

Macroscale, Microscale, and Nanoscale Structural and Optical Characterization on Hybrid InGaN Red Quantum Wells

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Abstract

Recent micro-light-emitting diode (μ LED), including liquid crystal displays (LCDs) and organic light-emitting diodes (OLEDs), has revolutionized the display industry. However, challenges related to their brightness, lifetime, response time and contrast ratio remain difficulties in the development of next generation displays. In this context, indium gallium nitride (InGaN) has attracted significant attention as a light source for μ LED displays due to its superior physical performance compared to LCDs and OLEDs.

The peak wall-plug efficiency reaches approximately 78% for blue and 56% for green LEDs. Increasing the In content of InGaN can provide yellow and red emission because of the bandgap energy range of 0.67–3.42 eV. However, the external quantum efficiency (EQE) of yellow and red InGaN-based LEDs is still low compared to that of blue and green LEDs. The EQE at RT is at most 10% for reported InGaN-based red LEDs on sapphire substrates. The low EQE and internal quantum efficiency (IQE) originate from the low-temperature growth, substantial lattice mismatch, and quantum-confined Stark effect (QCSE) of In-rich InGaN active layers. These issues also cause a substantial shift of the peak wavelength with increasing current.

For red InGaN LEDs, IQE is the most limiting factor, numerous research groups have focused on the characterization of InGaN-based red LEDs to improve the IQE. For the red InGaN hybrid double quantum well (DQWs) with EQE of approximately 1.6 %, it was reported that the IQE is as high as 24% under non-selective excitation. According to the calculation, the product of light extraction efficiency (LEE) and current injection efficiency (CIE) is only about 6.7%, which is too low and unreasonable. Additionally, photoluminescence (PL) lifetime evaluation is also important to study the IQE, and it was estimated to be only 5 ns at room temperature (RT). All the aforementioned experiments were conducted under non-selective excitation conditions, meaning that the PL lifetime and deduced IQE are not correct as demonstrated in a blue InGaN study. Moreover, the samples used in these experiments

were red InGaN DQWs. According to previous reports, red InGaN SQW exhibits higher crystal quality and lower defect densities than those of DQWs. Therefore, under selective excitation conditions, the estimation of the IQE and PL lifetime for red InGaN SQWs remains unexplored. For the spatial-resolved microscopy, previous studies on red InGaN SQW have shown optical electroluminescence (EL) images, where various dark emission spots of unclear origin were observed. Moreover, microscopic spectroscopic information for these spots is currently unavailable. Thus, for red InGaN SQW, studies ranging from macroscopic to nanoscopic scales remain insufficiently addressed.

This study investigates the optical and structural properties of on InGaN-based hybrid quantum wells for efficient red emitters from macroscopic and nanoscopic scale. The following provides a brief overview of the contents of each chapter.

Chapter 1 introduces the current status of InGaN-based LEDs and the challenges faced by high In-content InGaN-based LEDs. It briefly summarizes the characterization of red InGaN-based LEDs reported in recent studies and highlights the unresolved issues in these reports. Furthermore, it emphasizes the lack of research on red InGaN-based SQWs from macroscopic to nanoscopic scales, thereby establishing the objectives and significance of this study.

Chapter 2 discusses the estimation of the IQE at 6 K and 293 K, as well as the power- and temperature-dependent PL lifetimes. It is found that when the temperature is higher than 100 K, the shortening τ_{NR} strongly dominate the τ_{PL} , contributing to the thermal droop in InGaN-based red SQW. The power dependence of the τ_R at cryogenic temperatures suggests that the radiative rate is influenced by a combination of internal electric fields, Coulomb enhancement, and Coulomb interaction screening. Additionally, we demonstrate that disorder-induced linewidth plays a significant role in the broadening of the FWHM, particularly under high excitation conditions, resulting in a longer τ_R . Therefore, improving the compositional homogeneity of In in red QWs is identified as a promising approach to enhance the efficiency of InGaN-based red LEDs.

Chapter 3 presents the results of micro-photoluminescence (μ -PL) spectroscopy

for an InGaN-based red LED with a hybrid QW structure, which consists of blue and red SQW. The μ -PL mapping image of the integrated red emission intensity revealed various sizes/contrasts of dark spots. In addition, not only red and blue (from blue SQW) but green emission bands were observed at certain dark spots, suggesting that In segregation is one of the causes of dark red emissions. Comparing the blue and green emission maps to the red emission map, the dark spots in the intensity map of the red emission were classified into four types. Through the correlative analysis, the red dark spots correlated to the dark areas in the intensity map of the blue emission are the major nonradiative centers. Consequently, we establish a correlation in the distribution of nonradiative recombination centers (NRCs) between the blue SQW and red SQW.

Chapter 4 presents the structural and optical properties of a blue InGaN SQW and an efficient red InGaN active layer, using AFM and SNOM PL spectroscopy. Our findings reveal that the primary NRCs in the blue and red SQWs are threading dislocations (TDs) and trench defects, respectively. All the trench defects exhibit dark emission intensity due to the In segregation induced by high In content. Based on the previously established correlation in the distribution of NRCs between the blue and red SQWs, we reasonably infer that TDs must be a trigger in the formation of trench defect in red InGaN SQW. These results demonstrate that improving the EQE of InGaN-based red LEDs requires the elimination of In segregation within trench defects and the suppression of TD density.

Chapter 5 summarizes the research on the structural and luminescence properties of red InGaN-based SQW across macroscopic to microscopic scales. These findings will help in realizing efficient InGaN-based red LEDs. Finally, it outlines future research plans to achieve a more comprehensive evaluation of InGaN-based red SQWs.

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Chapter 1

1. Introduction

1.1 Status of Semiconductor Solid-State Visible Light Sources

Semiconductor solid-state light sources have revolutionized the field of illumination because of superior efficiency, extended lifetime, and reduced environmental impact, compared to traditional lighting solutions. [1, 2] These light sources are now integrated to a wide range of applications, as general lighting, displays, and advanced optoelectronic systems. [3]

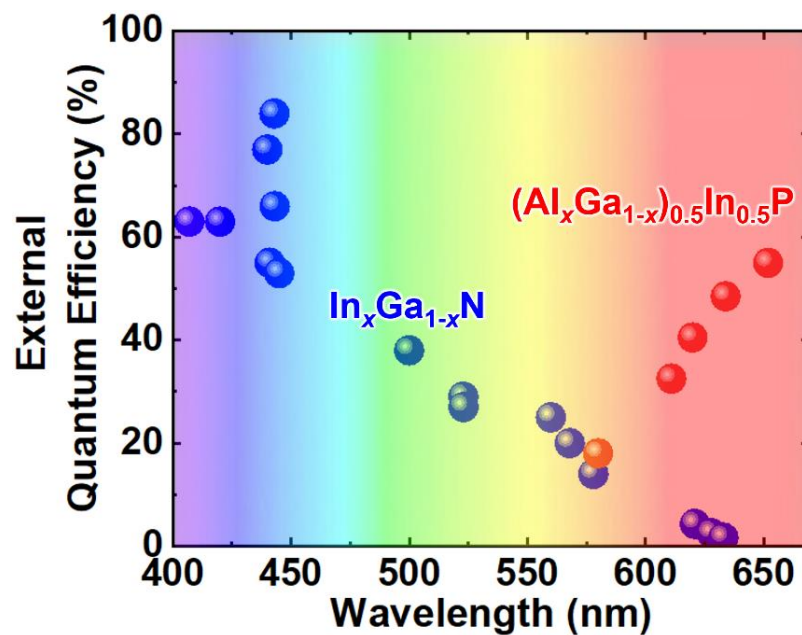


Figure 1-1. Reported EQE values of LEDs consisting of $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ [7] and $\text{In}_x\text{Ga}_{1-x}\text{N}$ active layer [8-13] as a function of emission wavelength.

The origins of semiconductor solid-state visible light sources can be traced back to the invention of the first practical red LEDs in the 1960s, using gallium arsenide phosphide (GaAsP) materials. [4] The early LEDs demonstrated the feasibility of

semiconductor-based light generation but were constrained by the low efficiency and limited color range. Subsequent innovations in other compound semiconductors, particularly group III-V materials, significantly broadened the range of emission wavelengths and enhanced the overall performance of LEDs. [5, 6]

A major milestone in the evolution of visible light sources was the development of high-efficiency blue LEDs in the 1990s, utilizing indium gallium nitride (InGaN) as the active material. [14-16] This breakthrough enabled not only white light generation through phosphor conversion but also the widespread adoption of LEDs in displays, lighting, and optical communication systems. Figure 1-1 presents the reported external quantum efficiency (EQE) values of AlGaInP LEDs [7] and InGaN LEDs [8-13]. The EQE is defined by a ratio of the number of extracted photons to the number of injected electrons. In the red spectral region, the EQEs of $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ -based LEDs decrease with shortening emission wavelength due to the transition from a direct to an indirect bandgap when x approaches 0.5. [17] On the other hand, the EQEs of InGaN-based green and blue LEDs are greater than 50% and 80%, respectively. [18, 19] However, as the emission wavelength gets longer, the EQE of InGaN-based LEDs significantly decreases. Currently, InGaN-based LEDs are mainly utilized for blue and green emission sources, [20, 21] whereas AlGaInP is the most mature semiconductor material to make red LEDs with high brightness and good reliability. [22]

Following the success of conventional LEDs, continuous improvements in material quality, device architecture, and manufacturing processes have driven the development of next-generation light-emitting devices. Among them, Micro-LEDs have attracted increasing attention for research and commercial applications such as micro-displays, visible light communications, and optogenetics because of the unique advantages, including lower power consumption, longer lifetime, and superior brightness. [23-27] However, a key challenge with the production of monolithic RGB micro-LEDs lies in the use of different material systems for red (AlGaInP) and blue/green (InGaN) pixels. This discrepancy requires the integration of different materials on a single substrate to achieve full-color displays, [28] leading to mismatches in the far-field radiation patterns that may degrade the visual quality. Additionally, from an environmental viewpoint,

phosphorus precursors used in the growth of AlGaInP are highly toxic, making it unsuitable for sustainable development strategies. [29] Although recent studies have revealed that AlGaInP μ LEDs can recover the EQE through a proper sidewall treatment, [30] monolithic InGaN-based RGB LEDs hold promise for the creation of matrices with smaller pixel dimensions. Furthermore, InGaN-based micro-LEDs have demonstrated the higher tolerance against size-related effects, making them more suitable for micro-scale applications. [31] Therefore, monolithic InGaN-based RGB LEDs with variable size possess high potential, attracting increasing attention in the related field.

1.2 InGaN

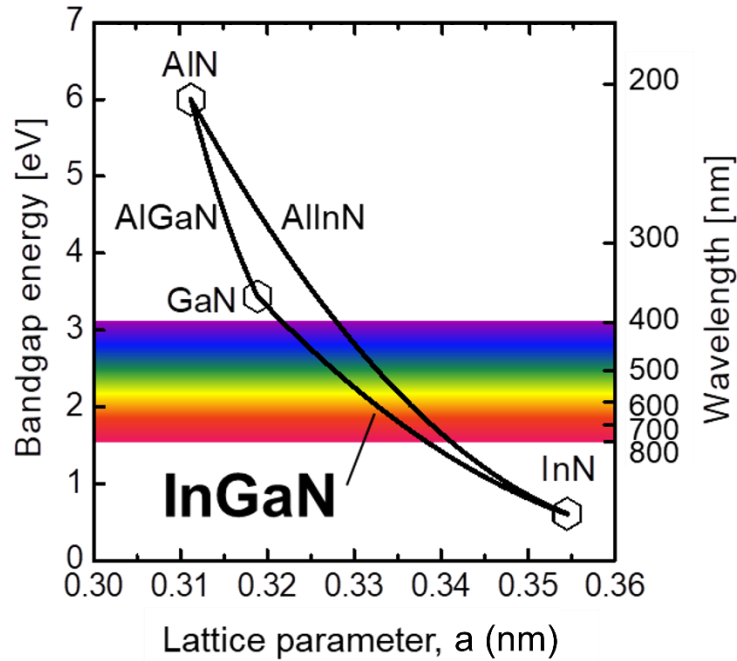


Figure 1-2. Bandgap energy and a -axis lattice constant of group III-nitride semiconductors.

The key advantage of InGaN lies in the ability to significantly change the bandgaps through the composition tuning. The bandgap energies and a -axis lattice constants of GaN, InN, and their ternary alloys are shown in Fig. 1-2. The bandgap energies of GaN and InN at 0 K are 3.51 eV and 0.69 eV, respectively. By forming ternary alloys, the

InGaN bandgap can be engineered to red, green, and blue colors through the tuning of the In composition. [32] The precise bandgap engineering enables the fabrication of vibrant and high-quality displays in addition to general lightings. Due to such great contributions, Nobel Prize in Physics was awarded to Profs. Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura “for the invention of efficient blue light emitting diodes which has enabled bright and energy-saving white light sources” in 2014. [33]

To advance the development of monolithic InGaN-based RGB LEDs, significant progress has been made in optimizing the performance. Notably, the peak wall-plug efficiency reaches approximately 78% for blue [35] and 56% for green LEDs. [19] However, the realization of efficient InGaN-based red micro-LEDs faces a critical challenge due to the material limitations and performance bottlenecks at longer wavelengths. The EQE is at most 10% for conventional InGaN-based red LEDs on sapphire substrates. [36] This remarkable decreasing trend should originate from several factors, such as the strong polarization field, [37] degradation of the crystalline quality, [38, 39] and phase separation, [40, 41] as shortly discussed in Sec. 1.3.

1.3 Challenging Issues on Red InGaN Emitters

The typical device structure of $\text{In}_x\text{Ga}_{1-x}\text{N}$ -based LEDs is shown in Fig. 1-3. The challenge issues mainly arise from the different material properties of each layer, resulting in the lattice mismatch between epilayer and substrate, significant piezoelectric polarization fields within the QWs, degradation of crystalline qualities, and In segregation. Understanding and addressing these issues are critical for the development of high-performance InGaN red emitters.

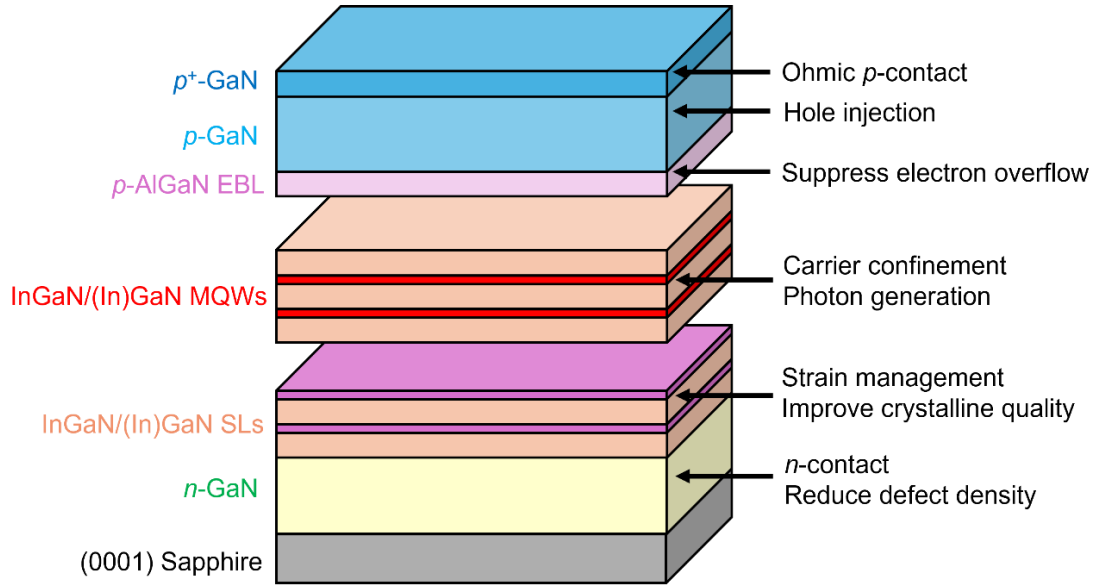


Figure 1-3. Typical InGaN-based LED structure and the functions for each layer.

1.3.1 Lattice Mismatch and Piezoelectric Polarization Field in QW

During the coherent growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum wells (QWs) on GaN substrates, significant lattice mismatch strain accumulates due to the difference between the lattice constants of GaN and InN. This lattice mismatch is approximately 11% and is a major source of strain in $\text{In}_x\text{Ga}_{1-x}\text{N}$ structures. [42] This strain induces piezoelectric polarization. When the polarizations induce an internal electric field along the growth direction, the electron (ψ_e) and hole (ψ_h) wavefunctions become spatially separated, significantly reducing their overlap integral $|\langle\psi_e|\psi_h\rangle|$ within the quantum well layer, as illustrated in Fig. 1-4. This separation reduces the radiative recombination rate, because the radiative recombination rate is proportional to the squared overlap integral $|\langle\psi_e|\psi_h\rangle|^2$. This is one aspect of the quantum confined Stark effect (QCSE). $|\langle\psi_e|\psi_h\rangle|^2$ is drastically reduced by the QCSE, particularly for the wide QWs. This issue is more pronounced in conventional polar (0001) InGaN QWs, where the internal electric field is significant.

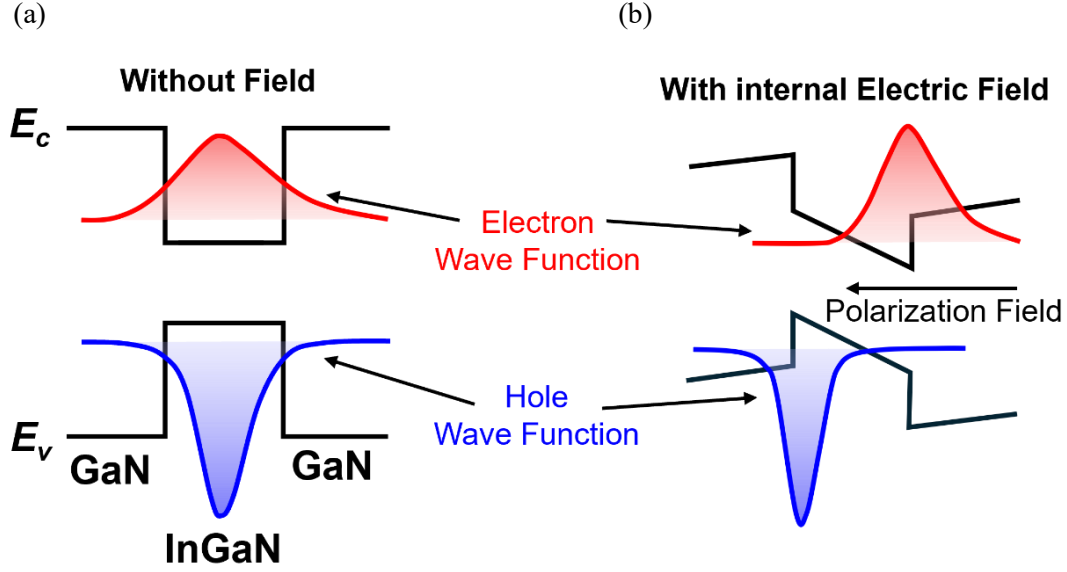


Figure 1-4. Wavefunctions of electrons and holes in InGaN well layer, when the internal electric field is (a) zero and (b) non-zero.

1.3.2 Degradation of Crystalline Qualities

The crystalline quality of epitaxial layers is crucial for the performance and reliability of optoelectronic devices. However, as In-content increases, the lattice mismatch between GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ QW becomes larger, reducing the critical layer thickness of the epitaxial layer. The critical thickness is defined as the maximum thickness of an epitaxial layer that can accommodate lattice-mismatch strain elastically without introducing defects. A general formula for the critical thickness is: [43]

$$\sigma b h_c \cos \lambda = \frac{1}{4\pi} (K_s b_s^2 + K_{e\perp} b_{e\perp}^2 + K_{e\parallel} b_{e\parallel}^2) \ln \left(\frac{h_c}{r_0} \right) \quad (1-1)$$

The left-hand side of the equation represents the force due to lattice mismatch acting on the slip plane, while the right-hand side corresponds to the dislocation line tension, which is equivalent to the dislocation energy per unit length. [44] Here, σ denotes the in-plane stress induced by the lattice mismatch. b represents the length of the Burgers vector. The angle λ describes the orientation between the Burgers vector and the interface direction normal to the dislocation line. Additionally, b_s , $b_{e\perp}$, and $b_{e\parallel}$ correspond to the screw, perpendicular edge components, and parallel edge components

of the Burgers vector, respectively, with K_s , $K_{e\perp}$, and $K_{e\parallel}$ being their respective energy coefficients, often called as “energy coefficients.” [45] Furthermore, r_0 , the dislocation core radius, is typically taken as a value between $b/4$ and b .

When the epitaxial layer thickness exceeds the critical thickness (h_c), lattice relaxation occurs, resulting in the formation of misfit dislocations at the interface, as shown in Fig. 1-5. Misfit dislocations are crucial for strain relaxation, but they also act as the precursors of threading dislocations (TDs), which can further weaken the crystal structure. It has been reported that TDs act as nonradiative recombination centers (NRCs), [46] significantly reducing the IQE of InGaN-based devices. Investigating the relationship between dislocations and IQE is a key to advance the development of high-efficiency InGaN optoelectronic devices.

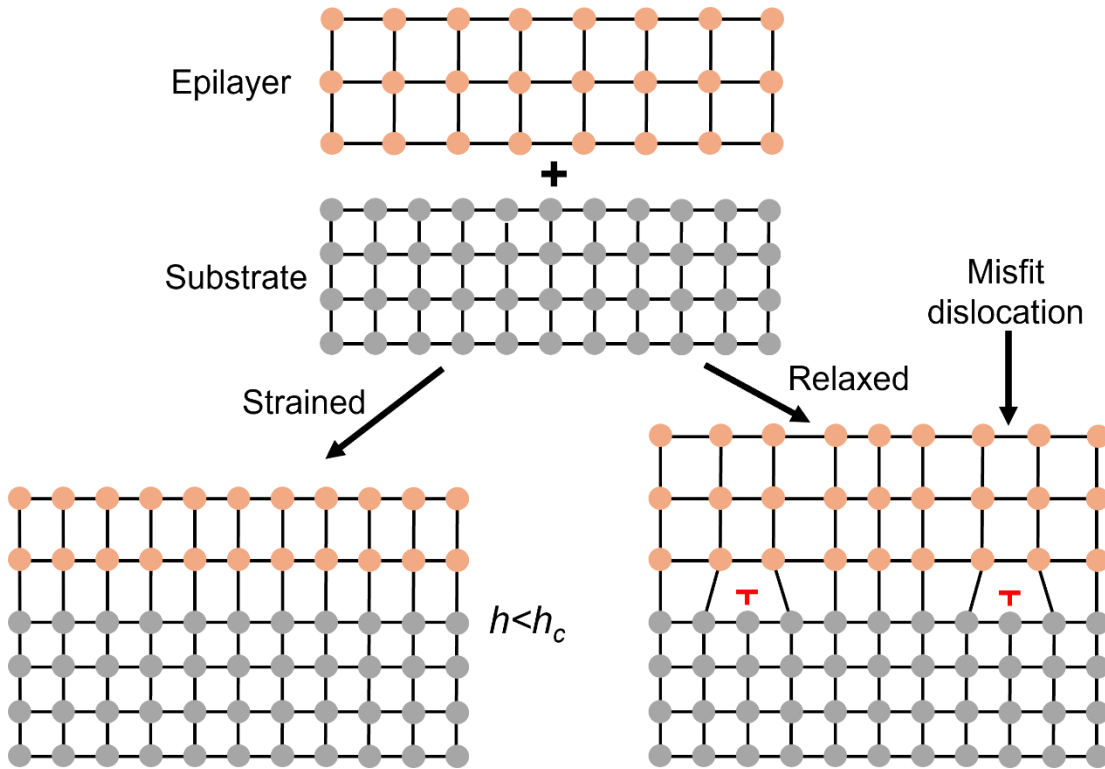


Figure 1-5. Formation of misfit dislocations and strain during heteroepitaxial growth.

1.3.3 In Segregation

In segregation refers to the non-uniform distribution of indium atoms within the crystal lattice, leading to compositional fluctuations on both microscopic and

macroscopic scales. The segregation of In atoms in InGaN epitaxial layers is closely related to the lattice mismatch between InN and GaN. At the microscopic level, lattice mismatch creates strain fields that result in the clustering of indium atoms, as the local strain energy can be minimized by accommodating larger In atoms in specific regions. This strain-induced segregation leads to the formation of compositional fluctuations, commonly called as phase separation. [47] Moreover, the lattice mismatch is also related to the thermodynamics of InGaN growth. The miscibility gap in the InGaN system limits the equilibrium solubility of InN in GaN. For example, at typical growth temperatures ($\sim 800^\circ\text{C}$), theoretical predictions suggest that the equilibrium solubility of InN is as low as 6%, [41] while metastable regions between 6% and 22% allow for the temporary incorporation of higher indium contents before segregation. The interaction between lattice mismatch and In segregation is a critical factor that determines the crystalline quality and optoelectronic properties of InGaN. Understanding and mitigating these effects, through growth optimization and defect engineering, are essential for improving InGaN device performance.

1.4 Recent Studies on InGaN-based Red LED

In order to improve the performance of InGaN-based red LED, there are many factors to solve. EQEs (η_{EQE}) mentioned in Sec. 1.1 can be divided into three efficiency terms, as described by the following equation [48],

$$\eta_{\text{EQE}} = \eta_{\text{CIE}} \times \eta_{\text{LEE}} \times \eta_{\text{IQE}} \quad (1-2)$$

η_{CIE} is the current injection efficiency, which is the ratio of number of injected electrons into QW against number of injected electrons. η_{LEE} is the light extraction efficiency, which is the ratio of number of extracted photons against number of generated photons. η_{IQE} is the internal quantum efficiency (IQE), which is the ratio of the number of generated photons with respect to the number of injected electrons into QWs.

To date, the EQE is at most 10% for conventional InGaN-based red LEDs on

sapphire substrates. [36] This value is significantly low compared to the EQE of efficient blue and green InGaN-based LEDs. [18, 19] Enhancing the EQE requires a comprehensive investigation of the CIE, LEE, and IQE. Among these factors, the LEE and CIE of InGaN red LEDs should reach currently approximately 45% [49] and 90% [50], respectively. Consequently, for InGaN-based red LEDs, the IQE is the most limiting factor. Therefore, improving the IQE should be a more crucial research direction for EQE of InGaN red LEDs. η_{IQE} can be described by the following equation,

$$\eta_{\text{IQE}} = \frac{\tau_{\text{rad}}^{-1}}{\tau_{\text{rad}}^{-1} + \tau_{\text{nrad}}^{-1}} \quad (1-3)$$

τ_{rad}^{-1} is the radiative recombination rate, representing the rate for carriers to recombine through photon emission. τ_{rad}^{-1} is an indicator of oscillator strength, reflecting the degree of internal electric field. τ_{nrad}^{-1} is the non-radiative recombination rate, representing the rate for carriers to recombine via non-emissive pathways. τ_{nrad}^{-1} is strongly related with defect density. To estimate τ_{rad}^{-1} and τ_{nrad}^{-1} , lifetime measurement is crucial. PL lifetime (τ_{PL}) is the time for excited carriers to return to the ground state. τ_{PL} can be estimated by fitting a PL decay curve with a single exponential function as follows:

$$I(t) = I_0 \times \exp\left(\frac{-t}{\tau_{\text{PL}}}\right) \quad (1-4)$$

where I_0 represents the initial time-resolved PL (TRPL) intensity, and $I(t)$ is the TRPL intensity at time t . τ_{PL} can be expressed by the radiative and nonradiative recombination lifetime as:

$$\tau_{\text{PL}}^{-1} = \tau_{\text{rad}}^{-1} + \tau_{\text{nrad}}^{-1} \quad (1-5)$$

Using equations (1-3) and (1-5), τ_{rad} and τ_{nrad} can be extracted. These two parameters provide critical insights and offer a guideline for improving the IQE.

To improve the IQE of InGaN-based red LEDs, numerous research groups have focused on the characterization of InGaN-based red LEDs from the viewpoint of macroscopic, microscopic, and nanoscopic scales.

1.4.1 Macroscale

Hou *et al.* studied the optical properties of InGaN red hybrid QWs LEDs, which are composed of red InGaN double quantum well (DQW) active layer and blue InGaN single quantum well (SQW), by non-selective excitation PL measurement. [51] The maximum EQE of the InGaN-based red LED was 1.6%. [52] According to the measurements by Hou *et al.*, the IQE of the red DQWs as a function of excitation energy at 293 K is presented in Fig. 1-6, showing an increase in the IQE to 24.03%. However, using Eq. (1-2), the product of the CIE and LEE is estimated to be only 6.7%. This estimation contradicts the commonly accepted values of CIE and LEE, which are typically above 90% and 45%, [49, 50] respectively. One potential factor contributing to the discrepancy is the neglect of the excitation power dependence of IQE at 6 K. Hou *et al.* assumed that IQE is 100% under any excitation energies at low temperatures, which may have led to an overestimation of the IQE. Additionally, the sample under investigation was composed of not only a red InGaN DQW but also a blue InGaN single quantum well (SQW). Non-selective excitations of both red and blue quantum wells may result in inaccurate IQE estimations, as demonstrated in prior studies of blue InGaN. [53] Therefore, a careful and accurate evaluation of the IQE of InGaN-based red LEDs is still lack.

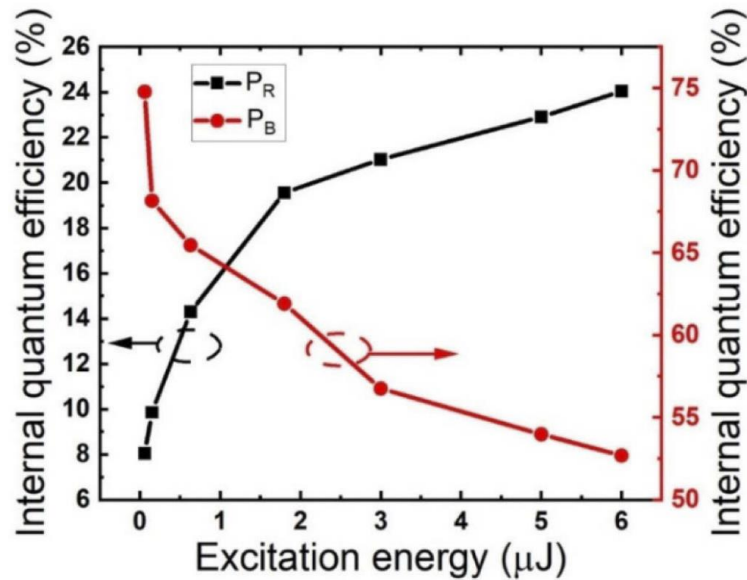


Figure 1-6. Internal quantum efficiency of two emission peaks as functions of the excitation energy, where P_R and P_B represent the red emission and blue emission,

respectively. [51] Reprinted with permission from [51] © Optical Society of America.

To gain a deeper precise understanding of recombination dynamics, Li *et al.* investigated the temperature-dependent PL lifetime of InGaN red hybrid QWs LEDs. [54] They revealed that the PL lifetime increases with increasing temperature initially and then τ_{PL} decreases, with a room-temperature value of 100 ns. However, because they did not measure the corresponding IQE, τ_{rad} and τ_{nrad} are unavailable. In another study, Hsiao *et al.* measured the temperature-dependent PL lifetime of high-V-defect-density InGaN red hybrid QWs LEDs. [55] The PL decay curve is shown in Fig. 1-7(a). Instead of using equations (1-3) and (1-5) to estimate τ_{rad} and τ_{nrad} , they applied a bi-exponential function to fit the time-resolved PL (TRPL) decay curves, assuming that the slow decay component corresponds to radiative recombination and the fast decay component originates from nonradiative recombination. The obtained temperature-dependent τ_{rad} and τ_{nrad} are presented in Fig. 1-7(b). However, it must be emphasized that their assumption that the slower decay component represents radiative recombination, and the faster one represents nonradiative recombination lacks a solid foundation. Moreover, as shown in Fig. 1-7(b), the radiative recombination lifetime is reported to be less than 15 ns at all the experimental temperatures. This contradicts the presence of a strong internal electric field in red InGaN QWs, as the QCSE would typically reduce the radiative recombination rate, resulting in a longer radiative recombination lifetime. Additionally, Hsiao *et al.* introduced many TD-related V-pits to enhance CIE. However, TDs may act as nonradiative recombination centers [56] and the intentional introduction of V-pits could alter τ_{PL} as well as τ_{rad} and τ_{nrad} .

Notably, all of the aforementioned studies investigate red DQWs under non-selective excitation condition PL. However, red DQWs have more defects compared to red SQW. [57] Furthermore, non-selective excitation condition can affect the estimation of both IQE and carrier recombination lifetimes. Therefore, from the macroscopic scale viewpoint a comprehensive analysis on carrier recombination dynamics in low-defect-density red InGaN QWs remains lacking.

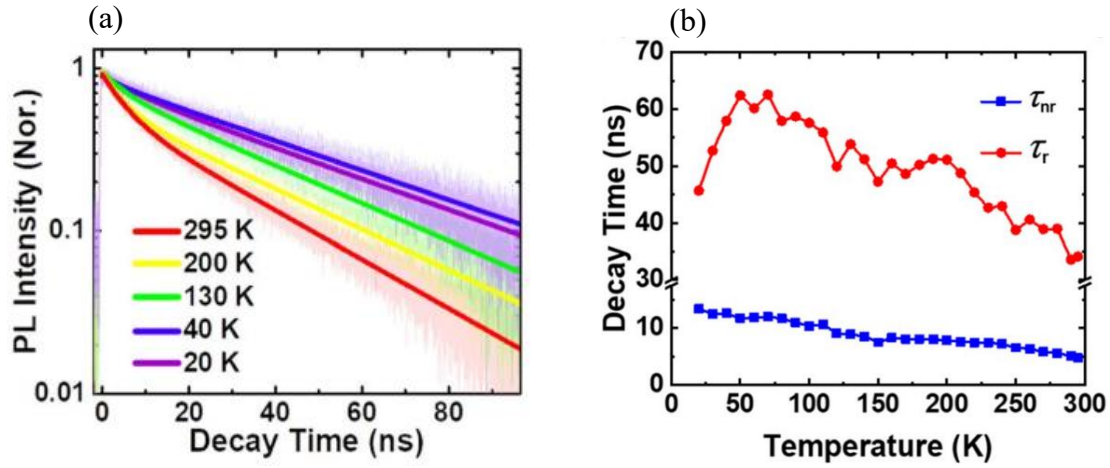


Figure 1-7. (a) TRPL decay at various temperatures. (b) Temperature dependence of the decay times derived from bi-exponential decay function fit. [55] Reproduced from [55] CC BY 4.0.

1.4.2 Microscale

To improve the IQE of InGaN-based red LEDs, the investigation on the microscopic origins of non-radiative recombination centers (NRCs) is crucial. Kirilenko *et al.* fabricated 649 nm InGaN red DQW LEDs and investigated the properties of the parasitic peak in the electroluminescence (EL) spectrum. [58] The EL image visualized many separated point-like emission spots as illustrated in Fig. 1-8(a). They demonstrated that the separated emission spots were related to the defect areas that contained lower In contents in red QWs. Subsequently, Iida *et al.* fabricated 621 nm InGaN red single quantum well (SQW) LEDs with an external quantum efficiency (EQE) of 4.3% at a current density of 10.1 A/cm². [49] They demonstrated that the formation of defects in second red QW leads to additional short-wavelength emissions. The EL image of the red SQW under a 20 mA injection current is shown in Fig. 1-8(b), revealing apparently homogeneous emissions. However, upon closer inspection, numerous dark emission spots can be observed. The underlying physics of these dark emission spots remains unclear. Additionally, because Fig. 1-8(a) and Fig. 1-8(b) were taken using a camera, no microscopic spectral information is given. Consequently,

microscopic characterizations of InGaN-based red LEDs are still lacking and further investigation is required.

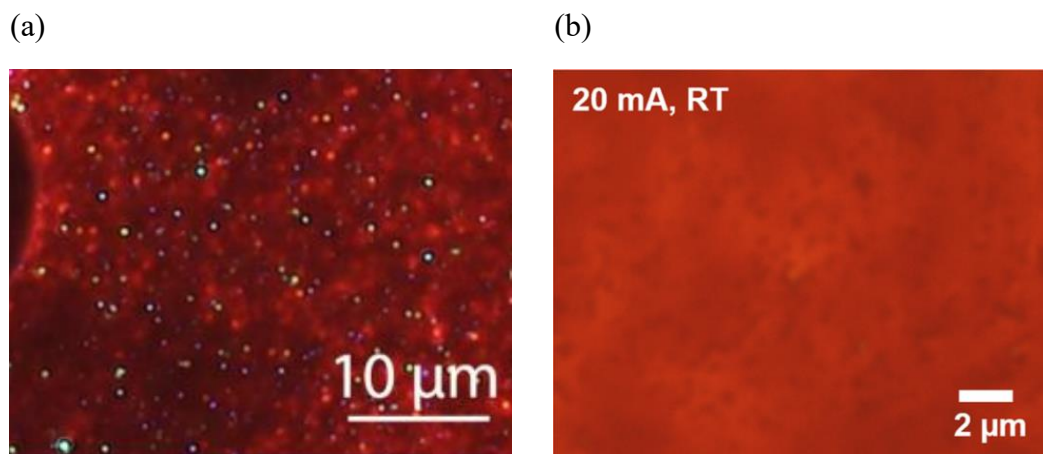


Figure 1-8. (a) EL image of InGaN-based red DQW LED at 1 mA. [58] Reproduced from [58]. CC BY 4.0. (b) EL image of InGaN-based SQW LED at 20 mA taken by high-resolution optical microscope. [57] Reproduced from [57]. CC BY 4.0.

1.4.3 Nanoscale

Currently, the number of nanoscale characterizations on InGaN-based red LEDs is limited. Most studies focus on nanoscale structural characterizations. For example, Iida *et al.* conducted atomic force microscopy (AFM) and cross-sectional scanning transmission electron microscopy (STEM) measurements on InGaN-based red DQW LEDs, revealing the presence of TD-related V-pits and trench defects. [52] Trench defects consist of basal stacking faults (BSFs) terminated by stacking mismatch boundaries (SMBs), which will be discussed in detail in Chapter 4. Previous studies have investigated the luminescence properties of trench defects in $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$, [59-62] suggesting that certain trench defects could contribute to higher luminescence intensity. A recent work by Pan *et al.* introduced a significant density of trench defects in red InGaN-based LEDs to enhance the luminescence intensity. [63] However, their macroscopic PL spectra exhibited a broad full-width at half maximum (FWHM), leaving it unclear whether this broadening originates from the high density of trench defects. Although cathodoluminescence (CL) mappings were conducted in their study,

microscopic spectral information was not provided, leaving the luminescence properties of trench defects in InGaN-based red LEDs still unexplored. Regarding TD-related V-pits, previous scanning near-field optical microscopy (SNOM) studies by Kaneta *et al.* identified TDs as NRCs in InGaN-based violet and green LEDs, while in blue LEDs, TDs were not NRCs. [64] However, the role of TDs in InGaN-based red LEDs remains unexplored. Furthermore, the impact of TDs and trench defects on the IQE is still unclear. Thus, nanoscopic characterizations, particularly investigations into the luminescence properties of these defects, are notably lacking. Such studies are crucial for understanding the role of these defects and for developing strategies to enhance the IQE of InGaN-based red LEDs.

1.5 Objective and Outline of This Study

As discussed in Sec. 1.4, investigating carrier recombination dynamics is crucial for enhancing the IQE of red InGaN LEDs. However, studies ranging from macroscopic to nanoscopic scales are lacking. Therefore, the object of this thesis is to elucidate the optical and structural properties of red InGaN hybrid QWs by macroscopic, microscopic and nanoscopic characterizations.

Chapter 2 discusses the estimation of the IQE at 6 K and 293 K, as well as the power- and temperature-dependent τ_{PL} . It is found that when the experimental temperature is higher than 100 K, the short nonradiative lifetime dominates the τ_{PL} , contributing to the thermal droop in the InGaN-based red SQW. The power dependence of the radiative lifetime at 6 K indicates that the radiative rate is affected by a combination of Coulomb enhancement and QCSE screening. Additionally, we demonstrate that the disorder-induced linewidth plays a significant role in the broadening of the FWHM. Therefore, the improvement of the In homogeneity should be a promising method for realizing efficient InGaN-based red LEDs.

Chapter 3 presents the results of micro-photoluminescence (μ -PL) spectroscopy for an InGaN-based red LED with a hybrid QW structure, which consists of a blue and a red SQW. The μ -PL mapping image of the integrated red emission intensity revealed

many dark spots. In addition, not only red and blue (from blue SQW) but green emission bands were observed at certain dark spots, suggesting that In segregation is one of the causes of dark red emissions. Comparing the blue and green emission maps to the red emission map, the dark spots in the intensity map of the red emission were classified into four types. Through the correlative analysis, the red dark spots correlated to the dark areas in the intensity map of the blue emission are the major nonradiative centers. Consequently, we establish a correlation in the distribution of nonradiative recombination centers (NRCs) between the blue SQW and red SQW.

Chapter 4 presents the structural and optical properties of a blue InGaN SQW and an efficient red InGaN active layer, using AFM and SNOM PL spectroscopy. We reveal that the origins of dark emission spots in the blue and red SQWs are TDs and trench defects, respectively. All the trench defects exhibit dark emission intensity due to the In segregation induced by high In content. Considering the previously established correlation in the distribution of NRCs between the blue and red SQWs, we conclude that TDs must be a trigger in the formation of trench defects in red InGaN SQW. These results demonstrate that improving the EQE of InGaN-based red LEDs requires the elimination of In segregation within trench defects and the suppression of TD density.

Chapter 5 summarizes this thesis on the structural and luminescence properties of red InGaN-based SQWs from macroscopic to nanoscopic scales. These findings will help in realizing efficient InGaN-based red LEDs. Finally, we outline future research works to achieve a more comprehensive evaluation of InGaN-based red SQWs.

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Chapter 2

2. Macroscopic Luminescence Characterization on Hybrid InGaN Red QWs

2.1 Introduction

As mentioned in Chap. 1, the external quantum efficiency (EQE) of InGaN-based red LEDs is at most 10%. The low EQE and IQE originate from the low-temperature growth, [1, 2] substantial lattice mismatch, [3, 4] and QCSE of In-rich InGaN active layers. [5] These issues also cause a substantial shift of the peak wavelength with increasing current.

Various approaches have been proposed to realize efficient III-nitride-based red LEDs, including using a micro-flow channel, [6] Eu-doped GaN, [7] lattice-matched substrates, [8] an AlGaIn interlayer, [9] a GaN underlying layer, [10, 11] *m*-plane growth, [12] and a hybrid quantum well structure. [13] Notably, Iida *et al.* have demonstrated efficient red LEDs using a hybrid quantum well (QW) structure composed of a blue single QW (SQW) underlayer and a red SQW layer. [13] The optical properties and carrier dynamics of red InGaIn hybrid DQWs have been studied under non-selective excitation condition. [14, 15] The maximum IQE at room temperature was estimated as high as 24.01%. [14] The estimated radiative (τ_{rad}) and nonradiative (τ_{nrad}) recombination lifetimes were from 35 to 60 ns and from 5 to 15 ns, respectively, for high-defect-density red InGaIn hybrid DQWs. [15] However, the intentional introduction of threading dislocations (TDs) might affect the estimation of PL lifetime (τ_{PL}), τ_{rad} , and τ_{nrad} . In addition, all the above experiments were conducted under non-selective excitation conditions. Therefore, the deduced IQE and τ_{PL} might be affected by carrier/photon transfer from blue SQW beneath-layer. [16] Furthermore, hybrid InGaIn red SQWs, which exhibit higher EQE due to the lower defect density

than hybrid InGaN red DQWs, [13] have yet to be investigated.

In this chapter, we study the optical properties of hybrid SQW InGaN red LEDs, using power- and temperature-dependent time-integrated (TI) and time-resolved (TR) PL spectroscopy. We estimate the maximum IQE of hybrid SQW InGaN red LEDs at room temperature as 5.9%. Based on the power-dependent TRPL, we reveal that the radiative recombination rate is affected by the internal electric field, Coulomb enhancement, and Coulomb interaction screening. The temperature dependence of τ_{rad} and τ_{nrad} is discussed, emphasizing the dominant contribution of the nonradiative recombination lifetime to the thermal droop. Additionally, the correlation between the radiative recombination lifetime and luminescence linewidth is discussed. These findings will lead to a comprehensive understanding of carrier dynamics in InGaN red LEDs.

2.2 Experiment

The studied sample was a red InGaN LED epitaxial structure grown on a patterned *c*-plane sapphire substrate by metal–organic vapor-phase epitaxy. Figure 2-1 shows a cross-sectional schematic of the sample. The precursors of Ga, Al, In, and N were trimethylgallium, trimethylaluminum, trimethylindium, and ammonia, respectively. [3] The epitaxial structure consisted of an 8- μm -thick n-GaN layer, a hybrid QW structure composed of a 2.5-nm-thick InGaN blue SQW and a 3.5-nm-thick InGaN red SQW, and a strain-compensation barrier structure. The blue SQW pre-strained layer was expected to suppress strain relaxation and reduce the defect densities in the red SQW layer, thereby improving the red emission efficiency. [17]

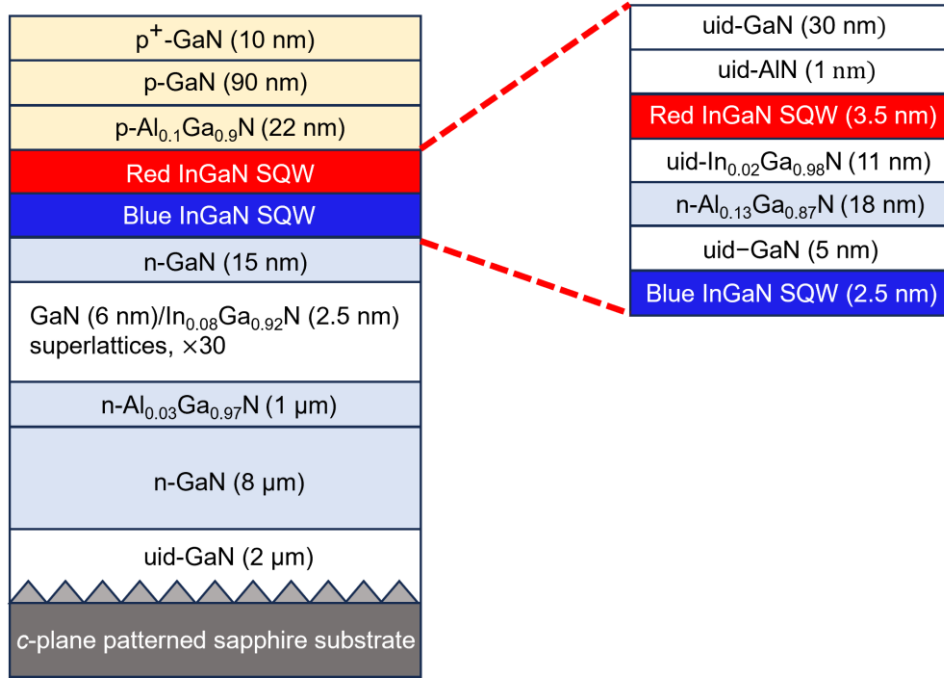


Figure 2-1. Epitaxial structure of the hybrid quantum-well InGaN red LED, where uid-GaN represents unintentionally doped GaN. The inset shows the details of the red and blue SQWs.

To estimate the IQE of the red InGaN hybrid red SQW and investigate the underlying origins of the efficiency and thermal droop, power-dependent and temperature-dependent macroscopic PL measurements were conducted. The measurement setups for macroscopic time-integrated PL (TIPL) (Fig. 2-2) and time-resolved PL (TRPL) (Fig. 2-3) were developed. A 513-nm continuous wave (CW) laser diode (LD) and a 508-nm pulsed LD served as the excitation sources. The pulsed LD had a pulse duration of 108 ps and operated at a repetition rate ranging from 100 kHz to 1 MHz. The laser spot with a diameter of 10 μm was achieved on the sample surface by an objective with a numerical aperture of 0.28. TIPL spectra were acquired using a 50 cm monochromator and a charge-coupled device. TRPL spectra were acquired using a 30 cm monochromator and a streak camera. A closed-cycle conduction-cooling cryostat was used to control the experimental temperatures between 6 K and 293 K.

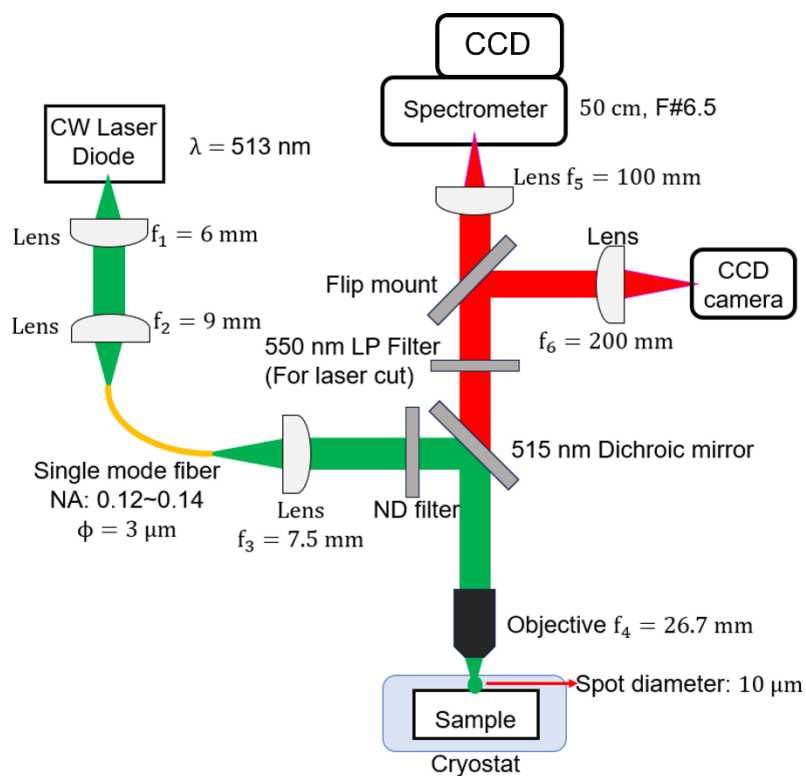


Figure 2-2. TIPL spectroscopy setup.

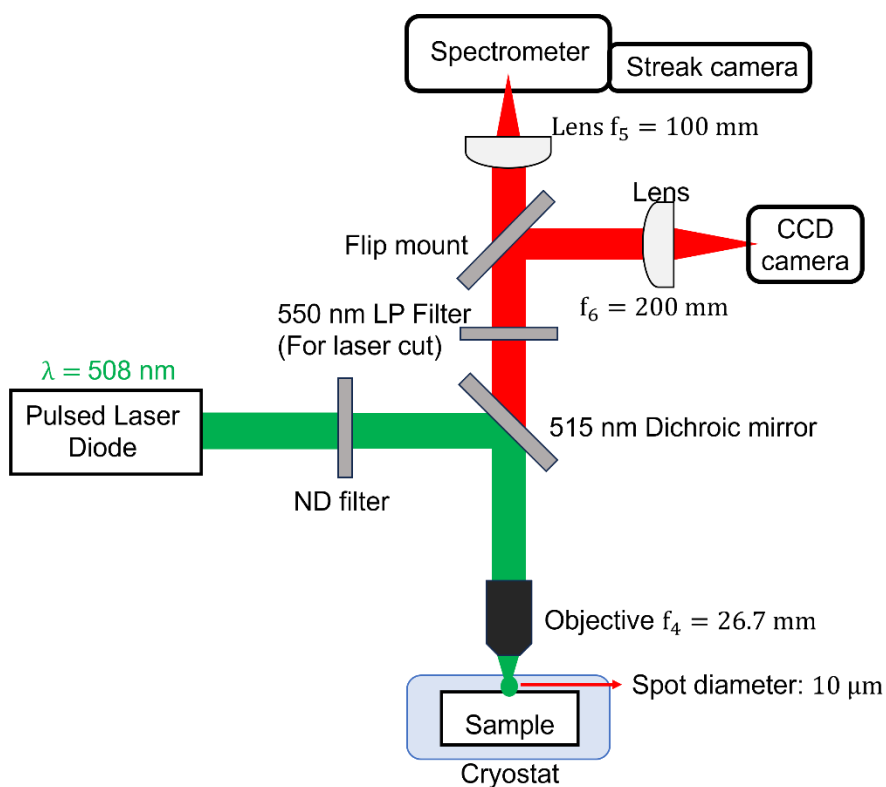


Figure 2-3. TRPL spectroscopy setup.

2.3 Result

2.3.1 Excitation Power Dependent IQE

Figure 2-4(a) depicts the normalized PL spectra obtained at 6 K and 293 K under CW LD excitation at 0.318 kW/cm^2 . The peak wavelength exhibits a notable blueshift from 6 K to 293 K, contrary to the typical temperature-induced bandgap shrinkage (redshift). [18] The abnormal blueshift behavior can be attributed to the strong localization effects arising from significant In compositional inhomogeneity in high In-content InGaN. Because of the substantial confinement energy of deep localized states, carriers are thermally activated to populate the higher energy state. This process overcomes the temperature-induced band-gap shrinkage, leading to a blueshift of the emission peak as temperature increases.

Figure 2-4(b) presents the dependence of the IQE on excitation power density at 6 K and 293 K, measured by CW (Solid circle) and pulsed (Hollow circle) LDs. The IQE is estimated from the PL efficiency normalized by the maximum value at 6 K. [19, 20] Under pulsed LD condition, the maximum IQE at 293 K was 5.1% at an excitation energy density of $124.8 \text{ } \mu\text{J/cm}^2$. Under CW LD condition, the IQE of 5.1% was estimated to an excitation power density of 4.4 kW/cm^2 at 293 K. Therefore, the excitation condition of $124.8 \text{ } \mu\text{J/cm}^2$ for the pulsed LD should be equivalent to that of 4.4 kW/cm^2 for the CW LD. Using the correspondence, the IQE curves for pulsed and CW excitation conditions are plotted at one figure as Fig. 2-4(b). The IQE curves measured by CW and pulsed LDs show consistent tendency as presented in Fig. 2-4(b). At 6 K, the IQE gradually decreases from 100% to 30% with increasing excitation power density, attributed to Auger recombination process, [21] absorption saturation, [22, 23] and carrier overflow [24]. At 293 K, as the excitation power density increases, the IQE increases initially and then decreases. Notably, at 293 K, the maximum IQE of 5.9% is obtained, which is significantly lower than the estimated value of 24.03% reported in previous studies. [14] We attribute the higher IQE estimated in Ref. 14 to the following possibilities: (1) In their work, IQE was defined as the ratio of the

integrated PL intensity at 300 K and 15 K under the same excitation energy density. They assumed that the IQE at 15 K was 100% for any excitation power. However, in our study, it was demonstrated that the IQE at 6 K decreases as the excitation power density increases. (2) In their work, the blue SQW was also excited due to non-selective excitation conditions. However, both the reabsorption of the blue SQW emission and the carrier relaxation from the blue SQW layer might affect the deduced IQE of the red SQW. [25, 26] As a result, the IQE at 293 K of red InGaN hybrid DQWs in Ref. 14 might be overestimated.

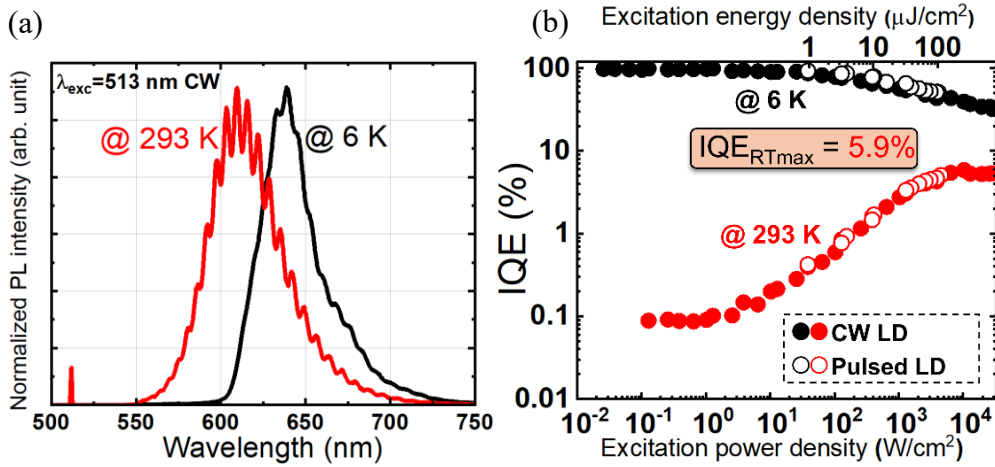


Figure 2-4. (a) PL spectra at 6 K and 293 K under CW LD excitation at 0.318 kW/cm². (b) Excitation power/energy density dependence of the IQE at 6 K (black circle) and 293 K (red circle), measured using CW and pulsed LDs.

2.3.2 Power-dependent Time-integrated PL Measurement

Figure 2-5(a) and (b) present the excitation-energy dependent PL spectra at 6 K and 293 K, respectively. The PL spectra are normalized and vertically shifted for clarification. The center wavelength shift and full width at half maximum (FWHM) as functions of excitation energy density are presented in Fig. 2-5(c) and (d). Here, the center wavelength is defined by following formula:

$$\lambda_{\text{center}} = \frac{\int \lambda \times I(\lambda) d\lambda}{\int I(\lambda) d\lambda} \quad (2-1)$$

where λ and $I(\lambda)$ are the wavelength and corresponding PL intensity, respectively. Here, the integrated wavelength range is from 550 to 750 nm.

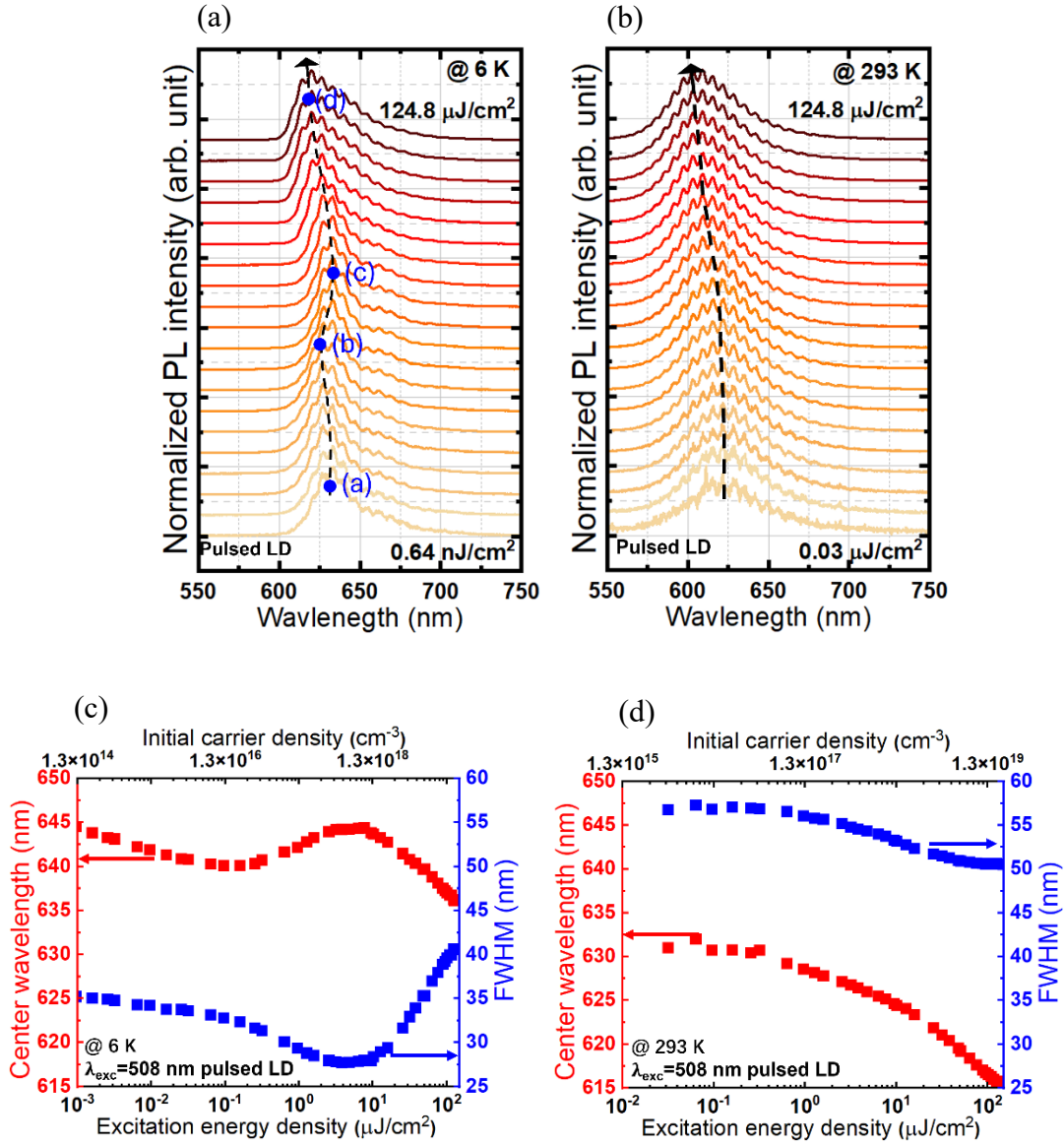


Figure 2-5. Normalized PL spectra with different excitation energy densities at (a) 6 K and (b) 293 K. PL center wavelength and FWHM as functions of excitation energy density at (c) 6 K and (d) 293 K.

At 6 K, as shown in Fig. 2-5(c), the PL center wavelength exhibits a blueshift-redshift-blueshift, while the FWHM decreases in the low excitation energy density range of $< 5 \mu\text{J}/\text{cm}^2$, and then increases rapidly as the excitation energy density increases. To explain the behaviors, the schematic diagrams representing the possible

mechanism of carrier transfer in the red InGaN SQW under different excitation power densities at 6 K are shown in Fig. 2-6. Here, two localization centers are introduced, classified as shallow (SLCs) and deep (DLCs) localization centers. The formation of SLCs and DLCs may be attributed to several mechanisms, such as In compositional fluctuations or interface morphology-related disorders in the alloy layers. [27-33] SLCs typically exhibit higher density compared with DLCs. [33] Under extremely low excitation energy density, carriers are randomly localized in different localization centers. Due to the higher density of SLCs, the total emission is dominated by SLCs as indicated in Fig. 2-6(a). As excitation power density increases ($< 0.1 \mu\text{J}/\text{cm}^2$), the initial blueshift and a reduction in FWHM, can be attributed to the screening of the QCSE. [34, 35] Miller *et al.* attributed the FWHM broadening by QCSE to the field-induced ionization of excitons. The process effectively shortens the lifetime of the excitonic state and destabilizes the exciton as a bound state, consequently broadening the emission linewidth. [35] With further increasing the excitation energy density ($0.1 \mu\text{J}/\text{cm}^2 \sim 5 \mu\text{J}/\text{cm}^2$), the gradual saturation of carriers in SLCs results in carrier relaxation into DLCs via hopping as indicated in Fig. 2-6(c). This process induces an anomalous redshift in the PL center wavelength, while the screening of QCSE causes a continuous reduction in the FWHM. As the excitation energy density further increases ($> 5 \mu\text{J}/\text{cm}^2$), carriers progressively occupy the higher energy state as indicated in Fig. 2-6(d), named as band-filling effect. [36] The saturation effect in DLCs becomes dominant, leading to a rapid blueshift of the PL center wavelength and a broadening of the FWHM. [34-36]

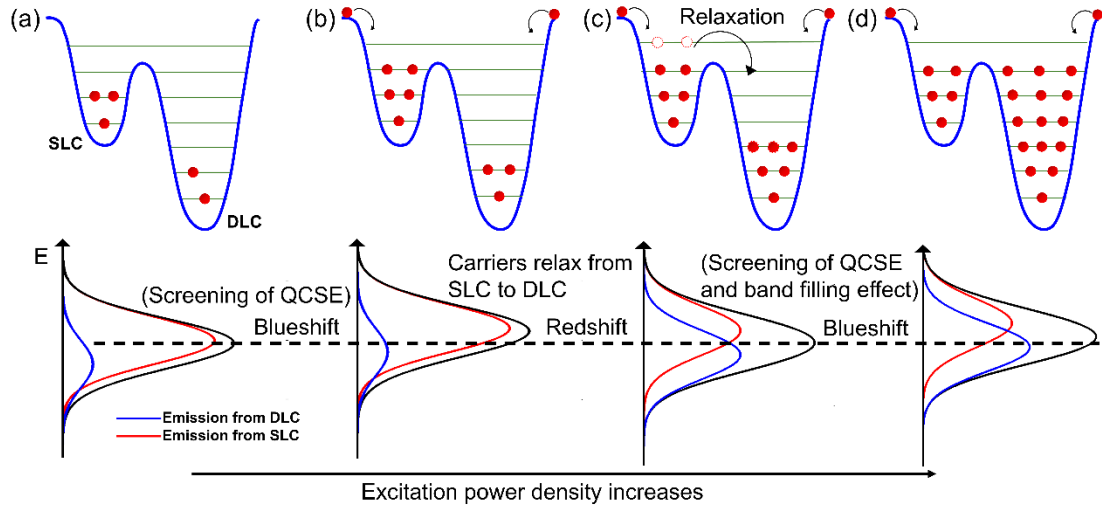


Fig. 2-6. Schematic diagrams of the possible mechanism of carrier transfer in the red InGaN SQW under different excitation power densities at 6 K. (a)-(d) represent the carrier distribution from low to high excitation power density in Fig. 2-5(a). The corresponding PL spectra are shown below.

At 293 K, different phenomena were observed as shown in Fig. 2-5(d). As the excitation energy density increases, the PL center wavelength shows a monotonic blueshift, accompanied by a narrowing of the FWHM. This can be attributed to the combined effects of the QCSE screening and the band-filling effect. Notably, the blueshift of the center wavelength progressively accelerates, while the narrowing of FWHM decelerates and approaches its minimum. It is because the band-filling effect gradually dominates over the QCSE screening as excitation energy density increases. Due to the sufficient thermal activation energy at 293 K, carriers can easily relax from SLCs to DLCs even under low excitation energy density. Consequently, at 293 K, carriers mainly exist in the DLCs, achieving thermal equilibrium with the lattice and occupying high-energy level. The high occupation in DLCs can effectively explain the blueshift of the PL center wavelength at 293 K.

2.3.3 Temperature-dependent Time-integrated PL Measurement

Figure 2-7(a) and (b) show the normalized temperature-dependent PL spectra, under excitation energy density of $7.6 \mu\text{J}/\text{cm}^2$ and $117.1 \mu\text{J}/\text{cm}^2$, respectively. Their center wavelength shift and FWHM as functions of temperature are presented in Fig. 2-7(c) and (d).

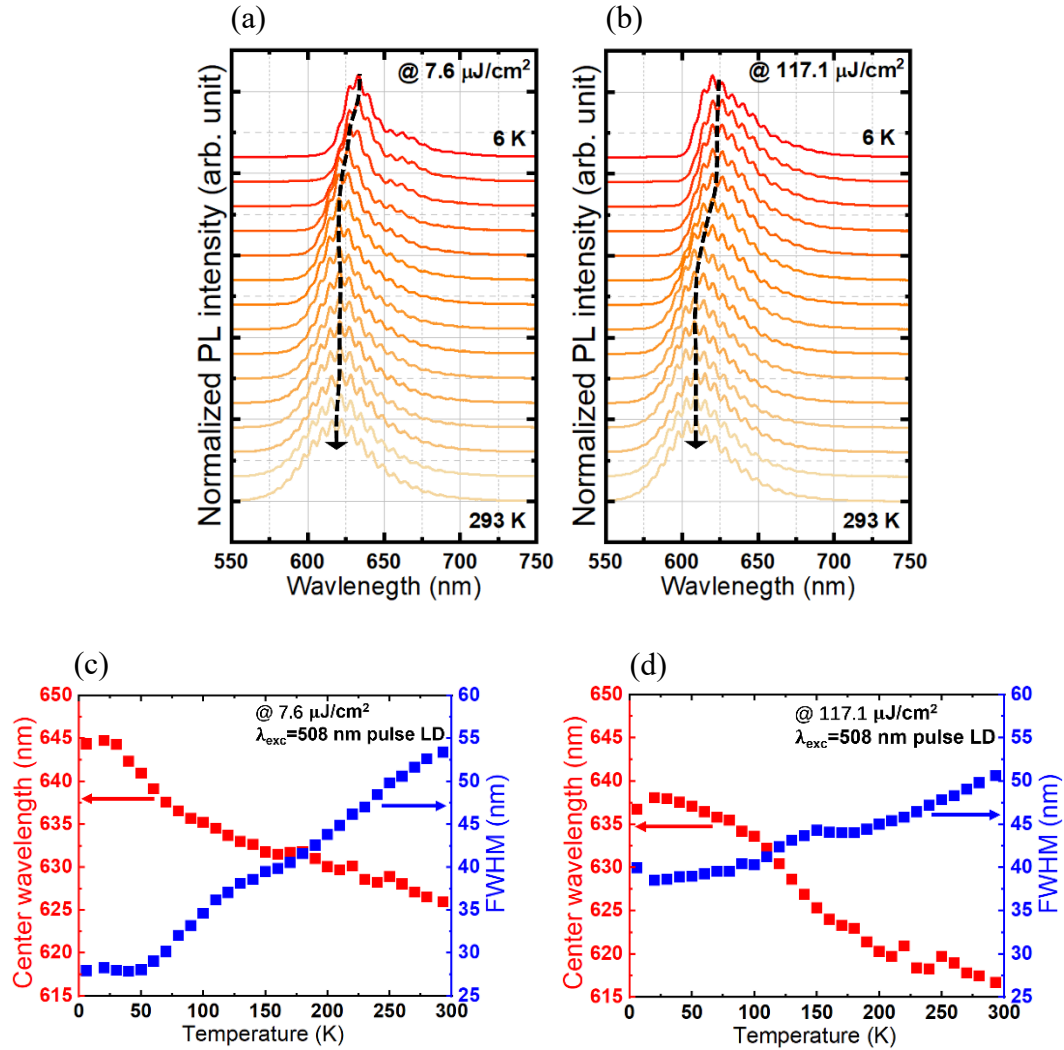


Figure 2-7. Normalized temperature dependent PL spectra under excitation energy density of (a) $7.6 \mu\text{J}/\text{cm}^2$ and (b) $117.1 \mu\text{J}/\text{cm}^2$. PL center wavelength and FWHM as functions of temperature under (a) $7.6 \mu\text{J}/\text{cm}^2$ and (b) $117.1 \mu\text{J}/\text{cm}^2$.

In Fig. 2-7(c)-(d), as temperature increases, the PL center wavelength exhibits an

anomalous blueshift behavior, accompanied by a broadening of the FWHM. The schematic diagrams of the possible mechanism of carrier transfer in the red InGaN SQW at different temperatures are shown in Fig. 2-8. As mentioned before, the anomalous continuous blueshift behavior can be attributed to the potential inhomogeneity and carrier localization due to the large compositional fluctuation in the red InGaN SQW. As the temperature increases, the localized carriers gain thermal energy and occupy the higher and broader energy state. However, they cannot easily escape from the deep localized state, resulting in a blueshift in the PL wavelength and a broadening of FWHM.

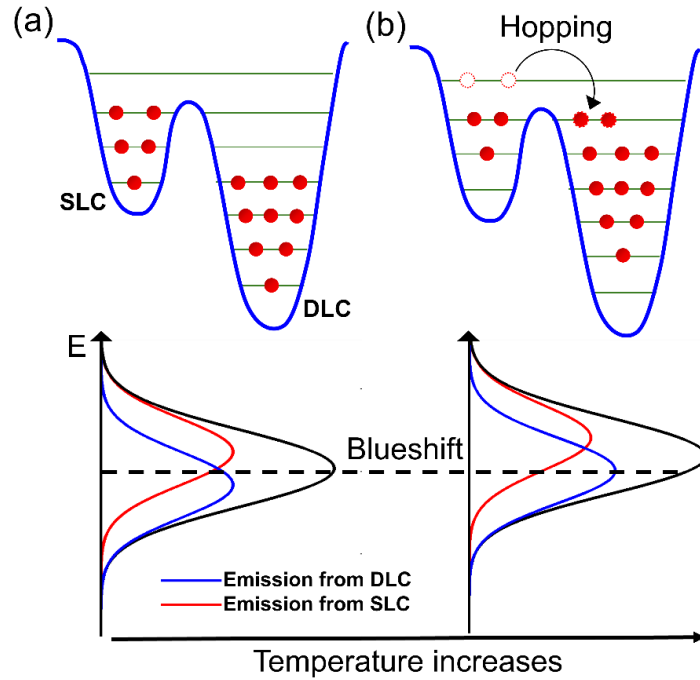


Fig. 2-8. Schematic diagrams of the possible mechanism of carrier transfer in the red InGaN SQW at different temperatures. (a) and (b) represent the carrier distribution at low and high temperature, respectively.

To further investigate the carrier localization effects under low and high excitation energy densities, one-channel Arrhenius model is used to analyze the temperature-dependent integrated PL intensity.

$$I(T) = \frac{I_0}{\left[1 + A \cdot \exp\left(-\frac{E_a}{k_B \cdot T}\right)\right]} \quad (2-2)$$

where I_0 is the integrated PL intensity at low temperature, A represents the contribution of nonradiative recombination pathway, E_a is activation energy and k_B is the Boltzmann constant. The fitting results under different excitation energy densities are shown in Fig. 2-9.

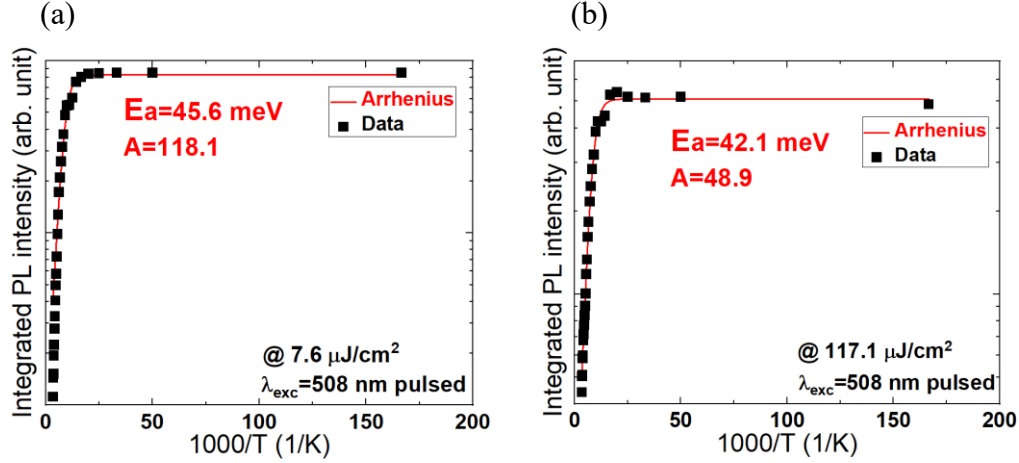


Figure 2-9. Integrated PL intensity versus temperature under excitation energy densities of (a) $7.6 \mu\text{J}/\text{cm}^2$ and (b) $117.1 \mu\text{J}/\text{cm}^2$.

We attribute the Arrhenius-like thermally activated behavior of integrated PL intensity to the defect-mediated nonradiative recombination processes. [37, 38] According to the fitting in Fig. 2-9(a)-(b), carriers have an activation energy of 45.6 and 42.1 meV under excitation energy density of $7.6 \mu\text{J}/\text{cm}^2$ and $117.1 \mu\text{J}/\text{cm}^2$, respectively. Our estimated E_a values lie between 40 and 50 meV, in agreement with those commonly reported for InGaN samples. [39, 40] Based on the fitting results, the activation energies are almost constant under different excitation energy densities. This indicates that the activation barriers for accessing defect-related nonradiative recombination pathways are unchanged under varying excitation energy densities. However, the decrease in A is observed under high excitation energy density, suggesting a reduced contribution from nonradiative recombination pathways. This can be attributed to the saturation of defect states under high excitation energy density, which decreases the probability of carriers being captured by NRCs. Consequently, the reduced contribution of nonradiative recombination pathways leads to slower thermal quenching of the integrated PL intensity under high excitation energy density.

2.3.4 Time-resolved PL Measurement

To investigate the underlying origins of the efficiency and thermal droop in red InGaN hybrid SQWs, we measured power-dependent and temperature-dependent TRPL curves. Normalized TRPL decay at two excitation energy densities are shown in Fig. 2-10(a), where the integrated wavelength range is from 550 to 700 nm. The TRPL decay curves can be well fitted with a single exponential decay function. $1/e$ PL decay time is used, where e is the Napier's constant. The fitting equation is shown as follows:

$$I(t) = I_0 \times \exp\left(-\frac{t}{\tau_{PL}}\right) \quad (2-3)$$

where τ_{PL} represents the PL lifetimes, and I_0 is the initial TRPL intensity.

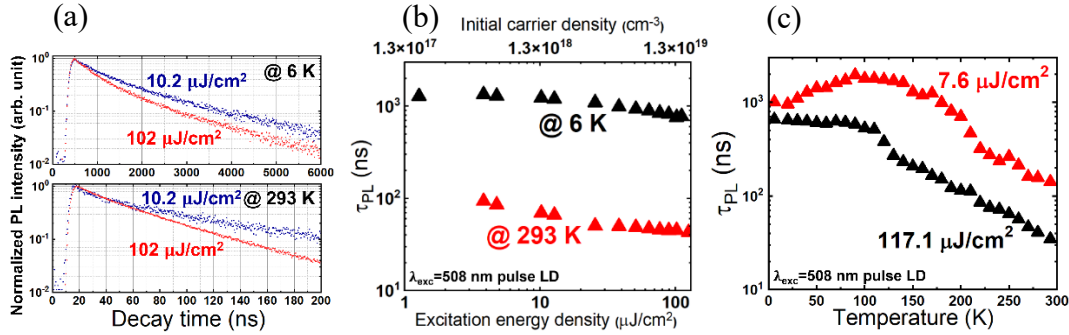


Figure 2-10. (a) TRPL decay at 6 K and 293 K. (b) Power-dependent and (c) Temperature-dependent PL decay times derived from single-exponential-function fitting at 6 K and 293 K.

The power dependence of τ_{PL} at 6 K and 293 K is depicted in Fig. 2-10(b). Both τ_{PL} at 6 K and 293 K exhibit a monotonic decrease with increasing excitation energy density. Under the same excitation energy density, τ_{PL} at 6 K is approximately 10 times longer than that at 293 K.

The temperature dependence of τ_{PL} under excitation energy density of 7.6 $\mu\text{J}/\text{cm}^2$ and 117.1 $\mu\text{J}/\text{cm}^2$ is depicted in Fig. 2-10(c). Under low excitation energy density of 7.6 $\mu\text{J}/\text{cm}^2$, τ_{PL} slightly increases and then decreases as the temperature increases, where the transitions temperature from increase to decrease is located at 100 K. Under high excitation energy density of 7.6 $\mu\text{J}/\text{cm}^2$, from 6 to 100 K, τ_{PL} is almost

constant, equal to about 700 ns. A rapid decrease of τ_{PL} is also observed above 100 K.

The τ_{rad} and τ_{nrad} are derived using the equations: [41]

$$IQE = \frac{\tau_{rad}^{-1}}{\tau_{rad}^{-1} + \tau_{nrad}^{-1}} \quad (2-4)$$

$$\tau_{PL}^{-1} = \tau_{rad}^{-1} + \tau_{nrad}^{-1} \quad (2-5)$$

where IQE corresponds to the internal quantum efficiency in Fig. 2-4(b).

2.3.5 Macroscopic and Microscopic PL Spectra

The PL spectra of the InGaN red SQW at room temperature (RT) are shown in Figure 2-11. These two spectra were recorded under macroscopic-PL (Diameter of laser spot onto sample surface: $\phi \sim 10 \mu\text{m}$) and microscopic-PL ($\phi \sim 0.2 \mu\text{m}$) measurement conditions. The PL FWHM is approximately the same between the macroscopic and microscopic PL measurements, indicating that the effect of long-range inhomogeneous broadening on the RT-PL FWHM of our InGaN red sample is negligible.

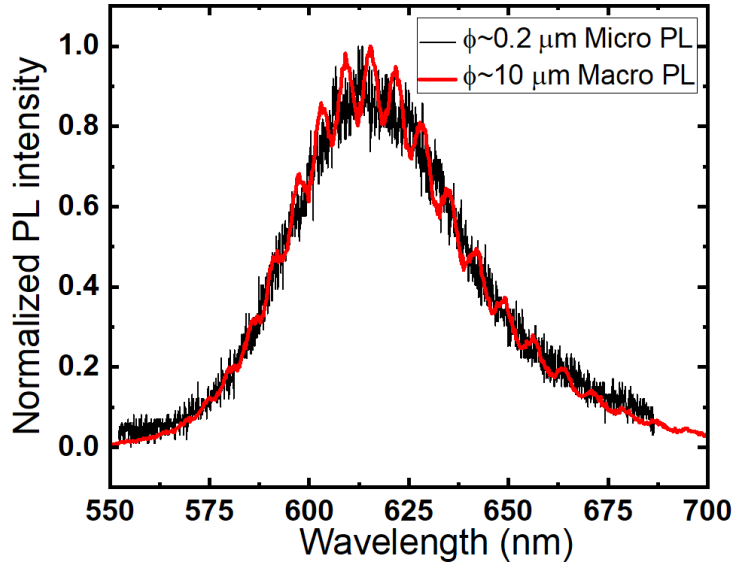


Figure 2-11. Room-temperature PL spectra of the InGaN red SQW layer as a function of the laser spot diameter. The 405 nm CW laser was used as an excitation source for micro-PL, while the 513 nm CW laser was used as an excitation source for macro-PL. Note that the PL spectra were not acquired at the same position on the sample.

2.4 Analysis

2.4.1 Power-dependent Radiative and Nonradiative Lifetime

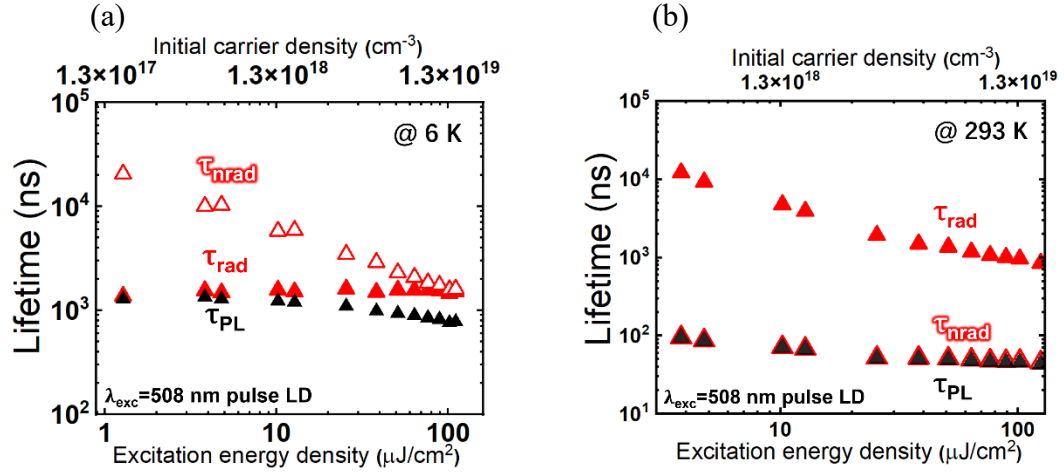


Figure 2-12. τ_{PL} , τ_{rad} , and τ_{nrad} as functions of excitation energy density at (a) 6 K and (b) 293 K.

The power-dependence of τ_{PL} , τ_{rad} , and τ_{nrad} at 6 K and 293 K is depicted in Fig. 2-12. At 6 K, as excitation energy density increases, τ_{rad} keeps a nearly constant value, while τ_{nrad} monotonically decreases. Firstly, we focus on the power dependence of τ_{rad} . τ_{rad} at cryogenic temperatures typically reflects the degree of an envelope-function overlap between electrons and holes in QW structure, and usually decreases as the carrier density increases due to the screening of QCSE. [42] In Fig. 2-5(a), the blueshift of the PL center wavelength and the narrowing of the FWHM confirm the presence of the screening of the QCSE. However, τ_{rad} keeps a nearly constant value as excitation energy density increases, implying that there must be another effect compensating the screening of the QCSE. τ_{rad} typically displays a complex behavior, influenced by not only the overlap of electron-hole wavefunctions, but also Coulomb interaction and carrier screening. [43] The attractive Coulomb interaction between electrons and holes will enhance the radiative recombination rate, named Coulomb enhancement. [44] This effect is progressively screened as carrier density increases

because the many-body effects reduce the exciton binding energy for carrier densities approaching the Mott density (around $2 \times 10^{18} \text{ cm}^{-3}$). [45, 46] The Coulomb screening will lead to a reduction in the radiative recombination rate as carrier density increases, and may compensate the effect of QCSE screening, resulting in the unchanged τ_{rad} .

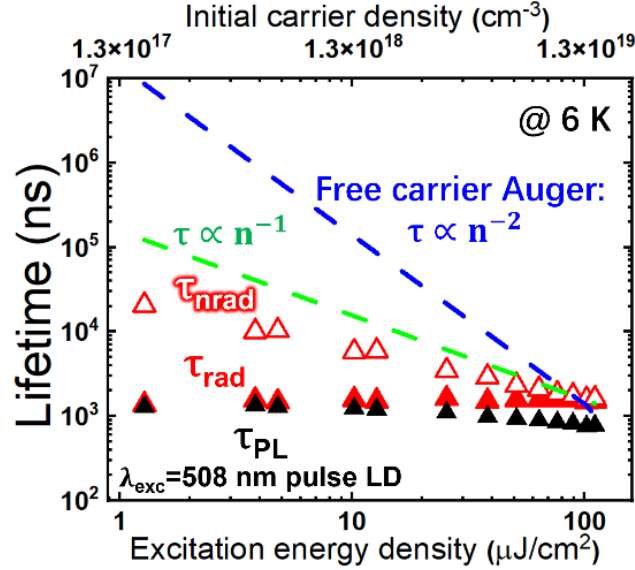


Figure 2-13. τ_{PL} , τ_{rad} , and τ_{nrad} as functions of excitation energy density at 6 K. The green and blue dashed lines represent the tendencies of $\tau_{\text{nrad}} \propto n^{-1}$ and $\tau_{\text{nrad}} \propto n^{-2}$ (free carrier Auger recombination), respectively. Here, n represents the initial photo-generated carrier density.

Next, we discuss the power dependence of τ_{nrad} at cryogenic temperature. Fig. 2-12(b) depicts the power dependence of τ_{nrad} plotted on a logarithmic scale. τ_{nrad} monotonically decreases from 10 to 1 μs with increasing excitation energy density, leading to a cause of the efficiency droop. In Fig. 2-13, the Auger recombination process of free carriers, whose lifetime is expected to decrease in proportion to the inverse square of carrier density ($\tau_{\text{Auger}} \sim \delta n^{-2}$), is shown by blue dashed line. Here, we assume that the photogenerated carrier density is proportional to the excitation energy density. However, τ_{nrad} is more consistent with the tendency proportional to δn^{-1} (green dashed line) instead of the trend of Auger recombination process (δn^{-2}). We attribute the weaker power-dependent τ_{nrad} at cryogenic temperature to the excitonic enhanced Auger recombination process, [47-49] exciton annihilation Auger recombination

process, [50] or two trap-assisted Auger recombination process. [43] These Auger nonradiative recombination lifetimes, all proportional to δn^{-1} , are more appropriate to describe the behavior of τ_{nrad} at cryogenic temperature in Fig. 2-13.

The dynamic Burstein-Moss shift of the absorption edge [22, 23] and carrier spillover might be taken into account. Both the effects will result in a saturation of the generated carrier densities under high excitation energy densities, and lead to the upward bending of carrier-dependent τ_{nrad} curve in Fig. 2-12. Thus, the decrease in τ_{nrad} cannot be explained by the three-body Auger recombination process of free carriers. Low-carrier-dependent Auger recombination process, threshold-less Auger process, Burstein-Moss shift of the absorption edge, and carrier spillover must play a role.

The power-dependent τ_{PL} , τ_{rad} , and τ_{nrad} at 293 K are plotted in Fig. 2-12(b). They all monotonically decrease as the excitation power density increases. Notably, the curves of τ_{PL} and τ_{nrad} nearly overlap, indicating that τ_{PL} is dominated by τ_{nrad} across all excitation energy densities at 293 K. τ_{nrad} shows a relatively weak carrier dependence. We can attribute it to the saturation of the nonradiative capture centers [45, 46] and negligible Auger recombination process. Unlike to the results at cryogenic temperature, τ_{rad} at 293 K shortens as the carrier density increases, which can be explained solely by the screening of the QCSE. Here, the Coulomb screening does not affect the tendency of τ_{rad} , because the thermal energy at 293 K is sufficient to dissociate the exciton into free electron-hole pairs. The fraction of carrier in excitonic phase in a quantum well at $T=300$ K is estimated in Ref. 43. It indicates that only a small fraction ($< 20\%$) of carriers may form excitons at room temperature, resulting in a negligible Coulomb enhancement. Therefore, the critical carrier density for the transition becomes low. In our present study, even if under the lowest carrier density ($1 \times 10^{17}/\text{cm}^3$) at 293 K, the Coulomb enhancement should be negligible. Therefore, the Coulomb screening is considered to be not dominant at room temperature in our study.

Compared to blue InGaN SQW ($\tau_{\text{rad}}=10$ ns), τ_{rad} is much longer in our red InGaN SQW. ($1 \sim 10$ μs). To investigate the origin of the longer τ_{rad} , we calculated the square of the overlap integrals of the electron-hole wave function for blue (In=20%)

and red (In=35%) InGaN SQWs via a self-consistent calculation approach. The predicted carrier-density dependent squares of the overlap integrals for blue and red InGaN SQWs are presented in Fig. 2-14.

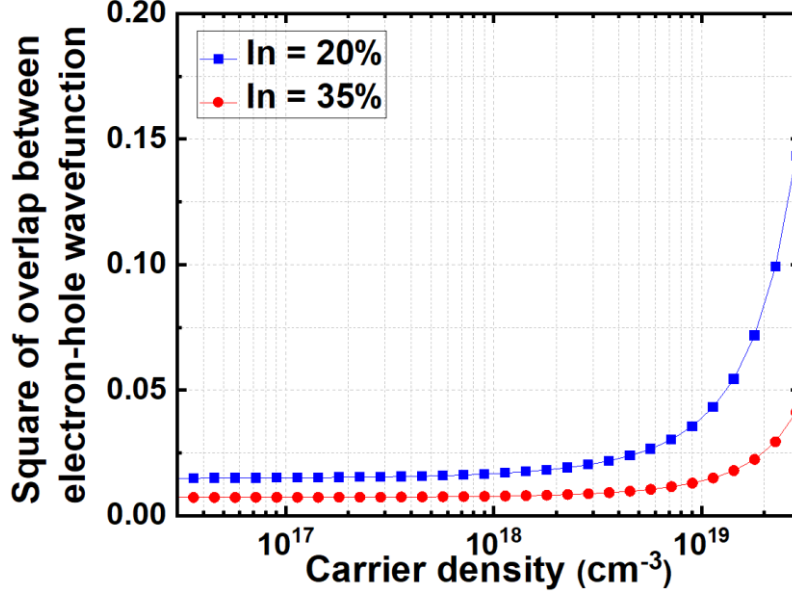


Figure 2-14. Calculated squares of overlap integrals of electron-hole wave function for blue and red InGaN SQW, as functions of carrier density.

From the calculation, the overlap integrals for the blue SQW are more than twice as large as those for the red SQW. This indicates that the stronger internal electric field is one of the factors contributing to the longer τ_{rad} in the red InGaN SQW. Focusing on the red InGaN SQW, as the carrier density increases, the square of the overlap integral between the electron-hole wavefunctions at highest carrier density becomes approximately six times larger than at lowest carrier density. This effectively explains the shortening in the radiative recombination lifetime of the red InGaN SQW as carrier density increases at 293 K in Fig. 2-12(b). Therefore, to enhance the radiative recombination rate, greater attention should be directed toward managing the wavefunction overlap in the red InGaN SQW.

In addition, compared with another study on a red InGaN SQW, [51] τ_{rad} and τ_{nrad} at 293 K have similar power-dependent tendency. However, τ_{rad} (1 μs ~10 μs) and τ_{nrad} (50 ns~100 ns) of our red InGaN hybrid SQW are much longer than those (τ_{rad} : 60 ns~35 μs , τ_{nrad} : ~15 ns) of a red InGaN SQW in Ref. 51. We attribute this

difference to the existence of the blue SQW beneath-layer, which can release the strain and suppress the defect density in the red InGaN active layer, leading to the longer τ_{nrad} . On the other hand, because the internal stress in the red InGaN SQW is retained, the strong QCSE result in the longer τ_{rad} . The relationship between τ_{rad} and τ_{nrad} can also be attributed to the degree of wavefunction-overlap on the Shockley-Read-Hall (SRH) coefficients. [52-54] It suggests that the capture processes by NRCs can be regarded as field-assisted recombination, resulting in a comparable IQE despite the much longer τ_{nrad} of red InGaN hybrid QWs. Therefore, to enhance the IQE of InGaN red LEDs, the relationship between τ_{nrad} and τ_{rad} under varying active layer characteristics should be further investigated.

2.4.2 Temperature-dependent Radiative and Nonradiative Lifetime

The temperature dependence of τ_{PL} , τ_{rad} , and τ_{nrad} is depicted in Fig. 2-15.

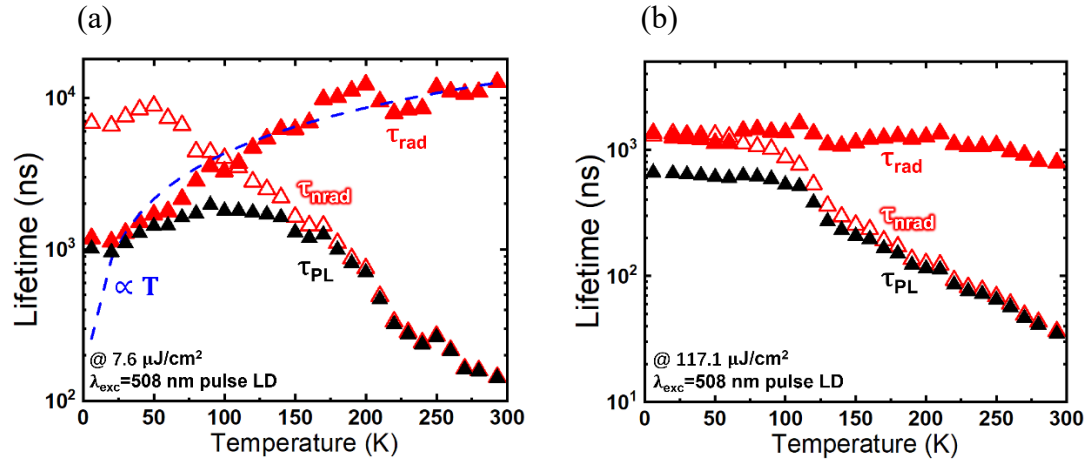


Figure 2-15. τ_{PL} , τ_{rad} , and τ_{nrad} as functions of excitation energy density under excitation energy densities of (a) 7.6 $\mu\text{J}/\text{cm}^2$ and (b) 117.1 $\mu\text{J}/\text{cm}^2$. The dashed line represents the tendencies of $\tau_{\text{rad}} \propto T$.

Under low excitation energy densities of 7.6 $\mu\text{J}/\text{cm}^2$ (Fig. 2-15(a)), as temperature increases, τ_{nrad} decreases monotonically due to the thermal activation of NRCs, while τ_{rad} exhibits a linear increase with temperature. The crossing temperature ($\tau_{\text{nrad}} =$

τ_{rad}) is 100 K. At temperature below 100 K, τ_{rad} is shorter than τ_{nrad} and dominates τ_{PL} , indicating a high radiative recombination probability. When the temperature increases above 100 K, the τ_{nrad} gradually dominates the τ_{PL} , contributing to the thermal droop. As indicated by blue dash line in Fig. 2-15 (a), τ_{rad} increases linearly with increasing temperature. As mentioned previously, due to the substantial confinement energy of deep localized states, carriers are strongly localized in deep localized states even at elevated temperatures (dimension (d) = 0). Therefore, the linear increase of τ_{rad} with temperature cannot be explained by Boltzmann statistics or the dimensionality-dependent density of states ($\tau_{\text{rad}} \propto T^{d/2}$). [41, 55] In a previous study, a relationship between τ_{rad} and homogenous linewidth $\Gamma_{\text{hom}}(T)$ in a GaAs/AlGaAs quantum-well system has been constructed and expressed as: [56]

$$\tau_{\text{rad}} \propto \frac{\Gamma_{\text{hom}}(T)}{|\langle \varphi_e(z) | \varphi_h(z) \rangle|^2 \left(1 - \exp\left[-\frac{\Gamma_{\text{hom}}(T)}{kT}\right] \right)} \quad (2-6)$$

where $|\langle \varphi_e(z) | \varphi_h(z) \rangle|^2$ represents the square of the electron-hole overlap integral, k and T are the (lattice) temperature and Boltzmann constant, respectively. In the limit $\Gamma_{\text{hom}}(T) \ll kT$, the τ_{rad} is linearly proportional to T , while for $\Gamma_{\text{hom}}(T) \gg kT$, τ_{rad} proportional to $\Gamma_{\text{hom}}(T)$ is expected. [56] Here, the electron-hole overlap integral is assumed to be temperature-independent. The homogenous linewidth $\Gamma_{\text{hom}}(T)$ is broadened by effects of alloying and exciton-phonon interactions. In our study, due to the significant alloy disorder and excitonic localization effects in high In-content InGaN QWs, the coherence area of the exciton is small, [56] resulting in a wide homogeneous linewidth. Therefore, we assumed $\Gamma_{\text{hom}}(T) \gg kT$, and τ_{rad} can be expressed as:

$$\tau_{\text{rad}} \propto \frac{\Gamma_{\text{hom}}(T)}{|\langle \varphi_e(z) | \varphi_h(z) \rangle|^2} \quad (2-7)$$

As indicated by Eq. (2-7), τ_{rad} is linearly proportional to homogeneous linewidth. The temperature dependences of τ_{rad} and PL FWHM at low and high excitation energy densities are compared in Fig. 2-16(a) and (b). At low excitation energy density of 7.6 $\mu\text{J}/\text{cm}^2$ (Fig. 2-16(a)), a clear correlation is indeed observed between the τ_{rad} and FWHM, and they both increase as temperature rises, suggesting that Eq. (2-7) could explain the temperature dependence of τ_{rad} for our InGaN QWs. Therefore, to gain a

deep understanding of τ_{rad} , it is crucial to investigate the PL FWHM.

To explain the behavior of temperature dependent PL FWHM, here we evaluated a model proposed by Phillips *et al.* [56] In this model, the PL FWHM is broadened by exciton-phonon interactions and effects of alloying. The effects of alloying can be divided into ensemble (long-range) and scattering (short-range) effects. [57, 58] The same PL FWHM for the laser-spot diameters from 10 μm to 0.2 μm in Fig. 2-11 suggests that the contribution of the ensemble effect is negligible. Consequently, we can assume that the PL FWHM is governed by the scattering of excitons within low temperature range where excitons remain stable, and expressed as:

$$\Gamma_{\text{hom}}(T) = \Gamma_{\sigma} + \Gamma_a T + \frac{\Gamma_{\text{LO}}}{\exp\left(\frac{E_{\text{LO}}}{kT}\right) - 1} \quad (2-8)$$

where Γ_{σ} is the short-range disorder-induced linewidth, related to the crystalline quality. Γ_a and Γ_{LO} describe the exciton-phonon coupling strength with acoustic and optical phonons, respectively. E_{LO} is the longitudinal-optical phonon energy. The short-range disorder-induced linewidth Γ_{σ} is related to the standard deviation of the potential fluctuations (σ). Ozaki *et al.* have investigated the temperature dependence of Γ_{σ} : as temperature increases, Γ_{σ} initially rises due to the thermal redistribution of excitons to higher-energy states within the potential energy landscape. [58] Once excitons populate nearly all available states, Γ_{σ} saturates and equals to those of the potential energy distribution ($=2\sqrt{2 \ln 2} \sigma$).

Therefore, under low excitation energy density, the broadening of homogeneous linewidth $\Gamma_{\text{hom}}(T)$ with increasing temperature can be attributed to both the short-range disorder-induced linewidth (Γ_{σ}) and enhanced exciton-phonon interactions (Γ_{ph}).

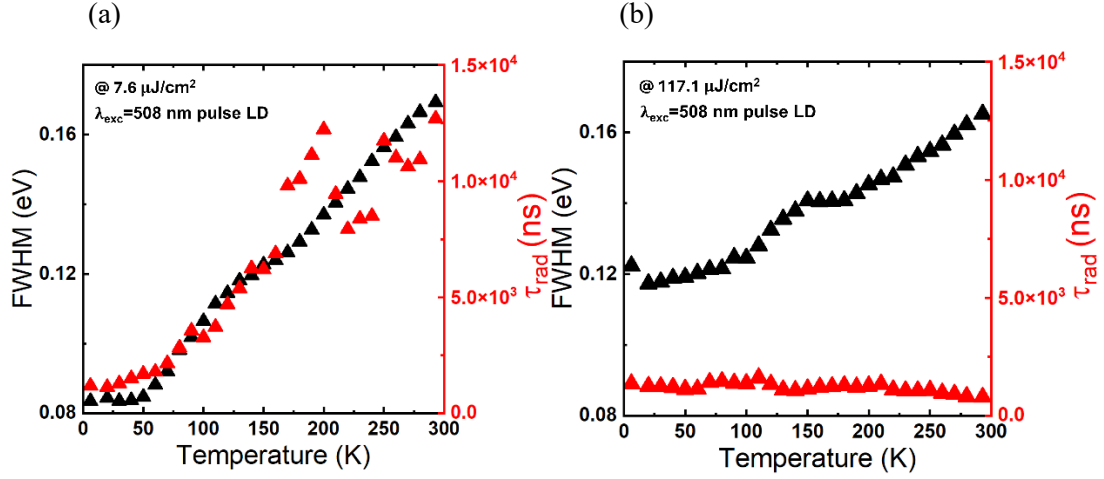


Figure 2-16. Temperature dependence of τ_{rad} and PL FWHM for InGaN red active layer under excitation energy densities of (a) 7.6 $\mu\text{J}/\text{cm}^2$ and (b) 117.1 $\mu\text{J}/\text{cm}^2$

Under high excitation energy densities of 117.1 $\mu\text{J}/\text{cm}^2$ (Fig. 2-16(a)), as the temperature increases, the τ_{PL} is shortened monotonically (Fig. 2-15(b)), remaining strongly dominated by τ_{nrad} . However, the τ_{rad} keep nearly unchanged (1 μs) as the temperature increases. For the FWHM, it shows a larger initial value compared with that under low excitation energy densities. With increasing temperature, the broadening trend is slower at low temperatures (6–200 K) and accelerates at higher temperatures (200–293 K). Given the larger initial FWHM value, as well as the assumption of the same exciton-phonon coupling constant (Γ_a and Γ_{LO}) for both high and low excitation energy densities, it is reasonable to infer that Γ_σ has a larger value and dominates under high excitation. This may result from carriers populating higher-energy localized states, thereby enhancing the observed linewidth associated with short-range potential fluctuations. At low temperatures (0–200 K), Γ_σ gradually increases with temperature and eventually reaches saturation. This behavior results in a noticeable plateau around 150 K. As the temperature continues to rise (200–300 K), the linewidth broadening induced by phonon interactions becomes more pronounced, leading to a significant increase in FWHM. Consequently, a similar increasing trend at high temperatures (200–300 K) is observed under both low and high excitation conditions, further supporting the assumption of the same exciton-phonon coupling constants (Γ_a and Γ_{LO}) for both excitation regimes. The calculated phonon-broadened PL FWHM for GaN is shown as

a red solid line in Fig. 2-17. Here, we use $\beta=28 \text{ } \mu\text{eV/K}$, $\gamma=510 \text{ meV}$, and $\hbar\omega_{\text{LO}}=90 \text{ meV}$ as reported for (0001) GaN [59] because there is no reliable data for InN. By subtracting the calculated phonon-broadened PL FWHM from the experimentally obtained FWHM, the temperature-dependent short-range disorder-induced linewidth (Γ_σ) can be deduced as shown as a black solid line in Fig. 2-17. It is evident that Γ_σ increases with temperature and gradually saturates, which aligns with the trends observed in previous simulations of Γ_σ . [58]

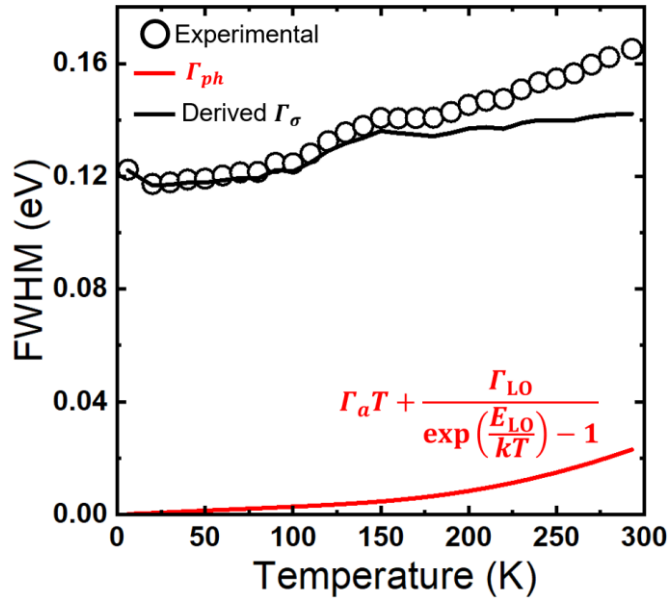


Fig. 2-17. Temperature dependence of the PL FWHM for InGaN red active layer under high excitation energy density (hollow circle), calculated phonon-broadened PL FWHM for GaN (red solid line), and deduced short-range disorder-induced linewidth (black solid line).

For τ_{rad} under high excitation energy density, it shows no temperature dependence and is uncorrelated with the FWHM. Here, we combine Eq. (2-7) and (2-8) for a discussion:

$$\tau_{\text{rad}} \propto \frac{\Gamma_{\text{hom}}(T)}{\left| \langle \varphi_e(z) | \varphi_h(z) \rangle \right|^2} = \frac{\Gamma_\sigma + \Gamma_a T + \frac{\Gamma_{\text{LO}}}{\exp\left(\frac{E_{\text{LO}}}{kT}\right) - 1}}{\left| \langle \varphi_e(z) | \varphi_h(z) \rangle \right|^2} \quad (2-9)$$

From Eq. (2-9), τ_{rad} is not only dependent on the PL FWHM but also influenced by the overlap integral of the electron and hole wavefunctions. Given the unchanging τ_{rad} as well as the broadening of the FWHM with increasing temperature, it can be

inferred that the overlap integral of the electron-hole wave functions may have temperature dependence. A temperature-dependent internal electric field has been observed in previous studies, [60] which demonstrated that the magnitude of the piezoelectric field decreases with increasing temperature at a rate of $1.08 \text{ kVcm}^{-1}\text{K}^{-1}$, attributed to the decrease in a mismatch between the thermal expansion coefficients of GaN and InGaN. We hypothesize that the temperature dependence of the internal electric field would be more pronounced in high-In-content InGaN. Therefore, given the increase in PL FWHM and overlap integrals of electron-hole wavefunctions, the τ_{rad} keep almost unchanged as excitation energy density increases.

2.5 Summary

Radiative and non-radiative recombination processes of red InGaN hybrid SQWs were investigated by temperature-dependent and power-dependent TRPL and TIPL spectroscopy. We demonstrated that the shortening of the τ_{nrad} is the main causes of efficiency and thermal droop in red InGaN hybrid SQWs. The radiative rate is affected by a combination of internal electric field, Coulomb enhancement, and Coulomb interaction screening. We successfully establish a positive correlation between τ_{rad} and full width at half maximum (FWHM) of PL spectra. We demonstrate that disorder-induced linewidth plays an important role in the broadening of the FWHM. Therefore, the improvement of the In homogeneity of red QWs should be a promising method for realizing efficient InGaN-based red LEDs.

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Chapter 3

3. Correlative Micro-PL Study on InGaN-based Hybrid Red QWs

3.1 Introduction

In chapter 2, we demonstrated that the shortening of the non-radiative lifetime with increasing temperatures is the main cause of the low IQE in red InGaN hybrid SQWs. However, the microscopic origins of NRCs are not understood. To further increase the EQE, the microscopic properties that govern the IQE and EQE should be elucidated, similar to the case of blue LEDs. [1, 2] In this chapter, we present the results of micro-photoluminescence (μ -PL) spectroscopy for an InGaN-based red LED with a hybrid QW structure, which consists of a blue and a red SQW. The μ -PL mapping image of the integrated red emission intensity revealed many dark spots. In addition, not only red and blue (from blue SQW) but green emission bands were observed at certain dark spots, suggesting that In segregation is one of the causes of dark red emissions. Comparing the blue and green emission maps to the red emission map, the dark spots in the intensity map of the red emission were classified into four types. Through the correlative analysis, the red dark spots correlated to the dark areas in the intensity map of the blue emission are assigned as the major nonradiative recombination centers (NRCs). Consequently, we establish a correlation in the distribution of NRCs between the blue SQW and red SQW.

3.2 Experiment

The studied sample was a red InGaN LED epitaxial structure grown on a patterned *c*-plane sapphire substrate by metal–organic vapor-phase epitaxy. Figure 3-1 shows a cross-sectional schematic of the sample. The precursors of Ga, Al, In, and N were trimethylgallium, trimethylaluminum, trimethylindium, and ammonia, respectively. [3]

The epitaxial structure consisted of an 8- μm -thick n-GaN layer, a hybrid QW structure composed of a 2.5-nm-thick InGaN blue SQW and a 3.5-nm-thick InGaN red SQW, and a strain-compensation barrier structure. The blue SQW pre-strained layer was expected to suppress strain relaxation and reduce the defect densities in the red SQW layer, thereby improving the red emission efficiency. [4]

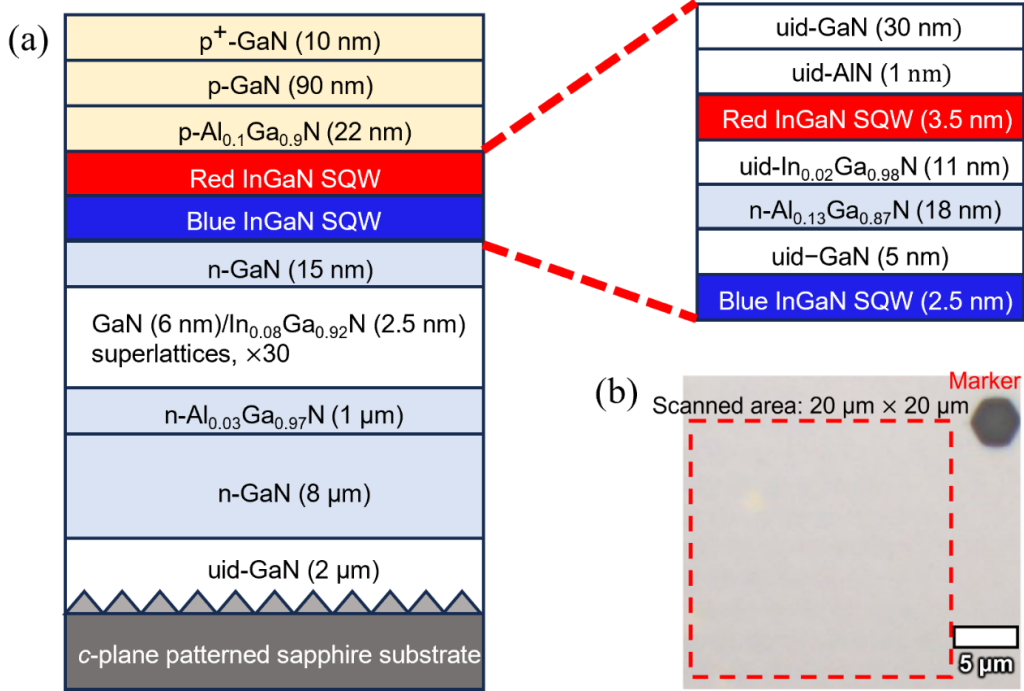


Figure 3-1. (a) Epitaxial structure of the hybrid quantum-well InGaN red LED, where uid-GaN represents unintentionally doped GaN. The inset shows the details of the red and blue SQWs. (b) Optical reflection image of the scanning area.

A confocal laser microscope (alpha 300S, WITec) was developed. The excitation source was a 405 nm continuous-wave laser diode. The spot diameter was approximately 200 nm. The laser beam was focused onto the sample surface by a short working distance objective with a numerical aperture of 0.9. Luminescence signals were detected by a high-throughput spectrometer (UHTS300 VIS, WITec). Figure 3-1(b) shows an optical reflection image of the red InGaN-based LED sample surface under white-light illumination. The scanning area was an optically homogeneous surface. The scanned area of the μ -PL mapping was 20 μm × 20 μm with a scanned step of 0.2 μm . The excitation power density was set at 4.6 kW/cm². All of the

experiments were performed at room temperature.

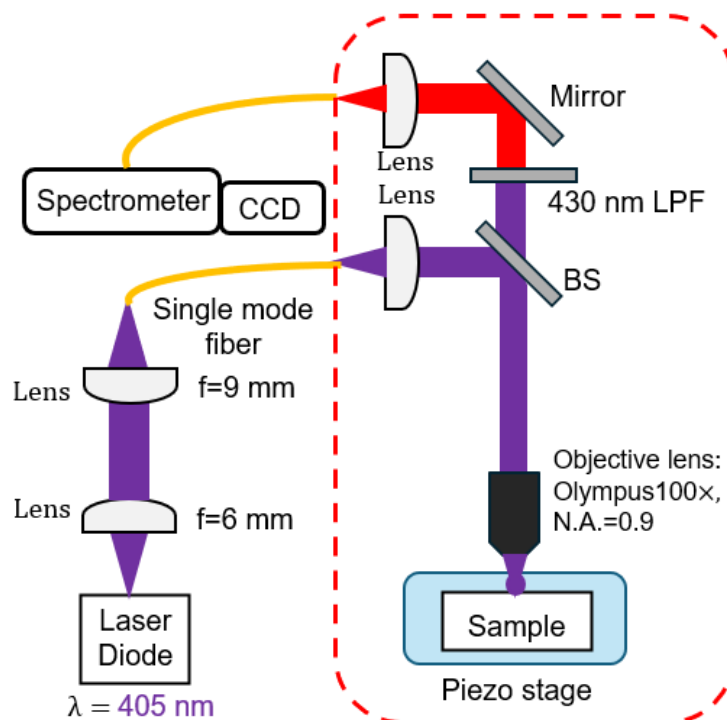


Figure 3-2. Confocal μ -PL spectroscopy setup.

3.3 Result

The integrated PL intensity map of the red emission is presented in Fig. 3-3(a), where the integrated wavelength range is from 575 to 700 nm. A number of dark spots with various sizes and contrasts are observed, indicating the presence of weak red emission areas in the red SQW. The PL spectra at points 1 and 2 in Fig. 3-3(a) are shown in Fig. 3-3(b). Contrary to the PL spectrum at point 1, not only red and blue but also green emissions are observed in the spectrum at point 2. The red PL intensity at point 2 is weaker than that at point 1, suggesting that In segregation in the red SQW is one of the causes of the dark-red emissions and results in parasitic green emissions. In addition, weak red emission areas are often accompanied by weak blue emission areas, as shown in the PL spectrum at point 2. This observation suggests a correlation between the blue and red SQW dark emissions, which will be discussed later. It should be noted that because of the high emission intensity of blue emissions, we assume that blue emissions originate from the blue SQW layer.

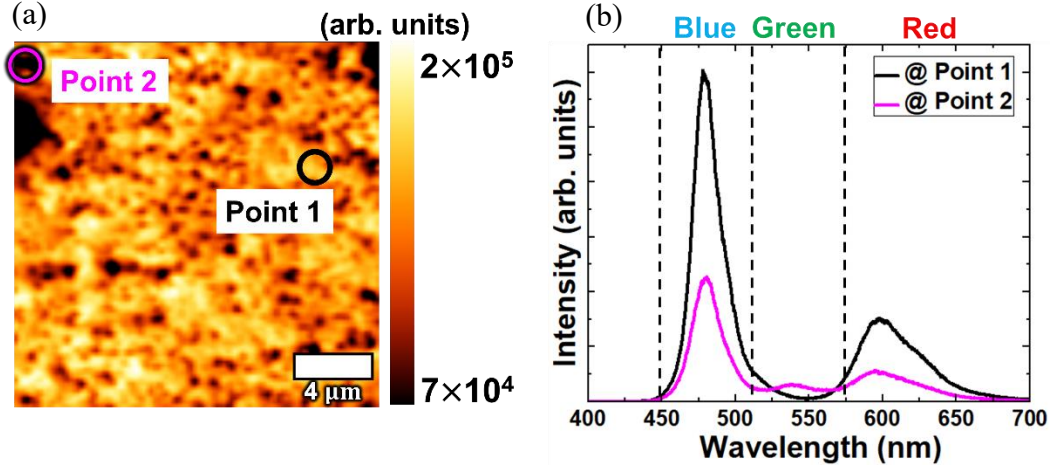


Figure 3-3. (a) Integrated PL intensity map of red emission. (b) PL spectra at points 1 and 2 in Fig. 3-2(a).

To understand the physics of the red dark spots, we classified them into four dark spots. Figures 3-4(a–c) present the red, green, and blue emission μ -PL mapping images. Comparing the blue (Fig. 3-4(c)) and green (Fig. 3-4(b)) emission images to the red emission image (Fig. 3-4(a)), we define four types of red dark spots denoted by black, purple, white, and yellow (abbreviated as B, P, W, and Y dark spots, respectively). The dark spots in both the blue and red emission images correspond to the P and B dark spots, whereas the dark spots in the red emission image but the bright spots in the green emission image correspond to the P and Y dark spots. The classification is summarized in Fig. 3-4(d).

Typical PL spectra corresponding to the four types of red dark spots and to a red bright point are shown in Fig. 3-4(e). In the case of blue emission, the peak intensity at the bright point is approximately 1.2×10^4 counts. The PL spectra at the W and Y dark spots show approximately the same peak wavelength as the bright point, whereas the PL spectra at the P and B dark spots show a peak wavelength shift and a peak emission intensity lower than 1.0×10^4 counts. The PL spectra at the P and Y dark spots show green emission bands, which implies In segregation, as previously mentioned. In the case of red emission, the PL spectra acquired at all the dark spots exhibit a redshift compared with the spectrum acquired at the bright point. Among the PL spectra of all of the dark spots, those of the B and W dark spots show a shorter peak wavelength

(approximately 605 nm) and higher red intensity, whereas those of the P and Y dark spots typically show a longer peak wavelength (approximately 620 nm) and a lower PL intensity.

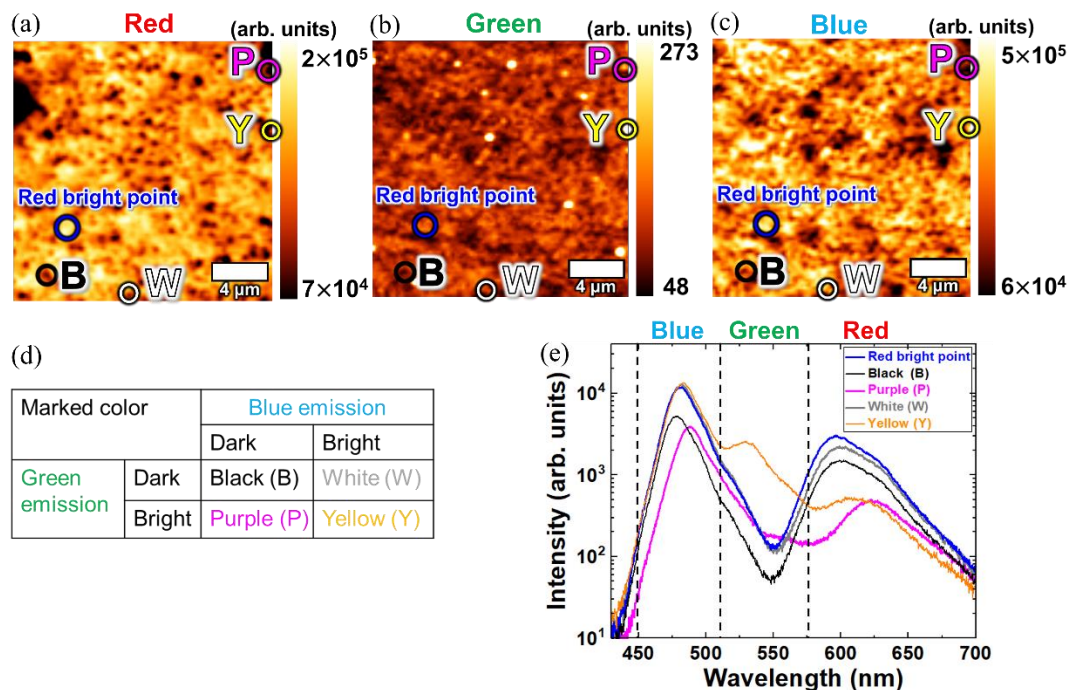


Figure 3-4. (a) Integrated PL intensity map of red emission. (b) PL intensity map at 540 nm (green emission). (c) Integrated PL intensity map of blue emission, where the integrated wavelength range of blue emission is from 450 to 510 nm. (d) Classification of red dark spots. (e) μ -PL spectra at points B, P, W, Y, and a red bright point in Fig. 3-4(a)–(c).

3.4 Discussion

The four types of dark spots are depicted in Fig. 3-5 and are summarized in Table 3-1. The number of B dark spots is the highest at 243. As previously mentioned, a majority of B dark spots exhibit a higher red PL intensity compared with the other dark spots. They are typically smaller. The number of P dark spots is 31. The P dark spots typically have a large size, a low PL intensity, and a large redshift. The numbers of the W and Y dark spots are relatively small at 30 and 7, respectively. Notably, the features of the W dark spots are similar to those of the B dark spots in that they exhibit a higher

PL intensity, smaller redshift, and smaller size. Their diameters are typically smaller than 0.5 μm , where the diameters are defined by the Full Width at Half Maximum (FWHM) value of the emission intensity drop. Conversely, the Y dark spots exhibit features similar to those of the P dark spots, including a lower PL intensity, a greater redshift, an additional green emission band, and larger size. Their diameters are typically larger than 1 μm . These behaviors suggest that the physical origins of the B and W dark spots should be the same, as should those of the P and Y dark spots. Based on our statistical analysis, nearly 90% of the red dark spots are associated with the dark areas in blue emissions (that is, the B and P dark spots).

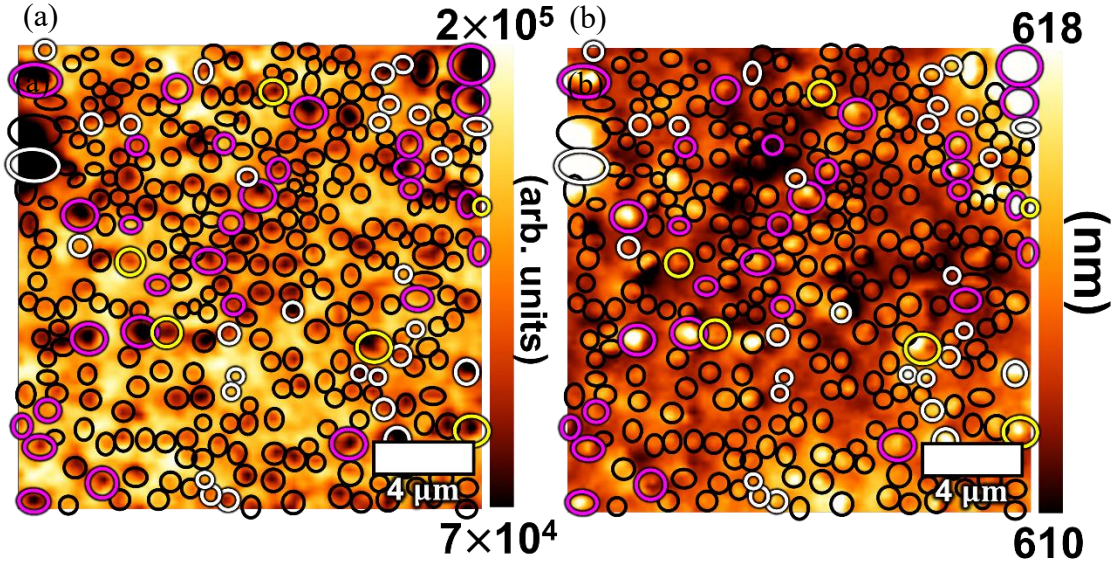


Figure 3-5. Classification of the four types of dark spots in the (a) integrated PL intensity map and (b) center wavelength map of red emission.

To assess the effect of the dark spots on the macroscopic optical properties, their impact on the macroscopic IQE is estimated in Table 3-1, where the local highest IQE refers to the IQE at the highest PL intensity point. The three local highest IQE values are assumed to be 100%, 50%, and 20% for our analysis. Here, we explain how to estimate the impact of the dark spots on the macroscopic IQE. As an example, we assume that the local highest IQE is 100% and one dark spot with finite size is recalled. First, the total PL intensity at the dark spot is summed $\sum_{\text{size}} I(r)$, where $I(r)$ is the PL intensity at the point r . The summation is performed for the dark spot size. Then,

the $\sum_{\text{size}} I_{\text{max}}(r)$ is calculated, where $I_{\text{max}}(r)$ is the PL intensity at the local highest IQE point. The impact of one dark spot on the macroscopic IQE can be estimated by $(\sum_{\text{size}} I(r) - \sum_{\text{size}} I_{\text{max}}(r)) / \sum_{\text{size}} I_{\text{max}}(r)$. Notably, the impact of all the dark spots on the macroscopic IQE (e.g., -25.5% in Table 3-1) does not correspond to the total macroscopic IQE reduction ($67-100 = -33\%$ in Table 3-1) because of the existence of the individually unresolved nonradiative recombination centers, such as point defects. According to the analysis in Table 3-1, the B dark spots prominently affect the macroscopic IQE despite their relatively high PL intensity among the dark spots. Compared with the W dark spots, the P dark spots have a twofold greater effect on the macroscopic IQE because of their lower PL intensity. The Y dark spots have the weakest effect on the macroscopic IQE because of their lowest number. This analysis illustrates that the B and P dark spots, which are related to the dark areas in the blue emission, are the major red nonradiative recombination centers, irrespective of the assumed IQE. Therefore, focusing on the growth of the blue SQW layer is important to increase the IQE of hybrid-quantum-well InGaN red LEDs.

Table 3-1. Impact of the four types of dark spots on the macroscopic IQE.

Dark spot	Related to blue dark area?	Number	Density (cm^{-2})	Impact on the macroscopic IQE		
				If local highest IQE is 100% (Macro IQE = 67%)	If local highest IQE is 50% (Macro IQE = 34%)	If local highest IQE is 20% (Macro IQE = 13%)
Black (B)	Yes	243	6.1×10^7	-18.1%	-9.1%	-3.6%
Purple (P)		31	7.8×10^6	-4.2%	-2.1%	-0.8%
White (W)	No	30	7.8×10^6	-2.0%	-1.0%	-0.4%
Yellow (Y)		6	1.8×10^6	-1.2%	-0.6%	-0.2%
All		310	7.8×10^7	-25.5%	-12.8%	-5.1%

Finally, we discuss the origins of the four red dark spots by classifying them into two categories based on the presence or absence of the green emission. The P and Y dark spots (with green emission) are typically larger in size and exhibit a greater redshift (Fig. 3-5(b)). Therefore, we speculate that the P and Y dark spots correspond to large

trench defects because the same behavior (i.e., a low PL intensity, large redshift, and typically large size) has been previously observed at such defects. [5-9] Kusch *et al.* found that the large trench defects have a higher In composition than the surrounding region. [10] This finding implies that In segregation easily occurs at the large trench defects, which can explain the observed parasitic green emission bands at the P and Y dark spots. In addition, the total density of the P and Y dark spots is approximately $1 \times 10^7 \text{ cm}^{-2}$ (Table 3-1). The trench defect density of a red double quantum well is approximately $1 \times 10^8 \text{ cm}^{-2}$ [11], and our red SQW has a lower trench defect density, [3] supporting our assignment. Given the combination of the weak emission intensity and wavelength shift of the blue emission peak, the P red dark spots must be related to nonradiative recombination centers in the blue SQW. On the other hand, the origins of the Y dark spots should exist in layers above the blue SQW. The B and W dark spots (without green emission bands) are typically present in larger quantities and exhibit a smaller size and a less-pronounced redshift than the P and Y dark spots. Consequently, several possible origins can be proposed, such as V-pits, edge threading dislocations, point defects, and small trench defects. [12-15] Among them, point defects are unlikely to be the origin because of their typically huge density. Confocal microscopy cannot resolve the individual point defects. The nanoscopic structural and luminescence properties of the B and W dark spots will be discussed in Chapter 4.

To conclude, the P and Y dark spots likely originate from large trench defects, whereas the B and W dark spots might originate from other defects, such as V-pits, edge threading dislocations, and small trench defects. Time-resolved PL measurements at each defect will provide additional information. Although we cannot conclude the origins of the four types of dark spots at this stage, we have convincingly established a correlation in the distribution of nonradiative recombination centers between the blue SQW and red SQW. To further improve the device performance of InGaN-based red LEDs, our study indicates that decreasing the dark spot density is crucial to enhance the PL intensity and decrease the FWHM of the spectrum. A narrower FWHM will improve the color purity which is one of the most important indicators of InGaN monolithic RGB emitters.

3.5 Conclusion

We studied the microscopic optical properties of hybrid QW InGaN red LEDs using correlative confocal micro-PL spectroscopy. We classified the dark spots in the intensity map of the red emission into four types by comparing the blue and green emission images to the red emission image. We concluded that the red dark spots, which are associated with the dark areas in the blue emission, serve as the primary nonradiative recombination centers. The presence of In segregation also contributed to the dark spots in the red emission, as indicated by the green emission. On the basis of the presence or absence of the green emission peak, these dark spots can be categorized into two distinct types, and we speculated that the P and Y dark spots correspond to large trench defects, whereas the B and W dark spots correspond to other defects, such as V-pits, edge threading dislocations, and small trench defects.

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Chapter 4

4. Nanoscale Structural and Optical Characterization on Blue InGaN SQW and Hybrid Red InGaN SQW

4.1 Introduction

In chapter 3, our study revealed that the red dark emission positions were strongly correlated with the blue dark emission positions. In addition, we hypothesized that B and W dark spots originate from threading dislocation V-pits and small trench defects, while P and Y dark spots are associated with trench defects. However, the structural origins of the dark emissions have not been explored.

In this chapter, using atomic force microscopy (AFM) and scanning near-field optical microscope (SNOM) photoluminescence (PL) spectroscopy, we study the structural and optical properties of a blue InGaN single quantum well (SQW) and efficient red InGaN active layer. We demonstrate that all of the threading dislocations (TDs) serve as nonradiative recombination centers (NRCs) in the blue InGaN SQW. The surrounding energy barrier partly prevents carriers from being trapped by the NRCs. For the red active layer, we demonstrate that all types of trench defects, as well as TDs, exhibit low emission intensity, indicating that they are NRCs. Interestingly, bright emission spots are observed within some trench defects, which are attributed to the regions with lower indium content caused by In segregation. In previous research, lower-center trench defects exhibited reduced emission intensity, while both level and raised center trench defects displayed higher emission intensities compared to the surrounding QW. [1] The difference should originate from the fact that we study InGaN samples with an In content of around 35%. Our findings suggest that the enhanced In segregation caused by high In-content significantly reduces the emission intensity. Given the correlation of dark emission positions between the blue and red emissions,

[1] as well as the lower TD density in red SQW, TDs must be a trigger in the formation of trench defects in the red InGa_N SQW. Therefore, to enhance the EQE of InGa_N red LEDs, it is crucial to eliminate In segregation within the trench defects and to suppress the TD density.

4.2 Experiment

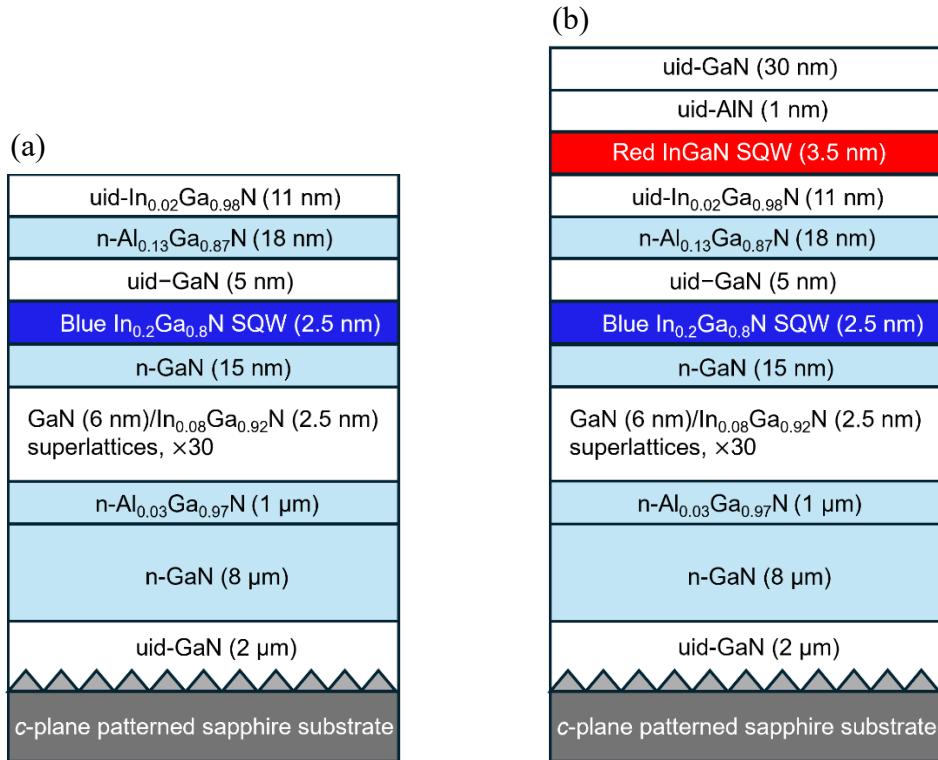


Figure 4-1. Epitaxial structure of (a) a blue InGa_N SQW and (b) a hybrid red InGa_N SQW, where uid-GaN represents unintentionally doped GaN.

The studied samples were a blue InGa_N SQW and a hybrid red InGa_N SQW grown on a patterned *c*-plane sapphire substrate by metal–organic vapor-phase epitaxy. The difference between the two samples is the existence of red InGa_N SQW and the above layer. The precursors of Ga, Al, In, and N were trimethylgallium, trimethylaluminum, trimethylindium, and ammonia, respectively. Figure 4-1 shows a cross-sectional schematic of sample 1 (Fig. 4-1(a)) and sample 2 (Fig. 4-1(b)). Sample 1 consisted of blue InGa_N SQW, whereas sample 2 consisted of blue InGa_N SQW and red InGa_N

SQW. The other epitaxial structures, which consisted of 30 periods of undoped $\text{In}_{0.08}\text{Ga}_{0.92}\text{N}$ (2.5 nm) / GaN (6 nm) superlattices (SLs), a heavily Si-doped n- $\text{Al}_{0.03}\text{Ga}_{0.97}\text{N}$ layer (1 μm), and a thick n-GaN layer (8 μm), were the same as those of a hybrid QW InGaN red LED studied in chapter 2 and 3, except that p-type layers were additionally grown in our previously investigated sample. The SLs function as underlayers to bury point defects. [2, 3]

To estimate the internal quantum efficiency (IQE) of the InGaN blue SQW, power-dependent macroscopic PL measurements were conducted at 6 K and 293 K. A continuous-wave (cw) laser diode with a wavelength (λ) of 405 nm was used as an excitation source. A laser spot diameter of 10 μm was achieved on the sample surface by an objective with a numerical aperture of 0.28. PL spectra were acquired using a 50 cm monochromator and a charge-coupled device detector. A closed-cycle conduction-cooling cryostat was used to control the experimental temperatures.

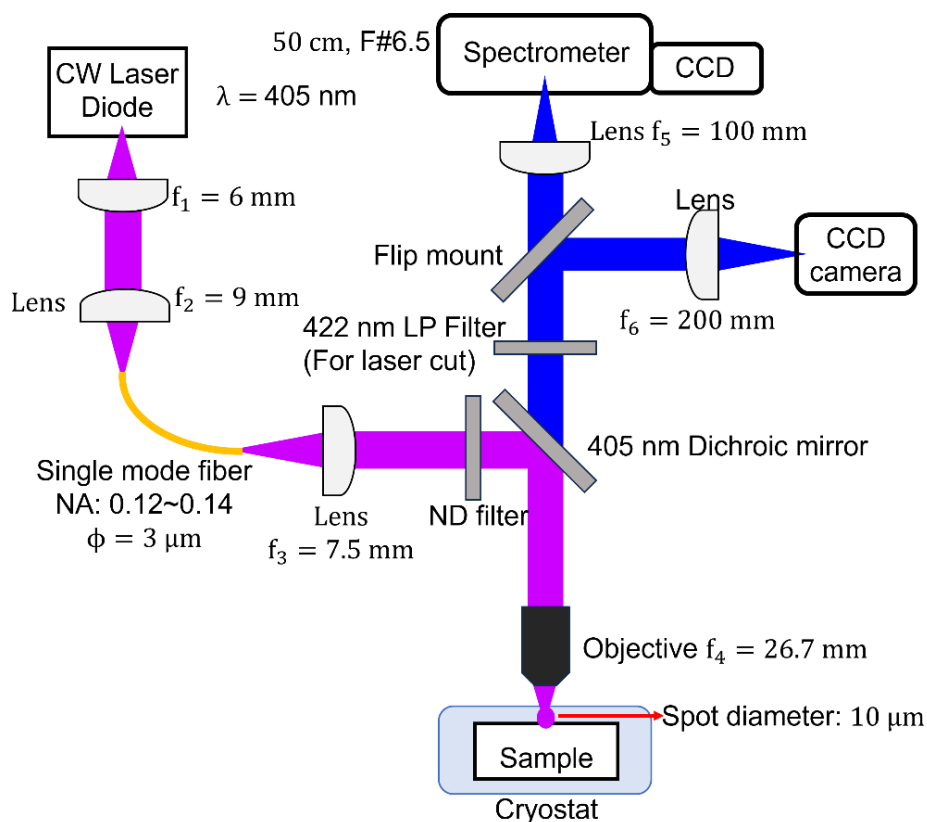


Figure 4-2. Macro-PL spectroscopy setup.

To estimate the TD density (TDD) of the InGaN blue SQW and hybrid red InGaN

SQW, an ω -scan was conducted with a Rigaku SLX-2000 X-ray diffractometer. The filament voltage and current were 50 kV and 300 mA, respectively. The Cu $K_{\alpha 1}$ line ($\lambda = 1.540562 \text{ \AA}$) was selected by a double-crystal Ge (220) monochromator.

The surface morphology of the samples was investigated by atomic force microscopy (AFM; Nanocute, Hitachi High-Tech). A Si probe mounted on a cantilever (OMCL-AC160TS) with a spring constant of 26 N/m was used. The resonant frequency and Q-factor of the cantilever were 300 kHz and 359 in air, respectively.

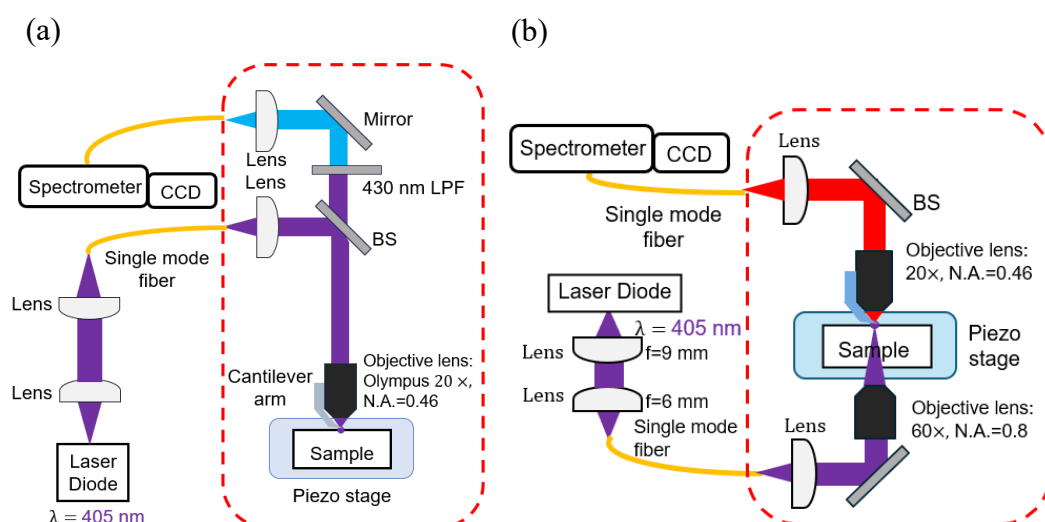


Figure 4-3. (a) I-C mode SNOM-PL spectroscopy setup. (b) C mode SNOM-PL spectroscopy setup.

The nanoscopic luminescence properties were investigated using illumination-collection (I-C)- and collection (C)-mode SNOM (Alpha 300S, WITec) setups. The schematic diagrams of the I-C- and C-mode setup are shown in Fig. 4-3(a) and (b), respectively. We used different cantilevers for the I-C-mode and C-mode measurements, with aperture diameters of approximately 90 nm and 150 nm, respectively. The excitation source was a 405 nm cw laser diode. For I-C-mode SNOM, the laser beam was focused onto the aperture of an SNOM cantilever by an objective with a numerical aperture of 0.46. The excitation power was set to 19 mW above the aperture of the SNOM cantilever. For C-mode SNOM, the laser beam was focused onto the sample surface by an objective with a numerical aperture of 0.8, and PL signals were collected through the SNOM aperture cantilever. The excitation power was set to 8 mW on the

sample surface. For both modes, luminescence signals were detected by a high-throughput spectrometer (UHTS300 VIS, WITec). All of the experiments were performed at room temperature, except the macroscopic PL measurements conducted at 6 K.

4.3 Result

4.3.1 X-ray Rocking Curves

4.3.1.1 Blue InGaN SQW

The ω -scan X-ray rocking curves (XRCs) of the (0002), (1-102), and (1-101) reflections for the 8- μm -thick GaN layer of sample 1 are shown in Fig. 4-4(a). The full-widths at half-maxima (FWHMs) of the (0002), (1-102), and (1-101) reflections are 203, 241, and 271 arcsec, respectively. Figure 4-4(b) shows the FWHMs as a function of the inclination angle χ of lattice planes (hkl) with respect to the c -plane. The twist angle (β_{twist}) and tilt angle (β_{tilt}) are estimated to be 284 arcsec and 201 arcsec, respectively, on the basis of a fitting using Eq. (4-1): [4]

$$\text{FWHM}(\chi) = \sqrt{\beta_{\text{tilt}}^2 \cos^2 \chi + \beta_{\text{twist}}^2 \sin^2 \chi} \quad (4-1)$$

The fitted curve is also represented in Fig. 4-4(b) by a solid line.

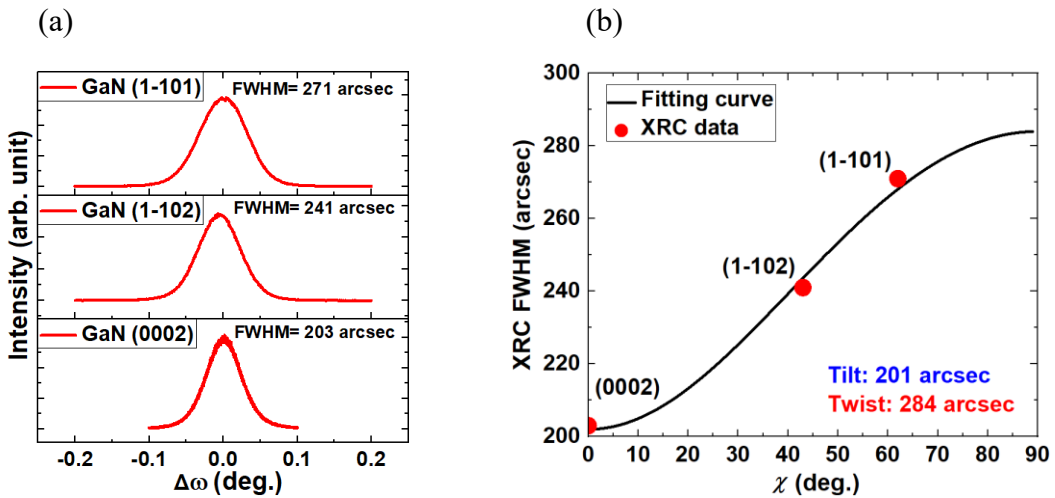


Figure 4-4. (a) Rocking curves of the (0002), (1-102), and (1-101) planes for the 8- μm -thick n-GaN layer of sample 1. (b) FWHM of (hkl) planes as a function of the lattice-

plane inclination angle χ , according to experimental data (red dot) and the results of the fitting using Eq. (4-1) (solid line).

The edge-type TDD (N_{edge}) and screw-type TDD (N_{screw}) are estimated using the following formulas: [5]

$$N_{\text{edge}} = \beta_{\text{twist}}^2 / (4.35 |b_{\text{edge}}|^2), \quad N_{\text{screw}} = \beta_{\text{tilt}}^2 / (4.35 |b_{\text{screw}}|^2), \quad (4-2)$$

where b_{edge} and b_{screw} are the Burgers vectors of edge-type and screw-type TDs, respectively ($|b_{\text{edge}}| = 0.3189 \text{ nm}$, $|b_{\text{screw}}| = 0.5185 \text{ nm}$) for GaN. The N_{edge} and N_{screw} values are estimated to be $4.4 \times 10^8 \text{ cm}^{-2}$ and $8.3 \times 10^7 \text{ cm}^{-2}$ in the 8- μm -thick n-GaN layer, respectively. In the following discussion, we assume that the TDDs are the same between the n-GaN and InGaN SQW layers because of the pseudomorphic growth of the sample.

4.3.1.2 Hybrid Red InGaN SQWs

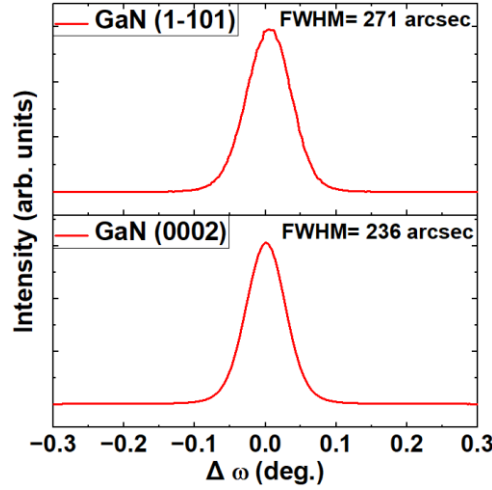


Figure 4-5. Rocking curves of the (0002) and (1-101) planes for the 8- μm -thick n-GaN layer.

The ω -scan X-ray rocking curves (XRC) of the (0002) and (1-101) reflections for the 8- μm -thick GaN layer are depicted in Fig. 4-5, with the FWHMs of 236 and 271 arcsec, respectively. Using the method outlined previously by Lee *et al.*, [4] we

estimated the twist angle β_{twist} and tilt angle β_{tilt} to be 280 arcsec and 236 arcsec, respectively.

On the basis of relationship between edge/screw-type TDD and twist/tilt angle, [5] the edge-type TDD N_{edge} and screw-type TDD N_{screw} in the 8- μm -thick n-GaN layer were estimated and listed in Table 4-1.

Table 4-1. TDD in n-GaN layer estimated by XRC analysis.

Type	Screw-type TDs	Edge-type TDs
Density/ cm^{-2}	1.1×10^8	3.8×10^8

Table 4-2. Defect density at surface estimated by AFM analysis.

Type	Screw-type TDs	Mixed-type TDs	Trench defects
Density/ cm^{-2}	1.8×10^7	7.9×10^7	8.8×10^7

4.3.2 Excitation Power Dependent IQE of Blue InGaN SQW

Figure 4-6(a) shows the excitation power density dependence of the IQE of sample 1 at 6 K and 293 K. The IQE is estimated from the PL efficiency normalized by the maximum value at 6 K. [6, 7] At 6 K, the IQE is almost constant at low excitation power densities, indicating the high quality of our sample. At 6 K, the IQE gradually decreases with increasing excitation power density. This decreasing tendency is attributable to an Auger recombination process, absorption saturation, and carrier overflow. At 293 K, the IQE increases and then decreases with increasing excitation power density. The maximum IQE of 37.3% is obtained at an excitation power density of 637 kW cm^{-2} . The tendency of the IQE to initially increase is attributable to the saturation of Shockley–Read–Hall recombination centers and to the screening of the quantum-confined Stark effect (QCSE). The subsequent decrease in IQE at high excitation power densities at 293 K can be explained by the same mechanism at 6 K. The excitation power density dependence of the center wavelength at 6 K and 293 K is shown in Fig. 4-6(b), where the integrated wavelength range is from 380 to 620 nm. Both center wavelengths exhibit a blueshift with increasing excitation power density, which is

attributed to the screening of the QCSE and the band-filling effect.

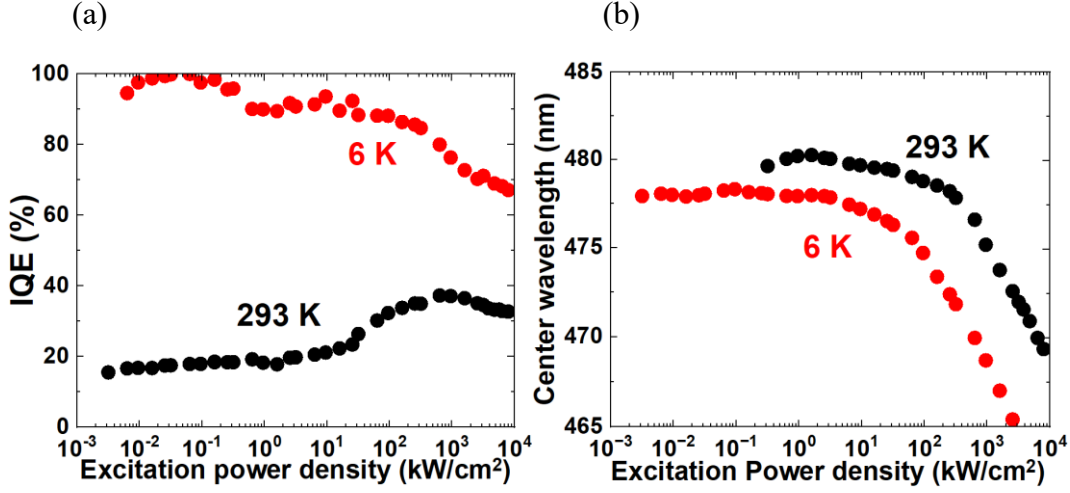


Figure 4-6. Excitation power density dependence of the (a) IQE and (b) center wavelength of sample 1 at 6 K (red) and 293 K (black).

4.3.3 Nanoscopic Structural and Optical Characterization

4.3.3.1 Blue InGaN SQW

An AFM image of the sample 1 surface (Fig. 4-7(a)) shows a step-flow growth morphology, with two kinds of V-pit defects with pinned steps (spiral growth). Deep (marked by blue circles) and shallow (marked by green circles) V-pits are observed. The deep V-pits are approximately 8–16 nm deep and exhibit a density of $8 \times 10^7 \text{ cm}^{-2}$. The shallow V-pits are less than 3 nm deep and exhibit a density of $1.2 \times 10^8 \text{ cm}^{-2}$. The V-pit defects and spiral growth are triggered by screw- or mixed-type TDs, [8, 9] whereas edge-type TDs do not contribute to spiral growth. Given that the depth of the V-pits originating from screw-type TDs is greater than that of V-pits originating from mixed-type TDs, [10, 11] the deep and shallow V-pits should originate from screw and mixed-type TDs, respectively. The deep V-pit density estimated from AFM images ($8 \times 10^7 \text{ cm}^{-2}$) is approximately the same as the screw-type TDD estimated from XRD measurements ($8.3 \times 10^7 \text{ cm}^{-2}$), supporting the aforementioned assignment.

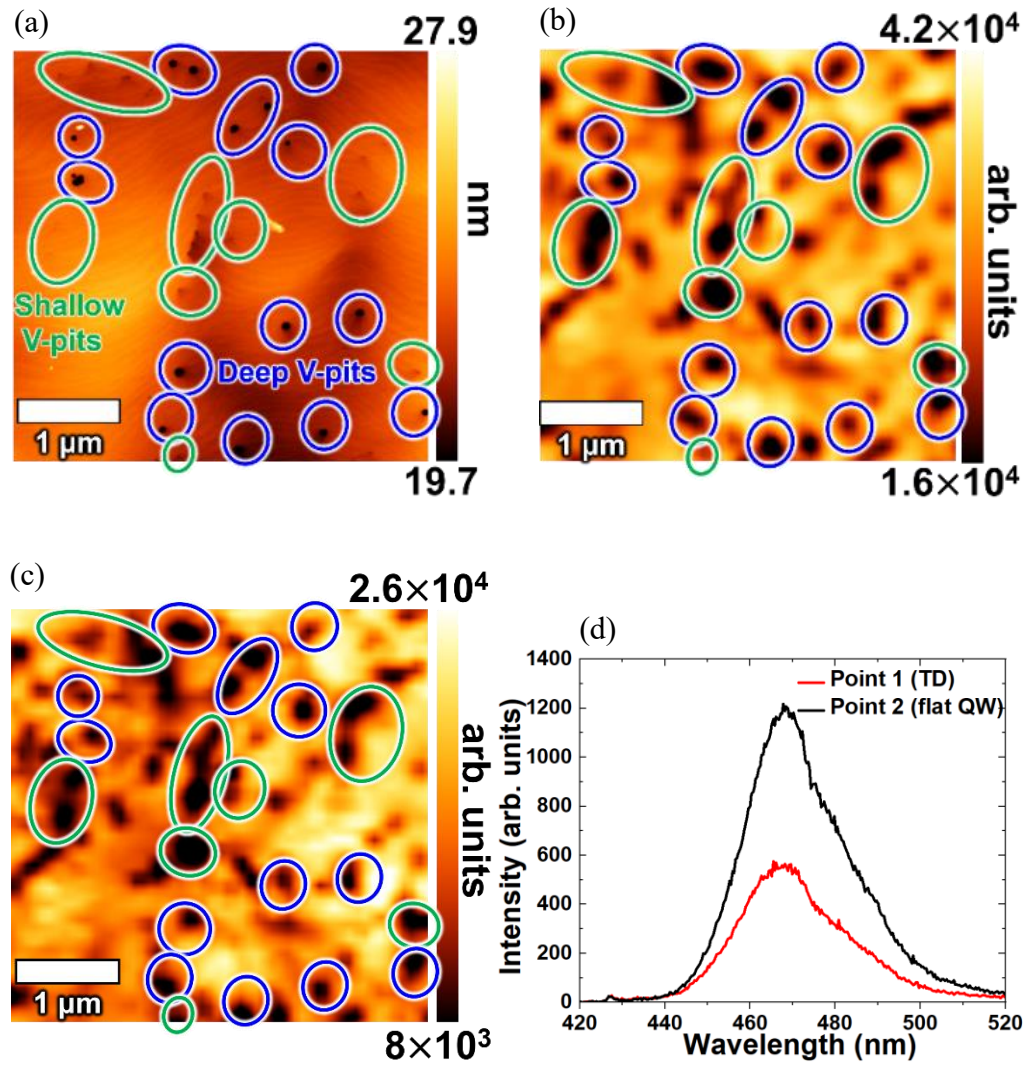


Figure 4-7. (a) AFM image, (b) I-C-mode SNOM integrated PL intensity mapping image, (c) C-mode SNOM integrated PL intensity mapping image, and (d) PL spectra corresponding to points 1 and 2 in Fig. 4-7(b).

The I-C- and C-mode SNOM integrated PL intensity mapping images acquired at the AFM scanned area are shown in Fig. 4-7(b) and Fig. 4-7(c), respectively, where the integrated wavelength range is from 400 to 550 nm. Both figures show numerous dark spots. The dark spots both in the I-C- and C-mode SNOM indicate that these dark spots originate from NRCs. [10] The PL spectra corresponding to points 1 (dark spot) and 2 (flat area) in Fig. 4-7(b) are shown in Fig. 4-7(d). The PL spectral shape is almost independent of the position. A comparison between the SNOM and AFM images reveals that the V-pits originating from screw- and mixed-type TDs exhibit dark

emissions and are NRCs. [10] Additional dark spots with a density of $2.9 \times 10^8 \text{ cm}^{-2}$ and not associated with any V-pits are observed in Fig. 4-7(b). The edge-type TDD estimated by XRD measurement ($4.4 \times 10^8 \text{ cm}^{-2}$) is similar to the additional dark spot density ($2.9 \times 10^8 \text{ cm}^{-2}$). Therefore, we attribute the origin of these additional dark spots to the edge-type TDs. Point defects can be ruled out here because the density is too high to be individually visualized. [12] In short, all the dark spots in the SNOM integrated PL intensity mapping images have been classified and attributed to three types of TDs.

4.3.3.2 Hybrid Red InGaN SQWs

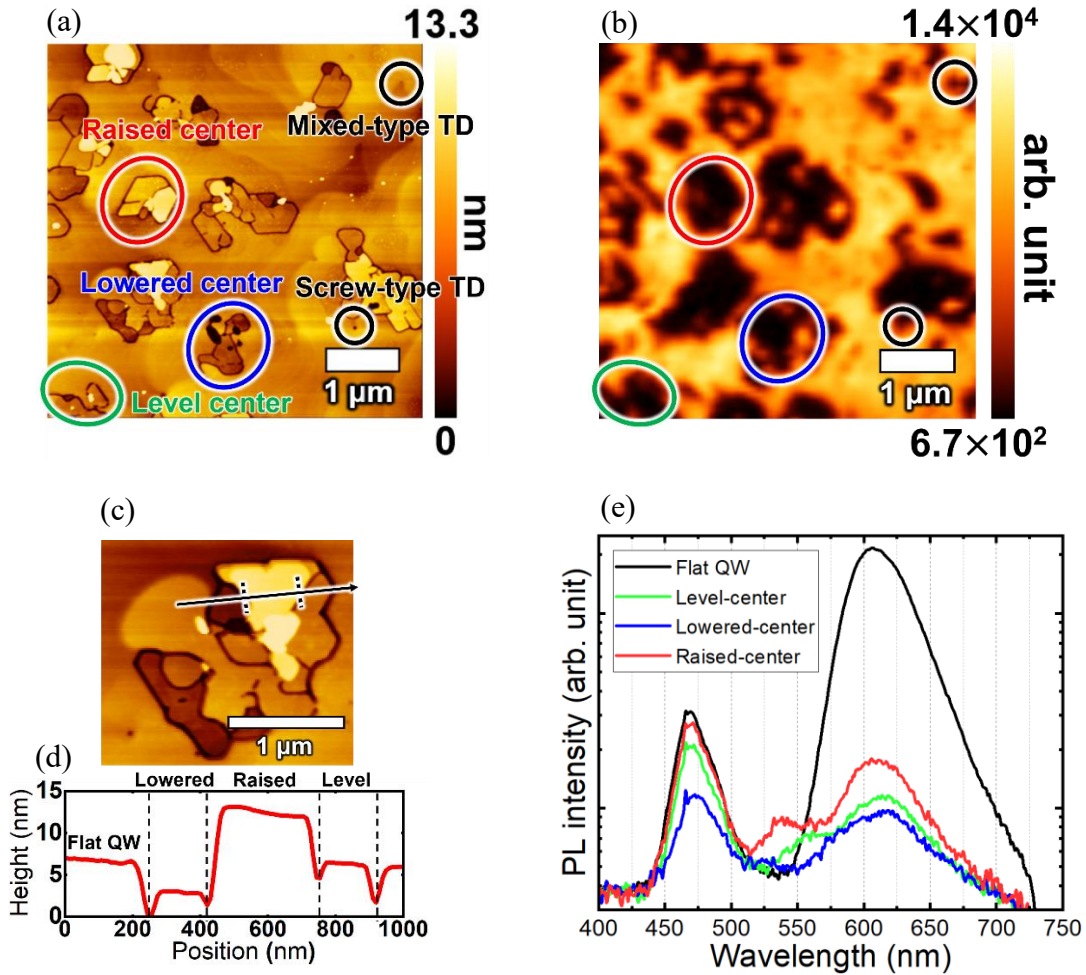


Figure 4-8. (a) AFM image. (b) C-mode SNOM integrated PL intensity mapping image of red emission. (c) Magnified AFM image. (d) Cross-sectional line profile. (e) PL spectra at flat QW and three types of trench defect.

Figure 4-8(a) shows an AFM image of the sample surface. Trench defects and hexagonal V-shaped pits are observed. The magnified image and the cross-sectional line profile of trench defects are shown in Figs. 4-8(c) and 4-8(d), respectively. The trench defects exhibit three height variations relative to the surrounding area. On the basis of the variations, trench defects are categorized into three types: (1) lowered-center, (2) level-center, and (3) raised-center trench defects, as proposed in a previous report study. [1] Two types of V-pit defect with pinned steps (spiral growth) are also observed: deep and shallow V-pits. The deep V-pits are approximately 8–16 nm deep, whereas the shallow ones are less than 3 nm deep. The V-pit defects originate from screw- or mixed-type TDs. [8, 9] Given that the depth of the V-pits originating from screw-type TDs is greater than that of V-pits originating from mixed-type TDs, [10, 11] the deep and shallow V-pits should originate from screw- and mixed-type TDs, respectively. The defect densities, as determined by AFM analysis, are presented in Table 4-2. Note that large trench defects are often composed of smaller trench defects. Here, we determined the trench defect density on the basis of the number of trench defects of different heights (If a large trench defect is composed of one lowered-, one level-, and one raised-center trench defects, we count it as three trench defects.)

Figure 4-8(b) shows a C-mode SNOM integrated PL intensity mapping image taken at the AFM scanned area, where the integrated wavelength range is from 570 to 700 nm. All of the V-pits and trench defects exhibit dark emission, indicating that they are NRCs. Notably, bright emission spots are observed within some trench defects. Their origins will be discussed later. Figure 4-8(e) shows the PL spectra at the flat QW, lowered-, level-, and raised-center trench defects. Not only blue (~470 nm) and red (~610 nm) but also parasitic green (~540 nm) emissions are observed. The additional green emissions originate from In segregation. For the red emissions, the peak emission wavelengths at all types of trench defects exhibit a redshift compared with that at the flat QW, which is in agreement with the findings of previous research studies. [1, 13] This redshift is attributed to the enhancement of In incorporation caused by the strain relaxation at trench defects. [13] In summary, all the dark spots in Fig. 4-8(b) have been identified as TDs and trench defects.

4.4 Discussion

4.4.1 Blue InGaN SQW

4.4.1.1 Origins of NRCs

In previous sections, we demonstrate that all of the TDs are origins of NRCs in a blue SQW serving as a beneath layer of hybrid InGaN QW red active layers. In our previous research on hybrid QW red InGaN LEDs [1], we established a correlation in the distribution of dark spots between the blue SQW beneath layer and red active layer. Collectively, the previous and present results reveal that all of the TDs are also likely origins of NRCs in the red active layer. The results of the present study suggest that reducing the TDDs is necessary to enhance the IQE of red emission in hybrid QW red InGaN LEDs.

4.4.1.2 Energy Barrier and Antilocalization

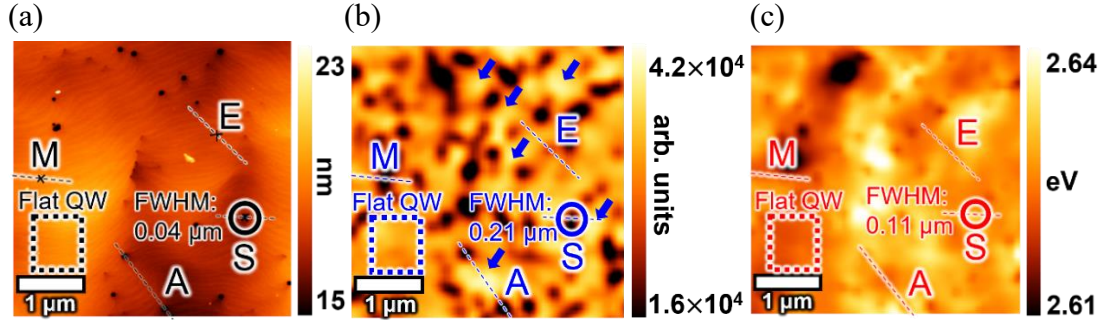


Figure 4-9. (a) AFM image, (b) I-C-mode SNOM integrated PL intensity mapping image, and (c) I-C-mode PL peak energy mapping image of sample 1.

The effect of TDs on the luminescence characteristics has been a popular topic in InGaN QW studies. Numerous groups have studied a correlation between luminescence and TDs using methods such as cathodoluminescence (CL) and scanning electron microscopy. Some direct correlation measurements have shown that screw-, mixed-, and edge-type TDs act as NRCs in $\text{In}_{0.28}\text{Ga}_{0.72}\text{N}$ QWs. [14] However, other studies have shown no correlation between the TD and PL intensity distributions in $\text{In}_{0.20}\text{Ga}_{0.80}\text{N}$

SQWs. [15, 16] In the present paper, we attributed all of the dark spots to screw-, mixed-, and edge-type TDs in a blue $\text{In}_{0.20}\text{Ga}_{0.80}\text{N}$ SQW. We speculate that, in the previous studies, [14, 15] the samples had dense point defects because of the absence of In-containing underlayers; consequently, point defects masked the effects of TDs, resulting in no correlation between the TD and PL intensity distributions in sample 1.

The AFM, I-C-mode SNOM integrated PL intensity mapping, and I-C-mode PL peak energy mapping images acquired at the same area are shown in Fig. 4-9(a)–(c). The average PL peak energy is 2.62 eV (472.7 nm), which corresponds to the center wavelength at $2.5 \times 10^3 \text{ kW/cm}^2$ in Fig. 4-6(b). Therefore, the estimated macroscopic IQE is 35.1% in Fig. 4-9(b). In Fig. 4-9(c), all of the TD cores exhibit a lower emission energy compared with their surroundings. This tendency has also been observed in previous studies. [15-19] The energy minima in TD cores should originate from an accumulation of In-rich InGa N at the center of the TDs. Several authors have proposed that the suppression of nonradiative recombinations in InGa N QWs is attributable to the shielding of NRCs by energy barriers, which leads to the antilocalization of carriers to NRCs. [15, 19] A barrier height on the order of 400 meV has been observed. [19] Such antilocalization behavior is also present in the present study. For example, the integrated PL intensity between two TDs is higher than that at a flat QW, as indicated by the line profile in Fig. 4-10(a). This higher integrated PL intensity is attributable to carrier confinement at the central region as a result of the existence of the surrounding energy barrier. In Fig. 4-9(b), such high-PL-intensity regions typically appear in the areas surrounded by dense defects (indicated by arrows), which further supports the antilocalization effect.

Although the carrier antilocalization behavior is observed, all of the TDs still appear as dark emission spots in the present work, as demonstrated by the line profiles of the dark spots "S" (screw-type TD), "M" (mixed-type TD), and "E" (edge-type TD) in Fig. 4-9(b)–(d). The dark spots are typically larger than the V-pits in the AFM image. For example, the FWHM (209 nm) of the "S" dark spot in the SNOM-PL intensity map (Fig. 4-9(b)) is much larger than that (39 nm) of the V-pit in the AFM image (Fig. 4-9(a)) and that (110 nm) of the dark spot in the peak energy map (Fig. 4-9(c)). We attribute the

larger size of the dark spots to (1) carrier diffusion driven by an excited carrier density gradient and (2) carrier drift due to the potential energy gradient around the TDs. [20] The larger size of the dark spot in the SNOM-PL intensity map indicates that the antilocalization effect does not perfectly prevent carriers from being trapped by TDs in sample 1. This imperfect antilocalization effect originates from the energy barriers being lower (~ 10 meV) than those in previous studies (~ 400 meV). [21] Nevertheless, sample 1 exhibits a relatively high IQE ($>30\%$) irrespective of the high TD density (10^8 cm $^{-2}$). This finding suggests that, even when the barrier height is low, the antilocalization effect still remains effective for achieving a high IQE in blue InGaN QWs.

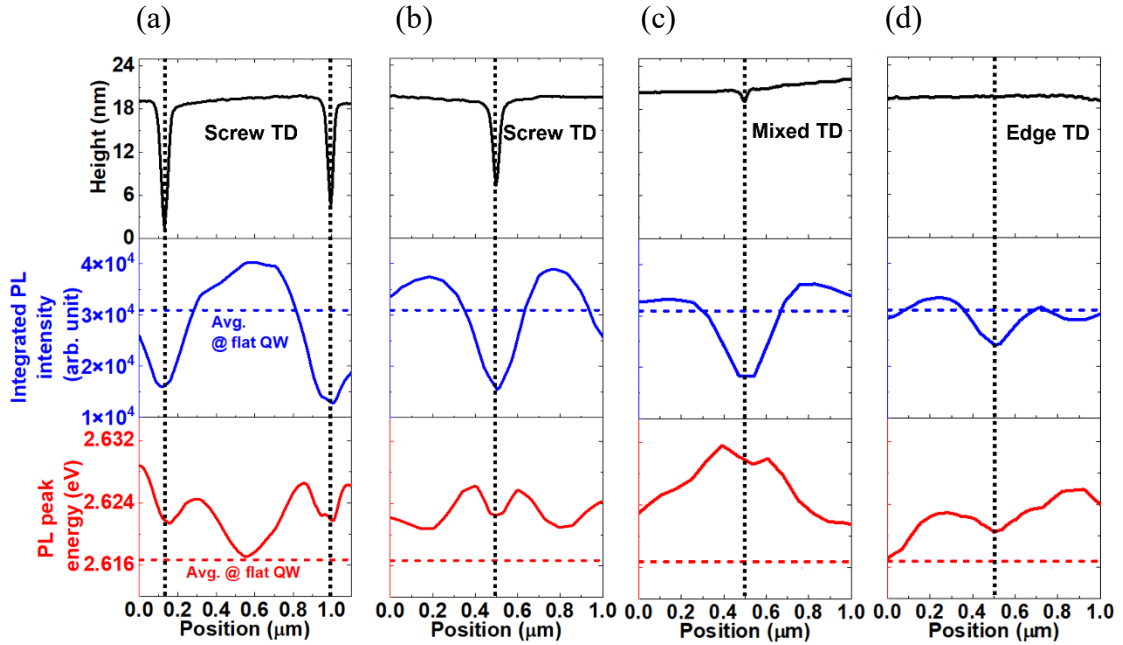


Figure 4-10. Cross-sectional line profile at the (a) "A" position, (b) "S" dark spot (screw-type TD), (c) "M" dark spot (mixed-type TD), and (d) "E" dark spot (edge-type TD) in Fig. 4-9(a)–(c). The "Avg. @ flat QW" refers to the average integrated PL intensity or PL peak energy at the flat QW (i.e., the area without V-pits in the AFM image and without dark spots in the SNOM integrated PL intensity map).

4.4.1.3 Effect of TDs on the Integrated PL Intensity

Table 4-3. Effect of the three types of TDs on the integrated PL intensity for sample 1.

TD type	TD density (cm^{-2})	Average integrated PL intensity reduction per dark spot (arb. units)	Total integrated PL intensity reduction (arb. units)
Screw	8.0×10^7	8.7×10^4	1.8×10^6
Mixed	1.2×10^8	6.0×10^4	1.8×10^6
Edge	2.9×10^8	3.4×10^4	2.8×10^6

Note: The total integrated PL intensity in Fig. 4-7(c) is 6.1×10^7 arb. units.

To assess the effect of the three types of TDs (i.e., screw, mixed, and edge) on the macroscopic optical properties, we estimated their effect on the integrated PL intensity (Table 4-3) using C-mode SNOM integrated PL intensity mapping images (Fig. 4-7(c)). According to the analyses, edge-type TDs, which have the highest density among the three TD types, exhibit a greater reduction in the integrated PL intensity compared with screw- and mixed-type TDs. Instead, screw-type TDs have the highest reduction in the integrated PL intensity on a per-defect basis. Overall, screw, edge, and mixed-type TDs have nearly the same effect on the integrated PL intensity. Therefore, all of the TDs contribute to the reduction in the IQE of sample 1. Given the correlation between dark emission regions of blue and red emissions in hybrid red InGaN LEDs, [22] all of the TDs should also function as NRCs, leading to a reduction in the IQE of the red emission. In a blue InGaN SQW studied in the present study, even if all of the TDs are eliminated, the total integrated PL intensity only increases from 6.1×10^7 to 6.7×10^7 (Table 4-1). Given the macroscopic IQE of 35.1% in Fig. 4-7(c), the presence of TDs alone cannot account for the whole reduction in the IQE. Individually unresolved point defects must also decrease the IQE. Our previous studies on a red active layer indicated that point defects are also significant factors in the reduction of the IQE. [22] Optimizing the underlayer [2] to effectively bury point defects in a red SQW is also a potential strategy for enhancing the IQE of red emission.

4.4.2 Red InGaN Hybrid SQW

4.4.2.1 Origins of the Bright spots

The origins of the bright spots within trench defects [see Fig. 4-11(a)] in red InGaN hybrid SQW are discussed here. The PL spectra at flat QWs, trench-defect bright spots, and dark areas [in Fig. 4-11(a)] are shown in Fig. 4-11(b). At the trench-defect bright spots, weak red and additional green (570 nm) emissions are observed. As mentioned above, the additional green emissions originate from In segregation. Because the integrated wavelength range for the red emission is from 570 nm to 700 nm, the additional green emissions appear as bright emission spots in Fig. 4-11(a).

To check whether all the trench-defect bright spots have the parasitic green emissions, the PL intensity image at 559 nm [Fig. 4-11(d)] and the PL center wavelength image of red emission [Fig. 4-11(e)] are depicted. The bright spots in Fig. 4-11(d) and short emission wavelength spots in Fig. 4-11(e) correspond to the bright spots in the integrated PL intensity mapping image of red emission [Fig. 4-11(a)]. Therefore, all of the bright emissions within trench defects originate from parasitic green emissions, namely, In segregation.

4.4.2.2 In Segregation

In segregation within trench defects has also been observed in previous studies on green InGaN QWs. [23] The occurrence of In segregation at trench defects is attributed to the high-In-content incorporation. [24, 25] In our sample, In segregation is more pronounced at trench defects because of the high indium content. To investigate the impact of In segregation, we classified trench defects into two types: with strong In segregation (trench defect 1) and with weak In segregation (trench defects 2 and 3). In trench defect 1 [indicated marked in blue in Fig. 4-11(a)], significant In segregation occurs, as evidenced by the bright green emissions in Fig. 4-11(d). As a result, trench defect 1 exhibits a notably low red emission intensity, as shown in Fig. 4-11(a). On the other hand, trench defects 2 and 3 [indicated marked in red in Fig. 4-11(a)] exhibit a

weak In segregation owing to a lack of distinct green emissions in Fig. 4-11(d). As a result, they exhibit a higher red emission intensity than trench defect 1. Thus, we conclude that In segregation is the primary origin of the dark red emissions from trench defects.

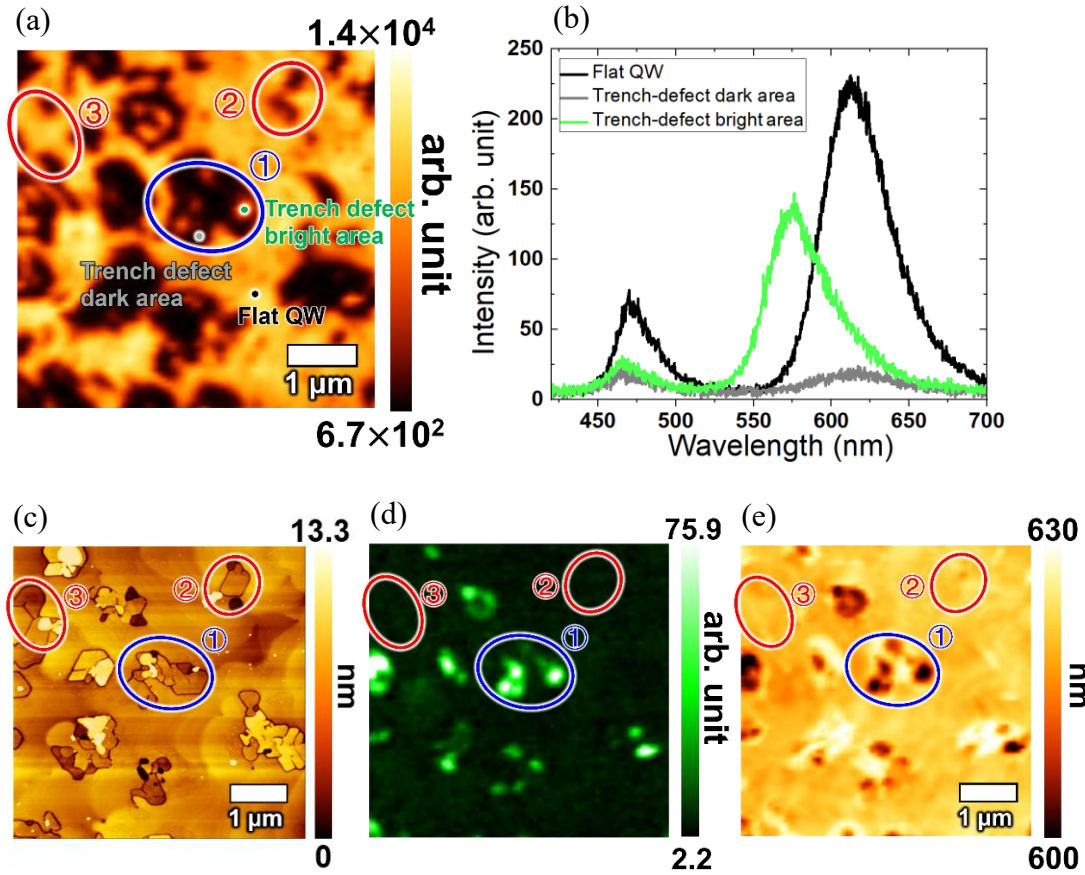


Figure 4-11. (a) C-mode SNOM integrated PL intensity map of red emission. (b) PL spectra at flat QW, trench defect dark area, and bright area in Fig. 4-11(a). (c) AFM image. (d) PL intensity map at 559 nm (green emission). (e) Center wavelength map of red emission.

We discuss the effects of trench defects on luminescence characteristics. Previous studies on $\text{In}_{0.20}\text{Ga}_{0.80}\text{N}$ QWs have shown that only lowered-center trench defects exhibit a lower emission intensity than their surroundings, whereas raised- and level-center trench defects show higher emission intensities. [1] In contrast, in this study, we demonstrated that in the hybrid InGaN red SQW, TDs and trench defects act as NRCs. The discrepancy should originate from the difference in the In content of the samples.

Unlike our sample, low-In-content samples in a previous study [1] were free of In segregation.

Pan *et al.* demonstrated that deep trench defects enhance the luminescence of red InGaN QWs, whereas shallow trench defects suppress the luminescence. [26] The difference between the deep and shallow trench defects lies in which layers they are generated. According to the definition of trench defects, all of the trench defects in our sample are classified as shallow trench defects. The low emission intensity at the shallow trench defects is consistent with the results of Pan *et al.*'s study. In the present study, we attribute the weaker luminescence in shallow trench defects to In segregation.

4.4.3 Relationship between TDs and Trench Defects

In our previous studies, we established a correlation between the dark emission positions in red and blue InGaN SQWs. [22] We demonstrated that the dark emissions in a blue InGaN SQW originated from the TDs. [27] In the present study, we demonstrated that the dark spots in a red InGaN SQW are mainly associated with trench defects. These findings indicate a strong correlation between TDs and trench defects in hybrid red InGaN QWs. To support the discussion, we compared the TD and trench defect densities at the n-GaN layer and surface. As shown in Tables 1 and 2, the trench defect density at the surface is $8.8 \times 10^7 \text{ cm}^{-2}$, which is very close to the decrease in the screw-type TDD ($1.1 \times 10^8 - 1.8 \times 10^7 = 9.2 \times 10^7 \text{ cm}^{-2}$) from the n-GaN layer to the surface. This coincidence suggests that screw-type TDs act as triggers for the formation of trench defects. Our conclusion differs from those in previous studies which suggested that V-defects (TDs) and trench defects are rather separate phenomena. [1, 28, 29]

According to our statistical analysis, the total integrated PL intensity is 6.1×10^7 in Fig. 4-11(a). The reduction in integrated PL intensity by trench defects is approximately 3.1×10^7 . This suggests that if all of the trench defects are eliminated, the total integrated PL intensity increases by nearly 50%. Therefore, to increase the EQE of InGaN red

LEDs, it is essential to decrease trench defect density. Since screw-type TDs play an important role in triggering the formation of trench defects, using a substrate with lower TDD or employing effective strain management techniques should be promising strategies.

4.5 Summary

Using SNOM and AFM techniques, we investigated the nanoscopic correlation between the structural and emission properties of a red InGaN hybrid SQW. The lowered-, level-, and raised-center trench defects, as well as TDs, exhibit a low emission intensity, indicating that they are NRCs. We demonstrate that the enhanced In segregation caused by the high In content of the sample significantly reduces the emission intensity. Given the correlation of dark emission regions between the blue and red emissions, as well as the observation that the reduction in the screw-type TDD is comparable to the increase in the trench defect density at the surface, it is reasonable to conclude that screw-type TDs must be one of the triggers in the formation of trench defects.

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Chapter 5

5. Conclusions and Future Works

5.1 Conclusion

In this thesis, the optical and structural properties of on InGaN-based hybrid quantum wells for efficient red emitters from macroscopic to nanoscopic scale have been investigated. The macroscopic internal quantum efficiency (IQE) and carrier dynamics are investigated in Chapter 2. The microscopic properties that govern the IQE and external quantum efficiency (EQE) are elucidated in Chapter 3. The nanoscopic structural origins of the nonradiative recombination center (NRCs) are explored in Chapter 4.

In chapter 1, the current status of InGaN-based LEDs and challenges of high In-content InGaN-based LEDs are introduced. The strain-induced piezoelectric polarization, the degradation of crystalline qualities, and In segregation of In-rich InGaN are main causes of the efficiency drop in InGaN-based red LED. The author briefly summarizes the characterization of red InGaN-based LEDs reported in recent studies and emphasizes the lack of research on red InGaN-based single quantum well (SQW) from macroscopic to nanoscopic scales, thereby establishing the objectives and significance of this thesis.

In chapter 2, power-dependent and temperature-dependent time-integrated and time-resolved photoluminescence (PL) measurements on a red InGaN LED with hybrid QW structure were performed. As excitation power density increased, the IQE at 6 K initially kept 100% but then monotonically decreased to 30 %, whereas the IQE at 293 K increased to a maximum value of 5.9%. The estimated maximum IQE (5.9%) at 293 K was substantially lower than the IQE (24.0%) estimated by Hou *et al.* [1], possibly due to the overestimation by their non-selective excitation measurements. The power-dependence of PL lifetime (τ_{PL}), radiative recombination lifetime (τ_{rad}), and nonradiative recombination lifetime (τ_{nrad}) at 6 K and 293 K were also examined. The

τ_{rad} values were much longer than those observed in InGaN blue and green LEDs. [3] The power independence of τ_{rad} at 6 K can be explained by a combination of Coulomb enhancement and quantum confined Stark effect (QCSE) screening. At room temperature τ_{nrad} exhibited little power dependence, indicating weak Auger recombination. The temperature dependence of τ_{PL} , τ_{rad} , and τ_{nrad} at $7.6 \mu\text{J}/\text{cm}^2$ and $117.1 \mu\text{J}/\text{cm}^2$ was also studied. When the experimental temperature exceeded 100 K, the short τ_{nrad} dominated the τ_{PL} , contributing to the thermal droop in the InGaN-based red SQW. The author successfully established a positive correlation between τ_{rad} and full width at half maximum (FWHM) of PL spectra. The author demonstrated that disorder-induced linewidth plays an important role in the broadening of the FWHM. Therefore, the improvement of the In homogeneity of red QWs should be a promising method for realizing efficient InGaN-based red LEDs.

In chapter 3, to experimentally investigate the non-radiative recombination processes of InGaN-based red LEDs, the author performed μ -PL spectroscopy for an InGaN-based red LED with a hybrid QW structure, which contains a red and a blue SQW. The μ -PL mapping image of the integrated red emission intensity reveals the presence of various sizes/contrasts of dark spots. The author found that not only red and blue (from blue SQW) but green emission bands were observed at certain dark spots, indicating that In segregation is one of the causes of dark red emissions. By comparing the blue and green emission maps to the red emission map, the author classified the dark spots in the intensity map of the red emission into four types. The author concluded that the red dark spots, which are associated with the dark areas in the blue emission, serve as the primary NRCs. On the basis of the presence or absence of the green emission peak, these dark spots can be categorized into two distinct types. The author speculated that the dark spots with In segregation correspond to large trench defects, whereas the dark spots without In segregation correspond to other defects, such as threading dislocations, and small trench defects. To further improve the device performance of InGaN-based red LEDs, this study indicates that decreasing the dark spot density is crucial to enhance the PL intensity and decrease the FWHM of the emission spectrum.

In chapter 4, using atomic force microscopy (AFM) and scanning near-field optical microscope (SNOM) PL spectroscopy, the author studies the structural and optical properties of a blue InGaN SQW and an efficient red InGaN active layer. For the blue InGaN SQW, The AFM images reveal deep and shallow V-pits, corresponding to screw- and mixed-type threading dislocations (TDs). The SNOM PL intensity image illustrates that all the pits correspond to dark spots. The author also observed dark spots not associated with the V-pits; given the correspondence between the dark spot density and edge-type TD density estimated via X-ray diffraction measurement, these dark spots likely originate from edge-type TDs. Unlike previous studies, the author found that TDs act as NRCs in the recent blue SQW, most likely because of the reduction of point defects by the InGaN/GaN superlattices. For the red InGaN active layer, the AFM image reveals not only the presence of V-pits but also trench-like defects. These trench defects can be classified into three categories based on their height relative to the flat area: lower, level, and raised center trench defects. The SNOM image further demonstrates that all types of trench defects, as well as TDs, exhibit low emission intensity, indicating that they act as NRCs. Interestingly, bright emission spots were observed within some trench defects, which are attributed to the regions with lower indium content caused by In segregation. However, in previous research on trench defects, only lower-center trench defects exhibited reduced emission intensity, while level and raised center trench defects displayed higher emission intensities compared to the flat QW. [1] In contrast to previous studies on low In content samples, the author investigated samples with In content of 40%. Our findings suggest that the enhanced In segregation associated with the high In-content significantly reduces the emission intensity. Given the correlation of dark emission positions between the blue and red emissions, as well as the lower TD density in red SQW, TDs must be a trigger in the formation of trench defects in the red InGaN SQW. Therefore, to enhance the EQE of InGaN red LEDs, it is crucial to eliminate the In segregation within trench defects and suppress the TD density.

5.2 Future work

5.2.1 Conduct I-C mode SNOM on Red InGaN Hybrid QWs to Investigate the Carrier Diffusion.

I-C mode SNOM enables to measure the spatial variation in emission intensity, which is affected by both carrier diffusion and local emission efficiency. This is particularly important for understanding the non-uniformities of carrier transport originating from material defects or compositional gradients in the quantum wells. Comparing the intensity maps of I-C mode SNOM with those of C-mode SNOM can provide clearer insights. Moreover, I-C mode SNOM can estimate the carrier diffusion lengths and the influence of localized recombination processes.

5.2.2 Develop Time-resolved SNOM PL System to Study the Carrier Dynamics at the Defect (V-pits and Trench Defects).

Time-resolved SNOM PL allows the direct observation of carrier lifetimes and recombination rates at defects. It can be used to trace how carriers diffuse toward or away from defect regions, providing insights into their impact on the overall device efficiency. This provides critical information on whether defects act as non-radiative recombination centers or facilitate other carrier dynamics.

5.2.3 Perform High-resolution Transmission Electron Microscopy to Examine the Relationship between TDs and Trench Defects.

In chapter 4, because of the less TDs density in the red SQW than that in the n-GaN

layer, we conclude that TDs should contribute to the formation of trench defects. Through high-resolution transmission electron microscopy, we can identify the structural characteristics and origins of the trench defects connected to the TDs at atomic scale, helping in optimizing growth processes to reduce trench defect densities.

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Appendix A

Exciton binding energy and excitonic fraction

In chapter 2, the author demonstrates that the radiative rate is influenced by not only the overlap of electron-hole wavefunctions, but also Coulomb interaction and carrier screening. To support the statement of Coulomb screening effect, it is essential to calculate the carrier density-dependent exciton binding energy and excitonic fraction. However, the effects of Coulomb interaction, disorder-induced localization and polarization field all compete in the calculation and lead to a computational problem. Here, we refer to approximate formulas for exciton binding energy derived in previous studies, which are based on both numerical calculations and experimental data. [1, 2] A numerical solution for the variation of the binding energy as screening increases in two-dimension (2D) by Portnoi and Galbraith, [3] while Snoke proposed an approximate formula for calculating the 2D exciton binding energy. [1] The carrier density-dependent exciton binding energy of 2D QWs at 6 K is approximated and presented in Fig. A(a), (Blue line) where the binding energy of the free exciton is normalized to 1. According to the simulation result, the normalized binding energy decreases monotonically as carrier density increases, indicating the Coulomb interaction screening. However, at high carrier densities, the exciton binding energy sharply decreases to zero, which leads to a breakdown of the mass-action equation in the following calculation. On the other hand, according to the investigation on a series of QWs with varying thickness by David *et al.*, the screening behavior follows a sigmoid-like pattern. [2] Based on this observation, they found an acceptable fit to the experimental data using the following function:

$$E_x(n) = \frac{E_x(0)}{1 + \left(\frac{n}{n^*}\right)^\alpha} \quad (\text{A-1})$$

Where $E_x(0)$ is the binding energy of free exciton, n is the total carrier density. n^* and α are both variable parameters, n^* corresponds to the point where the normalized binding energy equals 0.5, and α determines the extent to which the

exciton binding energy is screened as the carrier density increases.

In Ref. 2, $n^* \sim 2 \times 10^{17} \text{cm}^{-3}$ and $\alpha = 2/3$, were used for a bulk GaN. However, in a two-dimensional (2D) system, the carrier dependence of screening length ($l \propto n^{-1}$) is stronger than that in 3D system ($l \propto n^{-1/2}$). [1] It means the screening effect on Coulomb interactions in 2D QWs is significantly stronger at equivalent carrier concentrations, which leads to a more rapid decline in exciton binding energy as carrier density increases. Therefore, for 2D QWs, α should be higher than $2/3$ at least. Additionally, the thicker QW causes the electron-hole separation to dominate the physics, resulting in a lower exciton binding energy and shifting of n^* towards low carrier densities. [2] According to the normalized screening of binding energy with carrier density presented by Snoke et al., n^* is approximately $1.5 \times 10^{16} \text{cm}^{-3}$ for 2D QWs. Thus, for our 3.5 nm-thick red SQW, we substitute $n^* = 1.5 \times 10^{16} \text{cm}^{-3}$ and $\alpha = 1$ into Eq. (A-1), normalizing $E_x(0)$ to 1. As a result, based on the model proposed by David *et al.*, the carrier density-dependent exciton binding energy of InGaN at 6 K is approximated and presented in Fig. A(a). The simulation results are basically in agreement with those of Snoke *et al.*, except that at high carrier density the carrier density-dependent binding energy calculated from Eq. (A-1) shows a more moderate decrease. Moreover, the trend observed in this simulation with the new parameters closely resembles the calculated normalized binding energy for a 4 nm-thick QW in previous research. [2] Based on the simulated carrier-dependent normalized binding energy by Eq. (A-1), the excitonic population can also be conventionally computed with the Saha equation, [1] a mass-action law that relates the free and excitonic populations. For a 2D system, the Saha equation reads as the following equation: [2]

$$n_{ex} = \frac{n \cdot n_{free}^2}{\frac{nm_r k_B T}{\{2\pi\hbar^2 [\exp(\frac{E_x(n)}{k_B T}) - 1]\}} \quad (\text{A-2})$$

Where n_{ex} , n , and n_{free} represent the excitonic density, total carrier density, and free density of electrons (and holes). The total carrier density can be expressed as $n = n_{ex} + n_{free}$. All these are 2D densities, related to 3D densities by $n_{3D} = n_{2D}/t$, with t the QW thickness. m_r is the reduced effective mass of an electron and a hole, k_B is the Boltzmann constant, and T is the temperature. The carrier-dependent excitonic

fraction n_{ex}/n at 6 K obtained from Eq. (A-2) is shown in Fig. A(b). Here, the carrier density range matches that of our experiment, and the free exciton binding energy is assumed to range from 10 meV to 40 meV.

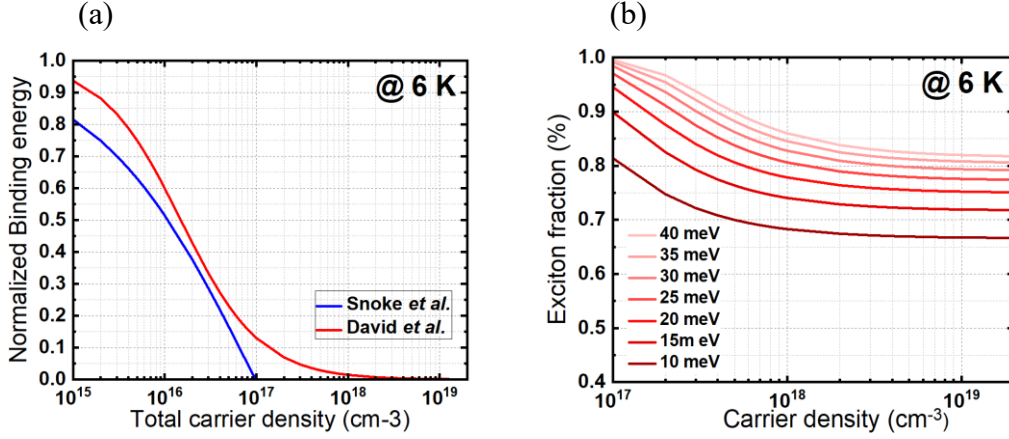


Figure A. (a) Simulation of normalized screening of the binding energy with carrier density. The red line is a simulation based on Ref. 2, while the blue line is a simulation based on Ref. 1. (b) Fraction of exciton versus total carrier density at 6 K under various assumed free excitonic binding energy, according to the Saha equation and Ref. 2.

According to the simulation shown in Fig. A(b), as the total carrier density increases, the excitonic fraction shows a decreasing trend under all assumed free excitonic binding energies, and the variation in the excitonic fraction is approximately 20% between lowest and highest carrier densities. Therefore, it is reasonable to consider that a high carrier density weakens Coulomb enhancement, thereby reducing the radiative rate. This Coulomb screening effect may offset the QCSE screening effect, resulting in an unchanged τ_{rad} in Fig. 2-12(a).

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List of Publications

Journal Papers

1. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,
 “Correlative Micro-Photoluminescence Study on Hybrid Quantum-Well InGaN Red Light-Emitting Diodes”
Phys. Status Solidi B 261, 2400036 (2024).
2. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,
 “Nanoscopic structural and optical investigations on blue InGaN single quantum wells serving as layers beneath efficient red active layers”
 Have been accepted by *Journal of Applied Physics*. ‘Editor’s Pick’
3. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,
 “Time-integrated and time-resolved photoluminescence study on red InGaN hybrid single-quantum-wells under selective excitation conditions”
 Have been submitted to *Applied Physics Letters*.
4. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,
 “Study on correlation between structural defects and local optical properties of red InGaN hybrid single-quantum-wells”
 In preparation.

International Conferences

1. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,
 “Correlative micro-photoluminescence spectroscopy on hybrid quantum-well InGaN red LEDs”
14th International Conference on Nitride Semiconductors, Fukuoka, CH1-3, oral.
2. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,
 “Study on blue InGaN single quantum well and efficient red InGaN active layer by atomic force microscopy and scanning near-field optical microscopy”
12th International Workshop on Nitride Semiconductors, (IWN 2024) O'ahu, Hawai'i — Hilton Hawaiian Village, 322, oral.

Domestic Conferences (Selected)

1. **Zhaozong Zhang**, Ryota Ishii, Mitsuru Funato, and Yoichi Kawakami,
 “Temperature-dependent microphotoluminescence study on green-emitting InGaN/GaN single quantum well grown on epitaxially laterally overgrown GaN”
83rd Japan Society of Applied Physics Spring Meeting, 20p-B202-3, Tohoku Univ., Sendai, Japan, (Sep. 2022), oral.
2. **Zhaozong Zhang**, Ryota Ishii, Mitsuru Funato, and Yoichi Kawakami,
 “Spatial- and time-resolved photoluminescence at high temperatures on green-emitting InGaN/GaN single quantum well grown on epitaxially laterally overgrown GaN”
70th Japan Society of Applied Physics Spring Meeting, 16a-B401-9, Sophia Univ., Tokyo, Japan, (March. 2023), oral.
3. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida,

Kazuhiro Ohkawa, and Yoichi Kawakami,

“Hybrid quantum-well InGaN red LEDs studied by correlative micro-photoluminescence spectroscopy”

84th Japan Society of Applied Physics Spring Meeting, Kumamoto-jo, Kumamoto, Japan, (Sep. 2023), oral.

4. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,

“Atomic force microscopy and scanning near-field optical microscopy on single quantum-well InGaN blue LEDs”

71st Japan Society of Applied Physics Spring Meeting, 22p-21C-2, Setagaya Campus, Tokyo City University, Tokyo, Japan, (March. 2024), oral.

5. **Zhaozong Zhang**, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,

“Time-resolved photoluminescence study on red InGaN hybrid single-quantum-wells under selective excitation conditions”

85th Japan Society of Applied Physics Spring Meeting, 19p-C42-15, TOKI MESSE Niigata Convention Center, Niigata, Japan, (Sep. 2024), oral.

Awards

1. Best Student Award

Zhaozong Zhang, Ryota Ishii, Kanako Shojiki, Mitsuru Funato, Daisuke Iida, Kazuhiro Ohkawa, and Yoichi Kawakami,

“Correlative micro-photoluminescence spectroscopy on hybrid quantum-well InGaN red LEDs”

14th International Conference on Nitride Semiconductors, Fukuoka, CH1-3, oral.