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Kyoto University
Nanosopic recombination processes in InGaN/GaN quantum wells emitting violet, blue, and green spectra

A. Kaneta,* M. Funato,† and Y. Kawakami‡

Department of Electronic Science and Engineering, Kyoto University, Kyoto 615-8510, Japan

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We investigated correlations between nanoscopic optical and structural properties in violet-emitting, blue-emitting, and green-emitting InGaN/GaN quantum wells (QWs) by means of scanning near-field optical microscopy (SNOM) and atomic force microscopy. Only in the blue-emitting QW, threading dislocations were not major nonradiative recombination centers (NRCs). SNOM data indicated that NRCs in the blue-emitting QW are surrounded by energy levels higher than those for radiative recombination. Such potential distributions realize “anti-localization” of carriers to NRCs, which is the cause of high emission quantum efficiencies in blue emitters.

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I. INTRODUCTION

In$_x$Ga$_{1-x}$N has a high potential in producing light emitters such as light emitting diodes (LEDs) and laser diodes (LDs). Because the band-gap energies of GaN and InN are 3.4 (Ref. 2) and 0.6 eV, respectively, In$_x$Ga$_{1-x}$N covers the full visible spectral range, and in fact, violet to green LEDs and violet to blue LDs have already been commercialized using this material. In recent years, much progress has been made to improve the external quantum efficiency (EQE) of In$_x$Ga$_{1-x}$N LEDs. As a result, despite high threading dislocation densities (TDDs) due to epitaxial growth on highly mismatched sapphire substrates, to date, the maximum EQE value of 75.5% has been achieved for blue LEDs, which has led to the fabrication of white LEDs with a luminous efficacy of approximately 169 lm/W (1). It is noteworthy that this luminous efficacy is much greater than that of fluorescent lamps. However, such a high efficiency is achieved only in the blue spectral band, and it tends to decrease outside this spectral range.3,5 One interesting finding is that reducing TDD in underlying GaN templates effectively improves EQE in the ultraviolet (UV) to violet spectral range but does not work in the blue to green spectral range.6 Apparently, threading dislocations (TDs) play a crucial role in determining carrier recombination dynamics in In$_x$Ga$_{1-x}$N, but questions arise as to why TDs affect the emission quantum efficiency of only UV to violet emitters and why blue emitters exhibit the highest emission quantum efficiency in spite of comparable TDDs in UV to green emitters.

To answer those questions, nanoscopic optical and structural properties have been assessed by correlating the cathodoluminescence (CL) mapping with structural analyses in heteroepitaxial GaN layers grown on sapphire substrates7–10 and in In$_x$Ga$_{1-x}$N QWs.11–14 Two different mechanisms have been proposed on the relationship between three types of TDs (edge, screw, and mixed TDs) and nonradiative recombination centers (NRCs). The first one is that the screw-type and mixed-type TDs act as NRCs, excluding the role of the edge-type TDs.7,9,11 The other one is that edge-type TDs as well as screw-type and mixed-type TDs act as NRCs.10,12,14 However, CL cannot generate carriers selectively in the QWs, and thus, generated carriers in the cladding layers may be captured in part by TDs before reaching the QWs. Hence, in addition to the intrinsic nature in QWs, this process contributes to the dark spot image in the CL. Furthermore, although the electron-beam diameter can be reduced to less than 10 nm, carrier diffusion within the material worsens the spatial resolution.

On the other hand, scanning near-field optical microscopy (SNOM)15–19 is advantageous over CL because of (1) selective photoexcitation in the well, (2) higher spatial resolution,16,17 and (3) feasibility to time resolve measurements.18,19 In addition, comparing images obtained from the illumination-collection (I-C) mode, which uses an identical fiber probe to excite and detect photoluminescence (PL), and those from the illumination (I) mode, which excites PL through a fiber and detects it in a far field, can provide insight into radiative recombination, nonradiative recombination, and diffusion processes.19 Remarkably, we like to emphasize that visualization of diffusion processes is achievable solely by SNOM. A drawback of SNOM was a difficulty in correlating PL mapping to topography with keeping high spatial resolutions for both the measurements simultaneously. To circumvent this issue, we have developed an experimental technique to precisely superimpose SNOM-PL images onto AFM ones. This technique is based on reference metal markers formed on the sample surface. Here we applied this characterization technique hybridized from multimode SNOM, which can operate simultaneously. To circumvent this issue, we have developed an experimental technique to precisely superimpose SNOM-PL images onto AFM ones. This technique is based on reference metal markers formed on the sample surface. We investigated correlations between nanoscopic optical and structural properties in violet-emitting, blue-emitting, and green-emitting InGaN/GaN quantum wells (QWs) by means of scanning near-field optical microscopy (SNOM) and atomic force microscopy. Only in the blue-emitting QW, threading dislocations were not major nonradiative recombination centers (NRCs). SNOM data indicated that NRCs in the blue-emitting QW are surrounded by energy levels higher than those for radiative recombination. Such potential distributions realize “anti-localization” of carriers to NRCs, which is the cause of high emission quantum efficiencies in blue emitters.

II. EXPERIMENT

A. Fabrication

The samples used in this study were In$_x$Ga$_{1-x}$N SQWs grown by metalorganic chemical vapor deposition. First, 15-μm-thick ELO-GaN templates were prepared on sapphire
TABLE I. Sum of screw-type and mixed-type TDDs estimated from the number of pits observed by AFM measurements.

<table>
<thead>
<tr>
<th>Dislocation density (cm$^{-2}$)</th>
<th>Wing</th>
<th>Seed</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN template</td>
<td>$&lt;1 \times 10^7$</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Violet</td>
<td>$&lt;1 \times 10^7$</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Blue</td>
<td>$&lt;1 \times 10^7$</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Green</td>
<td>$2 \times 10^6$</td>
<td>$5 \times 10^6$</td>
</tr>
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TABLE II. Summary of SNOM measurement conditions.

<table>
<thead>
<tr>
<th>Excitation wavelength (nm)</th>
<th>Violet</th>
<th>Blue</th>
<th>Green</th>
</tr>
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<tbody>
<tr>
<td>Fiber-type</td>
<td>Pure SiO$_2$</td>
<td>GeO$_2$ doped SiO$_2$</td>
<td>GeO$_2$ doped SiO$_2$</td>
</tr>
<tr>
<td>Probe structure</td>
<td>Single taper</td>
<td>Double taper</td>
<td>Double taper</td>
</tr>
<tr>
<td>Aperture diameter (nm)</td>
<td>$I$-$C$ mode</td>
<td>$I$-$C$ mode</td>
<td>Multimode mode</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>70</td>
<td>160</td>
</tr>
</tbody>
</table>

III. ROLE OF TDS

Generally, GaN heteroepitaxial layers involve three types of TDs, which are edge-type, screw-type, and mixed-type TDs. They appear as growth pits in AFM images. The screw-type and mixed-type TDs are always located at the growth steps and have large cores to be detected by AFM. Therefore, although they were indistinguishable from each other by AFM, their positions were clearly identified. On the other hand, the core of the edge-type TD is too small to be detected in large area AFM images similar to those in the figures below. Hence, we performed a high-resolution AFM mapping in a smaller area for a GaN template, by which the ratio of the edge-type TD against the density of the sum of screw-type and mixed-type TDs was determined to be $\sim 7$. This ratio depends on sample details such as growth conditions and impurity doping, and for example, Hino et al. reported a factor of $\sim 10$. Therefore, we precisely estimated the screw-type and mixed-type TDs from the growth pits revealed by AFM as summarized in Table I, whereas we roughly estimated the edge-type TD from the ratio of 7–10.

Figure 1 shows the SNOM-PL intensity mappings in the $I$-$C$ mode, AFM images, and PL intensity profiles of violet-emitting, blue-emitting, and green-emitting SQWs. The PL intensity profiles were obtained by averaging the SNOM-PL intensities along the ELO mask stripes. The averaged PL intensities were normalized by those in the wing regions. The open circles in the SNOM images indicate growth pits observed in the corresponding AFM images. Those pits were screw-type and mixed-type TDs, as mentioned above.

For the violet-emitting QW, comparison between the SNOM and AFM images confirmed that these screw-type and mixed-type TDs correspond well to the dark area in the SNOM-PL mapping in the seed region for the ELO growth. Moreover, the averaged PL intensity of Fig. 1(c) of the seed region was about 0.78 times as weak as that of the wing region. These results directly evidence that these TDs act as NRCs in the violet-emitting QW. How-
ever, the PL intensity fluctuated even in the wing region, although these types of TDs were only sparsely observed in the vicinity of the border between the seed and wing regions, and were nearly undetectable when the area was more than a few micrometers away from the border. Regarding the edge-type TD, it is difficult at this stage to correlate it with either radiative recombination centers (RRCs) or NRCs because its location cannot be identified in this large area AFM image. However, their number in the area surrounded by the white square in Fig. 1(b) was estimated to be less than 10. These results led us to a conclusion that the considerable PL intensity fluctuations in the wing region are not due to any types of TDs but due to spatial clustering of nanoscopic point defects related to other types of NRCs such as vacancies, interstitials, antisite defects, and their complexes.

Unlike the violet-emitting QW, the blue-emitting QW did not show correlations between the TD distribution [Fig. 1(d)] and the PL intensity distribution [Fig. 1(e)]. Furthermore, the spatially averaged PL intensities [Fig. 1(f)] were almost unchanged in both regions. These results indicate that the TDs hardly contribute to recombination dynamics as NRCs in the blue-emitting In,Ga1−xN SQW and two conclusions can be extracted: one is that the area rich in point defects and vacancies should be the main origin of the dark PL domains and the other is that the diffusion length of the carriers is too short to be captured at the core region of the TDs probably due to the large potential fluctuations, which is discussed below in more detail.

The green-emitting QW strikingly contrasted the blue-emitting QW. As can be estimated from Fig. 1(g), the TDD of the green-emitting QW became one order of magnitude higher than those in other QWs as well as the underlying ELO-GaN templates. Consequently, the TD distribution clearly correlated with the SNOM-PL image [Fig. 1(h)] and the spatially averaged PL intensity [Fig. 1(i)] of the seed region was about 0.58 times as weak as that of the wing region. Furthermore, although step and terrace structures were observed [Fig. 1(g)], undulation of their edges induced by the spiral growth was more pronounced. It is thus obvious that new TDs were generated during the QW growth. There are two possible mechanisms responsible for this; one is a lowered growth temperature for reaching higher In incorporations and the other is the critical layer thickness (CLT) of In,Ga1−xN on GaN. The CLT, which decreases as the In composition increases, was calculated to be 4 nm for In0.2Ga0.7N on GaN. The CLT is comparable to the well thickness of 3 nm, partial lattice relaxation may happen to create TDs. At present, no further conclusion can be reached before doing, for example, transmission electron microscopy measurements.

Because PL spectra were acquired during the SNOM measurements, the PL intensity mapping shown in Fig. 1 can
directly be correlated with the PL peak wavelength mapping. Thus, Fig. 2 plots the PL intensity in the I-C mode as a function of the emission wavelength. An inverse V-shape correlation was clearly observed, which can be interpreted as follows by considering the results of Fig. 1. When the In composition is small like in the violet-emitting QW, carriers can easily diffuse from the probing area (to be captured by TDs) due to small potential fluctuations. Then, increasing the In composition enhances potential fluctuations and suppresses carrier diffusion to TDs. Consequently, the PL intensity increases with increasing emission wavelength. This trend continues up to ~470 nm in the blue-emitting QW. Further increase in the In composition newly generates TDs as NRCs, and the PL intensity decreases with increasing emission wavelength.

IV. POTENTIAL FLUCTUATIONS IN InGaN QWS

The previous section suggested that potential fluctuations in In$_{x}$Ga$_{1-x}$N are an important factor to determine the sensitivity of carriers to dislocations. To clarify potential distributions, the SNOM-PL intensity mapping and local PL spectra were examined in more detail.

Figure 3 displays typical results of the SNOM-PL intensity mappings in the I-C mode and the PL spectra for the blue-emitting QW [Figs. 3(a) and 3(b), respectively] and the green-emitting QW [Figs. 3(c) and 3(d), respectively]. The PL spectra were acquired at positions A, B, C, and D marked in the respective SNOM images. The data shown are for the wing regions of the ELO growth. No growth pits were observed by AFM within Fig. 3(a) due to the reduction in TDDs by the ELO technique. In contrast, in Fig. 3(c), although the TDDs were reduced by the ELO technique, 23 growth pits, which are indicated by open circles, were observed in the AFM measurement. The numbers of the edge-type TDs are supposed to be ~<30 in Fig. 3(a) and <200 in Fig. 3(c), respectively.

For the blue-emitting QW [Figs. 3(a) and 3(b)], it was found that the PL spectra taken at the dark area (C) or at boundary between bright and dark area (A and B) were composed of double emission peaks, independent of the existence of dislocations, whereas those taken at the bright area (D) were composed of a single emission peak. The observed features of the PL intensity distribution in the seed region were nearly the same, despite the larger TDDs, and intense PL islands with a diameter of about 200 nm were surrounded by dark areas. Furthermore, the feature of the PL spectra was also the same in both regions. These findings suggest that NRCs are strongly related to point defects, which cannot be detected by AFM, and that the potential energy around NRCs

FIG. 3. (Color) (a) SNOM image in the I-C mode and (b) PL spectra taken at positions A to D in the wing region of the blue-emitting SQW. (c) and (d) are those for the green-emitting SQW.

FIG. 4. (Color) SNOM images in (a) the I-C mode and (b) the I mode. Images were taken in the seed region. (c) PL spectra observed at positions designated by A to C in (a) [or equivalently, A' to C' in (b)].

FIG. 5. (Color) (a) SNOM image in the I-C mode and (b) that in the I mode of the blue-emitting SQW. (c) and (d) are those for the green-emitting SQW. Images were taken in the wing region.
is higher than that around the area rich in RRCs, which prevent carriers and/or excitons from being captured by NRCs. On the other hand, for the green-emitting QW, Fig. 3(d) shows the PL spectra at positions A, B, C, and D. A and B represent strong PL positions, while C and D show weak PL ones. It was found that all the PL spectra were composed of a single emission peak, and that the PL peak wavelengths of the dark area (C and D) were longer than those of bright area (A and B). Such characteristics are not by chance but are reproducible in other monitored positions. Therefore, we presumed that areas with lower potential are associated with TDs and/or point defects so that carrier localization enhances the pathway to NRCs in the green-emitting QW.

V. CARRIER DIFFUSION IN InGaN QWS

To investigate carrier diffusion processes under the presence of potential fluctuations, we performed multimode SNOM-PL measurements. Let us begin by discussing the blue-emitting QW. Figure 4 shows (a) the spatial distribution of the PL intensity of the seed region in the I-C mode, (b) that in the I mode taken in the same scanning area, and (c) the PL spectra at positions A (A'), B (B'), and C (C') in Figs. 4(a) and 4(b). All positions were selected to be boundaries between bright and dark areas. The PL spectra at positions A and B were composed of double emission peaks in the I-C mode, whereas those at positions A' and B' in the I mode showed a single emission peak, which was located on the low-energy side of the PL in the I-C mode, as shown Fig. 4(c). This result strongly suggests that regions with high and low band-gap energies are formed in the vicinity of the PL intensity boundary and that photogenerated carriers very effectively diffuse to the low band-gap region. Comparing the two SNOM images showed two types of dissimilarities. The first type is that the weak PL in the I-C mode becomes strong in the I mode, as indicated by the white circles in Figs. 4(a) and 4(b). In such areas, the carriers and/or excitons that are photogenerated directly under the aperture of the fiber probe are diffused and captured into localization states beyond the fiber aperture, and they recombine radiatively. The second type is opposite, where the PL intensity in the I-C mode is higher than that around the area rich in RRCs, which prevents carriers from being captured by NRCs. As shown in Figs. 3(b) and 4(c), the PL spectra taken in the I-C mode around boundaries between bright and dark PL domains were often composed of double emission peaks with an energy separation of about 130 meV. In order to discuss the origin of this energy separation, we calculated the transition energies under the influence of two factors: the QW thickness fluctuation and the In compositional fluctuation.31 The nominal QW thickness and In composition were 3 nm and 20%, respectively. The AFM image of the sample surface consisted of one monomolecular layer (ML) steps and terraces as shown in Fig. 1(d), implying an atomically flat interface. However, an only 2.3 ML thickness fluctuation induces a difference in quantized energy levels of 130 meV. On the other hand, In compositional differences of 17% and 20% also lead to an energy difference of 130 meV. It should be noted that Hangleiter et al.32 reported that the V-shape defects formed at the TDs act as negative localization centers, which lead to a dislocation-insensitive PL property due to the locally thin QWs around the defects. Therefore, it is not clear at present stage whether the variation of well layer thickness (order of a few MLs) or In compositional fluctuation contributes to the observed energy separation.

In order to clarify the differences of carrier diffusion and recombination dynamics in blue-emitting and green-emitting QWs, multimode SNOM-PL measurements were performed in the wing regions for both the QWs, as shown in Fig. 5. The I-C and I modes were taken at the same area. The thick white circles represent where the PL intensity domains in the I-C mode were spread in the I mode, while the white dashed circles represent the opposite tendency. Comparing the green-emitting QW [Figs. 5(c) and 5(d)] with the blue-emitting QW [Figs. 5(a) and 5(b)], it was found that the area designated by the dashed circles increased in the green-emitting QW. This observation suggests that in the green-emitting QW, carriers are easily diffused from the aperture due to the potential fluctuation, and then, many of them recombine nonradiatively due to the trapping at NRCs. Although the diffusion length was highly anisotropic and fluctuated in the randomly localized system, it appears to be a few hundred nanometer long, especially at the border of the intensity domains. This diffusion length is much longer than those in the blue-emitting QW discussed above, probably because of a longer recombination lifetime due not only to the piezoelectric effect33,34 but also to the smaller localized RRCs35 in the green-emitting QW. It is noteworthy that such
dark PL domains observed in the \( I \) mode correlate much better with TDs than those in the \( I-C \) mode.

Figure 6 is a schematic summary of the current study. In the violet-emitting QW, less potential fluctuations enhance carrier diffusion, and consequently, PL intensity mapping is well correlated with TD distribution. In the blue-emitting QW with a higher In composition, potential fluctuations are pronounced to affect carrier recombination processes in two different ways. One is carrier localization to RRCs as supported by a short carrier diffusion length and the other is carrier antilocalization to NRCs including TDs, as supported by the variation observed between SNOM-PL spectra in the \( I-C \) and \( I \) modes. This antilocalization effect is realized because NRCs are surrounded by energy levels higher than those for radiative recombination. In the green-emitting QW, further increase in the In composition in the InGaN well causes the introduction of TDs. In addition, longer recombination lifetimes elongate carrier diffusion length. As a result, many of the carriers recombine nonradiatively before reaching RRCs. Those observations lead us to a conclusion that In\(_{x}\)Ga\(_{1-x}\)N blue emitters can exhibit such high emission quantum efficiencies owing to localization to RRCs and antilocalization to NRCs, which are difficult to be simultaneously realized in other spectral ranges. Finally, we like to point out that the results of the green-emitting QW encourage the use of nonpolar or semipolar QWs because much faster radiative recombination processes are expected to suppress carrier trapping to NRCs and, consequently, to realize improvement of emission quantum efficiencies.

VI. CONCLUSION

The carrier recombination processes in violet-emitting, blue-emitting, and green-emitting In\(_{x}\)Ga\(_{1-x}\)N SQWs were elucidated by assessing the same surface area with multimode SNOM and AFM. The violet-emitting and green-emitting QWs clearly showed that TDs act as NRCs, whereas such correlation was not found for the blue-emitting QW. For the blue-emitting QW, NRCs are surrounded by energy levels higher than those for RRCs. Such potential fluctuations realize antilocalization of carriers to NRCs, which is, we consider, why InGaN blue emitters exhibit such high emission quantum efficiencies. For the green-emitting QW, weak PL was observed in the area emitting at lower-energy bands. These results indicate that many of carriers recombine nonradiatively before reaching RRCs.

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\*akio.kaneta@optomater.kuee.kyoto-u.ac.jp
\^funato@kuee.kyoto-u.ac.jp
\^kawakami@kuee.kyoto-u.ac.jp

NANOSCOPIC RECOMBINATION PROCESSES IN…

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