that of the counterpart planar sample; and while the “S-shaped” peak energy versus temperature curves of both the \( P_M \) and \( P_D \) emissions of the NP sample have higher inflection point temperatures (\( T_{max} \)) than that of the counterpart planar sample, where the inflection point temperatures \( T_{min} \) and \( T_{max} \) respectively correspond to the minimum and maximum peak energy for both samples. For the \( P_M \) (\( P_D \) emission, \( T_{min} \) and \( T_{max} \) are 50 and 170 K (60 and 240 K) for the planar sample, and 70 and 190 K (90 and 270 K) for the NP sample, respectively. The features show that both the InGaN matrix region and QDs region of the NP sample should have a stronger localisation effect than that of the counterpart planar sample [30,31].

To confirm this argument, the degree of localisation effect of the two

![Fig. 2](image_url)

Fig. 2. (a) A cross-section HRTEM image of the InGaN/GaN MQWs-based planar sample. (b) A SEM image of the InGaN/GaN MQWs-based NP LED sample taken at 54° tilt angle.
samples can be obtained by fitting the peak energy v. temperature curves shown in Fig. 5 by using a band-tail model [30]:

$$E(T) = E(0) - \alpha T^2/(T + \beta) - \sigma^2/k_B T$$

(1)

where $E(T)$ is the emission energy at $T$, $E(0)$ the energy gap at 0 K, $\alpha$ and $\beta$ are Varshni coefficients, $k_B$ is the Boltzmann constant, and $\sigma$ indicates the degree of localisation. The fitting results (Fig. 5) show that, $\sigma$ values of the InGaN matrix and In-rich QDs are 20.9 and 23.5 meV for the planar sample, and 27.9 and 30.1 meV for the NP sample, respectively, indicating that the $\sigma$ values of both the InGaN matrix and In-rich QDs of the NP sample are larger than that of the counterpart planar sample. These results further confirm the aforementioned argument that both the InGaN matrix and QDs of the NP sample confer a stronger localisation effect than that of the counterpart planar sample [30,33,34].

To explain the physical mechanism responsible for the aforementioned excitation power- and temperature-dependent behaviours of the PL peak energies shown in Figs. 4 and 5, that is, the differences both in the QCSE and in the localisation effect between the two samples, schematic diagrams indicating the possible mechanism of carrier transfer and distribution in two different QWs, without (denoted by the $F_0$ structure), and with (denoted by the $F_1$ structure), a piezoelectric field, are supposed (Fig. 6). As can be seen from Fig. 6, the profiles of both the InGaN matrix and the QD regions are flat for the $F_0$ structure (Fig. 6(a)), and are significantly inclined for the $F_1$ structure due to the piezoelectric field (Fig. 6(b)). As a result, with increasing excitation power the Coulomb screening of the QCSE both in the InGaN matrix and in the QD regions, corresponding to the increase of the peak energy for both the $P_M$ and $P_D$ emissions, should be observed only in the $F_1$ structure. This can explain the aforementioned experimental results (Fig. 4), which with, upon increasing the excitation power from 0.5 µW to 50 mW, both the $P_M$ and $P_D$ emissions of the NP sample exhibit a smaller peak blue-shift than that of the counterpart planar sample, due to the reduction of the strain relaxation-induced QCSE both in the InGaN matrix and in the QD regions embedded in the nanopillars.

On the other hand, it is also seen from Fig. 6 that compared with the case of the $F_0$ structure, for the $F_1$ structure, the shallow localised carriers in the InGaN matrix and QD regions, easily escape and become free carriers in their respective regions, due to the role of the piezoelectric field (i.e., the inclination of the piezoelectric field-induced InGaN matrix and QD profiles), thus resulting in both the InGaN matrix and QD regions of the $F_1$ structure having a more significant localisation effect than that of the counterpart $F_1$ structure. The aforementioned analysis explains the experimental results (Fig. 5), in which both the InGaN matrix and the QD regions of the NP sample have stronger localisation effects than that of the counterpart planar sample, due to the reduction of the strain relaxation-induced piezoelectric field both in the InGaN matrix and in the QD regions embedded in the nanopillars.

To investigate the effect of the etching process on efficiency, the integrated PL intensity divided by the excitation power, i.e., relative external quantum efficiency (EQE), is plotted as a function of temperature for both the InGaN matrix and the In-rich QDs of the two samples (Fig. 7). As shown in Fig. 7, upon increasing the excitation power.
power from 0.5 µW to 50 mW, all EQEs for both the samples increase markedly in the lower excitation power range (below about 5 mW), and then increase at a lower rate. The former is mainly attributed to the dominant non-radiative recombination, the latter mainly is due to gradual saturation of the non-radiative recombination centres [30,35–37]. Moreover, it is also found from Fig. 7 that, both the InGaN matrix and In-rich QDs of the NP sample have a higher EQE than that of the counterpart planar sample. The improvement in the EQE for the NP sample is attributed to the following three factors: 1) the reduction of the strain relaxation-induced QCSE in the MQWs embedded in the nanopillars, including the InGaN matrix and In-rich QD regions (q.v., Fig. 4); 2) the enhancement of the localisation effect of the carriers both in the InGaN matrix and in the In-rich QD regions, due to the reduction of the probability of the carrier escaping from the localised states originating from the reduction of the strain relaxation-induced piezoelectric field after etching (Fig. 5); 3) the enhancement of the LEE, since the fabrication of the nanotexture improves the probability of escape of photons inside the LED due to the larger light-extracting surface area and light-guiding effect.

4. Conclusions

In summary, a conventional planar InGaN/GaN MQWs-based LED producing a blue-green dual-wavelength spectrum, due to phase separation in the InGaN well layers, is grown, and fabricated into an NP LED array structure with an etching depth penetrating through the MQW region using an ICP-RIE process. The excitation power and temperature dependences of the PL spectra of the two samples show that with increasing the excitation power from 0.5 µW to 50 mW both the emissions $P_M$ and $P_D$ of the NP sample exhibit a smaller peak blue-shift than that of the counterpart planar sample. This is attributed to the reduction of the strain relaxation-induced QCSE in the MQWs embedded in the nanopillars. In addition, interestingly, the NP sample also shows a stronger carrier localisation effect both in the InGaN matrix and in In-rich QDs than the planar sample. The behaviour for the NP sample is attributed to the suppression of the carrier escaping from the localised states, due to the reduction of the strain relaxation-induced polarisation field after etching. Moreover, the fabrication of the nanotexture also enhances the LEE, due to the increased probability of escape of the photons inside the NP LEDs and the light-guiding effect. These results are consistent with the experimental data that showed that both the InGaN matrix and In-rich QDs of the NP sample have a higher EQE than that of the counterpart planar sample, due to the aforementioned enhancement of the IQE and LEE after etching.

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References


