Enhanced performance of InGaN/GaN multiple-quantum-well light-emitting diodes grown on nanoporous GaN layers

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Abstract: We demonstrate the high efficiency of InGaN/GaN multiple quantum wells (MQWs) light-emitting diode (LED) grown on the electrochemically etched nanoporous (NP) GaN. The photoluminescence (PL) and Raman spectra show that the LEDs with NP GaN have a strong carrier localization effect resulting from the relaxed strain and reduced defect density in MQWs. Also, the finite-difference time-domain (FDTD) simulation shows that the light extraction efficiency (LEE) is increased by light scattering effect by nanopores. The output power of LED with NP GaN is increased up to 123.1% at 20 mA, compared to that of LED without NP GaN. The outstanding performance of LEDs with NP GaN is attributed to the increased internal quantum efficiency (IQE) by the carrier localization in the indium-rich clusters, low defect density in MQWs, and increased LEE owing to the light scattering in NP GaN.

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References and links


1. Introduction

Recently, GaN-based light-emitting diodes (LEDs) have been rapidly developed because of their tremendous potential for energy-efficient lighting and widespread LED applications. Many researchers have focused on improving the external quantum efficiency (EQE) of LEDs. Unfortunately, the optical performance of GaN-based LEDs still suffers from low internal quantum efficiency (IQE) and light extraction efficiency (LEE) [1–5]. Generally, it is believed that the low IQE is related to the poor crystal quality of the GaN epilayer and the polarization field in LEDs [6–9]. The large mismatch of lattice constants and thermal expansion coefficients between the GaN epilayer and sapphire substrate reduce the crystal quality of GaN layers by introducing threading dislocations that act as non-radiative recombination centers [10,11]. Furthermore, the quantum confined Stark effect induced by the strong built-in piezoelectric field in InGaN/GaN multiple quantum wells (MQWs) lowers carrier recombination rate by increasing the spatial separation between the electron and hole wavefunctions [12]. Another important reason for the low EQE of such devices is their low LEE, which results from the total internal reflection of light emitted from MQWs because of the large difference in the refractive indices of GaN (n = 2.5) and air (n = 1) [13–15]. Recently, NP GaN formed by electrochemical (EC) etching has shown promise as a way to improve the crystal quality of overgrown GaN [16,17]. Soh et al. [18] reported that a low
defect density and stress relaxation of GaN regrown on NP GaN were achieved by the presence of NP GaN and effect of dislocation annihilation. Although it has been shown that a NP GaN underlayer is a simple and effective method to reduce the defect density and compressive stress state of regrown GaN layers, the electroluminescence and electrical properties of LEDs grown on a NP GaN underlayer have not been reported. In this paper, we reveal that the optical and electrical characteristics of LEDs can be improved by growth on a NP GaN layer.

2. Experimental details

InGaN/GaN MQW LEDs were grown on a c-plane (0001) sapphire substrate by metal-organic chemical vapor deposition. Figure 1(a) shows a schematic diagram of a LED grown on a NP GaN layer. A 2.5 μm-thick undoped GaN layer and a 1.5 μm-thick n-type GaN layer with a doping concentration of $6 \times 10^{18}$ cm$^{-3}$ were deposited on the sapphire substrate. To obtain a NP GaN layer, the n-type GaN layer was etched in 0.2 M oxalic acid electrolyte at room temperature for 10 min using a platinum rod as the cathode. NP GaN layers with different porosities were obtained at applied voltages of 11, 17, and 30 V. Then, a 500 nm-thick undoped GaN layer was grown on NP GaN as a current-blocking layer to prevent current leakage to NP GaN. A 2 μm-thick n-type GaN layer and six periods of InGaN/GaN (2.3/7.7 nm) MQWs were grown on the undoped GaN current-blocking layer, followed by growth of a 200 nm-thick p-type GaN layer. Figure 1(b) shows that nanosized air voids formed in the NP GaN layer after an InGaN/GaN MQW LED was grown on NP GaN that was electrochemically etched at an applied voltage of 17 V.

3. Results and discussion

Figures 1(c) and 1(d) show top and cross-sectional scanning electron microscopy (SEM) images of NP GaN layers fabricated by EC etching at an applied voltage of 17 V. Figure 1(c) shows that the size distribution of nanopores is in the range of 23–53 nm and the area of pores on the surface is ~11.0%. Other two samples showed the size distribution of nanopores and area of pores on the surface in the range of 12–24 nm and ~1.1% at 11 V, and in the range of 28–240 nm and ~23.3% at 30 V, respectively. These results indicate that the size distribution and surface area of nanopores are increased with increasing the applied voltage in the EC etching of n-type GaN. The nanopores in the NP GaN layers had a columnar structure with a height of 1.5 μm, as shown in Fig. 1(d). The nanopores in NP GaN changed to nanosized sphere-like voids after regrowth of the LED epilayer (Fig. 1(b)). The NP GaN layer has a metastable morphology after EC etching because of its high surface area and high curvature, as reported for porous materials including NP silicon [19–21]. The marked shape transformation from columnar- to nanosphere-like voids occurs in NP GaN to minimize the surface energy of nanospheres by surface diffusion and atomic migration during the regrowth of LEDs on NP GaN.
Figure 2 shows the Raman spectra of GaN epilayers regrown on NP GaN layers. The NP GaN layers were etched at applied voltages of 11, 17, and 30 V. The $E_2$ phonon mode peak of the as-grown GaN and regrown GaN layers on NP GaN etched at 11, 17, and 30 V (denoted GaN(NP GaN)-1, GaN(NP GaN)-2, and GaN(NP GaN)-3, respectively), appear at 568.3, 568.3, 567.6, and 567.1 cm$^{-1}$, respectively. The shift of the $E_2$ phonon mode peak is related to the relaxation of residual strain and can be calculated using the following equation [22]:

$$\Delta \omega_y = \omega_y - \omega_o = K_y \cdot \sigma_{xx}$$

(1)

where $\omega_o$ and $\omega_y$ represent the Raman peaks of the 500 nm-thick regrown undoped GaN layer with and without a NP GaN underlayer, respectively. A proportionality factor $K_y$ of 4.2 cm$^{-1}$ GPa$^{-1}$ is used for hexagonal GaN [22]. GaN(NP GaN)-3 shows the largest red shift of 1.2 cm$^{-1}$ with respect to that of as-grown GaN, as shown in Fig. 2. This corresponds to a relaxation of compressive stress ($\sigma_{xx}$) of 0.286 GPa. Figure 2 also shows that the relaxation of the residual strain of the GaN layer regrown on NP GaN is increased with increasing porosity of the NP GaN layer. This indicates that the compressive stress in the regrown GaN layer on NP GaN is relaxed because of shape transformation and atomic migration in the nanovoids of NP GaN.
Room-temperature photoluminescence (PL) and temperature-dependent PL (TD-PL) spectra of LEDs grown on the NP GaN layers were measured. The LEDs grown on as-grown GaN, and GaN(NP GaN)-1, −2, and −3 are denoted reference LED and LED(NP GaN)-1, −2, and −3, respectively. Figure 3(a) shows that the integrated PL intensity is increased by 92% for LED(NP GaN)-1, 194% for LED(NP GaN)-2, and 235% for LED(NP GaN)-3 compared with that of the reference LED. Figure 3(b) shows the peak position and full width at half-maximum (FWHM) of the PL spectra of the NP GaN LEDs. The PL peak position exhibits a red shift from 2.81 to 2.68 eV with increasing porosity of NP GaN. In addition, FWHM increases as the integrated PL intensity of the NP GaN LEDs increases, indicating a high indium content and fluctuation of indium distribution in InGaN/GaN MQWs grown on the GaN(NP GaN) layers.

To further examine the inhomogeneity of indium in InGaN/GaN MQWs, the band-tail model is considered. The temperature-induced shift of the PL peak energy can be described by [23]:

\[ E_g(T) = E_g(0) - \frac{\alpha T^2}{T - \beta} - \frac{\sigma^2}{k_B T} \]  

where \( E_g(T) \) is the PL emission energy at temperature \( T \), \( E_g(0) \) is peak energy at 0 K, \( \alpha \) and \( \beta \) are Varshni coefficients, and \( k_B \) is the Boltzmann constant. The third term originates from the composition inhomogeneity, in which \( \sigma \) indicates the Gaussian broadening parameter of carrier localization states in MQWs induced by the fluctuation of indium. Figure 3(c) shows the shift of PL peak position and a fitting curve as a function of temperature. The fitting curve shows that \( \sigma = 22.5 \) meV for the reference LED, and \( \sigma = 24.1, 27.8, \) and \( 30.5 \) meV for LED(NP GaN)-1, −2, and −3, respectively. These results show that the carrier localization effect increases with increasing porosity in NP GaN because of the increased indium content and fluctuation in MQWs caused by the partially relaxed residual strain in the undoped GaN regrown on the NP GaN layers.

The Arrhenius plots of PL intensities of the NP GaN LEDs in Fig. 3(d) show the thermal quenching of PL intensity with increasing temperature. The TD-PL intensity is described by the following equation based on the non-radiative recombination process [24]:

\[ I(T) = I(0) e^{-\frac{E_{qu}}{k_B T}} \]
where $I(T)$ is the integrated PL intensity at temperature $T$, and $I(0)$ is the integrated intensity of the emission at 10 K in this study. $E_a$ and $C$ are the activation energy and a constant related to the density of the non-radiative recombination centers, respectively. The fitting curves in Fig. 3(d) show $E_a$ is 35.5, 36.1, and 36.2 meV for LED(NP GaN)-1, −2, and −3, respectively, and 26.2 meV for the reference LED. $C$ is 8.3, 7.2, and 7.1 for LED(NP GaN)-1, −2, and −3, respectively and 12.2 for the reference LED. The large $E_a$ for the NP GaN LEDs are ascribed to the deep potential wells of indium-rich regions in MQWs; a large $E_a$ leads to a high energy barrier for carrier capture by defects such as threading dislocations [24]. The larger $E_a$ of the NP GaN LEDs than that of the reference LED indicate that they have higher indium contents in their InGaN/GaN MQWs. The smaller $C$ for the NP GaN LEDs means that they have a lower density of non-radiative recombination centers such as threading dislocations in MQWs than in the reference LED. In addition, the estimated IQEs of the LEDs are 28.2, 38.5, and 36.3% for LED(NP GaN)-1, −2, and −3, respectively, and 19.2% for the reference LED according to Fig. 3(d), assuming that IQE is 100% at a low temperature of 10 K [25]. These results show that the distribution of carrier localization states in MQWs is enhanced by the reduced strain in MQWs grown on the regrown NP GaN layer. This results in a high IQE because of increased carrier localization and reduced defect densities in the NP GaN LEDs.

To analyze the contribution of the nanovoids in NP GaN to LEE, finite-difference time-domain (FDTD) simulations were performed using the FullWAVE™ program. Figures 4(a) and 4(b) show the calculated electric-field distributions of LEDs without and with a NP GaN
layer, respectively. A single dipole source was used to simulate the LEE of LED. The peak wavelength of light source was set at 450 nm. The light intensity in FDTD simulation was obtained by adding the results of 3 orthogonal polarizations states along the $x$, $y$, and $z$ direction incoherently [26]. The light intensity was measured by a detector located on top of the LED. The size distribution of nanovoids used in the simulation was extracted from the SEM image of LED(NP GaN)-3 shown in the inset of Fig. 4(c). Figure 4(c) reveals the size distribution of nanovoids over an area of $2.5 \times 2.5 \mu m$ of NP GaN-3 in LED(NP GaN-3). Figure 4(d) shows the light intensity of LEDs with and without NP GaN as a function of simulation time. The light intensity of the LED with NP GaN is increased by 50.7% compared with that of the LED without NP GaN. This means that the photons emitted from the active region can escape more easily into the air in LEDs with NP GaN than in those without NP GaN because of the light scattering effect. In addition, the FDTD simulation for LED(NP GaN)-1 and LED(NP GaN)-2 show that the LEE is also increased by 20.7% and 38.2%, respectively. The LEE is linearly increased with increasing pore size and density in nanoporous GaN, as shown in FDTD simulation of Fig. 4(e). However, IQE is linearly increased and then decreased, showing a maximum value at 17 V of applied voltage. Even though the increased pore size and density in nanoporous GaN decrease the residual stress and defects in the overgrown GaN layer and increase IQE, the larger pore size and density can deteriorate the GaN overgrowth condition, decreasing IQE at a higher voltage of 30 V. The calculated enhancement of output power (IQE × enhanced LEE) of LED(NP GaN)-3 (54.7%) was slightly higher than the enhancement of output power of LED(NP GaN)-2 (53.2%) and this is well agreed with the measured optical output values at 20 mA as shown in Fig. 5(b).
Figure 4. Schematic diagrams with calculated electric-field distributions of (a) LED without NP GaN, and (b) LED with NP GaN. (c) The size distribution of nanovoids used in FDTD simulations over an area of 2.5 × 2.5 μm of NP GaN-3 in LED(NP GaN-3). The inset shows an SEM image of NP GaN in LED(NP GaN-3). (d) Calculated light intensity as a function of simulation time for LEDs with and without NP GaN. (e) The IQE and enhanced LEE of reference LED and LED(NP GaN)s assuming that the LEE of LED without nanoporous GaN is 100%.

Figure 5(a) shows the current-voltage (I-V) characteristics of the reference LED and NP GaN LEDs. The forward voltages of the reference LED and LED(NP GaN)-1, −2, and −3 are 3.86, 3.52, 3.66, and 3.59 V at 20 mA, respectively. The low forward voltages of the NP GaN LEDs are attributed to the large degree of indium fluctuation and the higher crystal quality achieved by using a NP GaN underlayer. The total voltage at forward bias is given by [27]:

\[ V_F = \frac{n k_B T}{q} \ln \left( \frac{I_F}{A} \right) + \frac{E_g(T)}{q} + I_F R_S \]  

where \( I_F \) is the forward current, \( E_g(T) \) is the band gap at temperature \( T \), \( R_s \) is the series resistance, \( q \) is the elementary charge, \( A \) is a constant related to the materials of the \( p-n \) junction, and \( n \) is the ideality factor. Equations (2) and (4) show that the bias voltage is affected by \( E_g(T) \) and the crystal quality related to \( R_s \). Equation (2) reveals that \( E_g(T) \)
decreases as $\sigma$, which is associated with carrier localization, increases. This indicates that $V_F$ can be decreased by increasing the indium fluctuation in MQWs. Wu et al. [28] also reported that indium fluctuation in MQWs strongly affects IQE, $I$-$V$ curve, and droop behavior because carrier transport occurs along local potential minimum paths when the indium composition is varied in MQWs. Furthermore, $R_s$ estimated from the $I$-$V$ curves of the reference LED and LED(NP GaN)-1, −2, and −3 are 15.96, 15.39, 15.31, and 15.61 $\Omega$, respectively. These values indicate that decreasing the density of defects such as threading dislocations would improve the crystal quality of regrown MQWs, resulting in a reduction of $R_s$ and forward voltage. Figure 5(b) shows that the optical output powers of LED(NP GaN)-1, −2, and −3 are increased by 72.7%, 117.3%, and 123.1% at 20 mA, respectively, compared with that of the reference LED. The large increase of optical power is partly attributed to the increased indium content in MQWs with a lower density of threading dislocations because of the decrease of residual strain in MQWs grown on an NP GaN layer. The localized states caused by indium fluctuation can enhance the confinement of carriers at the potential minimum, and increase IQE [28,29]. Therefore, the large increase in optical output power can be attributed to an improvement of IQE caused by the increased rate of radiative recombination induced by the enhanced carrier localization in indium-rich regions of MQWs, reduction of defects such as threading dislocations, and increased light extraction by the nanopores in the NP GaN layer.

![Graphs](image)

Fig. 5. (a) $I$-$V$ curve and (b) optical output power of reference LED and LED(NP GaN)-1, −2, and −3.
4. Conclusion

In summary, we report the enhanced optical and electrical properties of InGaN/GaN MQW LEDs grown on electrochemically etched NP GaN layers. The Raman spectra of regrown undoped GaN layers on NP GaN show relaxation of compressive stress caused by nanosphere-like shape transformation and atomic migration in the NP GaN layer. The PL peak position of LEDs with NP GaN undergoes a red shift from 2.81 to 2.68 eV because of the increase of indium content and inhomogeneity in MQWs as the residual strain is relaxed in GaN regrown on NP GaN. Increases in output power of 72.7%, 117.3%, and 123.1% at 20 mA for LED(NP GaN)-1, −2, and −3 compared with that of the reference LED are attributed to the increased IQE caused by the strong carrier localization in the indium-rich regions in MQWs, low defect density in MQWs, and the increased LEE allowed by the nanopores in the NP GaN layer.

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