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Kyoto University
Optical properties of InGaN/GaN nanopillars fabricated by postgrowth chemically assisted ion beam etching

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The optical properties of InGaN/GaN quantum wells, which were nanopatterned into cylindrical shapes with diameters of 2 μm, 1 μm, or 500 nm by chemically assisted ion beam etching, were investigated. Photoluminescence (PL) and time-resolved PL measurements suggest inhomogeneous relaxation of the lattice-mismatch induced strain in the InGaN layers. By comparing to a strain distribution simulation, we found that partial strain relaxation occurs at the free side wall, but strain remains in the middle of the pillar structures. The strain relaxation leads to an enhanced radiative recombination rate by a factor of 4–8. On the other hand, nonradiative recombination processes are not strongly affected, even by postgrowth etching. Those characteristics are clearly reflected in the doughnut-shape emission patterns observed by optical microscopy. © 2010 American Institute of Physics. [doi:10.1063/1.3280032]

I. INTRODUCTION

Extensive scientific and technological efforts have been devoted to optoelectronic devices based on III-nitride semiconductors, which have led to dazzling blue light-emitting diodes with a record external quantum efficiency of 75.5%. Although the In composition in InGaN quantum well (QW) active layers can control the emission wavelength, the emission efficiency drastically decreases beyond the blue-green spectral range. This so-called green gap issue is due to two major factors: the potential fluctuations and quantum confinement Stark effect (QCSE). Using scanning near field optical microscopy (SNOM) and confocal laser scanning microscopy,5 we have investigated the emission mechanisms of InGaN QWs, and found that their optical properties strongly depend on submicron-scale potential fluctuations.

Quite recently, we have developed nanospectroscopy based on SNOM and atomic force microscopy.4 This newly developed technique to assess violet, blue, and green emitting QWs has revealed that in blue-emitting QWs, potential fluctuations prevent threading dislocations (TDs) from capturing carriers/excitons. In contrast in green-emitting QWs, potential fluctuations are associated with newly introduced TDs. Carriers/excitons with a radiative lifetime, τr, elongated by the QCSE easily diffuse to such TDs and recombine nonradiatively. Therefore, one promising way to increase the luminescence intensity in the green spectral range is to shorten the diffusion length of carriers/excitons, which corresponds to a reduction in τr. Thus, the stronger luminescence is a consequence of a better internal quantum efficiency, which is described as (1 + τr/τnr)−1, where τnr is a nonradiative recombination lifetime.

Of the several proposals to promote radiative recombination, such as nonpolar/semipolar QWs6–9 and plasmonics,10 nanostructures are one of the most promising approaches because the free side wall may relax the strain in QWs, and consequently, suppress the QCSE.11–19 In particular, InGaN/GaN nanocolumns, which are self-formed by molecular beam epitaxy, do not involve TDs11,12 and show a very fast τr due to strain relaxation in InGaN QWs.16 To date, the sizes and positions of nanocolumns are well controlled by selective area growth,17 and the homogeneity has drastically been improved.18 On the other hand, nanorings and nanopillars are constructed from conventional planar QWs by postgrowth processes.13,14,19 This top-down approach can be advantageous over the above-mentioned bottom-up approach because arbitrary structures can be fabricated at arbitrary positions, allowing well-established growth on the (0001) plane. Moreover, this approach will pave the way toward controlled artificial spatial inhomogeneity in InGaN light-emitting layers, which was proposed in Ref. 5 as an effective way to improve emission efficiency and, furthermore, to create novel functionality. However, to date, radiative and nonradiative recombination processes have yet to be thoroughly studied for bottom-up and top-down nanostructures. Particularly for top-down nanostructures, the generation of nonradiative recombination centers by postgrowth processes is a major concern. Herein the details of the recombination dynamics in InGaN/GaN nanopillars fabricated from planar QWs by chemically assisted ion beam etching (CAIBE) are investigated. It is demonstrated that CAIBE does not generate a nonradiative pathway, which enables the intrinsic properties of nanopillars to be extracted. Optical characterizations and theoretical considerations revealed that the lattice-mismatch induced strain is relaxed around the free side wall, whereas it remains around the middle of nanopillars, which lead to their unique optical properties.
II. NANOPILLAR FABRICATION

Initially, GaN was grown on a sapphire (0001) substrate using metalorganic vapor phase epitaxy. Then a 3-nm-thick InGaN single QW (SQW) and a 10-nm-thick GaN capping layer were grown on GaN. The In composition was 25%, unless stated. Cylindrical nanopillars with diameters of 2 μm, 1 μm, and 500 nm were fabricated ex situ. The patterns were defined into a 200-nm-thick polymethylmethacrylate resist spun onto the samples and exposed to a field emission electron beam lithography system. After lithography, the beam patterns were transferred into the samples using CAIBE. CAIBE employs both chemical and physical etching processes. Thus, anisotropic but fast etching is possible under gentle conditions. In this study, Xe was used for sputtering, while Cl₂ was used for chemical etching. The etched depth was 150 nm. Therefore, the side wall of the SQW was exposed to air. Figure 1 displays scanning electron microscopy (SEM) images of a fabricated nanopillar sample with a diameter of 500 nm. It is confirmed that well-defined structures are fabricated even for this minimum diameter.

III. RADIATIVE RECOMBINATION PROCESSES AFFECTED BY STRAIN RELAXATION AROUND THE FREE SIDE WALL

A. Optical characterizations

Figure 2 shows a fluorescent microscopy image of nanopillars with a 2 μm diameter acquired at room temperature (RT). The image was taken at the surface normal. Details of the emission pattern are discussed in Sec. V. As seen in Fig. 2, 8×8 nanopillars were fabricated within a 30×30 μm² square region, which was surrounded by an unprocessed region involving the planar SQW. Obviously, the emission from the nanopillars was much stronger than that from the planar SQW, even though the nanopillar fabrication decreased the emission area. Similar trends were observed for nanopillars with different diameters. Contrary to conventional III-V semiconductors, such as GaAs, where post-growth processes typically cause damage and degrade the emission properties, the external quantum efficiency was drastically improved for our InGaN/GaN nanopillars. This finding suggests that the surface recombination velocity of (In)GaN is very slow not only for the self-formed nanocolumns but also for the nanopillars. (The influence of the nanopillar fabrication on the nonradiative recombination rate is quantified in Sec. IV.) However, the mechanisms causing the striking difference between conventional III-V and nitride semiconductors have yet to be clarified.

The emission intensity is generally determined as the product of the internal quantum efficiency and light extraction efficiency. Therefore, to identify which factors play larger roles in the increased emission intensity observed in Fig. 2, photoluminescence (PL) measurements were performed at 4.2 K and RT under selective excitation by a frequency doubled Ti:sapphire laser emitting at 400 nm. The excitation spots were adjusted using confocal microscopy in order to assess a single nanopillar while maintaining an excitation spot density of 8.0×10¹⁷/cm³. Figure 3 shows the PL spectra at 4.2 K with the emission intensities normalized by the emitting areas. The PL integrated intensities were nearly the same for all samples, indicating that there is not a difference in the light extraction efficiencies among the samples. This was supported by fluorescent microscopy performed at 4.2 K, where the emission intensity was rather independent of the sample structures including the planar SQW. Our finite-difference time-domain (FDTD) simulation suggests that thicker GaN capping layers increase the light extraction efficiency, especially to the near-normal direction. Hence, the thin capping layer in the present nanopillar (10 nm) did not affect the light extraction efficiency. At RT, on the other hand, compared to the planar SQW, the PL integrated intensities increased by factors of 3.3, 7.7, and 6.6 for

FIG. 1. (a) Bird’s eye view of InGaN/GaN nanopillars observed by SEM and (b) the magnified image. Pillar diameter is 500 nm.

FIG. 2. (Color online) Fluorescent microscopy image observed at the surface normal of nanopillars. Image is acquired at RT and the pillar diameter is 2 μm.

FIG. 3. (Color online) PL spectra of a planar SQW and nanopillars with diameters of 2 μm, 1 μm, and 500 nm acquired at 4.2 K.
B. Discussion

To support the above experimental results, the polarization-induced electric field, the square overlap of the electron and hole wave functions, and the transition energy were calculated as a function of strain in 3-nm-thick In$_{0.25}$Ga$_{0.75}$N/GaN SQWs. It was assumed for simplicity that GaN is always unstrained, whereas In$_{0.25}$Ga$_{0.75}$N can be strained irrespective of the lattice mismatch. Therefore, only the InGaN layers involved electric fields. The piezoelectric polarization was first evaluated as a function of strain, and then, the internal electric field was deduced with considering the contribution from the spontaneous polarization. The obtained internal electric field determined the band profile of the 3-nm-thick In$_{0.25}$Ga$_{0.75}$N/GaN SQW, for which electron and hole wave functions, their square overlap, and transition energy were calculated.

Figure 5 shows the results. The in-plane strain ($\epsilon_{xx} = \epsilon_{yy}$) for fully strained In$_{0.25}$Ga$_{0.75}$N on GaN is $-2.65\%$ and the closed circle in Fig. 5(a) denotes the corresponding square overlap. Because square overlaps of the electron and hole wave functions are inversely proportional to radiative lifetimes, this plot represents the radiative lifetime of the planar SQW (210 ns) and relates the experimentally estimated radiative lifetime to the calculated square overlap, as indicated by two vertical axes on the left hand side of Fig. 5(a). Then, from the experimentally observed variation of the radiative lifetimes due to the nanopillars (Fig. 4), the open circles in Fig. 5(a) are determined on the square overlap.
As shown in Fig. 6, the strain distribution is not uniform, reducing the calculation time without degrading the accuracy. In the middle of the pillar, the in-plane strain on the side wall relaxes the strain to 1.5% to 1.0%. It was confirmed that nanopillars with diameters larger than 200 nm do not change the degree of strain relaxation at the side wall, which is why we selected 200 nm for the calculation to estimate radiative recombination lifetime (τr) at RT. This assumption seems valid because the PL intensity remained unchanged below 50 K; if nonradiative processes are not negligible, then the PL intensity should be weakened by higher temperatures. On the other hand, the PL decay expressed as 1/τPL = 1/τr + 1/τnr was measured at RT by TRPL. Using the experimentally obtained IRT/I4.2 K and τPL at RT, then τr and τnr can be evaluated.

Table I summarizes the results. For all samples, the estimated radiative recombination lifetime (τr) is longer than that at 4.2 K (Fig. 4), reflecting the temperature-dependence of radiative recombination of excitons in low-dimensional structures. Comparing all the samples indicates that the nanopillars shorten the radiative lifetimes; that is, the radiative recombination rates are heightened by factors of 1.9, 4.7, and 5.3 for the φ2 μm, φ1 μm, and φ500 nm nanopillars, respectively. The enhancement factors differ slightly from

\[
\frac{I_{RT}}{I_{4.2\ K}} = \frac{\tau_{PL}}{\tau_{r}} = \frac{\tau_{r}}{\tau_{nr}}
\]

IV. RADIATIVE AND NONRADIATIVE RECOMBINATION AT RT: INFLUENCE OF POSTGROWTH NANOPILLAR FABRICATION

To assess radiative and nonradiative recombination processes at RT, temperature dependence PL and TRPL measurements were performed. Assuming the internal quantum efficiency at low temperatures is nearly 100%, the PL intensity ratio between 4.2 K and RT, IRT/I4.2 K, can be regarded as the internal quantum efficiency, (1 + τr/τnr)−1, at RT. This assumption seems valid because the PL intensity remained unchanged below 50 K; if nonradiative processes are not negligible, then the PL intensity should be weakened by higher temperatures. On the other hand, the PL decay expressed as 1/τPL = 1/τr + 1/τnr was measured at RT by TRPL. Using the experimentally obtained IRT/I4.2 K and τPL at RT, then τr and τnr can be evaluated.

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<th>Sample</th>
<th>IRT/I4.2 K (%)</th>
<th>τPL (ns)</th>
<th>τr (ns)</th>
<th>τnr (ns)</th>
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<td>Planar SQW</td>
<td>0.9</td>
<td>3.7</td>
<td>463</td>
<td>3.7</td>
</tr>
<tr>
<td>φ2 μm</td>
<td>3.0</td>
<td>7.2</td>
<td>240</td>
<td>7.4</td>
</tr>
<tr>
<td>φ1 μm</td>
<td>7.0</td>
<td>6.9</td>
<td>99</td>
<td>7.4</td>
</tr>
<tr>
<td>φ500 nm</td>
<td>6.0</td>
<td>5.3</td>
<td>88</td>
<td>5.6</td>
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The emission wavelengths at RT and 4.2 K similarly distribute in doughnut shapes, as recognized in Figs. 7(e) and 7(f); the area for longer emission wavelength is surrounded by the area for shorter emission wavelength. Those observations are well accounted for by the doughnut-shape strain distribution [Fig. 6]. That is, the strain relaxation at the side wall reduces QCSE and shortens the emission wavelength. Longer-wavelength emission observed outside the nanopillar is probably due to light scattering within the sample, and the emission intensity is negligibly weak, as supported by Figs. 7(c) and 7(d).

In contrast, the fluorescent microscopy images revealed considerably different emission patterns for RT and 4.2 K [Figs. 7(a) and 7(b)]; at RT, the emission intensity is distributed in doughnut shapes, whereas at 4.2 K, it is rather uniform in spite of the presence of the strain distribution. Those observations are confirmed by the mappings of single nanopillars by confocal microscopy [Figs. 7(e) and 7(f)]. To understand the difference in the emission patterns at RT and 4.2 K, temperature-dependent physics have to be considered and we found that carrier/exciton recombination processes can well account for the phenomena. The PL intensity, \( I_{PL} \), is determined by competition between radiative and nonradiative recombination processes and can be expressed by \( I_{PL} = G / (1 + \tau_r / \tau_{nr}) \), where \( G \) is the generation rate of carriers/excitons by laser excitation. This equation tells us that at low temperatures where nonradiative recombination processes are negligible (i.e., \( 1 / \tau_{nr} \sim 0 \)), \( I_{PL} \) becomes independent of \( \tau_r \). This is consistent with Figs. 7(b) and 7(d). At RT, on the other hand, both \( \tau_r \) and \( \tau_{nr} \) may contribute to \( I_{PL} \). As listed in Table I, \( \tau_{nr} \) is not affected by the nanopillars, whereas \( \tau_r \) is drastically shortened by smaller nanopillars. Thus, the PL intensity is strengthened around the side wall where the strain is relaxed to shorten \( \tau_r \), and the doughnut-shape emission patterns are observed.

VI. RED-EMITTING NANOPILLARS

In this section, we discuss red-emitting nanopillars with a 4-nm-thick In_{0.30}Ga_{0.70}N SQW and a 120-nm-thick GaN capping layer. The purpose to assess these red-emitting nanopillars is twofold; one is to provide supporting data for strain relaxation phenomena in nanopillars using a different structure, and the other is to demonstrate the effect of capping layers on the light extraction.

Figure 8 displays PL spectra of the red-emitting planar SQW, \( \phi 2 \mu m \) and \( \phi 500 \mu m \) nanopillars at 4.2 K. The excitation conditions were the same as those for Fig. 3. The emission intensities were normalized by the emitting areas but were significantly structure-dependent, different from those of the green-emitting nanopillars. The cause of this observation is the light extraction, which is discussed later. Concerning the emission peak energy, the blueshift by the nanopillar fabrication suggests the strain relaxation. The degree of the shift in the red-emitting nanopillars is slightly larger than those in the green-emitting nanopillars, which may be accounted for by a wider well in the red-emitting nanopillars. Although two emission components due to the strain-relaxed and strained regions could not be well rec-
Thus, the strain-relaxation related phenomena observed in the red-emitting nanopillars are essentially the same as those for the green-emitting nanopillars, strongly suggesting that the current experimental results and their interpretations can be generalized. On the other hand, the light extraction properties can significantly be affected by the capping layer thickness. As mentioned above, the FDTD simulations have predicted that thicker capping layers enhance light extraction toward the surface normal. In fact, for the green-emitting nanopillars with a 10 nm capping layer, Fig. 3 demonstrates that the PL intensity at 4.2 K is rather insensitive to the pillar diameters, suggesting that light extraction is not affected by the pillar fabrication due to the very thin capping layer. In contrast, for the red-emitting nanopillars with a 120 nm capping layer, the PL intensity normalized by the emitting area increases by factors of 3.8 and 14.3 for \( \phi 2 \) \( \mu \)m and \( \phi 500 \) nm nanopillars, respectively, at 4.2 K, as shown in Figs. 8 and 9. Furthermore, Fig. 9 indicates that these factors remain unchanged up to 50 K. Such temperature independence implies that nonradiative processes are not activated in this low temperature range, and the intensity difference can chiefly be ascribed to the difference in light extraction efficiency. (For more precise evaluation of the light extraction efficiency, an integrating sphere must be used because the current PL setup using an objective lens with a numerical aperture of 0.60 preferentially collect the PL signal normal to the surface.) When the capping layer is thick, smaller nanopillars have stronger PL intensities because nanopillars with a higher aspect ratio can act as better waveguides directing toward the surface normal. Furthermore, fluorescent microscopy images of these red-emitting nanopillars acquired at 4.2 K confirm the strengthened emission for smaller nanopillars even at low temperatures.

VII. SUMMARY

In summary, we investigated InGaN/GaN nanopillars formed from a planar SQW by CAIBE. It is confirmed that CAIBE does not seriously induce nonradiative recombination centers, which enabled the intrinsic properties of the nanopillars to be extracted. The calculations and the experimental results by PL and TRPL consistently show that the compressive strain in InGaN QWs is relaxed mainly at the free side wall. Consequently, the radiative recombination rate is enhanced at the free side wall by a factor of 4–8, which indicates that nanopillars can control radiative recombination processes.

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5K. Okamoto, A. Kaneta, Y. Kawakami, S. Fujita, J. Choi, M. Terazima,