

Emission Mechanisms in Al-rich AlGa_N Quantum Wells
toward Deep Ultraviolet Light Emitters
by Electron Beam Pumping

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Abstract

Since the discovery of ultraviolet (UV) light, various UV light sources have been developed. Thanks to this development, the applications of UV light have been increasingly expanded. Deep UV (DUV) optical devices are expected to realize various applications, such as air and water purification/sterilization, biomedical research, and semiconductor processes. The current DUV light sources are mainly excimer gas lasers/lamps and mercury vapor lamps. However, these DUV light sources have a lot of disadvantages such as short lifetime, high cost and use of harmful materials. To overcome these problems, aluminum gallium nitride (AlGa_N) based solid-state optical devices are highly expected. Al_{*x*}Ga_{1-*x*}N has a direct bandgap that can be tuned from 3.4 eV to 6.0 eV covering the DUV region by changing the Al composition *x*. Recently, their crystal qualities have been drastically improved, and consequently the internal quantum efficiencies (IQEs) have reached $\sim 70\%$ at emission wavelengths between 240 nm and 280 nm, including our group. However, despite the high IQEs, the external quantum efficiencies (EQEs) of AlGa_N-based light emitting diodes (LEDs) are less than $\sim 10\%$ due to the main problems associated with p-AlGa_N. To obtain AlGa_N quantum wells (QWs) with higher quality and DUV optical devices with higher emission efficiencies, it is important to understand the optical properties in Al-rich AlGa_N QWs. However, their optical properties have not been investigated adequately.

This thesis addresses the problems described above. In this thesis, we performed various optical spectroscopy measurements to understand the emission mechanisms in Al-rich AlGa_N/AlN QWs. First, we measured photoluminescence (PL) using a Xe₂^{*} excimer lamp and assessed the temperature dependence of PL in order to investigate the fundamental emission mechanisms under weak excitation condition. As a result, we observed the emission properties derived from the localized excitons based on two types of localization states. In addition, temperature dependent cathodoluminescence (CL) mapping measurements were performed in order to observe the exciton dynamics directly in Al-rich AlGa_N/AlN QWs. From these analyses, we identify that the experimentally observed two types of localization states, that is, shallow and deep localization states originate from the statistically unavoidable alloy disorder effect and 2 ML (± 1 ML) fluctuation of the well width, respectively. Moreover, many excitons migrated to deep localization state derived from 2 ML fluctuation and emitted brightly in those regions for narrow QWs. Then, based on the results of the optical properties under weak excitation condition, the optical properties under intermediate and high excitation conditions were discussed. It was found that the excitation power dependence of PL properties could be explained by the above-mentioned potential model. Therefore, it is considered that the proposed potential model is

reasonable. The PL peak shift and its well-width dependence could be reproduced by considering the bandgap renormalization (BGR), the Burstein-Moss (B-M) shift, and the screening effect of the internal electric field. Among them, the major factor for the difference in the PL peak shift due to the well width was found to be the screening effect. Then, we performed TRPL measurements for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs under the selective excitation condition in order to investigate carrier recombination dynamics around the Mott transition. The fast and the slow lifetime components were observed under highly-excited conditions and were attributed to radiative recombination lifetimes of the electron-hole plasma (EHP) and the exciton many-body (EMB) effect, respectively.

Additionally, it is also important to obtain the guideline of the optimum QW structures and the design of DUV optical devices with high emission efficiencies. Toward the application of DUV optical devices in particular DUV solid-state lasers, we discussed the optical gain characteristics evaluated by the variable stripe length (VSL) method in Al-rich AlGaIn/AlN QWs at RT. Edge PL spectra were much narrower than surface spectrum and their emission intensities were increased exponentially as excitation length was increased. In the result of the well width dependence of VSL measurements in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQWs, the largest optical gain of 140 cm^{-1} was obtained for the QW with $L_w = 5\text{ nm}$. Furthermore, comparing the conditions between with and without gain saturation, it was found that the redshift was caused by the gain saturation. The dominant polarization was changed from transverse electric-field (TE) mode to transverse magnetic-field (TM) mode, as Al composition was increased. This result was derived from the turnover of valence band ordering of AlGaIn/AlN QWs. Next, to overcome the problems with p-type AlGaIn , we propose the DUV optical devices based on AlGaIn QWs by electron beam (EB) pumping. Using AlGaIn/AlN QWs as a phosphor, high output power and power efficiency are promising, because a QW structure has higher radiative recombination probabilities, lower re-absorption loss than a bulky film, and higher light extract efficiency due to the quantum confinement. We used an EB pumping technique, demonstrating an output of 100 mW from Al-rich AlGaIn/AlN QWs emitting at $\sim 240\text{ nm}$. This achievement is attributed to the carrier confinement within the high-quality quantum wells, as well as the appropriate design of sample structures for EB pumping.

Finally, these presented results contribute to the development of DUV optical devices and suggest that EB pumping method overcomes the low EQEs of state-of-the-art DUV LEDs. It should be emphasized that the EB operating conditions in this study are accessible using portable field-emission devices. We therefore believe that EB pumping of QWs is effective for generating UV light, and the present developments form a significant step toward a next-generation, compact, high-efficiency DUV light sources.

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Chapter 1

Introduction

1.1 Background

Generally, the electromagnetic wave ¹ is divided into regions based on the wavelength of radiation. Ultraviolet (UV) region is defined as the wavelength range from 10 nm to 400 nm and further sub-classified into four regions; UV-A (315 – 400 nm), UV-B (280 – 315 nm), UV-C (200 – 280 nm) and Vacuum UV (VUV) (10 – 200 nm) [1]. In the field of semiconductor optics, a term of deep UV (DUV) defined as UV light with a wavelength of 200 – 300 nm is often used.

Since the discovery of UV light, various UV light sources have been developed and thereby their applications have been increasingly expanded. First of all, let us introduce the history of UV light briefly [2–4]. Table 1.1 lists the key developments of UV light. UV light was discovered by a German physicist J. W. Ritter in a series of experiments using a silver chloride in 1801. In 1893, the discovery of VUV was made by V. Schumann. Thanks to these discoveries, a lot of applications had been developed. In 1901, the first mercury vapor lamp was invented by P. C. Hewitt. Additionally, the sterilizing effect, which is important for the application to industry, was discovered by H. Strebel in 1901. UV light around 265 nm is effective for absorption of the deoxyribonucleic acid (DNA). The germicidal UV light causes adjacent thymine molecules in DNA to dimerize. If these defects accumulate on a microorganism's DNA, its replication is lost. As a result, it becomes harmless even if the organism is not killed. In 1936, the first commercial UV light source for the sterilization was developed by General Electric Company. In 1970, the first excimer laser using a xenon excited dimer (Xe_2^* ²) was developed by N. Basov *et al.* [5]. Since the beginning of 2000's, solid-state UV optical devices have been developed for the purpose of ecological UV light sources. In 2006, Taniyasu *et al.* reported that the first AlN PIN (p-type/intrinsic/n-type) homojunction light emitting diode (LED) with an emission wavelength of 210 nm, which was the shortest for any kinds of LEDs [6]. However, the reported external quantum efficiency (EQE) was as low as $10^{-6}\%$. In the same year, the stimulated emission from AlN epitaxial layer was first achieved by Shatalov *et al.* [7]. In 2008, the first laser diodes (LDs) using AlGaIn MQWs as active layers were reported [8]. In 2009, the first EB-pumped DUV optical device using a boron nitride (BN) as a phosphor was developed [9]. In 2012,

¹J. C. Maxwell first postulated electromagnetic waves. After that, they were confirmed by H. Hertz.

²Superscript * stands for the excited state.

Table 1.1: Key developments of UV.

Year	Key Developments	Person/Group
1801	Discovery of UV light	J. W. Ritter
1893	Discovery of VUV light	V. Shumann
1901	First Mercury vapor lamp	P. C. Hewitt
1901	Discovery of germicidal effect	H. Sterebel
1936	First UV light sources for sterilization	General Electric
1970	First excimer laser	N. Bosov <i>et al.</i> [5]
2006	First AlN-based LED	Y. Taniyasu <i>et al.</i> (NTT) [6]
2006	Stimulated emission from AlN	M. Shatalov <i>et al.</i> [7]
2008	First UV-LD using In-free AlGaIn MQW	H. Yoshida <i>et al.</i> (Hamamatsu) [8]
2009	First EB-pumped DUV optical device	K. Watanabe <i>et al.</i> (NIMS) [9]
2012	EQE of DUV-LED over 10%	M. Shatalov <i>et al.</i> [10]

EQEs of AlGaIn based DUV-LEDs over 10% were first achieved, thanks to the development of crystal growth technology [10]. More details regarding the AlGaIn-based optical devices will be discussed in Sec. 1.4.

1.2 Current Ultraviolet Emitters and Their Applications

To date, DUV optical devices are expected to realize various applications, such as air and water purification/sterilization, biomedical research, and semiconductor processes (e.g. photolithography) [11]. The current DUV light sources are mainly excimer³ gas lasers/lamps and mercury vapor lamps. Here, the principles of these devices are briefly introduced [12]. An excimer laser typically uses a combination of rare gas (Ar, Kr, Xe) and/or halogen gas (F₂, Cl₂), such as Xe₂^{*} (172 nm), ArF^{*} (193 nm), KrCl^{*} (222 nm), and KrF^{*} (248 nm). Under the appropriate conditions of electric discharge and high pressure, an excimer, which is a dimeric or heterodimeric molecule formed from two atoms, is created. Because an excimer is unstable, an excimer decays into two atoms with the UV emission in the lifetime of several nanoseconds. Produced UV light is oscillated with a Fabry-Perot interferometer. A mercury vapor lamp is a gas discharge lamp, generated by an electric arc through vaporized mercury. However, these current DUV light sources have a lot of disadvantages such as short lifetime, high cost and use of harmful materials. This means that these optical devices are not environmentally-friendly.

1.3 Current Status and Challenges of AlGaIn

To overcome the problems about the current DUV light sources, solid-state optical devices are highly expected. Recently, AlN and Al_xGa_{1-x}N quantum wells (QWs) have been extensively studied. Al_xGa_{1-x}N has a direct bandgap that can be tuned from 3.4 eV [13] to 6.0 eV [14] covering the DUV region by changing the Al composition x (see Fig. 1.1). Here, QW is the structure that discontinuity is created in the conduction and valence band edges by sandwiching

³Excimer originates from the word of excited dimer.

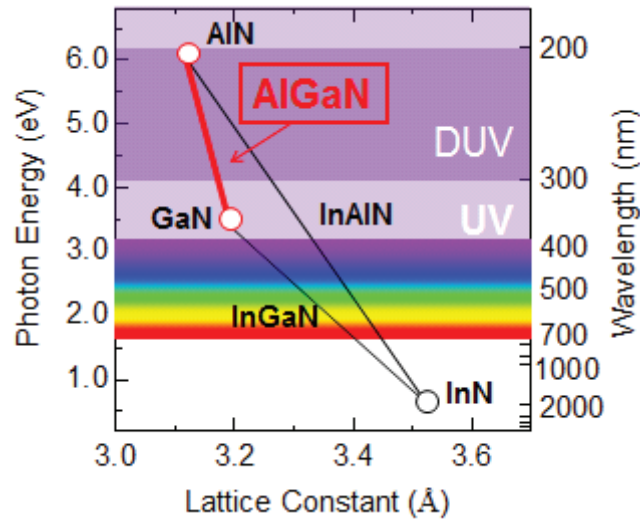


Figure 1.1: Relation between lattice constant and bandgap energy in nitride semiconductors. AlGa_N, which is the ternary alloy of AlN and GaN, covers DUV region defined as UV light from 200 nm to 300 nm.

a thin layer of one semiconductor between two layers of another semiconductor with larger band gap. In the QW structure, electrons and holes are confined in one dimension and they are free to move only in two dimension. Therefore this enhances the radiative recombination rates of the carriers, which leads to high emission efficiency. To date, their crystal qualities have been drastically improved, and consequently the internal quantum efficiencies (IQEs) have reached 70% at a wavelength of 280 nm [15], 68% at 245 nm [16], and 50% at 250 nm [17]. We have also achieved high-quality Al_xGa_{1-x}N/AlN QWs fabricated on sapphire (0001) substrates by the modified migration enhanced epitaxy (MEE) method [18,19], by which IQEs of 36% and 57% have been achieved at 240 nm and 237 nm, respectively [20–22]. Furthermore, IQEs as high as 69% were realized at room temperature (RT) in AlGa_N/AlN QWs emitting at 247 nm grown by metalorganic vapor phase epitaxy with simultaneous source supply [23]. The reported IQEs [15,17,20–23] are shown in Fig. 1.2 as a function of peak emission wavelength at RT. These IQEs are much lower at shorter wavelengths because of the smaller carrier confinement and localization degree.

Then, let us move on to the current status of optical properties in AlGa_N. So far, several groups have investigated the optical properties of AlGa_N films, in particular localization characteristics [24–27]. Exciton localization, which is caused by statistically unavoidable alloy disorder effect and additional Al compositional fluctuation, is one of the most important characteristics in AlGa_N films. Localization of carriers/excitons is favorable for the emission efficiency, because it prevents the trapping into nonradiative recombination centers (NRCs). However, exciton localization causes inhomogeneous broadening. The localization energy and linewidth have the maximum value at $x \sim 0.80$ [28]. On the other hand, the optical properties related to exciton localization have not been investigated yet in Al-rich AlGa_N QWs. For Al-rich AlGa_N, the localization effects are notable due to the small exciton Bohr radii. Furthermore, in QW structures, the well width fluctuation also causes the localization and inhomogeneous broadening in

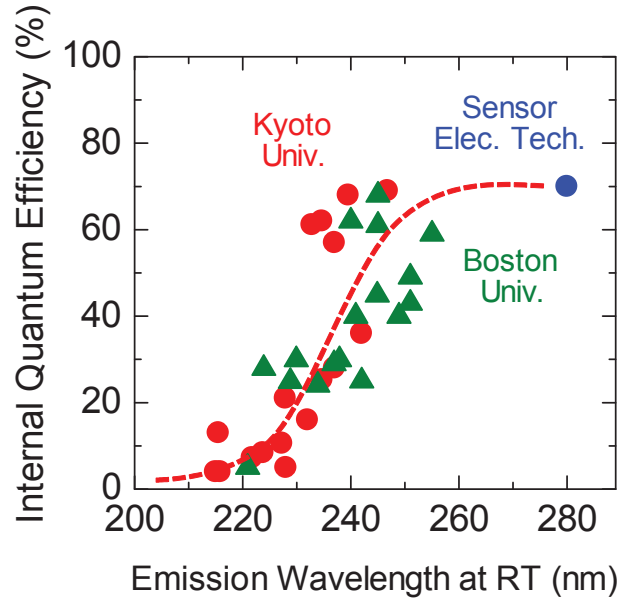


Figure 1.2: Reported internal quantum efficiencies in AlGaIn QWs as a function of emission wavelength at RT. The broken line is given only to indicate the data trend.

addition to the above-mentioned fluctuations. Thus, the optical properties are more complicated and localization characteristics are remarkable in Al-rich AlGaIn/AlN QWs. Because the actual light emitting devices are generally QW structures, a complete understanding of localization is essential for their optimization.

1.4 Current Status and Challenges of AlGaIn-based DUV Optical Devices

Light Emitting Diodes

Despite the high IQEs, the EQEs of AlGaIn-based LEDs are less than $\sim 10\%$ as shown in Fig. 1.3 [10, 29–43]. It is noteworthy that the record high EQE of blue-InGaIn LED is 84.3% at an emission wavelength of 444 nm [44]. Moreover, EQEs are also much lower at shorter emission wavelength. EQE is the product of IQE, light extraction efficiency (LEE) and carrier injection efficiency (CIE). Therefore, it is important to consider the contribution of each efficiency to the low EQE. Low LEE of 8% has been reported [32] due to the absorption loss in p-GaN, which is for compensating the poor electrical conductivity in p-AlGaIn, the absorption loss in p-type electrode, and the total reflection loss. CIE is also very low due to low hole concentrations in p-AlGaIn because of large acceptor (Mg) activation energies (GaN: 245 meV [45], AlN: 630 meV [6]). Therefore, it is considered that all these problems are associated with p-AlGaIn.

Laser Diodes

Recently, the lasing wavelength of the electrically-driven laser diodes (LDs) has been shortened to UV-A region [8, 46–48]. However, AlGaIn-based LDs for DUV region have not been achieved

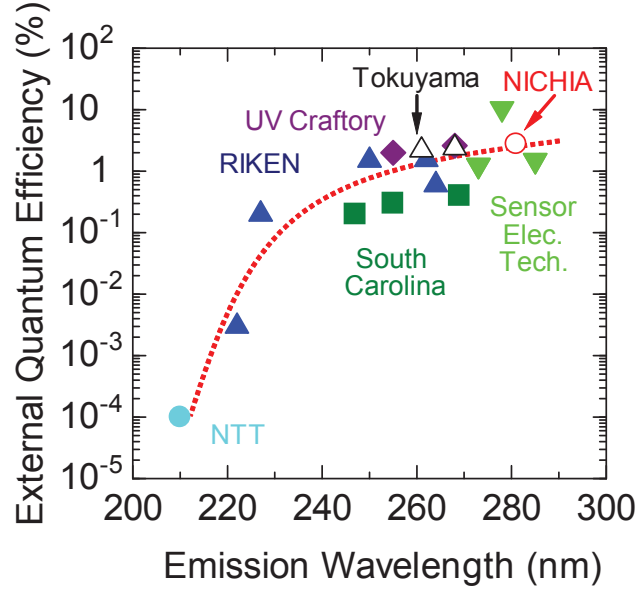


Figure 1.3: Reported external quantum efficiencies in AlGaIn based DUV-LEDs as a function of emission wavelength. The broken line is given only to indicate the data trend.

yet due to the poor characteristics of p-type AlGaIn like the same manner as LEDs. The minimum wavelength of LD is 336 nm [47, 48].

Electron Beam Pumped Optical Devices

To avoid the problems associated with p-type AlGaIn, several groups have proposed a promising alternative, electron beam (EB) pumped nitride semiconductor based light sources [9, 49–52]. UV light emitting devices using EB-pumped AlGdN has been reported at emission wavelength of 315 nm [49, 50]. These devices aim to replace the emission line of Hg vapor lamps. For DUV region, Watanabe *et al.* have first fabricated a handheld device using boron nitride (BN) powders with an emission wavelength of 225 nm, a maximum output power of 1 mW, and a power efficiency (PE) of 0.6% [9]. Additionally, it has been demonstrated that a silicon-doped AlGaIn bulk-like film excited by EB exhibits an output power of 2.2 mW at 247 nm with a PE of 0.22% [51, 52]. However, as well as LEDs, their performances are still insufficient for practical applications.

1.5 Research Purpose/Motivation

To obtain high-quality AlGaIn QWs and DUV optical devices with high emission efficiencies, it is important to understand the optical properties in Al-rich AlGaIn QWs adequately. However, except our group, the optical properties in Al-rich AlGaIn QWs have not been investigated, due to the lack of evaluation methods and/or high-quality Al-rich AlGaIn/AlN QWs. Additionally, many factors should be considered for the QWs with ternary alloy active layers ⁴. Considering the above, we thought that the variety of experimental methods should be developed.

⁴The factors which should be considered will be discussed in Chapter 2.

In this way, the main purpose of this study is to comprehensively understand the emission mechanisms from weak excitation condition to strong excitation condition in Al-rich AlGaIn/AlN QWs. To achieve this, in addition to the conventional photoluminescence (PL) spectroscopy using an ArF* excimer laser, we propose the weak excitation PL spectroscopy using a Xe₂* excimer lamp. Moreover, we perform the temperature dependent cathodoluminescence (CL) mapping studies to assess the exciton dynamics directly.

The other main purpose is to obtain the guideline for the design of DUV optical devices based on EB-pumped AlGaIn/AlN QWs. As described in the previous section, the solid-state DUV lasers have not been achieved yet. Toward the application of DUV optical devices in particular DUV lasers, we discuss the optical gain characteristics and the optical properties under EB-pumping. We propose to use AlGaIn MQWs as a phosphor, because a QW structure has higher radiative recombination probabilities, lower re-absorption loss than a bulky film, and higher LEE due to the quantum confinement.

1.6 Outline of This Thesis

In this thesis, the emission mechanisms of Al-rich AlGaIn/AlN QWs are mainly presented. The contents are systematically divided into seven chapters, as described below.

In chapter 1, the background of this study is introduced. After the history of UV light is introduced, current DUV light sources and AlGaIn based solid-state DUV emitters are explained. In the end of this chapter, the purpose and motivation of this study are presented.

In chapter 2, basic optical theories and properties in AlGaIn/AlN QWs are discussed. First, the optical theories of binary nitride semiconductors are explained. Then, the properties of AlGaIn films and QW structures are described. In this section, some calculations are performed to analyze the experimental data in AlGaIn QWs.

From chapter 3 to chapter 4, the emission mechanisms of Al-rich AlGaIn/AlN QWs are presented with a focus on the exciton localization phenomena. In Chapter 3, exciton localization phenomena due to the potential fluctuations are discussed in Al-rich AlGaIn/AlN QWs. The well width and Al composition dependences of the exciton localization characteristics are evaluated by the temperature dependent weak excitation PL and CL mapping measurements. In chapter 4, the emission mechanisms under intermediate and strong excitation conditions are discussed, based on the results in the weak excitation PL. Moreover, time-resolved PL (TRPL) measurements are performed to investigate the carrier dynamics in Al-rich AlGaIn/AlN QWs in detail.

From chapter 5 to chapter 6, the optical properties associated with the application of DUV solid-state emitters by EB pumping are presented. In chapter 5, the optical gain characteristics are described. The well width dependence of the optical gain properties and Al compositional dependence of the polarization properties are discussed. In chapter 6, the optical properties of Al-rich AlGaIn/AlN QWs pumped by EB are discussed toward the realization of the incoherent DUV optical devices with high emission efficiencies. These devices are the UV light sources without p-type AlGaIn which causes the low EQEs in AlGaIn-based DUV LEDs.

Finally, the conclusion of this thesis and future works are explained in chapter 7.

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Chapter 2

Fundamental Optical Properties in AlGaN QWs

2.1 Introduction

In chapter 2, the fundamental optical properties are discussed. First, the properties of AlN and GaN are briefly introduced. Secondly, the properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$, which is a ternary alloy semiconductor of AlN and GaN, are discussed with a focus on a QW structure. We perform some computational studies necessary to analyze the experimental results in Al-rich AlGaN/AlN QWs. Well width dependence of exciton Bohr radius is calculated by the variational method for the case of $x = 0.79$. After that, potential fluctuations were quantified solving the Schrödinger equations. Then, peak shifts of AlGaN/AlN QWs were calculated under intermediate and high excitation conditions as a function of carrier density. Finally, the properties of p-type AlGaN such as the acceptor ionization energy and hole concentration are explained.

2.2 Optical Properties of AlN and GaN

2.2.1 Band Structure

Nitride semiconductors such as AlN and GaN form the wurtzite structure (point group: C_{6v}) shown in Fig. 2.1 as a stabilized structure. For the nitride semiconductors, the conduction states transform like s-functions while the valence states transform like p-functions. $|X\rangle, |Y\rangle$ like wavefunctions and $|Z\rangle$ like wavefunction are split by the anisotropic crystal field. Using the irreducible representations of the group theory, the single-degenerate state is labeled as Γ_1 ($|Z\rangle$ like wavefunction), whereas the twofold-degenerate state is labeled as Γ_6 ($|X\rangle$ and $|Y\rangle$ like wavefunctions). Considering the spin-orbit interaction, the spin component (Γ_7) should be also considered. As a result, the twofold-degenerate Γ_6 is split into Γ_9 and Γ_7^{-1} , whereas the single-degenerate Γ_1 is labeled as Γ_7^{-2} . Thus, the valence band is split into three bands named heavy-hole band (HH, Γ_9), light-hole band (LH, Γ_7), and crystal-field split-off hole band (CH, Γ_7) by the crystal-field splitting (Δ_{cr}) and spin-orbit interaction (Δ_{so}) near the Γ point in the

¹ $\Gamma_6 \otimes \Gamma_7 = \Gamma_9 \oplus \Gamma_7$

² $\Gamma_1 \otimes \Gamma_7 = \Gamma_7$

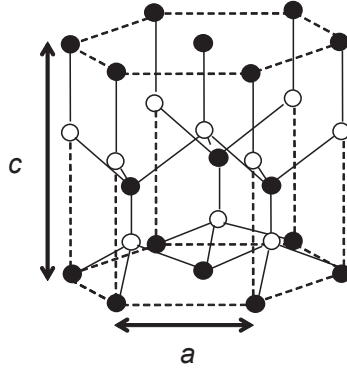


Figure 2.1: Crystal structure of wurtzite semiconductors. Point group of wurtzite structure is C_{6v} .

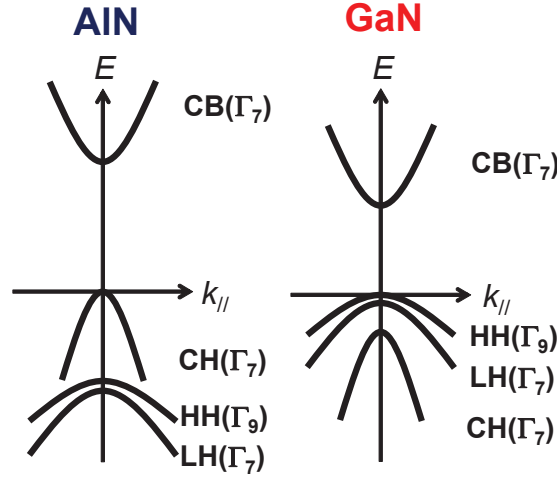


Figure 2.2: Band structures of AlN and GaN. The valence band order of AlN and GaN from top is CH, HH, LH and HH, LH, CH, respectively.

Brillouin zone. Figure 2.2 shows the band structure of AlN and GaN. It has been found that GaN has a positive $\Delta_{cr} = 12$ meV [1,2], while AlN has a large negative $\Delta_{cr} = -212$ meV [3–8]. The crystal-field splitting energy is strongly dependent on the structural parameters; the cell-internal structural parameter u and the ratio between the c -lattice and a -lattice constants c/a , where $u = 0.3819$ and $c/a = 1.601$ for AlN and $u = 0.3768$ and $c/a = 1.625$ for GaN. The lattice of AlN is strongly distorted from that of the ideal wurtzite structure with $u = 0.375$ and $c/a = 1.633$, due to the strong ionicity. In this result, AlN has the large negative crystal-field splitting energy. Consequently, the valence band ordering from the top is HH, LH, CH for GaN and CH, HH, LH for AlN.

2.2.2 Selection Rule of Optical Transition

From Fermi's golden rule, the optical transition rate w_s from the initial state $|\psi_i\rangle$ to the final state $|\psi_f\rangle$ is written as

$$w_s = \frac{2\pi}{\hbar} |\langle \psi_f | H_s | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega), \quad (2.1)$$

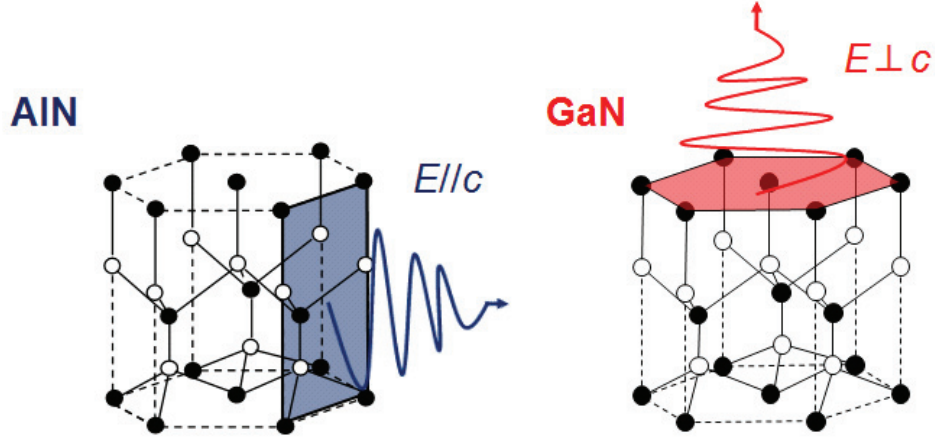


Figure 2.3: Polarization properties of AlN and GaN. The dominant directions of light extractions are $\mathbf{E} \parallel c$ for AlN and $\mathbf{E} \perp c$ for GaN, due to the difference of the valence band ordering.

where H_s is the perturbation hamiltonian of photon, and $E_{i(f)}$ is the energy of the initial (final) state. It is noted that δ function represents the conservation law of energy. Equation (2.1) indicates that the matrix element $\langle \psi_f | H_s | \psi_i \rangle$ decides whether the optical transition is allowed or forbidden. The irreducible representations of ψ_i , ψ_f and H_s are defined as Γ_i , Γ_f and Γ_s , respectively. From the group theory, we obtain the relationship described below [9–11],

$$\langle \psi_f | H_s | \psi_i \rangle \begin{cases} \neq 0 & (\text{if } \Gamma_1 \text{ is contained in } \Gamma_f \otimes \Gamma_s \otimes \Gamma_i) \\ = 0 & (\text{otherwise}) \end{cases}. \quad (2.2)$$

The irreducible representations of conduction band (CB), HH, LH and CH are Γ_7 , Γ_9 , Γ_7 and Γ_7 , respectively. Therefore, we obtain the selection rules³ of

$$\Gamma_7 \text{ (CB)} \longleftrightarrow \Gamma_9 \text{ (HH)} \quad \begin{cases} \text{allowed} & (\text{if } \mathbf{E} \perp c) \\ \text{forbidden} & (\text{if } \mathbf{E} \parallel c) \end{cases}, \quad (2.3)$$

$$\Gamma_7 \text{ (CB)} \longleftrightarrow \Gamma_7 \text{ (LH)}, \Gamma_7 \text{ (CH)} \quad \begin{cases} \text{allowed} & (\text{if } \mathbf{E} \parallel c) \\ \text{forbidden} & (\text{if } \mathbf{E} \perp c) \end{cases}. \quad (2.4)$$

The polarization properties of AlN and GaN are influenced by these selection rules. Because the top valence band is CH, Γ_7 (HH, Γ_9) for AlN (GaN), the polarization of light is $\mathbf{E} \parallel c$ ($\mathbf{E} \perp c$) (see Fig. 2.3). Therefore, the directions of light extractions are different for AlN and GaN. For AlN, it is noted that the LEE is low due to the polarization properties, which is the disadvantage for the device applications.

³The irreducible representations of photons with the polarization of $\mathbf{E} \parallel c$ and $\mathbf{E} \perp c$ are Γ_1 and Γ_5 , respectively.

2.2.3 Temperature Dependence of Optical Properties

Bandgap Energy

As explained in Chap. 1, AlN and GaN have the direct bandgap energies of 6.0 eV and 3.4 eV at RT, respectively. The bandgap energy has the temperature dependence due to the interaction between electrons and optical phonons. The bandgap energy at a given temperature $[E(T)]$ is obtained by the Bose-Einstein (B-E) equation [12],

$$E(T) = E(0) - \frac{2\alpha_B}{\exp(\Theta/T) - 1}, \quad (2.5)$$

where α_B is the strength of the electron-phonon coupling, and Θ is the average phonon temperature (Einstein characteristic temperature), which is related to Debye Temperature Θ_D ; $\Theta_D = (4/3)\Theta$ [13].

Linewidth

Linewidth of a spectrum is generally characterized by full width at half maximum (FWHM). As the temperature is increased, FWHM is increased due to the interaction between electrons and phonons. FWHM at a certain temperature $[\Gamma(T)]$ is given by [14],

$$\Gamma(T) = \Gamma_0 + \gamma_A T + \frac{\Gamma_{LO}}{\exp(\hbar\omega_{LO}/k_B T) - 1}, \quad (2.6)$$

where Γ_0 is the temperature independent homogeneous broadening, γ_A is the coupling constant between electrons and acoustic phonons, Γ_{LO} is the coupling constant between electrons and longitudinal-optical (LO) phonons, and $\hbar\omega_{LO}$ is the energy of an LO phonon.

2.2.4 Exciton

Electrons and holes are bound by the Coulomb attraction, because they have charges with the opposite signs. Electron-hole pair bound by the Coulomb attraction is called exciton. In the case of AlN and GaN, the effective mass is large and thereby the exciton binding energy is larger than thermal energy at RT. This indicates that excitons are stable at even RT for AlN and GaN.

For the case of excitons in a bulk semiconductor, the Schrödinger equation is described by

$$\left[-\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial \mathbf{r}_e^2} - \frac{\hbar^2}{2m_h} \frac{\partial^2}{\partial \mathbf{r}_h^2} - \frac{e^2}{4\pi\epsilon_0\epsilon_r|\mathbf{r}_e - \mathbf{r}_h|} \right] \Psi(\mathbf{r}_e, \mathbf{r}_h) = E\Psi(\mathbf{r}_e, \mathbf{r}_h), \quad (2.7)$$

where $m_{e(h)}$ is the effective mass of electron (hole), and $\epsilon_{0(r)}$ is the vacuum (relative) permittivity. Here, we replace $\mathbf{r}_e$ and $\mathbf{r}_h$ to new coordinates; a center of mass (CM) coordinate and relative coordinate defined by

$$\mathbf{R} = \frac{m_h \mathbf{r}_e + m_e \mathbf{r}_h}{M}, \quad (2.8)$$

$$\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h, \quad (2.9)$$

where $M = m_e + m_h$. Then, the Schrödinger Eq. (2.7) is divided into two equations,

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{d\mathbf{R}^2} \right] \psi(\mathbf{R}) = E_R \psi(\mathbf{R}), \quad (2.10)$$

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{d\mathbf{r}^2} - \frac{e^2}{4\pi\epsilon_0\epsilon_r r} \right] \phi(\mathbf{r}) = E_r \phi(\mathbf{r}), \quad (2.11)$$

where $\mu = (m_e^{-1} + m_h^{-1})^{-1}$,⁴ $\Psi(\mathbf{r}_e, \mathbf{r}_h) = \psi(\mathbf{R})\phi(\mathbf{r})$ and $E = E_R + E_r$. From Eq. (2.10), we obtain

$$E_R = \frac{\hbar^2 K^2}{2M}, \quad \psi(\mathbf{R}) = N_R \exp(i\mathbf{K} \cdot \mathbf{R}), \quad (2.12)$$

where N_R is the normalization factor. Equation (2.11) is the same form as the Schrödinger equation of a hydrogen atom. Therefore,

$$E_r = E_g - \frac{E_x}{n^2}, \quad \phi(\mathbf{r}) = N_r R_{nl}(r) Y_{lm}(\theta, \phi), \quad (2.13)$$

where N_r is the normalization factor, R_{nl} is the associated Laguerre polynomial, and $Y_{lm}(\theta, \phi)$ is the spherical harmonic function. E_x is the exciton binding energy described by

$$E_x = E_x^0 \frac{\mu}{m_0} \frac{1}{\epsilon_r^2}, \quad (2.14)$$

where $E_x^0 = 13.6$ eV is the binding energy of a hydrogen atom. Combining the above results of CM and relative motions, we obtain

$$E = E_g + \frac{\hbar^2 K^2}{2M} - \frac{E_x}{n^2}, \quad (2.15)$$

$$\Psi = N_R N_r \exp(i\mathbf{K} \cdot \mathbf{R}) R_{nl}(r) Y_{lm}(\theta, \phi). \quad (2.16)$$

Especially, for the case of the ground (1s) state,

$$E = E_g + \frac{\hbar^2 K^2}{2M} - E_x, \quad (2.17)$$

$$\Psi = N_R N_r \exp(i\mathbf{K} \cdot \mathbf{R}) \exp\left(-\frac{r}{a_B}\right). \quad (2.18)$$

a_B is the exciton Bohr radius described by

$$a_B = a_B^0 \frac{m_0}{\mu} \epsilon_r, \quad (2.19)$$

where $a_B^0 = 0.053$ nm is the Bohr radius of a hydrogen atom.

⁴ μ is called reduced mass

2.3 Optical Properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$

2.3.1 Vegard's Law

Material parameters A of a ternary alloy $\text{Al}_x\text{Ga}_{1-x}\text{N}$ composed of binary semiconductors AlN and GaN are generally obtained by the linear interpolation between those of AlN and GaN [15]. Therefore,

$$A_{\text{Al}_x\text{Ga}_{1-x}\text{N}} = xA_{\text{AlN}} + (1-x)A_{\text{GaN}}. \quad (2.20)$$

This relationship is called Vegard's law. However, this relationship is not true for the bandgap energy (E_g). In the case of the bandgap energy,

$$E_{g,\text{Al}_x\text{Ga}_{1-x}\text{N}} = xE_{g,\text{AlN}} + (1-x)E_{g,\text{GaN}} - bx(1-x), \quad (2.21)$$

where $b = 0.98$ eV [16] is a bowing parameter.

2.3.2 Energy Levels in AlGaIn

Using the $\mathbf{k} \cdot \mathbf{p}$ perturbation theory for the strained wurtzite semiconductors [17,18], the valence band energies (E_0^1, E_0^2, E_0^3) at $\mathbf{k} = 0$ are obtained by

$$E_0^1 = E_v^0 + \Delta_1 + \Delta_2 + \theta_\epsilon + \Delta_\epsilon, \quad (2.22)$$

$$E_0^2 = E_v^0 + \frac{\Delta_1 - \Delta_2 + \theta_\epsilon}{2} + \lambda_\epsilon + \sqrt{\left(\frac{\Delta_1 - \Delta_2 + \theta_\epsilon}{2}\right)^2 + 2\Delta_3^2}, \quad (2.23)$$

$$E_0^3 = E_v^0 + \frac{\Delta_1 - \Delta_2 + \theta_\epsilon}{2} + \lambda_\epsilon - \sqrt{\left(\frac{\Delta_1 - \Delta_2 + \theta_\epsilon}{2}\right)^2 + 2\Delta_3^2}, \quad (2.24)$$

where E_0^1, E_0^2 and E_0^3 correspond HH, LH and CH for GaN, and LH, CH and HH for AlN, respectively. Δ_1, Δ_2 and Δ_3 are represented by

$$\Delta_1 = \Delta_{\text{cr}}, \quad \Delta_2 = \Delta_3 = \frac{1}{3}\Delta_{\text{so}}. \quad (2.25)$$

The strain effects Δ_ϵ and θ_ϵ are defined as

$$\Delta_\epsilon = D_1\epsilon_{zz} + D_2(\epsilon_{xx} + \epsilon_{yy}), \quad (2.26)$$

$$\theta_\epsilon = D_3\epsilon_{zz} + D_4(\epsilon_{xx} + \epsilon_{yy}). \quad (2.27)$$

Here, D_i ($i = 1, 2, 3, 4$) is deformation potential. In the case of coherent AlGaIn layers grown on the (0001) plane,

$$\epsilon_{xx} = \epsilon_{yy} = \frac{a_s - a_l}{a_l}, \quad (2.28)$$

$$\epsilon_{zz} = -\frac{2C_{13}}{C_{33}}\epsilon_{xx}, \quad (2.29)$$

where a_s and a_l are lattice constants of substrate and epitaxial layer, and C_{13} and C_{33} are elastic stiffness constants. On the other hand, the conduction band energy is given by

$$E_c^0 = E_v^0 + E_g + \Delta_1 + \Delta_2, \quad (2.30)$$

while the top valence band is E_2^0 (CH) for AlN, therefore

$$E_c^0 = E_2^0 + E_g. \quad (2.31)$$

2.3.3 $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QW Structure

QW is a hetero-structure where there is only one dimensional confinement. The quantum confinement takes place when the well thickness becomes comparable to the de Broglie wavelength of carriers or the exciton Bohr radius. Discrete energy levels called energy subbands are formed by the quantum confinement.

Internal Electrical Field

The internal electrical field in a well layer (E_{int}^w) and a barrier layer (E_{int}^b) along the growth direction (z direction) is expressed by the piezoelectric polarization (P_z^{pz}) and the spontaneous polarization (P_z^{sp}). In the case of multiple QWs (MQWs), the electrical field in well and barrier layers are calculated from the continuity condition of the electric flux density and the periodic boundary condition [19, 20],

$$E_{\text{int}}^w = \frac{L_b \{ (P_{z,b}^{\text{pz}} + P_{z,b}^{\text{sp}}) - (P_{z,w}^{\text{pz}} + P_{z,w}^{\text{sp}}) \}}{L_w \varepsilon_b + L_b \varepsilon_w}, \quad (2.32)$$

$$E_{\text{int}}^b = -\frac{L_w}{L_b} E_{\text{int}}^w, \quad (2.33)$$

where ε is the dielectric constant, L is the thickness of layer, and the subscript b (w) represents well (barrier). In the case of single QWs (SQWs), from the conditions of $L_b = \infty$ and $P_{z,b}^{\text{pz}} = 0$,

$$E_{\text{int}}^w = \frac{P_{z,b}^{\text{sp}} - P_{z,w}^{\text{sp}} - P_{z,w}^{\text{pz}}}{\varepsilon_w}, \quad (2.34)$$

$$E_{\text{int}}^b = 0. \quad (2.35)$$

Here, $P_{z,w}^{\text{pz}}$ is obtained by

$$P_{z,w}^{\text{pz}} = \frac{2(a_w - a_b)}{a_b} \left(e_{31} - e_{33} \frac{C_{13}}{C_{33}} \right), \quad (2.36)$$

where e_{31} and e_{33} are the piezoelectric constants.

Quantum Confinement Stark Effect

Without an internal electric field, electrons and holes in QWs occupy the discrete states of energy subbands. When an internal electric field is applied, the triangle potential is formed

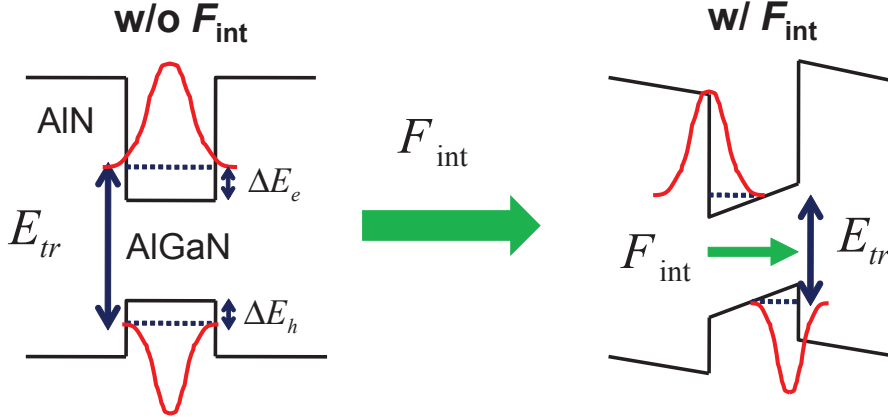


Figure 2.4: The schematic image of QCSE. With an internal electrical field F_{int} , the wavefunctions of electron and hole spatially separate and the transition energy E_{tr} is redshifted.

and the transition energy is redshifted, as shown in Fig. 2.4. Additionally, the internal electric field pushes electrons and holes to the opposite sides of the well layer, and consequently the overlap integral of the wavefunctions between electrons and holes is reduced. This indicates that the radiative recombination rate is reduced, because the radiative recombination rate w_r is proportional to the squared overlap integral $|\langle\psi_e|\psi_h\rangle|^2$. Figure 2.5 shows the squared overlap integral $|\langle\psi_e|\psi_h\rangle|^2$ in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs as a function of well width. $|\langle\psi_e|\psi_h\rangle|^2$ is drastically reduced by the QCSE in particular for the wide QWs. These effects within the internal electrical field are called the quantum confined Stark effect (QCSE), which is important in order to understand the optical properties in nitride semiconductors.

2.3.4 Schrödinger Equations of AlGaN QWs

Schrödinger Equations of Electrons and Holes

The quantum confinement with the internal electrical field F_{int} can be calculated solving the one-dimensional Schrödinger equation,

$$\left(-\frac{\hbar^2}{2m_i} \frac{d^2}{dz_i^2} + eF_{\text{int}}z_i + V_i(z_i) \right) \psi_i(z_i) = E_i\psi_i(z_i), \quad (2.37)$$

where E and V are the energy of carrier and potential energy, respectively. It is noteworthy that the electrostatic potential is negligible under weak excitation condition and the excitonic effect is not included in this calculation. The transition energy in QWs is calculated by

$$E_{\text{tr}} = E_g + E_i + E_h - eF_{\text{int}}L_w, \quad (2.38)$$

where $eF_{\text{int}}L_w$ is due to the polarization effect.

Schrödinger Equation of Exciton

In the QW structure, the exciton Bohr radius and binding energy are strongly dependent on the quantum confinement effect and the internal electrical field. The Hamiltonian of an exciton

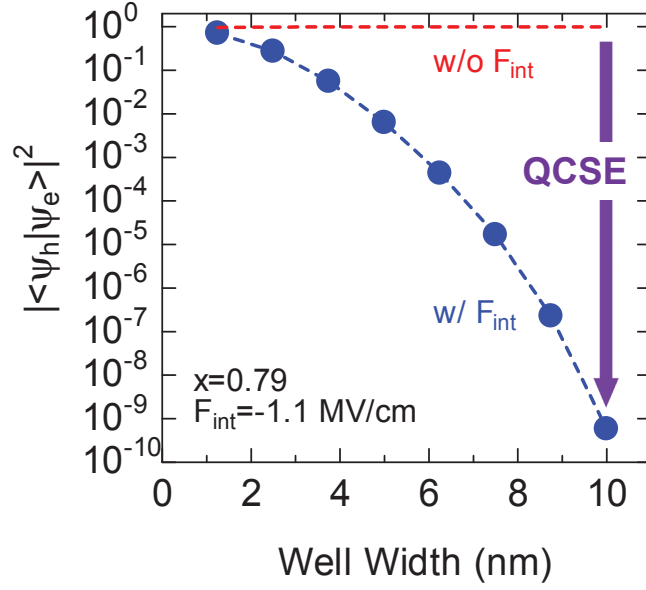


Figure 2.5: Well width dependence of the squared overlap integral $|\langle\psi_e|\psi_h\rangle|^2$ in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with and without internal electrical field F_{int} .

in the well layer is given by [21]

$$\mathcal{H} = -\frac{\hbar^2}{2} \frac{\partial}{\partial z_e} \frac{1}{m_e(z_e)} \frac{\partial}{\partial z_e} - \frac{\hbar^2}{2} \frac{\partial}{\partial z_h} \frac{1}{m_h(z_h)} \frac{\partial}{\partial z_h} - \frac{\hbar^2}{2\mu} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right) - \frac{e^2}{4\pi\epsilon_0\epsilon_r\sqrt{\rho^2 + (z_e - z_h)^2}} + V_e(z_e) + V_h(z_h) + eF_{\text{int}}(z_e)z_e - eF_{\text{int}}(z_h)z_h, \quad (2.39)$$

where ρ is in-plane relative coordinate. We solve the Schrödinger equation with this Hamiltonian by the variational method. We set a trial envelope function with a reference of Eq. (2.18) and envelope functions within QW structures,

$$\Psi(z_e, z_h, \rho) = N_c \psi_e(z_e) \psi_h(z_h) \exp \left(-\frac{\sqrt{\rho^2 + (z_e - z_h)^2}}{\alpha} \right). \quad (2.40)$$

Here, N_c is the normalization factor and

$$\psi_e(z_e) = \begin{cases} \exp(-\beta_e z_e) \cos(k_e z_e) & \left(|z_e| \leq \frac{L_z}{2} \right) \\ \exp(-\beta_e z_e) \exp(-q_e |z_e|) & \left(|z_e| > \frac{L_z}{2} \right) \end{cases}, \quad (2.41)$$

$$\psi_h(z_h) = \begin{cases} \exp(\beta_h z_h) \cos(k_h z_h) & \left(|z_h| \leq \frac{L_z}{2} \right) \\ \exp(\beta_h z_h) \exp(-q_h |z_h|) & \left(|z_h| > \frac{L_z}{2} \right) \end{cases}, \quad (2.42)$$

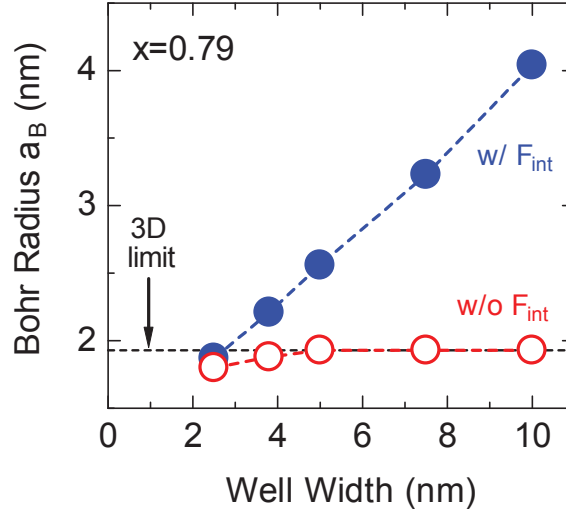


Figure 2.6: Well width dependence of the calculated exciton Bohr radius both with and without the internal electrical field F_{int} in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. The three dimensional exciton Bohr radius in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}$ is also shown.

where α , β_e and β_h are variational parameters. From the boundary conditions at $z_i = \pm L_z/2$ ($i = e, h$), we obtain three equations described below,

$$\begin{cases} k_i^2 = \frac{2m_i V_i}{\hbar^2} \cos^2\left(\frac{k_i L_z}{2}\right) \\ q_i = k_i \tan\left(\frac{q_i L_z}{2}\right) \\ A_i = \exp\left(\frac{q_i L_z}{2}\right) \cos\left(\frac{k_i L_z}{2}\right) \end{cases} . \quad (2.43)$$

Solving the above equations, k_i , q_i and A_i can be obtained. From the principle of the variational method, we should calculate α , β_e and β_h in the condition that $\langle \Psi | \mathcal{H} | \Psi \rangle$ has the minimum value. The obtained α corresponds the exciton Bohr radius a_B .

Figure 2.6 shows the well width dependence of the exciton Bohr radius a_B with and without internal electrical field in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. In the absence of the internal electrical field, a_B is gradually increased and comes close to a constant value due to the smaller quantum confinement effect, as the well width is increased. This value is the three dimensional (3D) exciton Bohr radius described by Eq. (2.19). On the other hand, when the internal electric field is applied, the exciton Bohr radius is significantly increased as the well width is increased. This is because the Coulomb attraction is reduced due to the spatial separation between electrons and holes.

2.3.5 Potential Fluctuation and Inhomogeneous Broadening

In reality, there are various inhomogeneities in the QW structures; well width fluctuation, compositional fluctuation, and statistically unavoidable alloy disorder effect. These inhomogeneities cause the potential fluctuation. The optical properties are highly influenced by the potential fluctuation.

tuations, that is, carriers/excitons are localized or thermally delocalized. Additionally, potential fluctuations broaden the linewidth of a spectrum (inhomogeneous broadening). Therefore, it is important to understand the potential fluctuations to assess the emission mechanisms in QW structures. These potential fluctuations can be experimentally investigated by the temperature dependence of PL measurements [22]. As temperature is increased from very low temperature, the peak shift was blueshifted, because carriers/excitons are delocalized from the potential minima. Here, localization energy is defined by the difference between experimental peak energy and calculational peak energy by the B-E equation. In this section, each potential fluctuation is quantified, based on the Schrödinger equations.

Well Width Fluctuation

In general, it is difficult to fabricate the QW structure with perfectly uniform interfaces. Therefore, the well widths are different from place to place. To evaluate the well width fluctuation quantitatively, we consider two regions (region A and region B) where the well width differs by ΔL_w ($\pm\Delta L_w/2$). We calculate the transition energy in each region ($E_{\text{tr,A}}^{\text{well}}, E_{\text{tr,B}}^{\text{well}}$) by the Schrödinger equation described in the previous section, and then define the well width fluctuation $\Delta E_{\text{tr}}^{\text{well}}$ as

$$\Delta E_{\text{tr}}^{\text{well}} = E_{\text{tr,A}}^{\text{well}} - E_{\text{tr,B}}^{\text{well}}. \quad (2.44)$$

Al Compositional Fluctuation

We calculate the Al compositional fluctuation $\Delta E_{\text{tr}}^{\text{comp}}$ with the same method as the well width fluctuation. Two regions (region C and region D) where the Al composition differs by Δx ($\pm\Delta x/2$) are considered and then $\Delta E_{\text{tr}}^{\text{comp}}$ is defined by

$$\Delta E_{\text{tr}}^{\text{comp}} = E_{\text{tr,C}}^{\text{comp}} - E_{\text{tr,D}}^{\text{comp}}. \quad (2.45)$$

Statistically Unavoidable Alloy Disorder Effect

In ternary alloys, random distribution of atoms (cations or anions) causes the linewidth broadening and the shallow localization of excitons like the Anderson localization. This indicates that the statistically unavoidable alloy disorder effect exists even if the ternary alloy is perfectly fabricated. Let us consider a case of $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}$ as an example. Figure 2.7 shows a schematic figure of alloy disorder effect for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}$. The probability of finding an Al atom on any cation side is given by the Al composition x . The sample volume is represented by the exciton volume, which is expressed by

$$V_{\text{exc}} = 8\pi a_B^3, \quad (2.46)$$

from the statistical model reported by Zimmermann [23]. Within the exciton volume, there are cations with a number of KV_{exc} , where K is the density of cations. The probability $p(n)$ that the number of Al atom in the exciton volume is n is obtained by the binominal distribution [24],

$$p(n) = \binom{KV_{\text{exc}}}{n} x^n (1-x)^{KV_{\text{exc}}-n}. \quad (2.47)$$

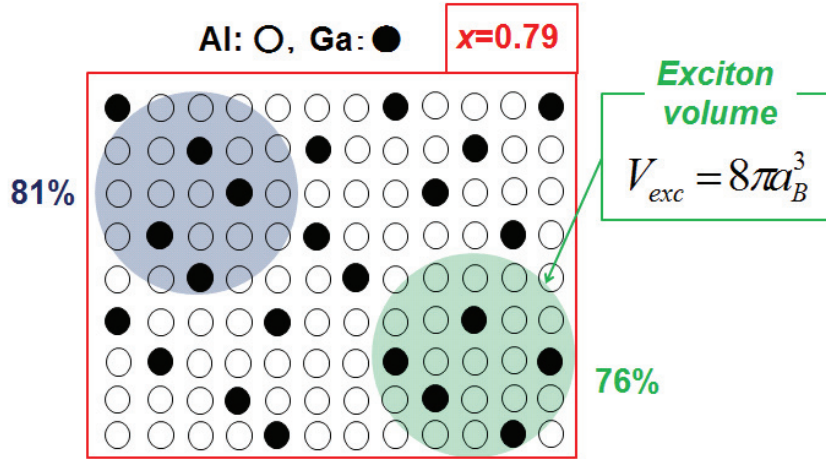


Figure 2.7: Schematic image of statistically unavoidable alloy disorder effect for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}$. Opened and closed circles show Al and Ga atoms, respectively. In the exciton volume $V_{\text{exc}} = 8\pi a_B^3$, there are cations with a number KV_{exc} . By statistically random distribution, the local Al compositions are different from place to place, such as 81% for blue region and 76% for green region.

From the central limit theorem, this binominal distribution is approximated by the standard distribution.⁵ Therefore, we obtain

$$\sigma(x) = \frac{dE_g}{dx} \sqrt{\frac{x(1-x)}{KV_{\text{exc}}}}, \quad (2.48)$$

as the standard energy deviation due to the alloy disorder effect.

Figure 2.8 shows Al composition dependence of the standard energy deviation due to the alloy disorder effect for HH and CH bands in AlGaIn. Because of the difference between HH and CH bands, the alloy disorder effect for HH is larger than that for CH.

Summary

Figure 2.9 shows the summary of each potential fluctuation described above in $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs with $x = 0.79$.⁶ It was found that the well width fluctuation and the alloy disorder effect become larger, while the Al compositional fluctuation becomes smaller, as the well width becomes narrower.

⁵This is a good approximation because of $KV_{\text{exc}} \gg 1$.

⁶1 ML is corresponded to $c/2$.

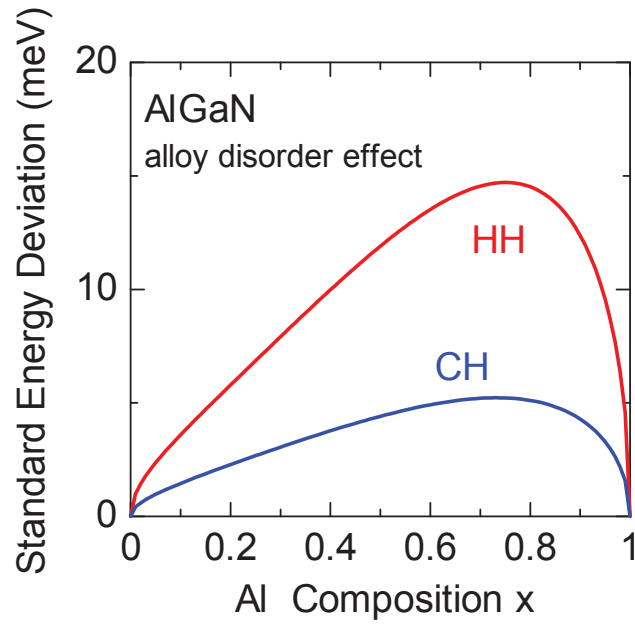


Figure 2.8: Al composition dependence of the standard energy deviation due to the alloy disorder effect for HH and CH bands in AlGaN.

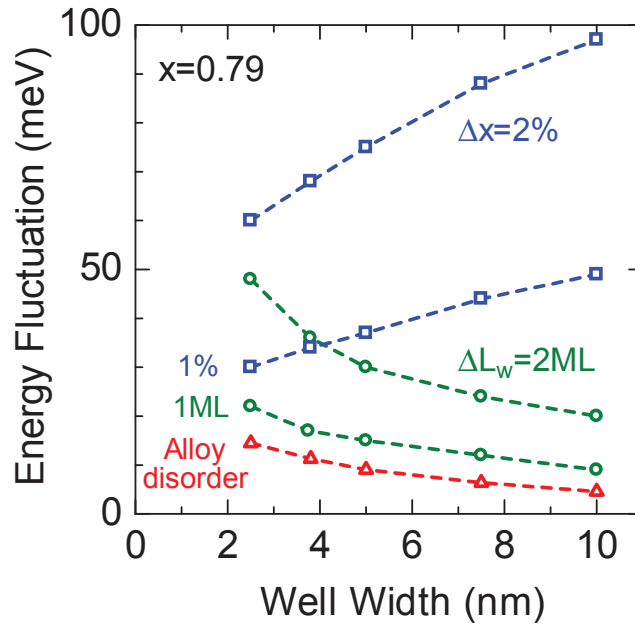


Figure 2.9: Well width dependence of calculated potential fluctuations in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW. As examples, well width fluctuations with $\Delta L_w = 1$ ML and 2 ML, Al compositional fluctuations with $\Delta x = 1\%$ and 2% , and alloy disorder effect are plotted.

2.4 Polarization Properties in AlGa_xN QWs

In AlGa_xN, interesting optical polarization phenomena occur, because the topmost Γ_7 in AlN is the $|Z\rangle$ -like CH state and Γ_9 in GaN is the $|X \pm iY\rangle$ -like HH state. The emission polarization of AlGa_xN is expected to be switched from $\mathbf{E} \perp c$ to $\mathbf{E} \parallel c$ as Al composition is increased. This turnover of the valence band is strongly dependent on the structure, because the valence band energies are influenced by strain and quantum confinement [25]. Let us discuss the quantitative analysis of polarization properties. Figure 2.10 shows schematic images of the band structures for (a) unstrained AlGa_xN, (b) strained AlGa_xN on AlN, and (c) AlGa_xN/AlN QWs. From Eqs. (2.22) – (2.24), the energy separation between HH and CH is given by

$$E(\text{CH}) - E(\text{HH}) = -\frac{\Delta_{\text{cr}} + \Delta_{\text{so}} + \theta_{\epsilon}}{2} + \sqrt{\left(\frac{\Delta_{\text{cr}} + \Delta_{\text{so}} + \theta_{\epsilon}}{2}\right)^2 - \frac{2}{3}\Delta_{\text{so}}(\Delta_{\text{cr}} + \theta_{\epsilon})}. \quad (2.49)$$

Therefore, $E(\text{CH}) - E(\text{HH})$ can be zero at a certain x , where the polarization switching occurs. As seen from Eq. (2.49), the condition of $E(\text{CH}) - E(\text{HH}) = 0$ corresponds to $\Delta_{\text{cr}} + \theta_{\epsilon} = 0$. In unstrained AlGa_xN, the Al composition at the turnover (x_t) was estimated to be 0.044 from the condition of $\Delta_{\text{cr}} = 0$ ($\theta_{\epsilon} = 0$). For strained AlGa_xN on unstrained AlN, the condition of $\Delta_{\text{cr}} + \theta_{\epsilon} = 0$ provides $x = 0.60$. This increase in x_t can be qualitatively understood by considering the strain effects on valence bands. The in-plane compressive strain in AlGa_xN pushes the $|X \pm iY\rangle$ related bands upward, whereas it is tensile strain along the growth direction which pushes the $|Z\rangle$ related band downward. As a result, the energy separation is decreased and thereby a larger Al composition is necessary for the turnover. An additional factor that can affect the valence-band structure is quantum confinement. Because of the difference of the effective masses between CH and HH (see Appendix A), the energy of CH is drastically lowered by the quantum confinement effect. The change of energy due to the quantum confinement can be calculated by Eq. (2.37).

The experimental characteristics have been reported for AlGa_xN thick layers in which the polarization switched from $\mathbf{E} \perp c$ to $\mathbf{E} \parallel c$ at $x = 0.25$ as the Al composition is increased [26]. This result also implies that the weak surface emission is already observable in AlGa_xN layers with Al compositions as low as 0.25. Moreover, Banal *et al.* reported the systematic polarization properties of coherently-grown Al_xGa_{1-x}N/AlN QWs [27, 28]. The emission with the polarization along $\mathbf{E} \perp c$ is observed up to $x \sim 0.82$, particularly for thinner QWs. This large Al composition for the polarization switch is explained by the in-plane compressive strain and the large quantum confinement. Similar result was reported by Hirayama *et al.* [29]. They demonstrated that the light emission polarized in the direction of $\mathbf{E} \perp c$ can be obtained even when the Al composition of the AlGa_xN QW is as high as 83%.

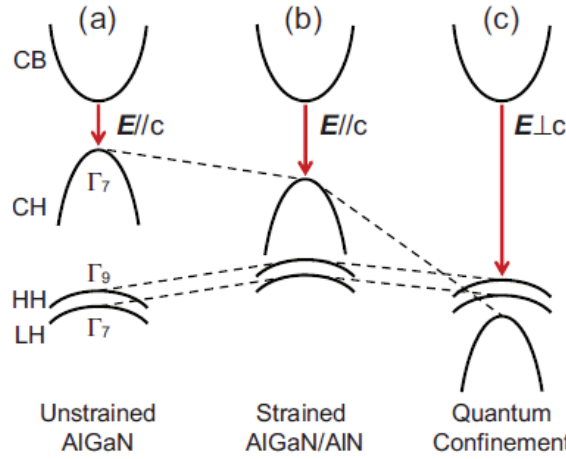


Figure 2.10: Schematic images of band structures for (a) unstrained AlGaIn, (b) strained AlGaIn on AlN, and (c) AlGaIn/AlN QWs. This figure is quoted from Ref. [28].

2.5 Effects of Strong Excitation

The various characteristics occur under strong excitation condition. In this section, the characteristics are presented and then the peak shifts due to their effects are calculated.

Bandgap Renormalization

Figure 2.11 shows schematic images of bandgap renormalization (BGR). If electrons and holes are completely randomly distributed in semiconductors, the Coulomb attraction and repulsion energies cancel. As a result, bandgap energy does not have the dependence on carrier density. However, in reality, carriers are not randomly distributed due to the exchange and correlation interactions at the request of the Pauli's exclusion principle. The exchange and correlation energies increase the average distance between electrons and reduces the total energy of electrons. The same discussion holds for holes. This means that the energy bandgap is shrinked by these interactions. The shrinkage of the bandgap is called BGR. In two dimensional system, the shift due to BGR (ΔE_{BGR}) is given by

$$\Delta E_{\text{BGR}} = -3.1(n^{2\text{D}} a_{\text{B}}^2)^{1/3} E_{\text{x}}, \quad (2.50)$$

where $n^{2\text{D}}$ is the sheet carrier density, and minus means the red shift [30].

Burstein-Moss Shift

The Burstein-Moss shift is enlargement of optical transition energy due to the carrier injection. Injected electrons occupy the bottom of the conduction band, depending on the density of state, and push the quasi Fermi level upward. The same mechanism pushes the quasi Fermi level for holes downward. As a result, the lowest band-to-band transition energy increases as the number of injected carriers increases.

For the current calculation, the density of states for two dimensional system with infinite

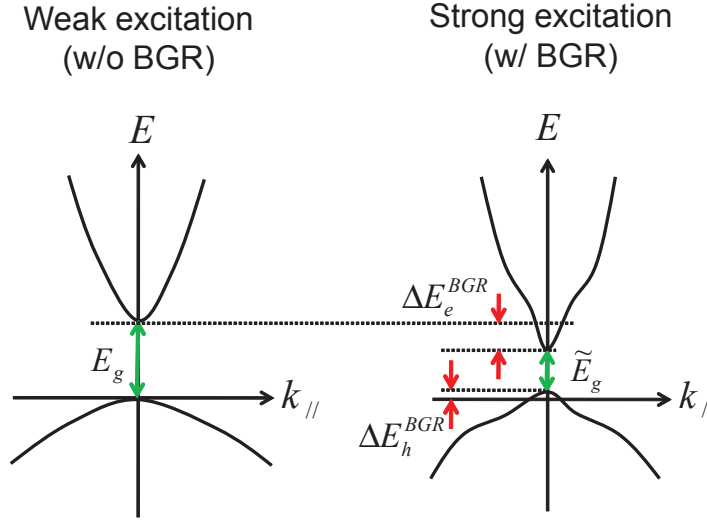


Figure 2.11: Schematic images of BGR. Under strong excitation, the energy bandgap is shrunk by the exchange and correlation interactions.

potential barriers was assumed,

$$\rho_i(E_i) = \sum_n \frac{m_i}{\pi \hbar^2 L_z} H(E_i - E_{ni}), \quad (2.51)$$

where H is the Heaviside function and E_{ni} is the minimum energy of n th subband,

$$E_{ni} = \frac{\hbar^2}{2m_i} \left(\frac{n\pi}{L_z} \right)^2. \quad (2.52)$$

Then, the quasi-Fermi level E_{fi} can be obtained by

$$N = \int f_i(E_i) \rho_i(E_i) dE_i \quad \left(f_i(E_i) = \frac{1}{1 + \exp\{(E_i - E_{fi})/k_B T\}} \right), \quad (2.53)$$

where N is the carrier density. The spontaneous emission rate r_{spon} can be calculated by [31]

$$r_{\text{spon}}(E) = B \int \rho_e(E') f_e(E') \rho_h(E - E') f_h(E - E') dE' \quad \left(B = \frac{n_r e^2 \omega |M_{cv}|^2}{\pi \hbar m_0^2 \varepsilon_0 c_0^3} \right). \quad (2.54)$$

Here, we assume that the matrix element $|M_{cv}|$ is constant. We can calculate the blueshift due to the Burstein-Moss shift by the carrier density dependence of the peak energy of $r_{\text{spon}}(E)$.

Screening Effect of Internal Electrical Field

The piezoelectric and spontaneous polarizations cause the internal electric fields in strained QWs. The electric field spatially separates injected electrons and holes, which, in turn, generates an additional electric field in the inverse direction. Therefore, carrier injection may screen the polarization-induced electric field to enlarge the transition energy. This so-called screening effect was evaluated by solving self-consistently the Schrödinger and Poisson equations described

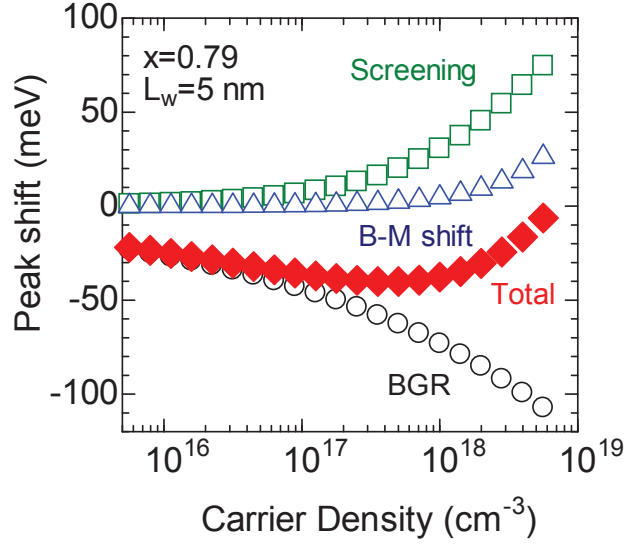


Figure 2.12: Calculated PL peak shifts of $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 5$ nm. The contributions from BGR, B-M shift, and screening effect, and the total shift are plotted.

below,

$$\left(-\frac{\hbar^2}{2m_i} \frac{d^2}{dz_i^2} + eF_{\text{int}}z_i + V_i(z_i) + e\phi(z_i) \right) \psi_i(z_i) = E_i \psi_i(z_i), \quad (2.55)$$

$$\frac{d^2\phi(z)}{dz^2} = -\frac{e}{\varepsilon} (p|\psi_h(z)|^2 - n|\psi_e(z)|^2). \quad (2.56)$$

Summary

Figure 2.12 shows the calculated contributions of the three factors to the peak shifts of Al-GaN/AlN QW with $x = 0.79$ and $L_w = 5$ nm as a function of carrier density. The total shift was obtained by summing these contributions.

2.6 Properties of p-type AlGaN

Hole concentration p of p-type semiconductor is obtained by the electroneutrality condition

$$\frac{p(p + N_D)}{N_A - N_D - p} = \frac{1}{2} N_V \exp\left(-\frac{E_A}{k_B T}\right), \quad (2.57)$$

where $N_{A(D)}$ is the density of acceptors (donors), N_V is the effective density of states of the valence band, and E_A is the activation energy of acceptors. E_A is given by the hydrogen atom model,

$$E_A = E_x^0 \frac{m_h^*}{m_0} \frac{1}{\varepsilon_r^2}. \quad (2.58)$$

Experimentally, $E_A = 630$ meV was reported [32] from temperature dependence of hole concentration estimated by Hall measurements, while $E_A = 245 \pm 25$ meV for GaN was reported [33]. Figure 2.13 shows the Al compositional dependence of hole concentration, assuming the hydrogen atom model. As Al composition is increased, the hole concentration is drastically decreased

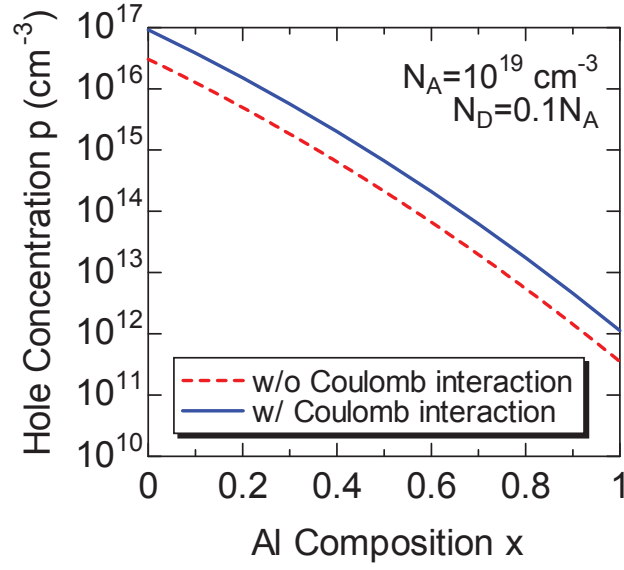


Figure 2.13: Calculated hole concentration p as a function of Al composition x at RT. $N_A = 10^{19} \text{ cm}^{-3}$ and $N_D = 0.1N_A$ are assumed.

due to the larger acceptor activation energy. These calculated results indicate that the p-type Al-rich AlGaIn with high hole concentration is difficult to be achieved in principle.

More strictly speaking, E_A has the ionized acceptor N_A^- dependence, because of the Coulomb interaction between ionized acceptor and hole. Therefore, the N_A^- dependence of E_A is calculated by [34]

$$E_A(N_A^-) = E_A(0) - \Gamma\left(\frac{2}{3}\right) \left(\frac{4\pi}{3}\right)^{1/3} \frac{e^2}{4\pi\epsilon_0\epsilon_r} (N_A^-)^{1/3}, \quad (2.59)$$

where Γ is the Gamma function. In Fig. 2.13, the calculated hole concentration contained the Coulomb effect is also plotted. It was found that the hole concentration are larger thanks to the Coulomb interactions, but still insufficient for diode-based devices.

2.7 Summary

We discussed the fundamental optical properties in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs. The polarization switching occurs in AlGaIn due to the different valence band ordering of GaN and AlN. For AlGaIn QW structures, it is important to understand the QCSE and the localization effect due to the potential fluctuation. Furthermore, we performed some calculations for $\text{Al}_x\text{Ga}_{1-x}\text{N}$. First, the well dependence of potential fluctuations was calculated. As the well width becomes wider, the well width fluctuation and statistically unavoidable alloy disorder effect are smaller, whereas the Al compositional fluctuation is wider. After that, the excitation power dependence of the peak shifts was calculated under strong excitation conditions. Finally, Al compositional dependence of hole concentrations is calculated. The hole concentration of p-type Al-rich AlGaIn was very low. These results suggest that it is difficult to fabricate the AlGaIn-based LEDs with high EQEs. The results described in this section will be used in the discussions after chapter 3.

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Chapter 3

Exciton Localization Characteristics in Al-rich AlGa_N/AlN QWs

3.1 Introduction

In the initial stage of the studies related to optical properties in Al_xGa_{1-x}N, fundamental optical properties of AlGa_N films (not QWs) have been investigated for epitaxial layers grown on foreign substrates (e.g. sapphire, SiC) by temperature dependent PL measurements and time resolved PL (TRPL) measurements [1–13]. Localization of carriers/excitons due to the alloy disorder effect and additional Al compositional fluctuation have been clearly observed in so-called “S-shaped” temperature dependence of peak energy [14]. Additionally, it was reported that the localization energy and FWHM has the maximum value at $x \sim 0.80$ [6, 12]. Furthermore, by means of TRPL measurements, the decay of carriers/excitons can be explained not only due to radiative/nonradiative recombinations, but also due to exciton transfer processes to lower energy states [15].

As for AlGa_N QWs, Al-rich AlGa_N/AlN QW structures have a great potential to realize DUV solid-state emitters with high emission efficiencies. Though IQEs as high as 70% have been achieved at 240–280 nm in AlGa_N QWs, the IQEs are much lower at shorter wavelengths. To obtain higher IQEs, it is important to understand the emission mechanisms in Al-rich AlGa_N/AlN QWs as well as reduction of the threading dislocation densities. This is because the optical properties would provide the significant information for optimizing designs of device structures. However, their optical properties have not been investigated adequately. One of the reasons is that the excitation source is quite limited and is mostly an ArF* excimer laser with a center wavelength of 193 nm [16]. The ArF* excimer laser strongly excites the samples. In such a condition, the localization states may be saturated, and furthermore, the emission mechanisms become complicated due to the occurrence of various transition processes. To investigate the fundamental optical properties in Al-rich AlGa_N/AlN QWs under weak excitation condition, we measured PL using a Xe₂* excimer lamp with a center wavelength of 172 nm. In addition, temperature dependent CL mapping measurements were performed in order to directly observe and assess the exciton dynamics in Al-rich AlGa_N/AlN QWs.

3.2 Experimental Procedure

3.2.1 Samples

The samples were grown on sapphire (0001) substrates by the modified MEE method [17, 18] based on metal-organic vapor phased epitaxy (MOVPE) at a reactor pressure of 76 Torr. The growth sequence of the modified MEE is shown in Fig. 3.1. First, thermal etching of a (0001) sapphire substrate was performed for 10 minutes at 1220 °C. After that, AlN with a thickness of ~ 600 nm was grown on the sapphire substrate at 1200 °C. One cycle of the modified MEE method was composed of 1 s NH₃ supply, 1 s simultaneous supply, and 1 s trimethylaluminum (TMA) supply. Then, Al_{*x*}Ga_{1-*x*}N/AlN QW was fabricated by the same method at a growth temperature T_g [19, 20]. In the case of AlGa_N/AlN QWs, trimethylgallium (TMG) was flew into the reactor simultaneously with TMA, but separately from NH₃. The flow rates of NH₃, TMA and TMG were 893, 4.11, and 8.18 $\mu\text{mol/min}$, respectively. Al_{*x*}Ga_{1-*x*}N/AlN QWs with different x were fabricated by changing T_g . The well width L_w was controlled by the growth time (cycles) and barrier width L_b was constant (15 nm). In the typical case, x and L_w were changed between 0.70 and 0.91 and between 1 nm and 10 nm, respectively.

Let us discuss the structural properties of Al_{*x*}Ga_{1-*x*}N/AlN QWs fabricated by the modified MEE method. Figure 3.2(a) shows the reciprocal space mapping (RSM) of 10-period Al_{0.79}Ga_{0.21}N/AlN MQWs with $L_w = 16$ nm. AlGa_N/AlN QW was coherently grown on underlayer AlN, because the AlGa_N satellite peaks were vertically aligned with the AlN peak. Therefore, it was considered that all of the Al_{*x*}Ga_{1-*x*}N/AlN QWs with both $x \geq 0.79$ and $L_w \leq 16$ nm were coherently grown on the underlayer AlN. To investigate the surface morphology of AlGa_N/AlN QW, the atomic force microscopy (AFM) measurement was performed. The AlGa_N/AlN QW with the atomically-smooth surface and step-terrace structure were achieved, as shown in Fig. 3.2(b). The transmission electron microscope (TEM) bright-field (BF) image shown in Fig. 3.2(c) confirmed successful fabrication of ten-period QWs with the homogeneous well and barrier thicknesses. From the typical X-ray diffraction (XRD) measurements, the densities of screw and edge dislocations were estimated to be $\sim 4.0 \times 10^6 \text{ cm}^{-2}$ and $\sim 7.2 \times 10^8 \text{ cm}^{-2}$, respectively.

3.2.2 Weak Excitation PL Setup

Figure 3.3 shows the experimental setup of our proposed weak excitation PL measurements. A Xe₂^{*} excimer lamp (USHIO Inc., SUS02) with a center wavelength of 172 nm was used as an excitation light source. The sample was placed in a cryostat and the excimer lamp was placed in front of the cryostat. Absorption of vacuum UV by ambient oxygen was prevented by nitrogen purge. The lamp was incident at the surface normal, and PL was collected in the direction of 60° from the surface normal by focusing on the entrance of a 50-cm monochromator (Princeton Instruments, SP2500) with a 600-grooves/mm grating. The PL detection was ensured by a liquid-N₂-cooled charge coupled device (CCD) camera (Princeton Instrument, 400B/LN). The wavelength resolution was about 0.045 nm. Excitation power density $P_{\text{ex}} = 3.5 \text{ mW/cm}^2$ was measured by an irradiance monitor (USHIO Inc., VUV-S172). Then, we estimated the carrier

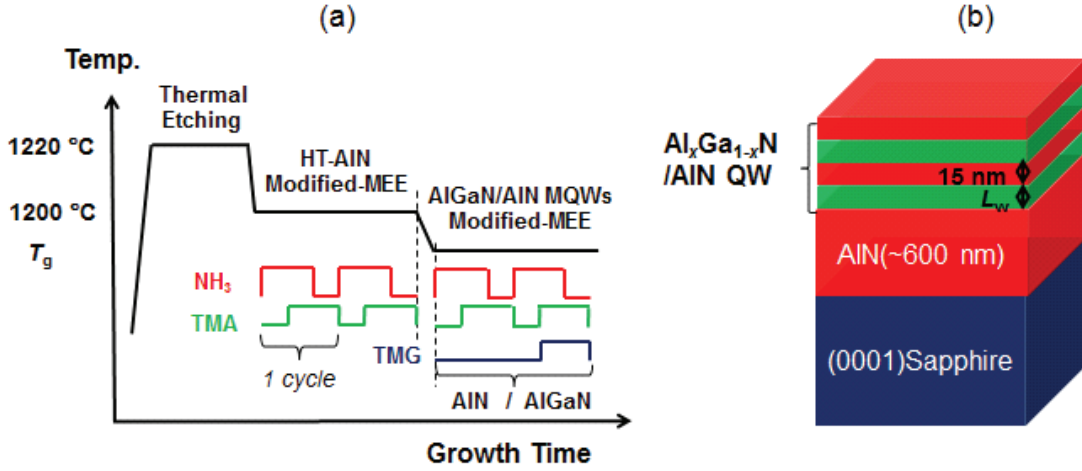


Figure 3.1: (a) Growth sequence of modified MEE method for AlGaIn/AlN QWs. One cycle of AlN growth is composed of 1 s NH_3 supply, 1 s simultaneous supply, and 1 s TMA supply. In the growth of AlGaIn/AlN QW, TMG was flow into the reactor simultaneously with TMA, but separately from NH_3 . (b) Schematic image of sample structure. The samples are AlGaIn/AlN QWs on (0001) AlN/sapphire templates grown by the modified MEE method.

density N by the following equation,

$$N = \frac{P_{\text{ex}}(1 - R)\tau}{E_{\text{ph}}c_{\text{QW}}L_w}(1 - e^{-\alpha_{\text{abs}}d}), \quad (3.1)$$

where R is the reflectance at the interface between air and AlN, τ is the lifetime, E_{ph} is the photon energy of the excitation source, c_{QW} is the number of QWs, α_{abs} is the absorption coefficient, and d is the sum of the thickness of AlN and AlGaIn layers. Thus, we obtained $N \sim 10^{12} \text{ cm}^{-3}$ with an assumed α_{abs} of 10^5 cm^{-1} [21] and $\tau = 2 \text{ ns}$ [22]. As shown in the inset of Fig. 3.3, PL spectra were clearly obtained in Al-rich AlGaIn/AlN QWs under weak excitation condition.

3.2.3 CL Mapping Measurements Setup

CL mapping measurements were performed by two types of CL equipments. One is the SEM system (JEOL Ltd., JSM-6500F) with a CL detection system (Gatan Inc., Mono CL3) in Kyoto University (CL System 1). CW electrons emitted from a field emission gun were focused by magnetic lenses. Acceleration voltage and emission current were 5 kV and 0.1 nA, respectively. CL was collected by an aluminum parabolic mirror, and then detected by a monochromator dispersed by a 2400-grooves/mm grating and detected by a photomultiplier tube (PMT). Selecting whether the grating is used or not, we can choose monochromatic or panchromatic CL measurements, respectively.

The other is the product of Attolight AG (Attolight Rosa 4634) in Switzerland (CL system 2). Figure 3.4 shows the CL system 2. CW electrons emitted from the Schottky field emission gun of the Attolight Rosa 4634 were focused by a gun lens and irradiated onto the sample. The acceleration voltage was set to 2 kV. The current measured at the level of the gun was between

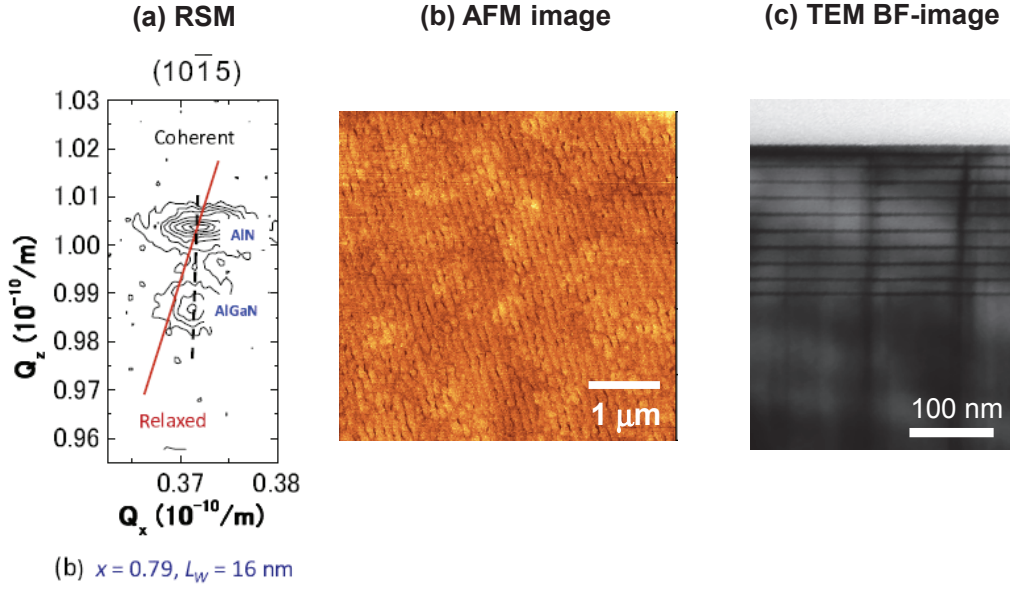


Figure 3.2: (a) RSM, (b) AFM image, and (c) TEM BF-image of $Al_{0.79}Ga_{0.21}N/AlN$ QWs fabricated by the modified MEE method. These figures are quoted from Ref. [20].

120 and 135 μA and the emission current was estimated to 30 pA – 20 nA.¹ The position and temperature were controlled by a cryogenic nano-positioning stage. CL was collected by a 0.72NA reflective objective and focused on the entrance of a 320 mm focal length monochromator dispersed by 600-grooves/mm grating and detected by a CCD camera. More details regarding the CL equipment are given in Ref. [23]. To measure the optical properties at the same area, metal masks with a few square micrometers were deposited on the samples.

¹From the datasheet of Rosa 4634.

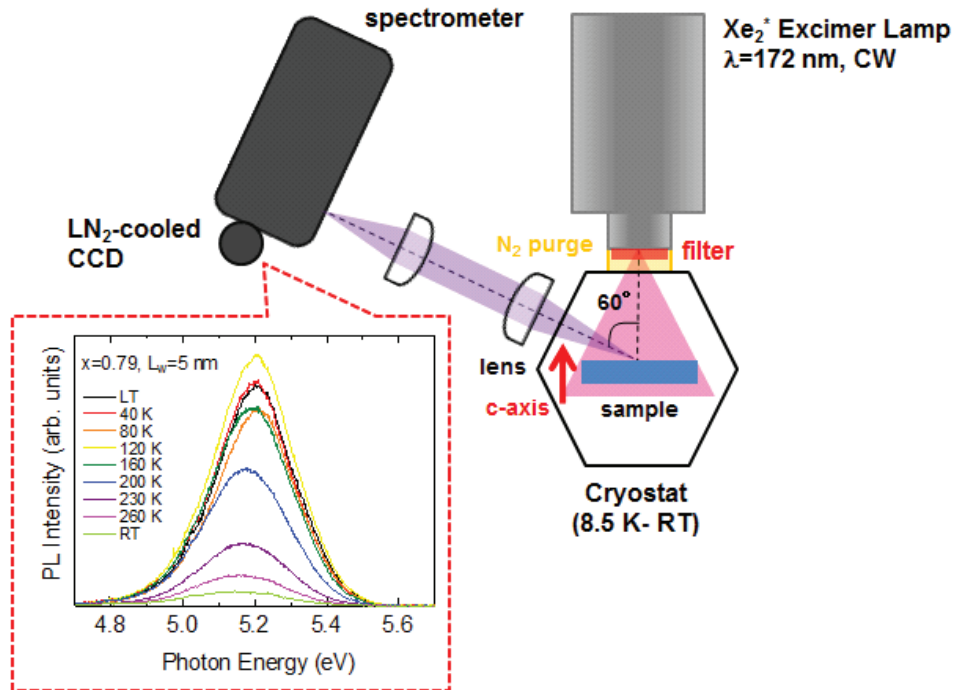


Figure 3.3: Weak excitation PL measurement setup. The inset shows the temperature dependent PL spectra in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with $L_w = 5$ nm.

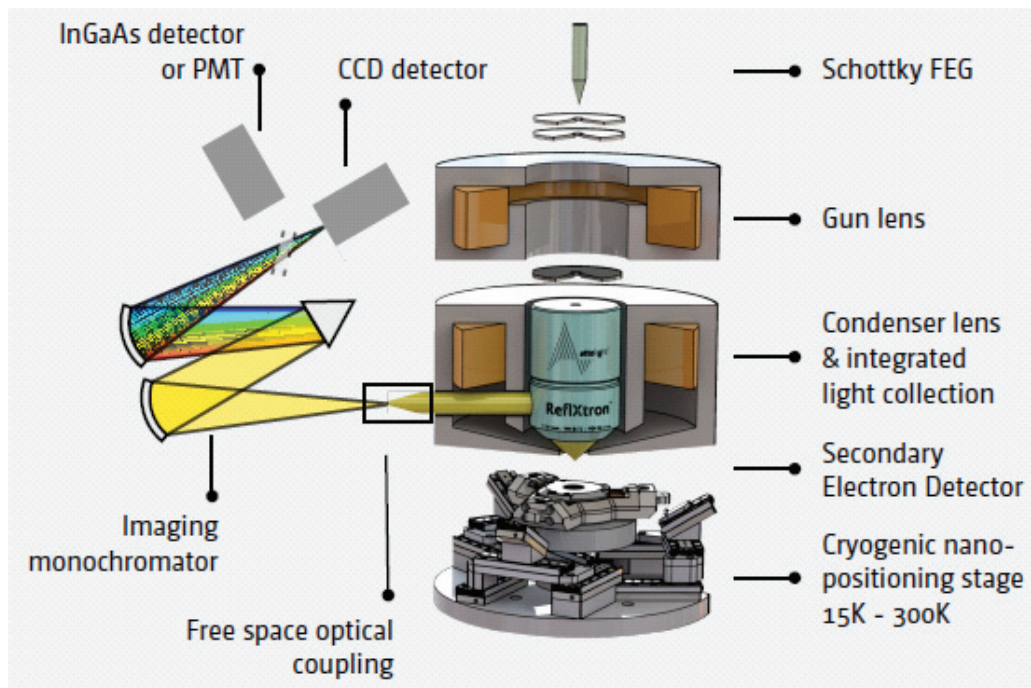


Figure 3.4: Attolight CL measurement system (Attolight Rosa 4634).

3.3 CL Mapping Measurements at RT

To observe the in-plane potential inhomogeneity and evaluate the exciton localization directly in Al-rich AlGa_N/AlN QWs, CL intensity mapping measurements were performed at RT by using the CL system 1. Figure 3.5 shows the CL intensity mappings for Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 2.5$ and 5 nm on the same scale of CL intensity. Island-like CL intensity distributions were observed on a sub-micrometer scale. Comparing these mappings, it was found that there were a lot of areas with intense CL intensity for the narrow QW ($L_w = 2.5$ nm). To express this observation clearly, Fig. 3.6 shows the histograms of CL intensities in Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 2.5$ and 5 nm. The histogram of Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 2.5$ nm had tail state to higher CL intensity. Then, some CL spectra at local spots were measured to investigate the relationship between the CL intensity and peak energy. Figure 3.7 shows the CL spectra at bright and dark regions in intensity. As a result, the peak energies of bright regions were ~ 60 meV lower than those of dark regions. Therefore, we summarize that the stronger CL intensity tail for $L_w = 2.5$ nm in Fig. 3.6 corresponds to the areas emitting at lower energies. The calculated energy fluctuation shown in Fig. 2.9 tells us that the average peak energy difference between bright and dark regions corresponds to the 2 ML (± 1 ML) fluctuation (see Fig. 3.8). This fluctuation may be caused by monolayer step and terrace structures with different spatial distributions at the top and bottom interfaces in QWs, as shown in Fig. 3.9 [24]. Furthermore, the linewidths of CL spectra at submicron-scale local areas were comparable to those at the macroscopic areas. This result suggests that Al compositional fluctuations superimpose on ± 1 ML fluctuations, which denotes the same tendency of Ga-rich AlGa_N films [25–27].

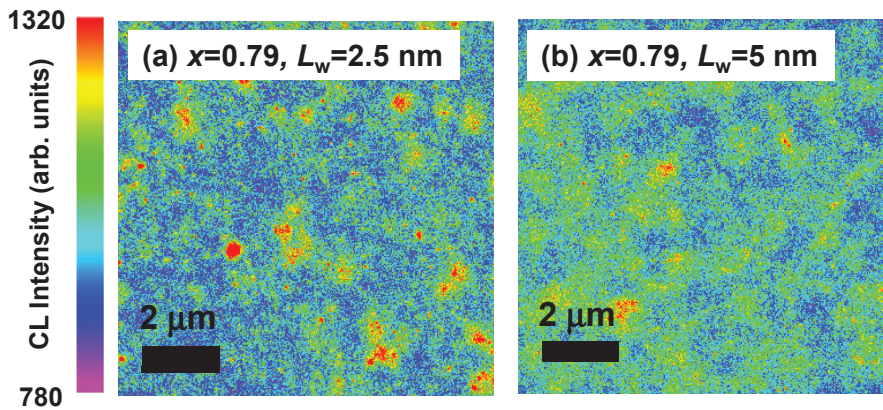


Figure 3.5: CL intensity mappings for Al_{0.79}Ga_{0.21}N/AlN QWs with (a) $L_w = 2.5$ nm and (b) $L_w = 5$ nm at RT.

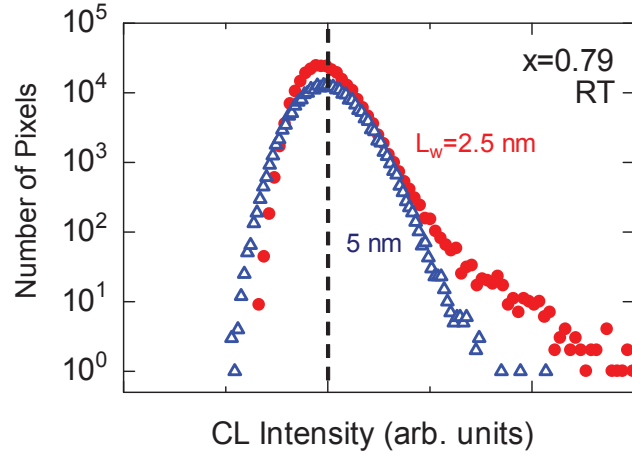


Figure 3.6: Histograms of CL intensities for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with $L_w = 2.5$ and 5 nm at RT. The broken line shows the average CL intensity.

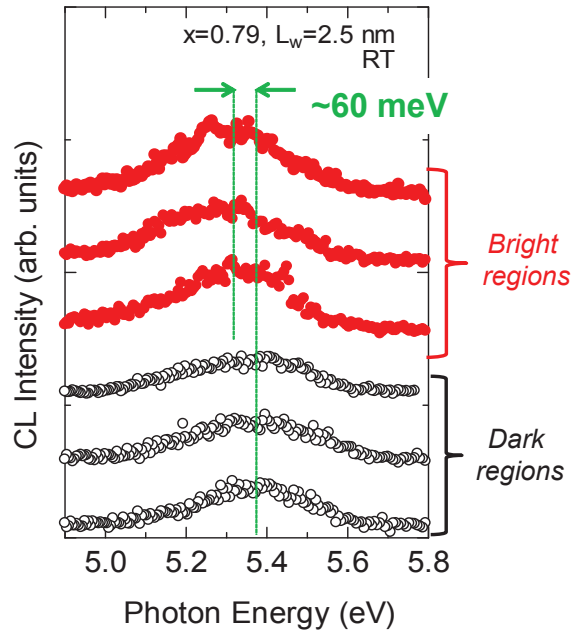


Figure 3.7: CL spectra at local bright and dark regions for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with $L_w = 2.5$ nm at RT. Emission energies in bright regions were ~ 60 meV lower than those in dark regions.

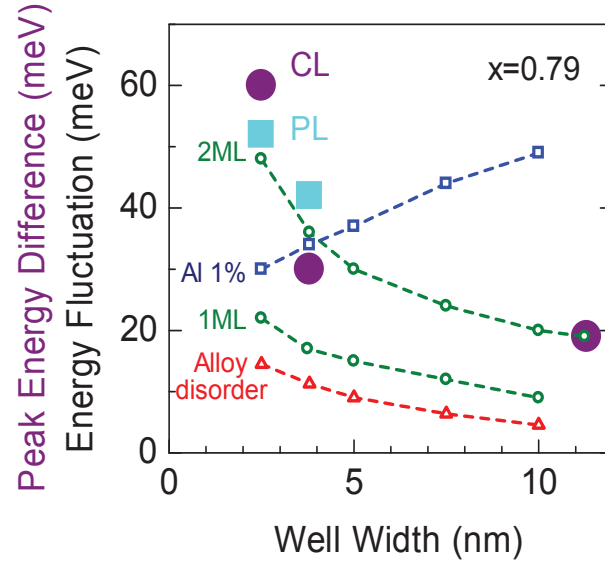


Figure 3.8: CL Peak energy difference between bright and dark regions in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs as a function of the well width. Energy fluctuations calculated in chapter 2 are also plotted. In addition, the energy difference is also shown between the experimental PL peak energy and the theoretical transition energy calculated by the B-E equation at RT, which is discussed in Sec. 3.4.

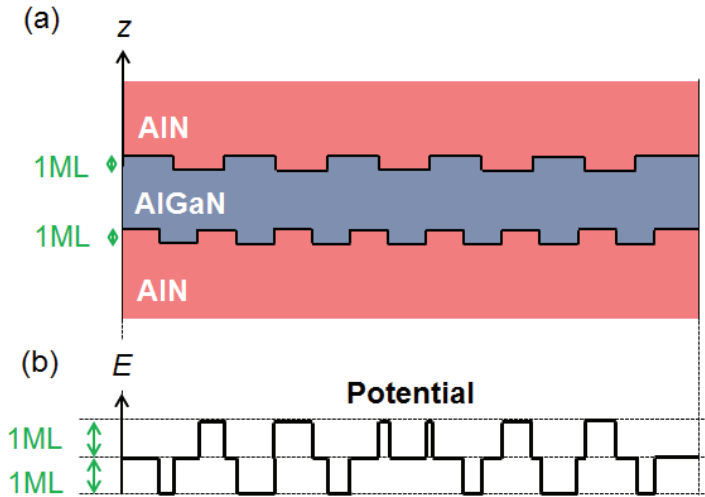


Figure 3.9: (a) Schematic image of QW structure with monolayer step and terrace structures with different spatial distributions at the top and bottom interfaces. (b) Considering the above-mentioned QW structure, the island-like potential with 2 ML fluctuation is formed.

3.4 Temperature Dependence of PL Properties

To investigate the exciton dynamics under the presence of localization states, the temperature dependence of weak excitation PL was assessed. Figure 3.10(a) shows the temperature dependence of the peak energy for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}$ QW with $L_w = 2.5$ nm. Here, the broken line shows the expected temperature dependence of the peak energy estimated from the B-E equation [Eq. (2.5)] for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. The parameters α_B and Θ for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ were calculated by the linear interpolation of GaN and AlN values [28,29] (see Table 3.1) and the peak energy at 0 K [$E(0)$] was shifted with the correspondence to the experimental results. The experimentally observed variation of peak energy cannot be explained by the temperature dependence of the bandgap energy. To account for this unique shift, a potential model with two types of localization states shown in Fig. 3.10(b) was considered. Considering this potential model, temperature dependent peak energy can be explained as follow. As the temperature is increased up to ~ 80 K, the peak energy is blueshifted because of the delocalization from shallow localization states. With the further increase in temperature, the peak energy is redshifted from the broken line. This result implies that excitons thermally delocalized from shallow localization states move to deeper localization states in Al-rich AlGaN/AlN QWs. Then, to prove thie model, the same measurements were performed for Al-rich AlGaN/AlN QWs with various well widths and Al compositions.

Well Width Dependence

To investigate the influence of the well width on the localization degree, the temperature dependent PL measurements were performed for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with the different well widths of 2.5, 3.8, 5 and 10 nm. Figure 3.11(a) shows the temperature dependence of the peak energy in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. Here, the shallow localization energy E_{loc} was defined by the difference between the experimental peak energy and the B-E equation at a LT. As shown in Fig. 3.11(a), the shallow localization energy was larger for the narrower QW. Moreover, the peak energy was redshifted from the B-E equation at elevated temperatures for the QWs with $L_w \leq 3.8$ nm, whereas the migration to deep localization states was not observed for the QWs with $L_w \geq 5$ nm. This is probably because many excitons recombined before they migrated to deep localization states for the wide QWs. The two possible reasons for this consideration are described below. One is the lower spatial density of deep localization states for the wider QWs, as suggested in Sec. 3.3. The other is the PL lifetime. It was reported that the PL lifetime was longer for the narrower QWs by TRPL measurements using the fourth harmonic wave of a Ti: Sapphire laser as an excitation source [22]. The diffusion length is proportional to the squared root of lifetime,² thereby this report supports our experimental results. Then, Figure 3.11(b) shows the temperature dependence of PL FWHM in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. Temperature dependence of FWHM can be also explained by not the Eq. (2.6) but the model with two types of localization states shown in Fig. 3.10(b). As temperature was increased up to ~ 80 K, FWHM was increased due to the delocalization. As temperature was increased from 80 K to 200 K, FWHM was decreased due to the migration to deep localization states. With further

²The diffusion length $L = \sqrt{D\tau}$, where D is diffusion coefficient and τ is the lifetime.

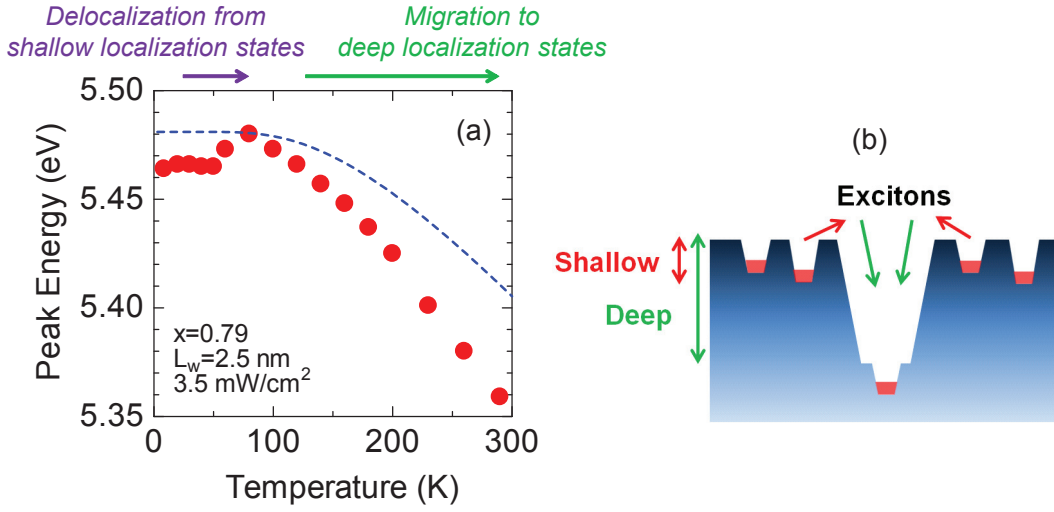


Figure 3.10: (a) Temperature dependence of peak energy in Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 2.5$ nm at $P_{ex} = 3.5$ mW/cm². The broken line shows the calculational peak energy estimated by the B-E equation. (b) Proposed potential model of Al-rich AlGa_N/AlN QWs. Shallow and deep localization states co-exist.

Table 3.1: Parameters α_B and Θ in calculation.

	α_B [eV]	Θ [K]	Ref.
GaN	0.075	350	[28]
AlN	0.20	558	[29]
Al _{0.79} Ga _{0.21} N	0.17	518	

increase in temperature, FWHM was increased again due to the exciton-phonon interaction, as described in Eq. (2.6).

Al Composition Dependence

To investigate the influence of Al composition on the localization degree, the same measurements were performed for AlGa_N/AlN QWs with various Al compositions. Figure 3.12 shows the temperature dependence of the peak energy in the Al_{*x*}Ga_{1-*x*}N/AlN QWs with $L_w = 1.3$ nm and various x of 0.71, 0.82, and 0.87. It was found that E_{loc} was gradually increased as the Al composition was decreased. The migration to deep localization states was also observed in Al_{*x*}Ga_{1-*x*}N/AlN QWs with $L_w = 1.3$ nm. This results agree with the consideration that the peak energy was redshifted from the B-E equation for the QW with $L_w \leq 3.8$ nm.

Summary

The potential model with two types of localization states can clearly explain the temperature dependence of both peak energy and FWHM in all the Al-rich AlGa_N/AlN QWs, thus indicating that our proposed potential model is quite reasonable.

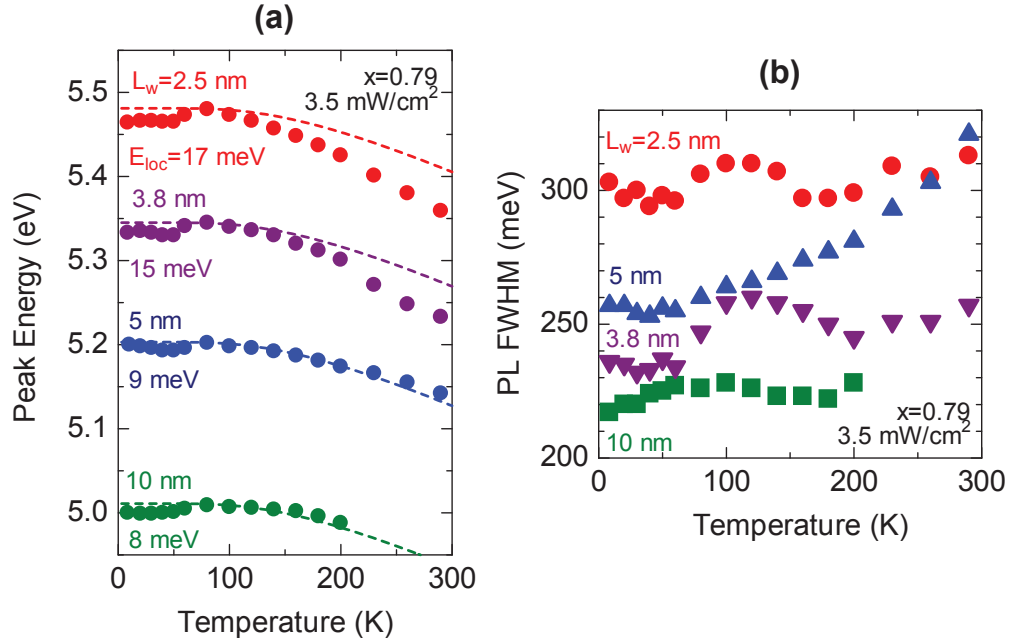


Figure 3.11: Well width dependence of (a) peak energy and (b) FWHM for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with $L_w = 2.5, 3.8, 5$, and 10 nm at 3.5 mW/cm^2 . The broken lines show the peak energy calculated using the B-E equation.

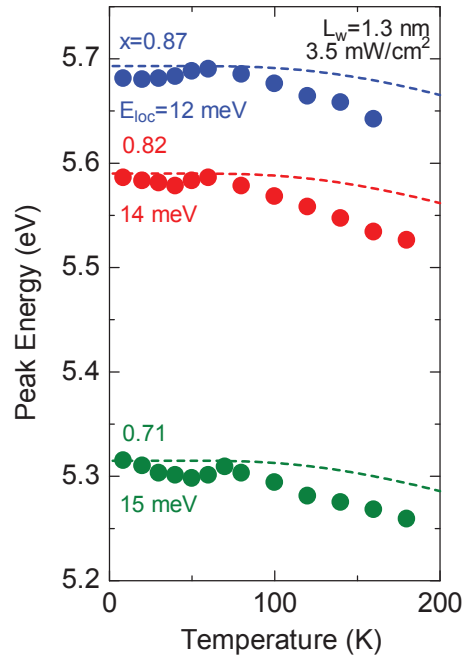


Figure 3.12: Al compositional dependence of PL peak energy for $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs with $L_w = 1.3 \text{ nm}$ and $x = 0.71, 0.82$, and 0.87 at 3.5 mW/cm^2 . The broken lines show the peak energy calculated using the B-E equation.

3.5 Origins of Localization States

To investigate the origins of localization states, we consider and calculate three types of fluctuations; well width fluctuation, Al compositional fluctuation, and statistically unavoidable alloy fluctuation. The details in the calculational procedures were described in Chap. 2.

Shallow Localization States

It was found that only the alloy disorder effect among the three possible factors quantitatively reproduced the dependence of the experimentally observed shallow localization energy on x and L_w , as shown in Fig. 3.13.

Deep Localization States

Figure 3.8 also shows the deep localization energies estimated from the difference between the experimental PL peak energy and the theoretical transition energy calculated by the B-E equation at RT. For the QWs with $L_w \leq 3.8$ nm, the estimated deep localization energy corresponds to the 2 ML (± 1 ML) fluctuation energy, as shown in Fig. 3.8. On the other hand, for the QWs with $L_w \geq 5$ nm, the migration to deep localization states was not observed, because many excitons recombined before they migrated to deep localization states, as explained in the previous section. Furthermore, the CL peak energies of bright regions were 2 ML fluctuation energy smaller than those of dark regions at RT, as discussed in Sec. 3.3. Therefore, it is concluded that the deep localization states originate from the 2 ML fluctuation of well layers.

Summary

Comparing the calculated energy fluctuations and the experimental results, we identify that the experimentally observed two types of localization states, that is, shallow and deep localization states originate from the statistically unavoidable alloy disorder effect and 2 ML fluctuation of the well width, respectively. It is noteworthy that we have obtained the consistent results about the origins of the localization states for the QWs with various Al compositions and well widths.

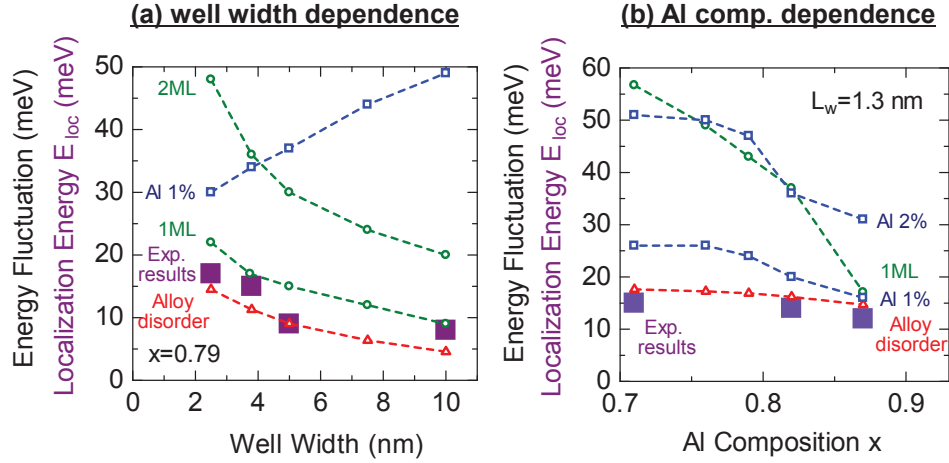


Figure 3.13: (a) Well width dependence of shallow localization energies E_{loc} in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. (b) Al composition dependence of shallow localization energies in $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs with $L_w = 1.3$ nm. Comparing the calculational energy fluctuation and experimental localization energy, only the alloy disorder effect can reproduce the experimental results.

3.6 Temperature Dependent CL Mapping Measurements

To investigate the exciton dynamics directly, temperature dependent CL mapping measurements were performed for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs using the CL system 2 .

3.6.1 CL Mappings

Figure 3.14 shows the normalized CL intensity mappings around the same metal mask on the $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm at (a) 18 K, (b) 100 K, (c) 200 K, and (d) 300 K. Figure 3.15 shows the CL peak wavelength mappings around the same metal mask on the $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm at (a) 18 K, (b) 100 K, (c) 200 K, and (d) 300 K. We performed CL measurements on 128×128 points at 18 K and 100 K, 64×64 points at 200 K, and 32×32 points at 300 K.

CL Intensity and Peak Wavelength Mappings

First, let us discuss the mappings at LT (18 K). A few areas with higher CL intensities (red areas) on a scale smaller than 100 nm were observed in Fig. 3.14(a). Comparing the Fig. 3.14(a) and Fig. 3.15(a), it was found that the emission wavelengths at bright regions were longer than those of dark regions. Figure 3.16 shows the CL spectra at bright and dark regions at 18 K. The average energy difference between bright and dark areas was ~ 50 meV, which was also corresponded to the 2 ML fluctuation energy. Therefore, the bright emissions from small areas were derived from deep localization states. Except the regions with the intense CL, CL intensities were relatively uniform. Ideally, the distribution of CL intensity at LT should be homogeneous because of homogeneous carrier distribution and negligible influence of NRCs. However, in reality, a little distribution exists most likely due to the drift effect and the capture into radiative/nonradiative recombination centers [32,33]. It is noted that we could not directly

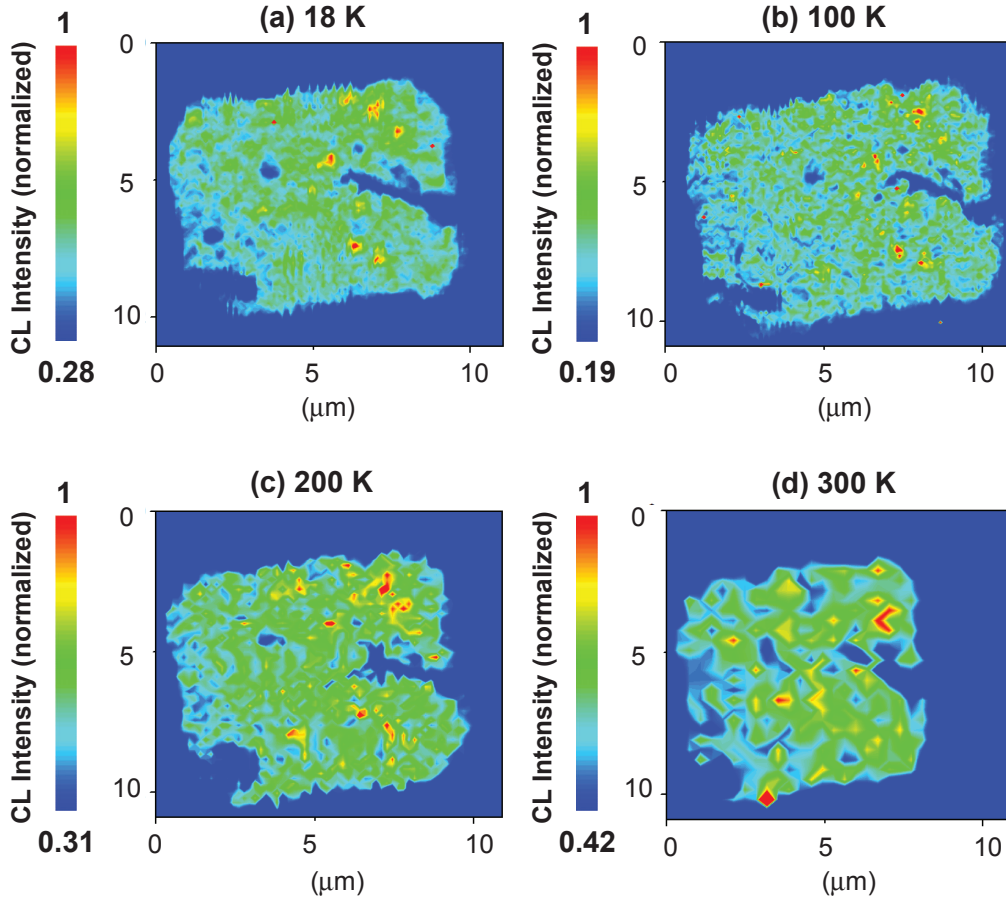


Figure 3.14: Normalized CL intensity mappings of Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 2.5$ nm at (a) 18 K, (b) 100 K, (c) 200 K, and (d) 300 K.

observe shallow localization states, because their spatial size was the same as the exciton Bohr radius.

As temperature was increased up to 100 K, the distributions of both CL intensity and peak wavelength mappings were expanded due to the delocalization. Further increase in temperature increases the areas with bright emissions. Figure 3.17 shows the CL spectra at bright and dark regions at 200 K. The emission energies at bright regions were ~ 45 meV lower than those in dark regions. Therefore, these results also indicate that the thermally delocalized excitons move to deeper localization states. Additionally, it is noteworthy that the average energy differences between bright and dark areas were comparable to the 2 ML fluctuation energy at any temperatures. Combined with the results in CL mappings obtained by the CL system 1 at RT, it is concluded that the emissions from the deep localization states exist at any temperatures.

Emissions of Deep Levels and Phase Separation

The emissions from deep levels probably related to Al vacancies [30,31] were observed between 280 nm and 300 nm in some dark regions, as shown in Fig. 3.17. Interestingly, another new peak was observed at around 260 nm, as shown in Fig. 3.17. It is noted that the new peak at

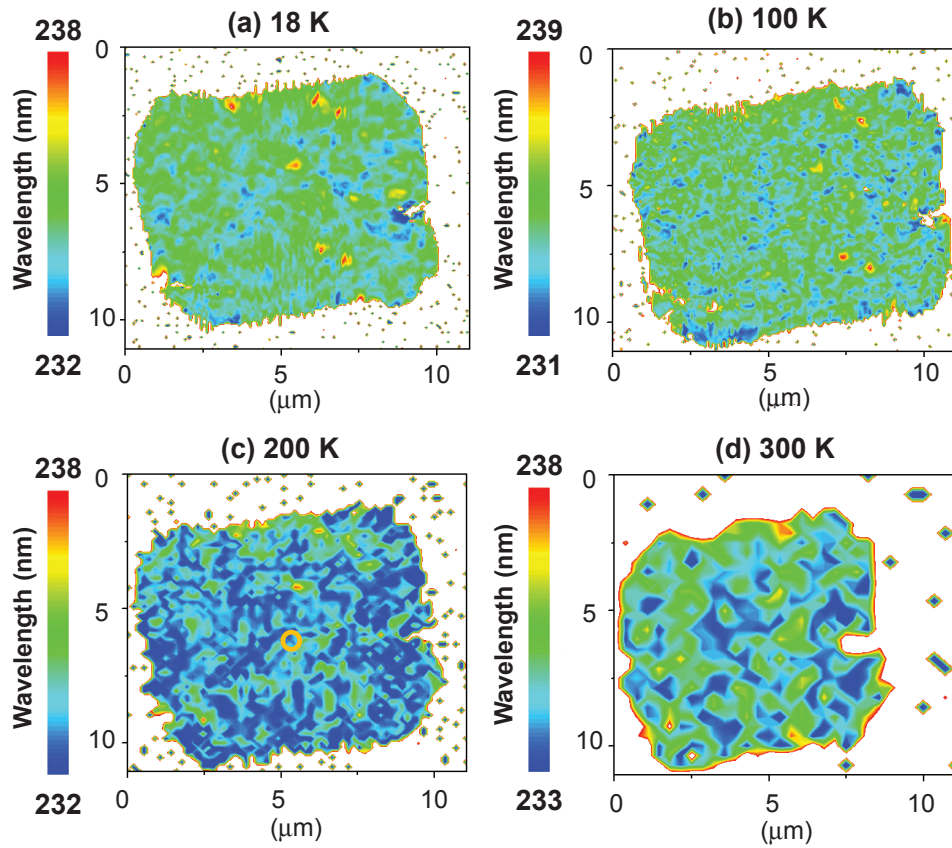


Figure 3.15: CL peak wavelength mapping of $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm at (a) 18 K, (b) 100 K, (c) 200 K, and (d) 300 K.

around 260 nm was observed for the first time by the CL system 2, thanks to the CL mapping measurements using the CCD detector. To investigate this peak in more detail, Fig. 3.18 shows the CL spectra at a local area shown in the solid circle. The relative intensity of this new peak to the near band edge was stronger at higher temperatures. This is probably because the diffusion length of excitons may be longer and thereby more excitons are captured into these regions at higher temperatures. The origin of this peak is under investigation, but now we are considering that this peak is due to local phase separation. Figure 3.19 shows the integrated CL spectra inside the metal mask. The new peak described above was not observed at any temperatures. Therefore, these results mean that there are few areas with the emission of ~ 260 nm. As the temperature was increased, the deep level around 280 nm was increased, because the influence of NRCs was larger at higher temperature.

3.6.2 Correlation between CL Intensity and Peak Energy

To investigate the correlation between CL peak energies and intensities, we plotted the CL intensity as a function of CL peak energy at all the measurement positions inside the metal mask. Figure 3.20(a)–(d) show it as a function of temperature. Here, the color scale represent the number density, and the vertical and horizontal broken lines show the average photon energy and CL intensity, respectively. As seen, the negative correlations of -0.39 were obtained

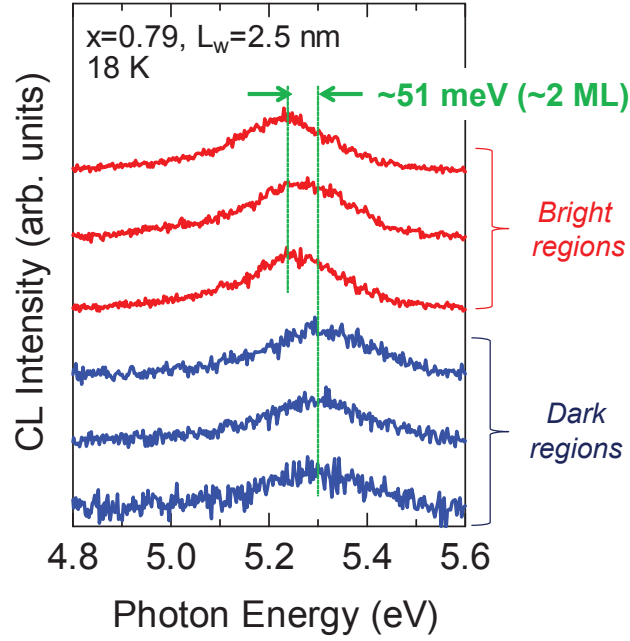


Figure 3.16: CL spectra at bright and dark regions in Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 2.5$ nm at 18 K. Emission energies in bright regions were ~ 51 meV lower than those in dark regions.

by calculating the Pearson product-moment correlation coefficient at LT. Here, the negative correlation means the localization effects were worked effectively. As temperature was increased from 18 K to 100 K, the areas with higher photon energies were increased and the average photon energy was increased, due to the exciton delocalization. As temperature was increased from 100 K to 200 K, the regions with higher photon energies were decreased. This result indicates that the migration to deep localization states is larger at higher temperature. To express the exciton dynamics clearly, Fig. 3.21 shows the histograms of CL intensities and peak energies in Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 2.5$ nm as a function of temperature. Here, the solid line shows the average photon energy. As temperature was increased up to 100 K, the distribution of photon energy was expanded and the average photon energy was increased, due to the delocalization from shallow localization states. With further increase in temperature, the areas with higher photon energies were drastically reduced. Moreover, the histogram of CL peak energy had tail state to lower CL peak energy. These results strongly indicate that excitons migrated to deep localization states. The results obtained by CL mappings correspond to those in the weak excitation PL. Consequently, the comprehensive understandings related to the exciton dynamics in AlGa_N/AlN QWs were obtained.

3.7 Summary

The exciton localization characteristics were presented for Al-rich AlGa_N/AlN QWs. The weak excitation PL measurements using a Xe₂^{*} excimer lamp and the CL mapping studies revealed that the emission mechanisms were governed by the two types of localization states. From the quantitative analysis, we identify that the experimentally observed two types of localization

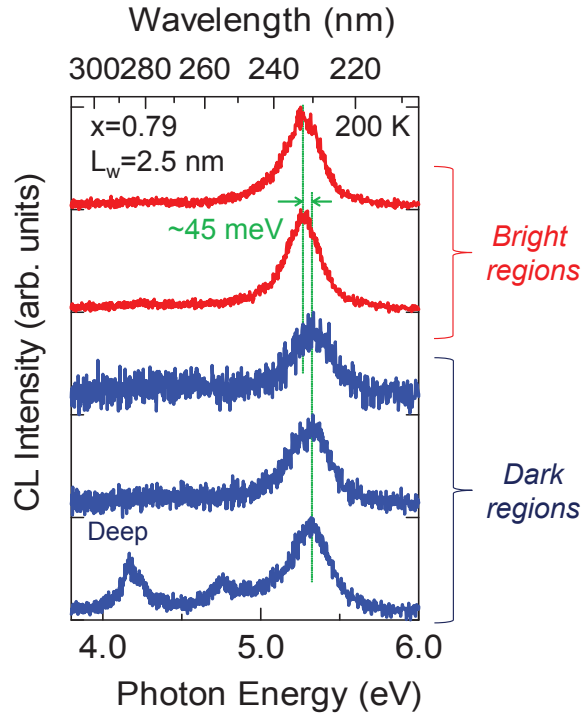


Figure 3.17: CL spectra at bright and dark regions in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm at 200 K. The emission energies at bright regions were ~ 45 meV lower than those in dark regions. The emission from deep levels around 280 nm and the new peaks around 260 nm were observed.

states, that is, shallow and deep localization states originate from the statistically unavoidable alloy disorder effect and 2 ML fluctuation of the well width, respectively. It is noteworthy that we have obtained the same results related to the origins of the localization states for the QWs with different well widths and Al compositions. For narrow QWs, many excitons migrated to deep localization state derived from 2 ML fluctuation and emitted brightly in those regions, because of large density of deep localization states and long PL lifetime. The emissions probably originating from the deep levels around 280 nm and the local phase separation around 260 nm were observed by CL mapping measurements. Because it was not observed in the average CL spectra, the regions with this emission around 260 nm are only a few.

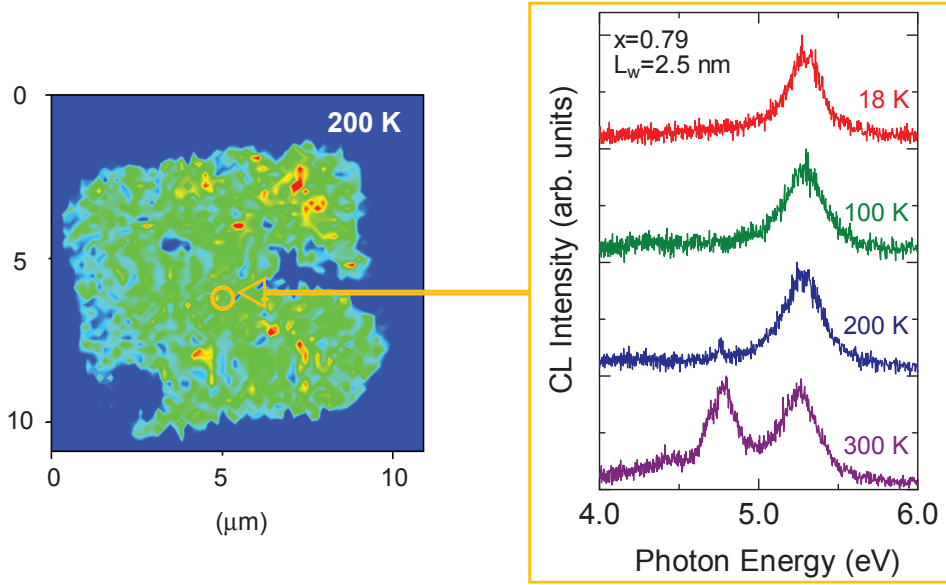


Figure 3.18: Temperature dependence of the CL spectra at the same area shown in the solid circle in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm.

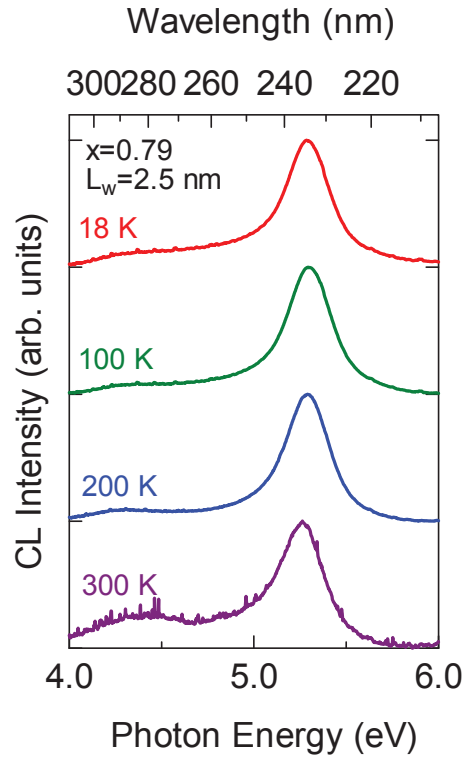


Figure 3.19: Integrated CL spectra inside the metal mask in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm as a function of temperature.

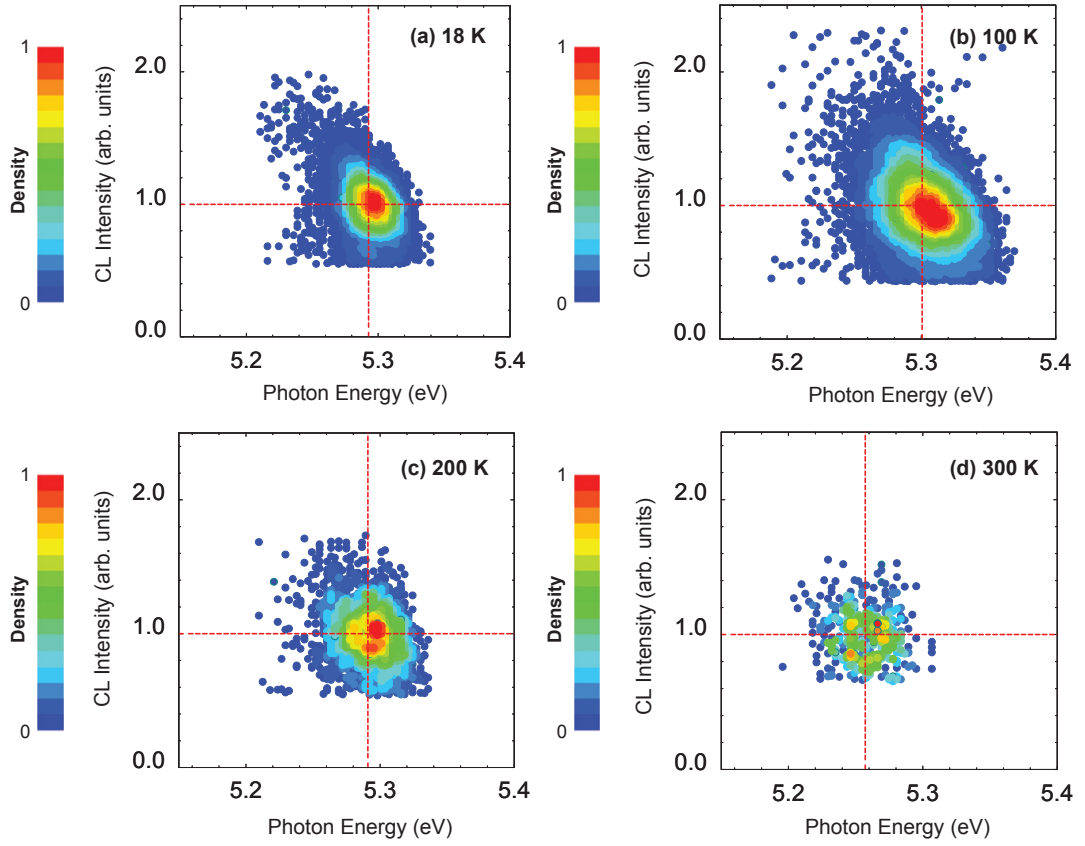


Figure 3.20: Correlation between photon energy and CL intensity in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm at (a) 18, (b) 100, (c) 200, and (d) 300 K. The vertical and horizontal broken lines show the average photon energy and CL intensity, respectively.

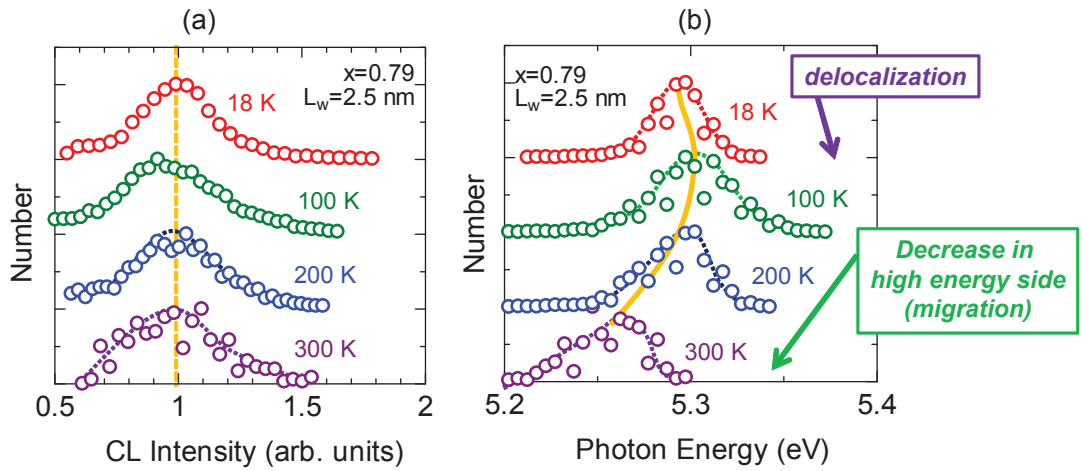


Figure 3.21: Histograms of (a) CL intensities and (b) CL peak energies in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 2.5$ nm as a function of temperature. The broken line in (a) and the solid line in (b) show the average CL intensity and the average CL peak energy, respectively.

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Chapter 4

Optical Properties in Al-rich AlGaN/AlN QWs under Increasing Excitation

4.1 Introduction

Highly excited emission mechanisms have been studied for various binary semiconductors such as GaN [1–10], AlN [11–13] and ZnO [14] and ternary semiconductors such as InGaN [3, 15] and AlGaN [16–22]. For GaN, the Mott transition from the exciton many body (EMB) effect to electron-hole plasma (EHP) was observed as the excitation intensity was increased [1]. Furthermore, it was theoretically predicted [23] and experimentally demonstrated [2] that the Mott density depends on temperature and is larger at higher temperatures. The Mott transition happens when high carrier densities shorten the screening length below a certain value (l_c). a_B and l_c have the relationship [24]:

$$a_B l_c^{-1} = 1.19. \quad (4.1)$$

Moreover, the red shift of PL peak energy was reported as excitation power increased [1]. It has also been reported that the momentum conservation model with Lorentzian broadening well reproduces EHP-emission spectra [3]. For AlN and AlGaN, PL under high excitation conditions below the Mott density was reported. M-line related to biexciton [19–22] and P-line related to exciton-exciton scattering [12, 13] was clearly observed. Additionally, it was reported that P_M line related to the biexciton-biexciton scattering [25] was observed [21, 22].

In this chapter, we assess power dependence of PL in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQWs excited by an ArF^* excimer laser and the DUV emission mechanisms are discussed in terms of localization effect and PL peak shift. Excitation power dependence of PL properties was investigated in high-quality $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. Then, we performed TRPL measurements for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs under selective excitation condition in order to investigate carrier recombination dynamics around the Mott transition.

4.2 Experimental Procedure

4.2.1 PL Setup

The experimental setup for strong excitation PL measurements was the same configuration as Fig. 3.3. An ArF* excimer laser (MPB Communications, PSX-100 and Ximer-300, center wavelength: 193 nm, pulse duration: 4 ns, pulse rate: 25–100 Hz) was used as an excitation light source. The laser power was tuned by two film polarizers and $\lambda/2$ wave plate. The sample was placed in a cryostat and the excimer laser was placed in front of the cryostat. The laser was incident at the surface normal, and PL was collected in the direction of 60° from the surface normal by focusing on the entrance of a 50-cm monochromator with a 600-grooves/mm grating. The PL detection was ensured by a liquid-N₂-cooled CCD camera. The excitation power density ranged from 1 to 600 kW/cm². The carrier density N was calculated by the Eq. (3.1) with an assumed α_{abs} of 10^5 cm^{-1} .

4.2.2 TRPL Setup

Figure 4.1 shows the experimental setup of TRPL measurement under high excitation condition. TRPL measurements were performed at 5.5 K. The DUV laser was used as the excitation source, which was composed of a Ti: sapphire laser (Spectra Physics, Tsunami, wavelength: 800 nm, pulse duration: 150 fs, repetition frequency: 80 MHz), a regenerative amplifier (Spectra Physics, Spitfire), an optical parametric oscillator (Light Conversion Ltd., TOPAS), and nonlinear optical crystals. The OPO converted the output laser from the regenerative amplifier into the two output waves called “signal” and “idler”. Here, wavelengths of the signal and the idler are 1150–1160 nm and 1600–2600 nm, respectively.¹ Signal light was converted by nonlinear optical crystals, and consequently the DUV laser with a wavelength between 189 nm to 240 nm was able to be generated. The pulse duration and the repetition rate were 2 ps and 1 kHz, respectively. To selectively excite the AlGaN QWs, the laser wavelength was set at 215 nm. TRPL spectra were acquired by a streak camera (Hamamatsu, C5680) with a time resolution of 1.5 ps. The excitation power density was $150 \mu\text{J}/\text{cm}^2$.

¹In this experiment, the idler wave was not used.

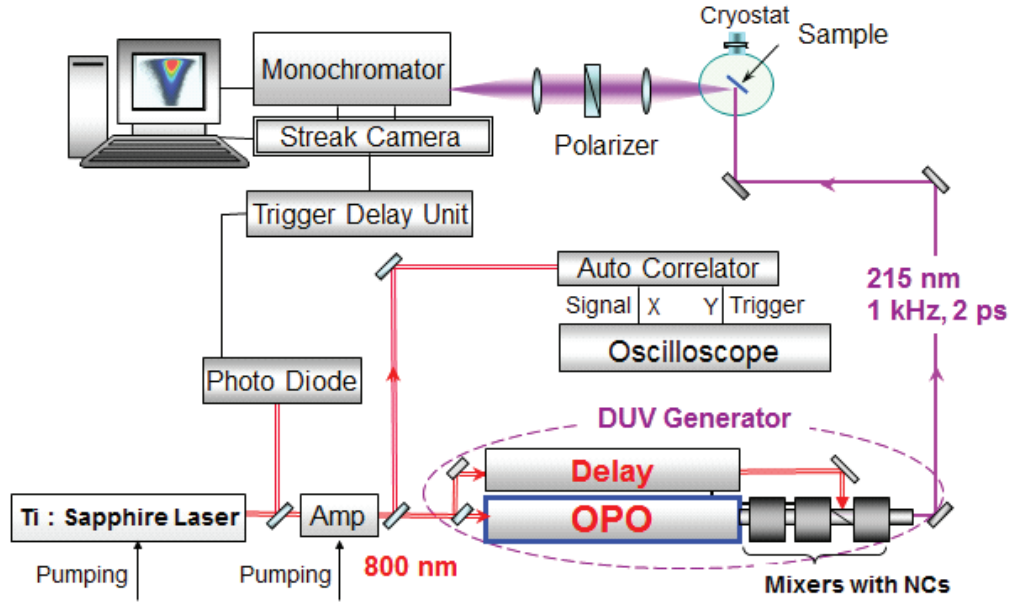


Figure 4.1: Experimental setup of TRPL measurement under high excitation condition.

4.3 Excitation Power Dependence of PL Properties

4.3.1 Localization Phenomena

Figure 4.2(a) shows the temperature dependences of PL peak energy under intermediate and strong excitation conditions (10 and 200 kW/cm²) in the Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 5$ nm. For comparison, that at an excitation power density (P_{ex}) of 3.5 mW/cm² is also shown. Here, the broken lines show the peak energy calculated by the B-E equations. The S-shaped temperature dependence due to the localization states was observed at 3.5 mW/cm², as described in Chap. 3. At $P_{ex} = 10$ kW/cm², a localization energy of 30 meV, which was larger than that of 3.5 mW/cm², was observed. Generally, localization states are filled with carriers/excitons as an excitation power is increased. Therefore, these results cannot be explained by one kind of localization state but can be by two types of localization states shown in Fig. 3.10(b). Figure 4.2(b) shows schematic images of localization states and filling of excitons as a function of excitation power density. At $P_{ex} = 3.5$ mW/cm², excitons are delocalized from shallow localization states and this localization energy was 9 meV. At $P_{ex} = 10$ kW/cm², shallow localization states were saturated and deep localization states were filled up to a certain energy level. Thus, excitons delocalized from deep localization states were observed and this localization energy was 30 meV. On the other hand, blueshift of peak energy was not observed at 200 kW/cm². This result means that the localization states were filled with excitons at 200 kW/cm².

To investigate the well width dependence of the emission mechanisms, we performed the temperature dependent PL measurements for the Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 3.8$ and 10 nm. Figure 4.3 shows the results for the Al_{0.79}Ga_{0.21}N/AlN QWs with (a) $L_w = 3.8$ and (b) 10 nm at excitation power densities of 3.5 mW/cm², 10 kW/cm², and 200 kW/cm². The temperature dependence of peak energy for the QWs with the different well widths can be

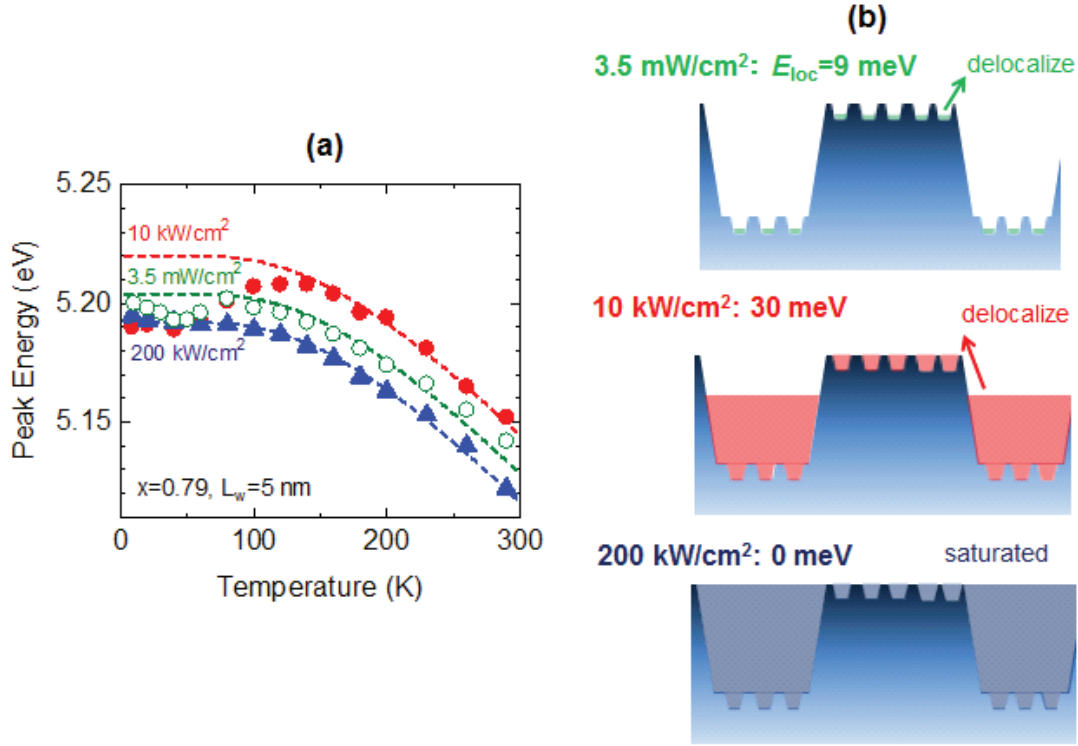


Figure 4.2: (a) Temperature dependence of PL peak energy in Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 5$ nm at $P_{ex} = 3.5$ mW/cm², 10 kW/cm², and 200 kW/cm². (b) Localization-states-filling of excitons at $P_{ex} = 3.5$ mW/cm², 10 kW/cm², and 200 kW/cm². The broken lines show the peak energy calculated by the B-E equations.

explained by the potential model shown in Fig. 3.10(b) as follow. For the QW with $L_w = 3.8$ nm at $P_{ex} = 3.5$ mW/cm², the migration of excitons to deep localization states was observed, as explained in the previous chapter. Comparing the excitation conditions of $P_{ex} = 3.5$ mW/cm² and 10 kW/cm², it was found that the redshift was smaller at higher excitation condition. This result means that the deep localization states were filled with excitons at some energy level, and thereby the migration to deep localization states was decreased. At $P_{ex} = 200$ kW/cm², the blueshift was not observed. Therefore, the localization states were saturated in the same manners as the QW with $L_w = 5$ nm. For the QW with $L_w = 10$ nm, the blueshift was not observed even at $P_{ex} = 10$ kW/cm², against the results of other QWs. This suggests that the localization states were already saturated at $P_{ex} = 10$ kW/cm², that is, the densities of deep localization states are smaller for the wider QWs. This tendency agrees with the results of the CL mapping measurements discussed in Chap. 3.

In summary, Fig. 4.4 shows schematic images of potential fluctuation and filling with excitons for the QWs with different well widths of 3.8, 5, and 10 nm under $P_{ex} = 10$ kW/cm². The emission mechanisms are quite different for the QWs with the different QW due to the different densities of deep localization states and the diffusion lengths of excitons.

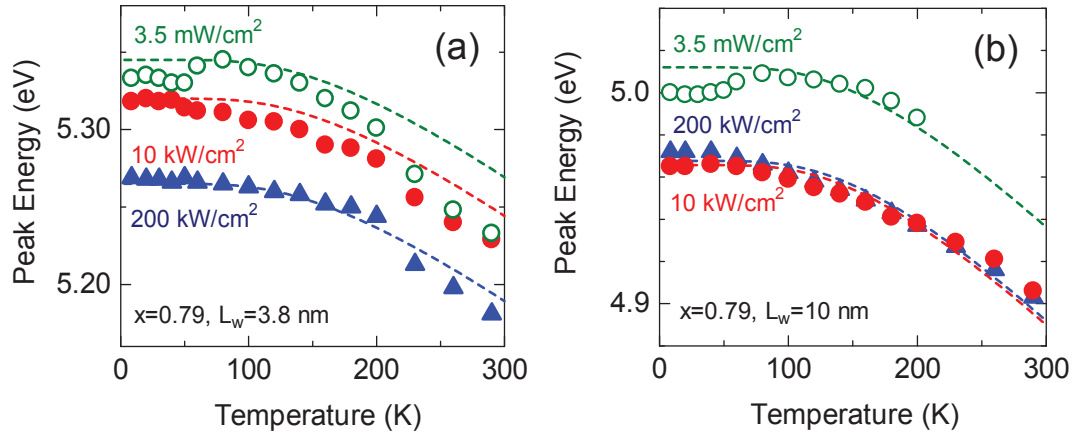


Figure 4.3: Temperature dependence of PL peak energy in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with (a) $L_w = 3.8$ nm and (b) $L_w = 10$ nm at excitation power densities of 3.5 mW/cm², 10 kW/cm², and 200 kW/cm². The broken lines show the peak energy calculated by the B-E equations.

4.3.2 Peak Energy

Figure 4.5 shows power dependent PL spectra of an $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQWs with a well width (L_w) of 5 nm, as an example. The peak position depended on the excitation power, and the mechanisms behind these observations are discussed.

Figure 4.6(a) shows the shift of the experimental peak energy as a function of excitation power density at a LT. The large difference was observed among the QWs with the different well width. To account for this difference, Fig. 4.6(b) shows the calculated total peak shifts of $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQWs with different well widths as functions of carrier density. The detail in the calculational procedure was described in Chapter 2. The calculated results reasonably reproduce the experimental results shown in Fig. 4.6(a). The screening effect of internal electrical field becomes more remarkable for wider wells. Therefore, the difference of PL peak shifts due to the well width is mainly caused by the screening effect.

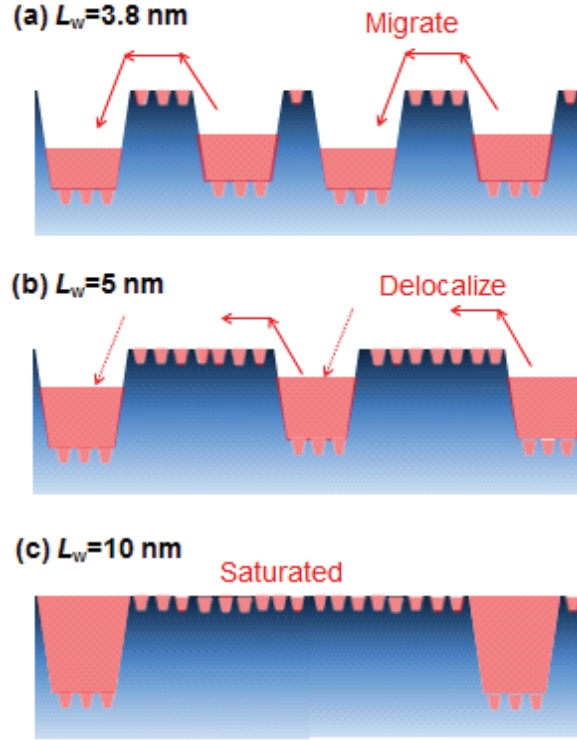


Figure 4.4: Schematic images of the potential fluctuation and filling with excitons for the QWs with different well widths of 3.8, 5, and 10 nm. These potential models are based on Fig. 3.10(b).

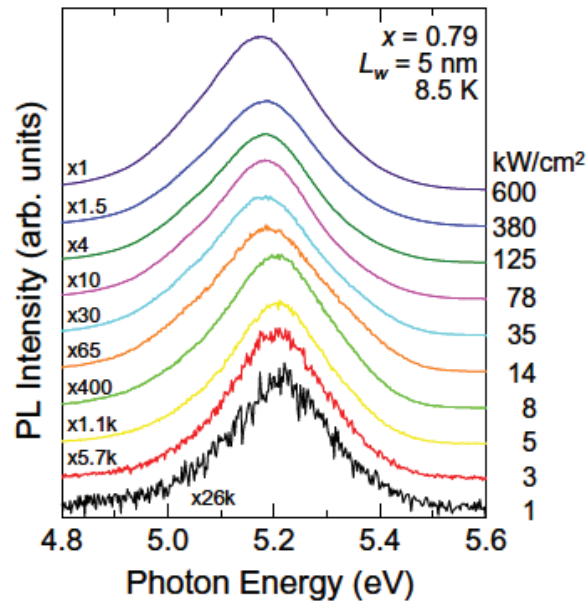


Figure 4.5: Excitation power dependent PL of $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}$ (5 nm)/AlN MQW. The PL spectra under excitation from 1 to 600 kW/cm^2 were shown. This figure is quoted from Ref. [26].

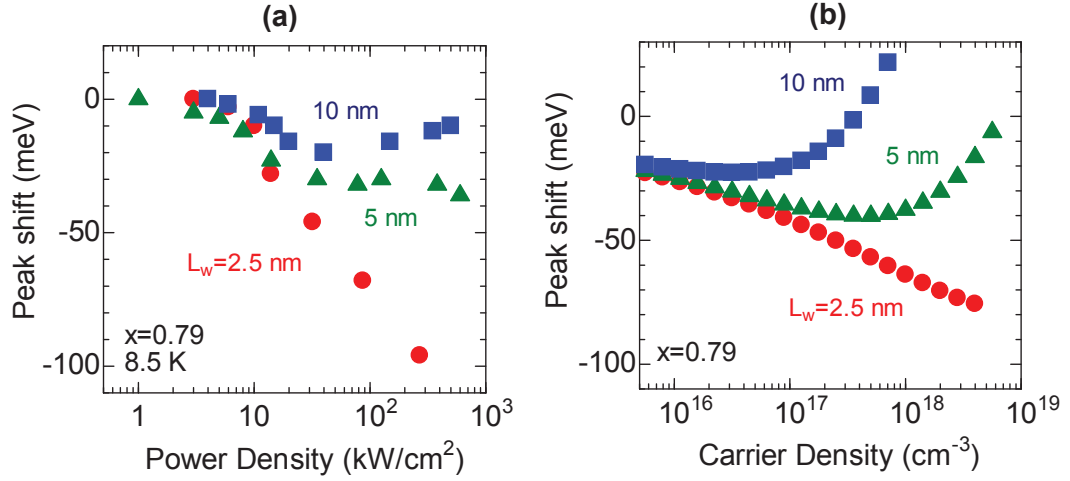


Figure 4.6: (a) Experimental and (b) total peak energy shifts of Al_{0.79}Ga_{0.21}N/AlN MQWs with $L_w = 2.5, 5$, or 10 nm. The total peak energy shift was calculated by summing the contributions of BGR, B-M shift, and screening effect. These figures are quoted from Ref. [26].

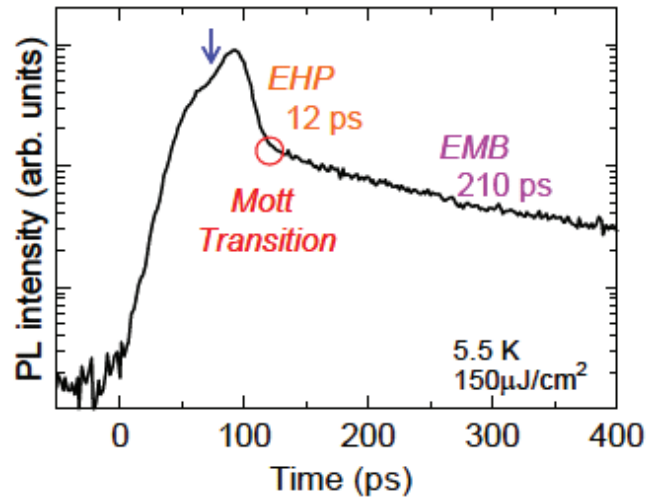


Figure 4.7: PL decay curve in Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 5$ nm under an excitation power of $150 \mu\text{J}/\text{cm}^2$. The slope change from the fast to the slow decay indicates the Mott density. This figure is quoted from Ref. [27].

4.4 TRPL around Mott Transition

To investigate the emission mechanisms in more detail, time resolved PL was measured by the DUV ps-pulse laser system described in Sec. 4.2. Figure 4.7 shows the time dependent PL intensity of the Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 5$ nm under an excitation power of $150 \mu\text{J}/\text{cm}^2$, where the PL intensity was summed over the entire spectrum. In Fig. 4.7, the fast and the slow decays were apparently observed. Because the AlGa_{0.79}N QWs were selectively excited, the observed decays can simply be attributed to intra-well radiative processes under the assumption that nonradiative processes can be neglected at low temperatures (LTs) [28]. To quantify those decay components, the time dependence was fitted by the double exponential equation described by

$$I(t) = A_{\text{fast}} \exp\left(-\frac{t}{\tau_{\text{fast}}}\right) + A_{\text{slow}} \exp\left(-\frac{t}{\tau_{\text{slow}}}\right), \quad (4.2)$$

where $I(t)$ is the PL intensity at a time of t , and τ is the lifetime. The subscripts represent the fast and the slow components. The estimated fast and slow lifetimes were 12 and 210 ps, respectively. The initial carrier density was estimated to be $\sim 1 \times 10^{19} \text{ cm}^{-3}$, which are beyond the two dimensional Mott density $n_{\text{M}}^{2\text{D}}$ [26]. Here, the two dimensional Mott density was estimated as follow. From the Thomas-Fermi model [23], the three dimensional Mott density $n_{\text{M}}^{3\text{D}}$ is given by

$$n_{\text{M}}^{3\text{D}} = a_{\text{B}}^{-3} \frac{\pi(1.19)^6}{4^3 \cdot 3} \left\{ \frac{m_e m_h}{(m_e + m_h)^2} \right\}^3. \quad (4.3)$$

We obtained $n_{\text{M}}^{3\text{D}} = 2.8 \times 10^{15} \text{ cm}^{-3}$ in Al_{0.79}Ga_{0.21}N. Unfortunately, the description of the Mott density in two dimensional system ($n_{\text{M}}^{2\text{D}}$) has not been well established yet, and here, we simply estimated $n_{\text{M}}^{2\text{D}}$ by the relationship expressed as $n_{\text{M}}^{3\text{D}} \leq n_{\text{M}}^{2\text{D}} \leq n_{\text{M}}^{2\text{D},\text{limit}} = 8n_{\text{M}}^{3\text{D}}$. The superscript, limit, represents the two dimensional limit with the conditions of $L_w \rightarrow 0$ and $V \rightarrow \infty$.² Thus, we obtained $2.8 \times 10^{15} \text{ cm}^{-3} \leq n_{\text{M}}^{2\text{D}} \leq 2.2 \times 10^{16} \text{ cm}^{-3}$ in Al_{0.79}Ga_{0.21}N/AlN QWs. Therefore, we considered the fast and the slow components represented radiative processes due to EHP and the EMB effect, respectively. With this regard, the slope change from the fast to the slow decay in Fig. 4.7 indicates that the dominant emission mechanism changes from EHP to the EMB effect, and corresponds to the Mott transition. As a result, the experimental Mott density was calculated to be $5.9 \times 10^{16} \text{ cm}^{-3}$. On the other hand, while the PL intensity increased until 95 ps, a kink was observed at $t \simeq 70$ ps, as designated by the arrow in Fig. 4.7. It was considered that this was related to the Coulomb screening of the internal electric field, which was predicted to be $-1.1 \text{ MV}/\text{cm}$. For InGa_{0.79}N/GaN QWs, pump and probe spectroscopy has revealed that the Coulomb screening takes about 15 ps [30]. Taking this value and the current excitation condition that exceeds the Mott transition into account, the presence of the kink is interpreted as the following; the initial rise of the PL intensity (< 70 ps) is due to an exciton-related emission such as the EMB effect under the presence of the internal electric field, whereas the second rise later than the kink is due to EHP.

²Exciton Bohr radius in two dimensional limit is half of that in three dimension [29].

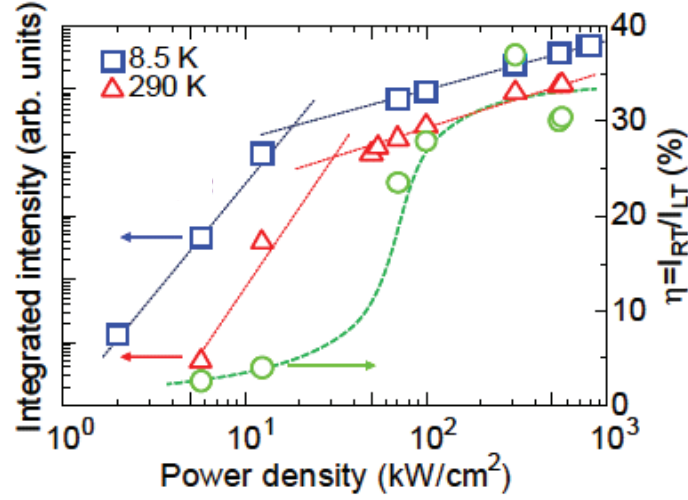


Figure 4.8: Excitation power dependence of PL integrated intensity acquired at 8.5 K (I_{LT}) and 290 K (I_{RT}), and their ratio of $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQW with $L_w = 5$ nm. This figure is quoted from Ref. [27].

4.5 Excitation Power Dependent IQE

The difference of the radiative recombination lifetimes between EMB effect and EHP can influence on the IQE. Figure 4.8 shows the IQE of $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 5$ nm as a function of excitation power density. Here, IQEs were estimated from the PL integrated intensity ratio between at LT and at RT. The remarkable difference of the IQE was observed. The high IQE has been achieved at $P_{\text{ex}} > 100 \text{ kW/cm}^2$ ($N > 10^{18} \text{ cm}^{-3}$), which is above the Mott density. Therefore, such excitation conditions are very effective for the applications of DUV optical devices with high power and efficiency.

To investigate the well width dependent IQE, Fig. 4.9(a) shows the IQEs under a power density of 3.5 mW/cm^2 and 200 kW/cm^2 as a function of well width. The dotted line shows their ratio. The IQEs at 200 kW/cm^2 are larger than those of 3.5 mW/cm^2 . This is because the faster radiative lifetime and the filling of NRCs. Moreover, this ratio was larger for the wider QWs, due to the larger screening effect of internal electrical field. To account for the tendency of IQE, we calculated the squared overlap integral $|\langle\psi_e|\psi_h\rangle|^2$ at carrier densities of 10^{12} cm^{-3} ($\sim 3.5 \text{ mW/cm}^2$) and 10^{18} cm^{-3} ($\sim 100 \text{ kW/cm}^2$), as shown in Fig. 4.9(b). In addition, their ratio was calculated. It is noted that τ_r^{-1} is proportional to $|\langle\psi_e|\psi_h\rangle|^2$ and IQE is given by

$$\text{IQE} = \frac{\tau_r^{-1}}{\tau_r^{-1} + \tau_{nr}^{-1}} = \frac{1}{1 + (\tau_r/\tau_{nr})}. \quad (4.4)$$

Assuming that τ_{nr} is almost the same for the QWs with different well widths, $|\langle\psi_e|\psi_h\rangle|^2$ has the same tendency as the experimental IQE. However, comparing the experimental IQEs and the calculational squared overlap integral, the experimental results can be reproduced by the calculation of the overlap integral qualitatively but qualitative fit requires further investigation. The possible reason of this discrepancy is the difference of nonradiative recombination lifetime and/or internal electrical field.

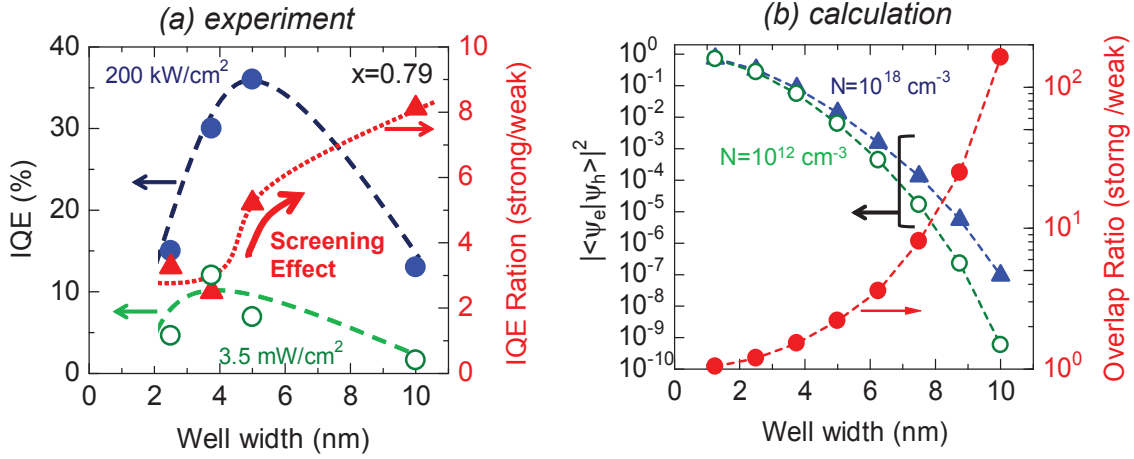


Figure 4.9: (a) IQEs estimated from PL integrated intensity ratio between at LT and at RT under a power density of 3.5 mW/cm² and 200 kW/cm² as a function of well width. The ratio of IQEs is also shown. (b) Calculated squared overlap integral at carrier densities of 10¹¹ cm⁻³ and 10¹⁸ cm⁻³, and these squared overlap integral ratio as a function of well width.

4.6 Summary

The emission mechanisms under intermediate and strong excitation conditions were discussed for Al_{0.79}Ga_{0.21}N/AlN MQWs with different well widths. The difference of temperature dependent peak energies for the QWs with the different well widths were explained by the potential model with two types of localization states with the different spatial densities of localization states. Moreover, the PL peak shift and its well-width dependence could reasonably be reproduced by considering BGR, the B-M shift, and the screening effect. Among them, the major factor for the difference in the PL peak shift due to the well width was found to be the screening effect. TRPL measurements for the Al_{0.79}Ga_{0.21}N/AlN QWs with $L_w = 5$ nm were performed at 5.5 K. The fast and the slow lifetime components were observed under highly-excited conditions and were attributed to radiative recombination lifetimes of EHP and the EMB effect, respectively. It was found that the high IQE has been achieved at $P_{\text{ex}} > 100$ kW/cm², which is beyond the Mott density. Therefore, the strong excitation conditions are very effective for the applications of DUV optical devices with high power and efficiency.

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Chapter 5

Optical Gain Characteristics in Al-rich AlGa_N/AlN QWs

5.1 Introduction

The properties of DUV lasing from AlGa_N QW structures have been extensively investigated by the optical-pumping method [1–7]. In the initial stage, a threshold power density of 1.2 MW/cm² and a transverse magnetic-field (TM) mode polarization of lasing were reported at a wavelength of ~ 240 nm at room temperature for Al_{*x*}Ga_{1–*x*}N/Al_{*y*}Ga_{1–*y*}N MQWs grown on a 4H-SiC substrate [1, 2]. Recently, high quality AlN substrates with a threading dislocation densities of $\sim 10^3$ cm^{–2} have been available [8]. By using these substrates, the threshold power density of lasing has been drastically reduced. In 2011, Wunderer *et al.* reported lasing at a wavelength of 267 nm with a threshold power density as low as 126 kW/cm² for Al_{*x*}Ga_{1–*x*}N/Al_{*y*}Ga_{1–*y*}N MQWs [6]. In 2013, Xie *et al.* reported a lower threshold density of 84 kW/cm² at a wavelength of 280 nm for Al_{0.5}Ga_{0.5}N/Al_{0.7}Ga_{0.3}N MQWs (1.6 nm well/ 4 nm barrier) [7].

On the other hand, optical gain characteristics have been reported for Al_{0.7}Ga_{0.3}N/AlN QW structures. A large modal gain of 118 cm^{–1} was reported at a energy density of 15 μ J/cm², which corresponded to a carrier density of 4.2×10^{17} cm^{–3} [9]. Additionally, the modal gain with transverse electric-field (TE) mode was reported by the same group [10]. However, the optimum structure has not been discussed yet in terms of the optical gain characteristics in Al-rich AlGa_N/AlN QW structures.

In this chapter, the optical gain characteristics measured by the variable stripe length (VSL) method are discussed in detail. To investigate the mechanisms of the optical gain formation in Al-rich AlGa_N/AlN QWs, the gain consumption phenomena, the well width dependence of the optical gain properties, and the polarization properties are discussed.

5.2 Experimental Procedure

5.2.1 Samples

The samples are the same QW structures as those used in Chapters 3 and 4. The 10-period Al_{*x*}Ga_{1–*x*}N/AlN QWs were fabricated on (0001) AlN/sapphire templates by the modified MEE

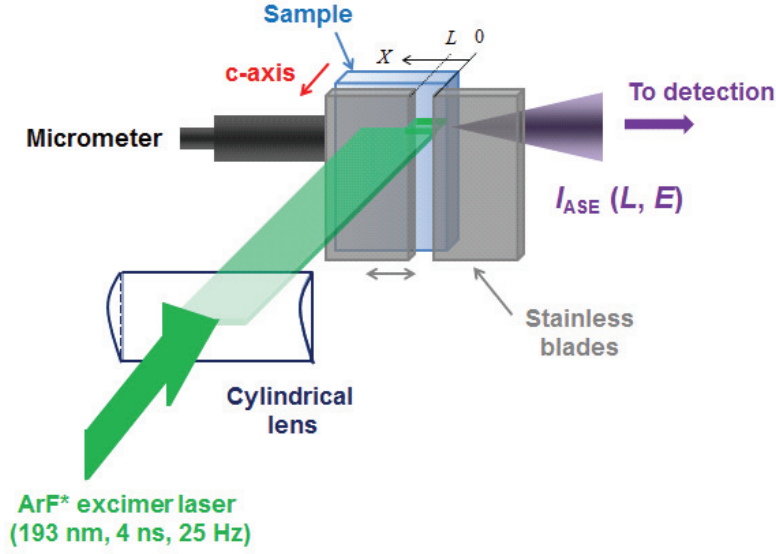


Figure 5.1: Experimental setup of variable stripe length method

method. The $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs were coherently grown on the AlN underlayers, as demonstrated by RSM. To investigate the optical properties of edge PL, cleaving and lapping of samples were performed exposing the m -plane of the AlN.

5.2.2 VSL Method

The VSL technique, which was first demonstrated by Shaklee *et al.*, is one of the established methodology for measuring the optical gain [11, 12]. The excited area is a stripe shape with small width and the PL spectra from edge plane are measured as a function of the excitation length L . If the optical gain occurs in the excited stripe region, the excited stripe serves as a one-pass light amplifier. Thus, the observed spontaneous emission is amplified along the stripe through the stimulated emission process. This emission is called amplified spontaneous emission (ASE).

Our experimental setup is shown in Fig. 5.1. An ArF* excimer laser (center wavelength: $\lambda = 193$ nm, repetition frequency: $f = 25$ Hz, and pulse duration: $\tau = 4$ ns) was used as an excitation light source. The ArF* excimer laser was uniformized by micro lens arrays (fly-eye lenses) and then focused in the striped shape by a cylindrical lens. The excitation length L can be adjusted by stainless blades operated by a micrometer. The excitation laser was incident at the surface normal and the PL was collected from the edge plane by one lens and focused at the entrance of a 50-cm monochromator with a liquid-nitrogen-cooled CCD by another lens. Moreover, this configuration allowed the polarization properties of TE and TM to be directly evaluated by using a Glan-Thomson polarizer inserted between these lenses.

5.3 How to Analyze Optical Gain

ASE is usually interpreted within a one-dimensional light amplifier model. The photons generated by spontaneous emission are amplified through the simulated emission process along the

X axis (see Fig. 5.1), which is monitored by recording the output PL intensity I_{ASE} from the edge of the sample.

The increase in the detected intensity dI_{ASE} related to the increase in the stripe length dX is given by

$$dI_{\text{ASE}}(X, E) = G_{\text{mod}}(E)I_{\text{ASE}}(X, E)dx + I_{\text{sp}}(E)dX, \quad (5.1)$$

$$G_{\text{mod}} = \Gamma g_{\text{mat}} - \alpha, \quad (5.2)$$

where G_{mod} is the modal gain, Γ is the optical confinement factor, g_{mat} is the material gain, and α is the internal loss. I_{sp} stands for the intensity of spontaneous emission coming from the unit length of the stripe and being independent of X . Solving the differential equation (5.1) in the range of $0 \leq X \leq L$, we obtain

$$I_{\text{ASE}}(L, E) = \frac{I_{\text{sp}}(E)\{\exp(G_{\text{mod}}(E)L) - 1\}}{G_{\text{mod}}(E)}. \quad (5.3)$$

Therefore, the gain spectra $G_{\text{mod}}(E)$ can be obtained by measuring $I_{\text{ASE}}(L, E)$ as a function of L . However, in reality, the equality (5.3) holds in only the condition of $L < L_s$.¹ If $L \geq L_s$, the ASE intensity is saturated. The detail in the saturation phenomena will be discussed in the next section. Finally, it is noteworthy that the VSL method has one disadvantage. If $|G_{\text{mod}}|L \ll 1$, the I_{ASE} is approximated as $I_{\text{ASE}} \simeq I_{\text{sp}}L$ from Eq. (5.3).² Consequently, this method cannot distinguish small positive gain from absorption [13].

5.4 ASE Saturation by Gain Consumption

As explained in the previous section, the gain consumption occurs in the condition of $L \geq L_s$. We discuss the effects caused by the gain consumption in this section.

We consider the excitation condition that excitation power density is constant and excitation length L is increased. Figure 5.2 shows schematic images of one-pass light amplification of photons generated at X in the conditions of (a) $L < L_s$ and (b) $L \geq L_s$. If $L < L_s$, the photons, which is generated by spontaneous emission at X , are amplified as $\exp(G_{\text{mod}}X)$. As L is increased, this amplification degree of photons is increased and stimulated emission is enhanced. When L is above L_s , the stimulated emission becomes dominant, especially near the edge of the stripe, because the rate of stimulated emission is proportional to photon density. This causes the decrease in the inversion population due to the decrease in the energy separation between electron and hole quasi-Fermi levels. Thus, the carrier density in the excited stripe is spatially inhomogeneous [14]. In addition, the peak energy is redshifted due to the decrease in the optical gain on the higher energy side.

¹ L_s is called saturation length.

² $\exp(G_{\text{mod}}L) \simeq 1 + G_{\text{mod}}L$ is used.

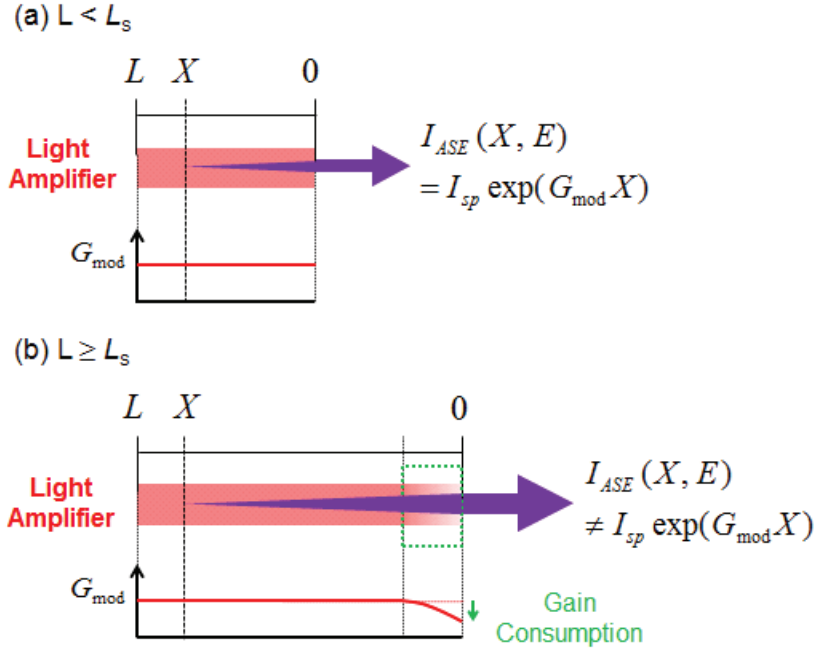


Figure 5.2: Schematic images of one-pass light amplification of photons generated at X in the conditions of (a) $L < L_s$ and (b) $L \geq L_s$. If $L \geq L_s$, ASE intensity is saturated by the gain consumption, in particular near the edge of the light amplifier.

5.5 Edge PL Properties Compared to Surface PL

Figure 5.3 shows the excitation length L dependence of edge PL spectra in Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 5$ nm at an excitation power density (P_{ex}) of 270 kW/cm². For comparison, the surface PL spectrum of the same QW at $P_{\text{ex}} = 540$ kW/cm² is also shown in Fig. 5.3. It was found that the linewidths of edge PL spectra were much narrower than that of the surface PL spectrum. This is because the amplification degree in the edge PL is much larger than that in surface PL due to much longer length of the light amplifier, though their optical gains are the same [15]. Furthermore, PL intensity was increased superlinearly (exponentially) as L was increased up to ~ 300 μm (L_s), as shown in Fig. 5.4. These results support that the ASE can be observed from this QW. On the other hand, with further increase in the excitation length from L_s , the ASE intensity was increased sub-exponentially due to the gain consumption. In the result of fitting the experimental results by the theoretical equation (5.3) in the region without the ASE saturation, large $G_{\text{mod}} = 140$ cm⁻¹ was obtained. Additionally, the peak energy was redshifted at $L \geq L_s$, as shown in Fig. 5.4. This result means that the redshift may be influenced by the gain consumption.

To confirm this observation, Fig. 5.5 shows the excitation length dependence of the ASE intensity at power densities of 70 kW/cm² and 270 kW/cm² for Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 5$ nm. The gain saturation was observed at 270 kW/cm², whereas it was not observed at 70 kW/cm². It was found that the redshift was observed only in the condition of the ASE saturation (270 kW/cm²). Therefore, these results strongly indicate that the redshift was caused by the gain consumption.

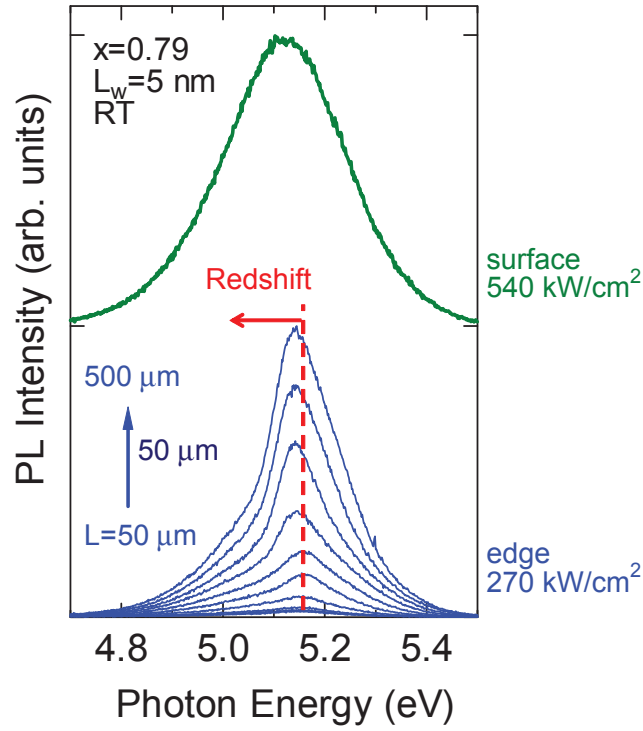


Figure 5.3: Edge PL spectra as a function of the excitation length (with $50 \mu\text{m}$ increments between $50 \mu\text{m}$ and $500 \mu\text{m}$) in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 5 \text{ nm}$ at $P_{\text{ex}} = 270 \text{ kW/cm}^2$. For comparison, the surface PL is also shown at $P_{\text{ex}} = 540 \text{ kW/cm}^2$.

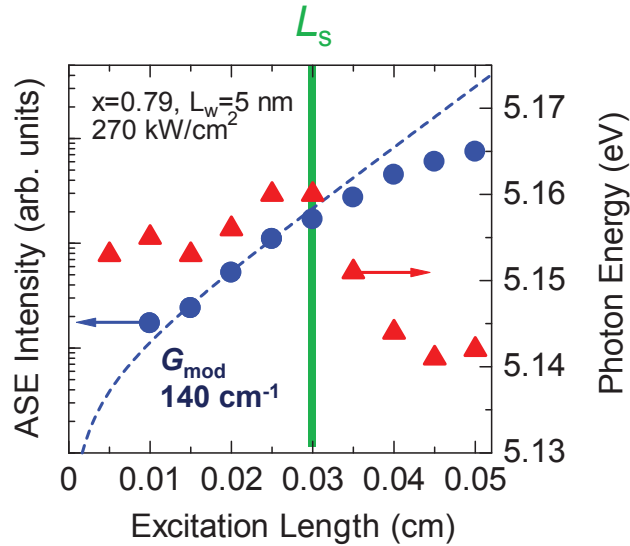


Figure 5.4: Excitation length dependence of ASE intensity and peak energy in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 5 \text{ nm}$ at $P_{\text{ex}} = 270 \text{ kW/cm}^2$. The dashed line represents the least-square fit obtained from Eq. (5.3). In the result of fitting, a modal gain of 140 cm^{-1} was obtained. Thick line shows the saturation length L_s .

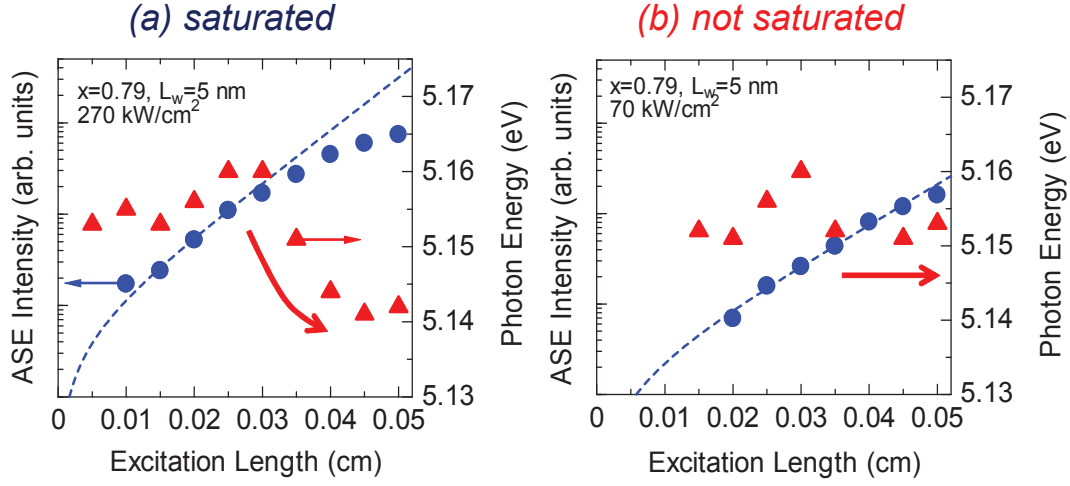


Figure 5.5: Excitation length dependence of ASE intensity and peak energy at (a) 70 kW/cm² and 270 kW/cm² in Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 5$ nm. The dashed lines represent the least-square fit obtained from Eq. (5.3).

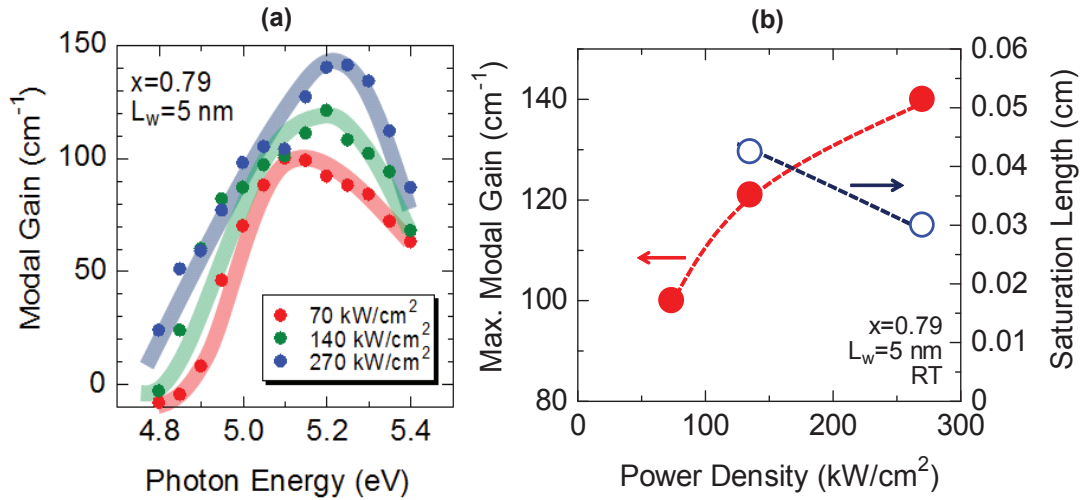


Figure 5.6: (a) Excitation power dependence of optical gain spectra and (b) power density dependence of maximum modal gain and saturation length in Al_{0.79}Ga_{0.21}N/AlN QW with $L_w = 5$ nm.

5.6 Excitation Power Dependence

Figure 5.6(a) shows the excitation power dependence of the gain spectra analyzed by Eq. (5.3) in the region without the gain saturation for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW with $L_w = 5$ nm and Fig. 5.6(b) shows the excitation power density dependence of the maximum modal gain and the saturation length L_s . As the excitation power was increased from 70 kW/cm^2 to 270 kW/cm^2 , the optical gain was increased from 100 cm^{-1} to 140 cm^{-1} and the peak energy was blueshifted due to the increase in the energy separation between electron and hole quasi-Fermi levels. As shown in Fig. 5.6(b), the larger modal gain caused the smaller saturation length.

5.7 Well Width Dependence

To investigate the optimum well thickness for the largest optical gain, the well width dependence of VSL measurements was performed. Figure 5.7 shows the optical gain spectra for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with different well widths of 2.5, 3.8, and 5 nm. It was noted that the optical gain was not observed at $L_w = 10$ nm. The largest modal gain of 140 cm^{-1} was obtained at $L_w = 5$ nm.

To account for this tendency, we calculate the optical confinement factor Γ and the maximum g_{mat} for TE mode in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with different well widths, as shown in Figs. 5.8 (a) and (b). For the wider QW, Γ is larger due to the wider active region. We calculated g_{mat} for QW structure by the simple two-bands model [16],

$$g_{\text{mat}}(E) = \frac{\pi e^2}{nc\varepsilon_0 m_0^2 \omega} \int |M_{\text{cv}}|^2 \rho_e(E') \rho_h(E - E') \{f_e(E') + f_h(E - E') - 1\} dE', \quad (5.4)$$

where $|M_{\text{cv}}|^2$ is the matrix element given by [17]

$$|M_{\text{cv}}|^2 = \frac{\hbar^2}{2m_0} \left(\frac{m_0}{m_e} - 1 \right) \frac{(E_g + 2\Delta_2)(E_g + \Delta_1 + \Delta_2) - 2\Delta_3^2}{E_g + 2\Delta_2} |\langle \psi_e | \psi_h \rangle|^2. \quad (5.5)$$

g_{mat} is proportional to the square overlap integral of wavefunctions between electron and hole, $|\langle \psi_e | \psi_h \rangle|^2$. As a result, g_{mat} was drastically reduced as the well width was increased. Assuming that the internal loss α is constant for all the QWs, G_{mod} is larger for the QW with larger Γg_{mat} . Figure 5.8(c) shows the well width dependence of Γg_{mat} , which should reproduce the well width dependence of the maximum modal gain, G_{mod} . However, the experimentally-observed optical gain was much larger than the calculated optical gain, and the well width at the maximum gain was different. This is probably because of the potential fluctuation [18]. Pecora *et al.* reported that a large net modal gain of $\sim 120 \text{ cm}^{-1}$ for the QW with cluster-like features, while the absorption was obtained for the homogeneous QWs. As discussed in Chap. 3, the two kinds of potential fluctuations co-exist in Al-rich AlGaIn/AlN QWs. Therefore, it is considered that the optical gain is much higher than what can be achieved with uniform QW structures, due to the benefits of potential fluctuations.

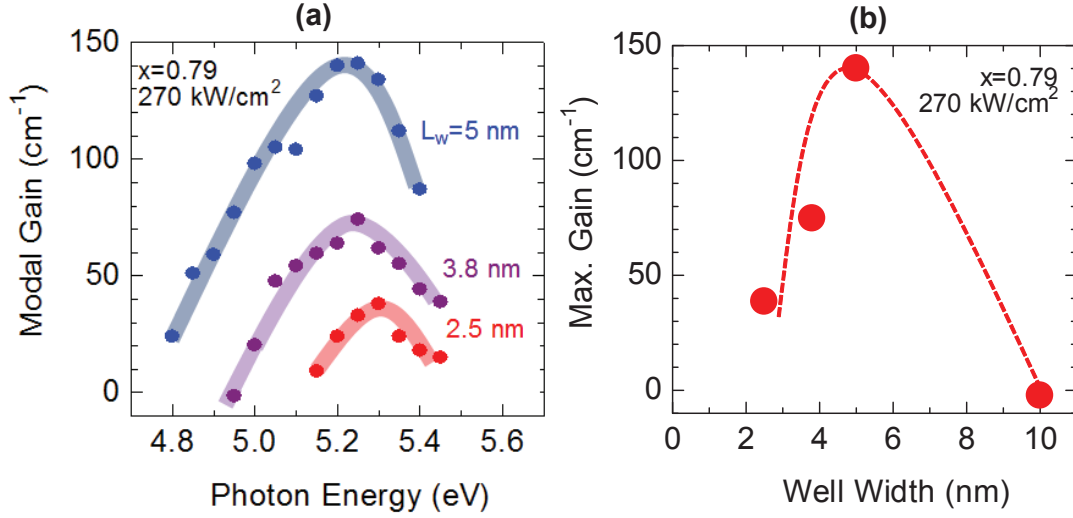


Figure 5.7: Well width dependence of (a) gain spectra and (b) maximum gain in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. The broken line is given only to indicate the data trend.

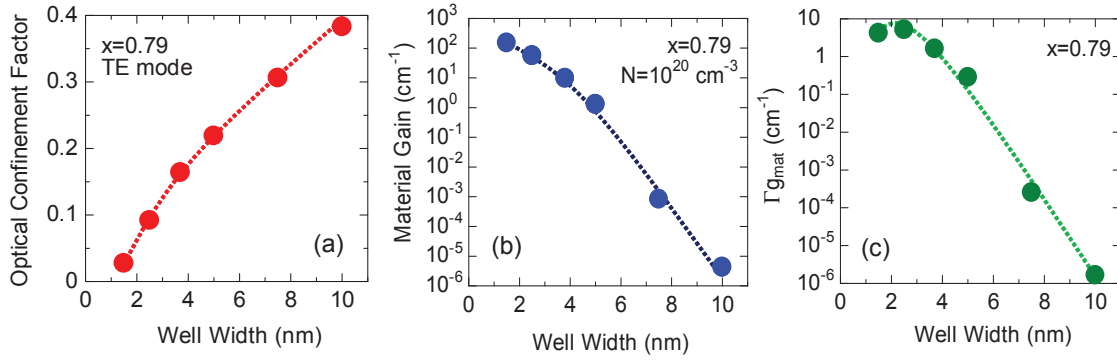


Figure 5.8: Well width dependence of (a) optical confinement factor Γ , (b) material gain g_{mat} and (c) Γg_{mat} in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs. The broken line is given only to indicate the data trend.

5.8 Polarization Properties

As described in Chap. 2, the optical transition between the conduction band and the top valence band is mainly TE polarized for GaN and TM polarized for AlN. For Al-rich AlGaN QWs, the polarization is switched at a certain Al composition due to the turnover of valence band order, depending on the strain and well width. The polarization switching phenomena of coherently-grown AlGaN/AlN QWs on AlN were experimentally observed around $x = 0.8$ [19], consistent with the theoretical suggestions [20,21]. As for the polarization of the optical gain, it was reported that the large modal gain of 52 cm^{-1} with TE-mode was obtained, whereas the negative gain (absorption) of -22 cm^{-1} with TM-mode was observed in $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ MQW [10]. To investigate the polarization switching of the optical gain, Al compositional dependence measurements of the optical gain were performed by the VSL method.

Figure 5.9 shows the I_{ASE} with TE and TM modes as a function of L for $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with $L_w = 5$ nm at RT. Interestingly, the modal gains with both TE and TM modes

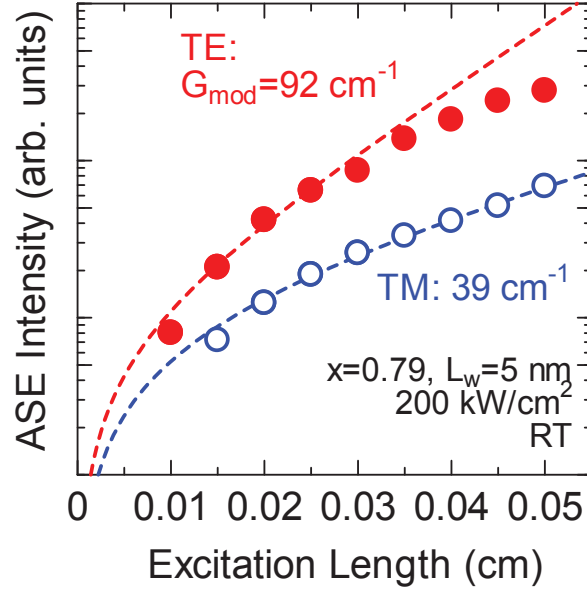


Figure 5.9: The modal gains with TE and TM modes in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQWs with $L_w = 5 \text{ nm}$ at $P_{\text{ex}} = 200 \text{ kW/cm}^2$. The dashed lines represent the least-square fit obtained from Eq. (5.3).

were obtained and their values were 92 cm^{-1} and 39 cm^{-1} , respectively. To characterize the effects of Al composition on the optical gain, Fig. 5.10 shows the polarization properties of the optical gain as a function of Al composition x . For reference, the estimated optical gain for an AlN thin film with a thickness of $\sim 1 \mu\text{m}$ is also shown. As x was decreased from 0.8, the modal gain with TM mode was reduced and came close to zero. On the other hand, as x was increased from 0.8, the modal gain with TE mode was drastically reduced and came close to zero. Furthermore, the polarization switching phenomena of optical gain was observed at a given Al composition between 0.79 and 0.91. These results are derived from the experimental and calculational results that the switching of valence band ordering occurs at about $x = 0.8$ in $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs (see Fig. 5.11).

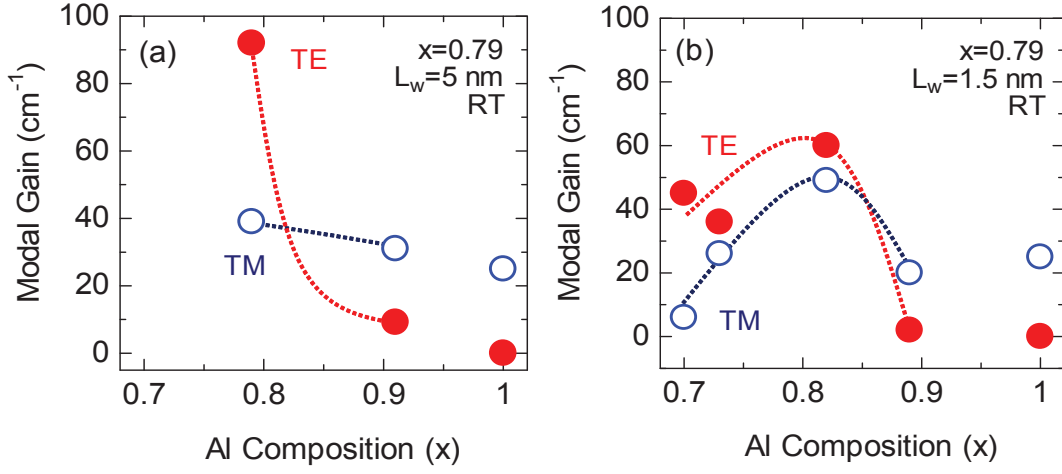


Figure 5.10: The modal gains with TE and TM modes for $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ MQWs with (a) $L_w = 5 \text{ nm}$ and (b) $L_w = 1.5 \text{ nm}$ as a function of Al composition. For reference, the result of AlN thin film with a thickness of $\sim 1 \mu\text{m}$ is also shown.

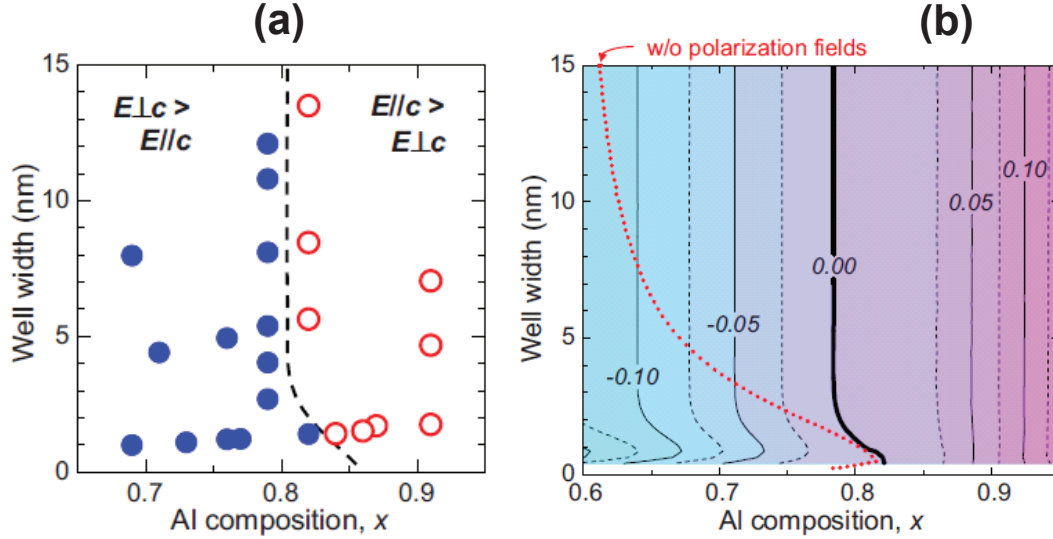


Figure 5.11: (a) Plot of polarization in AlGa_N/AlN QWs as functions of Al composition and well width. (b) Contour plot of the calculated energy difference of $E(\text{CH}) - E(\text{HH})$ in the unit of eV. Red dotted line and black solid line are the $E(\text{HH}) = E(\text{CH})$ lines for flat-band QWs without a polarization field and for QWs with polarization fields, respectively. The assumed spontaneous polarization was -0.040 C/m^2 . These figures are quoted from Ref. [19]

5.9 Summary

We discussed the optical gain characteristics evaluated by the VSL method in Al-rich Al-GaN/AlN QWs at RT. Edge PL spectra were much narrower than surface spectrum and their intensities were increased exponentially as excitation length was increased. In the result of well width dependence of VSL measurements in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQWs, the largest optical gain of 140 cm^{-1} was obtained for the QW with $L_w = 5\text{ nm}$. This observation can be qualitatively explained by the calculated optical confinement factor Γ and material gain g_{mat} . However, the experimentally-observed optical gain was much larger than the calculated optical gain with uniform two-bands model, and the well width at the maximum gain was different, probably because of the potential fluctuation. Moreover, by comparing the conditions between with and without the ASE saturation, we found that the redshift beyond L_s was caused by the gain consumption. We experimentally demonstrated that dominant polarization was changed from TE mode to TM mode as Al composition was increased, for the first time. This result is derived from the turnover of the valence band ordering of $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs.

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Chapter 6

Optical Properties in Electron Beam Pumped Al-rich AlGa_N/AlN QWs

6.1 Introduction

As explained in Chapters 1 and 2, a critical issue in electrically driven devices based on p-n junction diodes is the EQE, which is the product of IQE, CIE, and LEE. Despite the high IQE, the EQE of AlGa_N-based LEDs is about 10% and is smaller at shorter wavelengths. Although a low LEE of 8% has been reported [1], device configurations such as patterned substrates [2] may improve this value. A more essential factor for a low EQE may be intrinsically low hole concentrations in p-type AlGa_N. Generally, the wider the bandgap is, the deeper the acceptor activation energy becomes, which has been observed in the Mg acceptor activation energies in AlN (630 meV [3]) and GaAs (29 meV [4]). A simple calculation based on the Maxwell-Boltzmann statistics predicts that the hole concentration in AlN with a Mg acceptor concentration of $1 \times 10^{19} \text{ cm}^{-3}$ is as low as $\sim 2 \times 10^{10} \text{ cm}^{-3}$ at RT (see section 2.6). This very low value hampers current injection from the p electrodes into the diodes as well as that from the p-type cladding layers into the light emitting QW regions. Recently, several groups have proposed a promising alternative, EB pumped nitride semiconductor based light sources, which use a structure similar to a field emission display. It is noted that EB pumping method has been also proposed for II-VI semiconductors, which has the difficulty of controlling the electrical conductivity [5, 6]. Watanabe *et al.* have fabricated a handheld device using boron nitride powders with an emission wavelength of 225 nm, a maximum output power of 1 mW, and a power efficiency (PE) of 0.6% [7]. Additionally, Shimahara *et al.* have demonstrated that a Si-doped AlGa_N bulky film excited by EB exhibits a 2.2 mW output at 247 nm with a PE of 0.22% [8]. However, similar to electrically driven LEDs, these powers and efficiencies are insufficient for practical applications.

In this chapter, we propose to use Al_xGa_{1-x}N MQWs as a phosphor. First, the advantages of using QW structures is presented. Then, toward high-power, highly efficient DUV optical devices, we discuss the optical properties in EB-pumped AlGa_N/AlN QWs.

6.2 Advantages of QW Structures for EB Pumping

There are three major reasons for the relatively low output powers and efficiencies from EB pumped bulks and powders. First, self-absorptions degrades bulks and powders can emit light, but at the same time, those host materials can absorb the emitted light, which degrades the availability of emitted light. (Also in LEDs, p-type GaN used for improving the carrier (hole) transport property absorbs emitted light.) On the other hand, in the case of QWs, the light-emitting layer has a narrower bandgap than the host material, and so absorption by the host material can be avoided in principle. Second, radiative recombination probabilities of QWs are much higher than those of bulks and powders [9]. Finally, there is the optical anisotropy in AlGa_N/AlN QWs [10]. In thick AlGa_N coherently grown on AlN, the valence band ordering prevents surface emission from the (0001) plane for $x > 0.6$, that is, for emission wavelengths shorter than 250 nm. In contrast, we have found that the quantum confinement strongly affects the valence band ordering and promotes (0001) surface emission [10]. The detail regarding the polarization properties was described in Chap. 2. To overcome these issues and to extract the potential high performance from EB pumped UV light emitters, we propose to use highly luminous QWs as a phosphor for EB pumping.

6.3 Experimental Setup

Figure 6.1 schematically depicts the setup of the EB pumping experiments. The sample, EB gun, and photo-detector were loaded in the same vacuum chamber. EB was focused on the sample surface with a diameter of ~ 0.14 mm, measured by the knife edge method. The photo-detector, which was a 1×1 cm² AlGa_N photo-diode (PD) (ALGAN K.K., JAPAN) [11], was placed 3 mm behind the sample. Hence, the emission power was monitored through the sapphire substrate. To enhance light extraction, the back of the substrate was roughened by a mechanical process to avoid the total reflection at the substrate/vacuum interface. We confirmed that this roughened surface enhanced the light extraction by approximately 50%.

6.4 Optimization of QW Structures

As discussed in Sec. 6.2, a thin AlGa_N wells is desirable to avoid self-absorption and QCSE in AlGa_N wells. Furthermore, in AlGa_N/AlN QWs with a very thin well layer, the large quantum confinement promotes (0001) surface emission, which motivated us to use the 1-nm-thick QW. Thus, we used the 8-period Al_{0.69}Ga_{0.31}N/AlN MQWs fabricated by the modified MEE method on a (0001) AlN (600 nm)/sapphire template. To assess the fundamental optical properties, PL measurements were performed at 8.5 K and RT. Figure 6.2 shows the acquired PL spectra with an emission wavelength of ~ 237 nm at RT. Assuming that non-radiative recombination processes can be neglected at low temperatures [12], the PL intensity ratio between LT and RT estimates the IQE at RT, which was as high as 57%. It is noteworthy that the IQE of an AlN bulky film has been estimated to be about 5% at RT [14]. The much higher IQE of our QW, which promises superior properties under EB pumping, is owing to the carrier

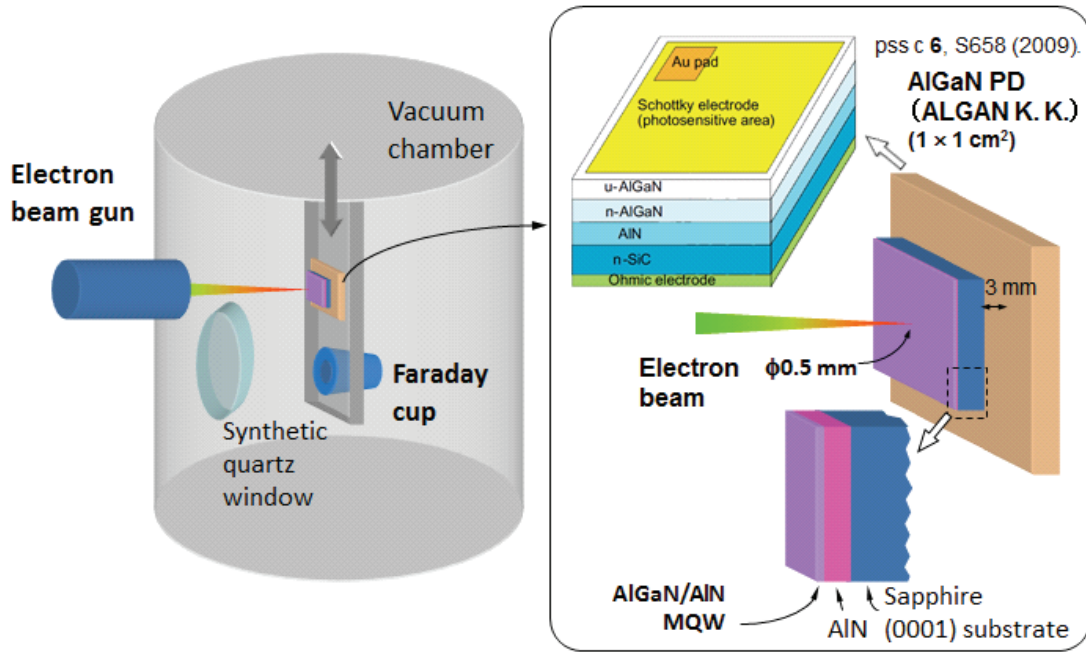


Figure 6.1: Schematic configuration of EB pumping experiments. $\text{Al}_{0.69}\text{Ga}_{0.31}\text{N}/\text{AlN}$ MQW with a rough back side is irradiated with a focused EB. An AlGaIn photo-diode is placed 3 mm behind the sample and monitors the emission power through the substrate.

confinement within the very high quality QW. Another important finding in Fig. 6.2 is that the emission from AlN is not observed, which indicates that carriers generated in the AlN barriers are eventually captured in the AlGaIn wells. That is, the AlN barriers work as a reservoir for supplying carriers to the AlGaIn wells.

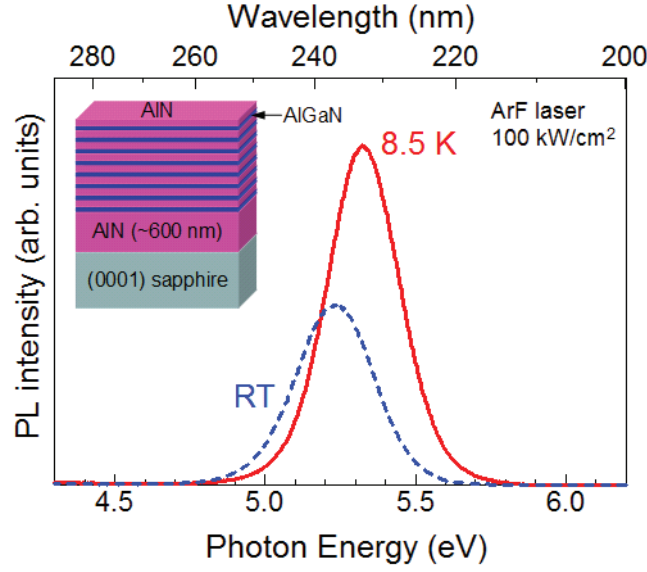


Figure 6.2: PL spectra of Al_{0.69}Ga_{0.31}N/AlN MQW were acquired at 8.5 K and RT, from which the IQE was evaluated to be 57%. The inset is a schematic of an Al_{0.69}Ga_{0.31}N/AlN MQW grown on an AlN (600 nm)/sapphire (0001) template. This figure is quoted from Ref. [13].

6.5 Optimization of EB Conditions by Monte Carlo Simulation

Electrons irradiated on a solid surface penetrate into the solid and experience mutual interactions with other electrons and atomic nucleus. The electron penetration depths are generally larger for higher acceleration voltages (V_A) and lighter density solids. As the simplest semi-empirical model reported by Kanaya and Okayama (Kanaya-Okayama model), penetration length R [nm] for a bulky semiconductor is given by [15],

$$R = \frac{2.76 \times 10^{-11} A E_0^{5/3}}{\rho Z^{8/9}}, \quad (6.1)$$

where A is the weight of nucleus [g/mol], E_0 [eV] is the energy of electron, ρ [g/cm³] is density, and Z is the average atomic number. Though the mutual interaction is considered only once in Eq. (6.1), this equation gives us the guideline for the optimization of penetration length of electrons.

Let us consider the case of QW structures. If the penetration depth is much greater than the thickness of the QW region, part of the irradiated electrons may go through that region and recombine in the underlying AlN layer, degrading the emission efficiency. On the other hand, if the penetration depth is too narrow, then QWs located deeper from the surface do not receive sufficient numbers of carriers. Hence to maximize the emission efficiency and the output power, properly selecting the acceleration voltage to match a given QW structure, or inversely, designing a QW structure to meet the acceleration voltage is crucial. To elucidate the appropriate combination between the QW structure and the acceleration voltage, we simulated numerous electron trajectories in our Al_{0.69}Ga_{0.31}N/AlN MQW under different acceleration voltages via a Monte Carlo method [16,17]. Figure 6.3(a) shows an example result for $V_A = 8$

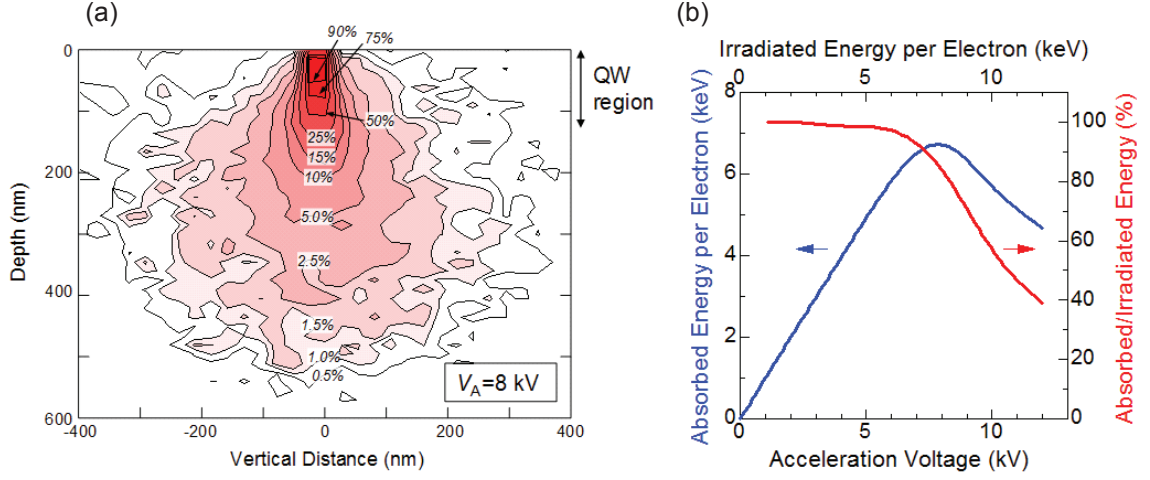


Figure 6.3: (a) Contour plot of the electron energy for $V_A = 8$ kV simulated by the Monte Carlo method. The assumed structure is an $\text{Al}_{0.69}\text{Ga}_{0.31}\text{N}$ (1 nm)/ AlN (15 nm) eight-period MQW. Percentages represent the electron energy with respect to the initial value. (b) Summary of the Monte Carlo simulation showing the V_A dependence of the absorbed electron energy within the quantum well region (left axis) and the ratio between absorbed energy and irradiated energy onto the sample (right axis). These figures are quoted from Ref. [13].

kV.

To analyze the simulated results more quantitatively, Fig. 6.3(b) summarizes the acceleration voltage dependences of the absorbed electron energy within the QW region (left axis) and the ratio between that absorbed energy and the irradiated energy onto the sample (right axis). The former corresponds to the energy used to generate electron-hole pairs in the QW region, and was maximized at $V_A = 8$ kV. Further increasing the acceleration voltage decreased the absorbed energy by the mechanism explained above. Therefore, $V_A = 8$ kV should be the best in terms of the output power. On the other hand, the energy ratio (right axis of Fig. 6.3(b)) represents the utilization of irradiated electrons within the QW region and corresponds to CIE. Again, $V_A > 8$ kV degraded the ratio by the same mechanism. Although the ratio is high for $V_A < 8$ kV, the penetration of electrons is insufficient to cover the entire QW region. Thus, the simulation indicates an acceleration voltage of ~ 8 kV is suitable for the current MQW structure.

6.6 Output Power and Power Efficiency

To confirm the Monte Carlo analysis, the output power was experimentally evaluated using the setup shown in Fig. 6.1. Figure 6.4(a) shows the UV output power and PE as a function of irradiated current (I_E). The acceleration voltages were parameters (6, 8, and 10 kV). The output power exceeded 100 mW with $V_A = 8$ kV and $I_E = 45$ μA . However, further increasing V_A did not increase the output power, which is consistent with the simulation [see Fig. 6.3(b)]. Furthermore, the PE was also the highest with $V_A = 8$ kV, and was $\sim 40\%$ for $I_E = 5$ μA . These experimental results indicated that $V_A = 8$ kV is the most suitable acceleration voltage

for our MQW. It is noteworthy that the attained 100 mW output power and 40% PE are about one order of magnitude higher than the values reported for LEDs emitting at 250 nm [1] and EB pumped nitride semiconductors [7, 8]. One discrepancy with the simulation was that $V_A = 6$ kV did not provide a PE comparable to that for $V_A = 8$ kV. One possible reason is the carrier density dependent IQE, as discussed in Sec. 4.5. Additionally, the mechanism of the PE drop observed for a larger current has been not clarified yet.

Figure 6.4(b) shows a photograph of a phosphor-coated glass excited by UV emission from our $\text{Al}_{0.69}\text{Ga}_{0.31}\text{N}/\text{AlN}$ MQW under the conditions of 8 kV and 45 μA . The coated phosphors were identical to those used for fluorescent lamps. In this particular case, the distance between the MQW and the target phosphors was 15 mm, which is much larger than that between the MQW and photodiode used for Fig. 6.4(a) (~ 3 mm). Nevertheless, the phosphors emitted a dazzling white color, confirming the high output power from our MQW.

6.7 Estimation of Each Efficiency

Let us discuss efficiencies, assuming $\text{IQE} = 57\%$, an emission energy (E) of 5.2 eV (238 nm), and a light output power (P_{out}) of 100 mW when $V_A = 8$ kV and $I_E = 45 \mu\text{A}$, according to the experimental results. It should be noted that one irradiated electron generates multiple electron-hole pairs in solids. Using the yield from an irradiated electron to electron-hole pairs (η_{EH}), the number of electron-hole pairs N_{EH} is given by

$$N_{\text{EH}} = \frac{\eta_{\text{EH}} V_A}{E} \quad (0 \leq \eta_{\text{EH}} \leq 1). \quad (6.2)$$

Then, taking

$$\text{PE} = \frac{P_{\text{out}}}{IV_A}, \quad (6.3)$$

$$\text{EQE} = \frac{\frac{P_{\text{out}}}{eE}}{N_{\text{EH}} \frac{1}{e}}, \quad (6.4)$$

$$\text{EQE} = \text{IQE} \times \text{LEE} \times \text{CIE}, \quad (6.5)$$

into account, we obtain

$$\frac{\text{PE}}{\eta_{\text{EH}}} = \text{IQE} \times \text{LEE} \times \text{CIE}. \quad (6.6)$$

It is difficult to experimentally quantify CIE. Therefore, the CIE estimated by the Monte Carlo simulation [the right axis of Fig. 6.3(b) was used, which was 84% for $V_A = 8$ kV]. Substituting those quantities into $\text{PE}/\eta_{\text{EH}} = \text{IQE} \times \text{LEE} \times \text{CIE}$ deduces $\eta_{\text{EH}} \times \text{LEE} = 0.58$. Although to determine each value, we have to determine either of them by other experiments, the condition of $\eta_{\text{EH}} \times \text{LEE} = 0.58$ seems reasonable, because the emitted UV light is efficiently extracted from the roughened back of the sapphire substrate.

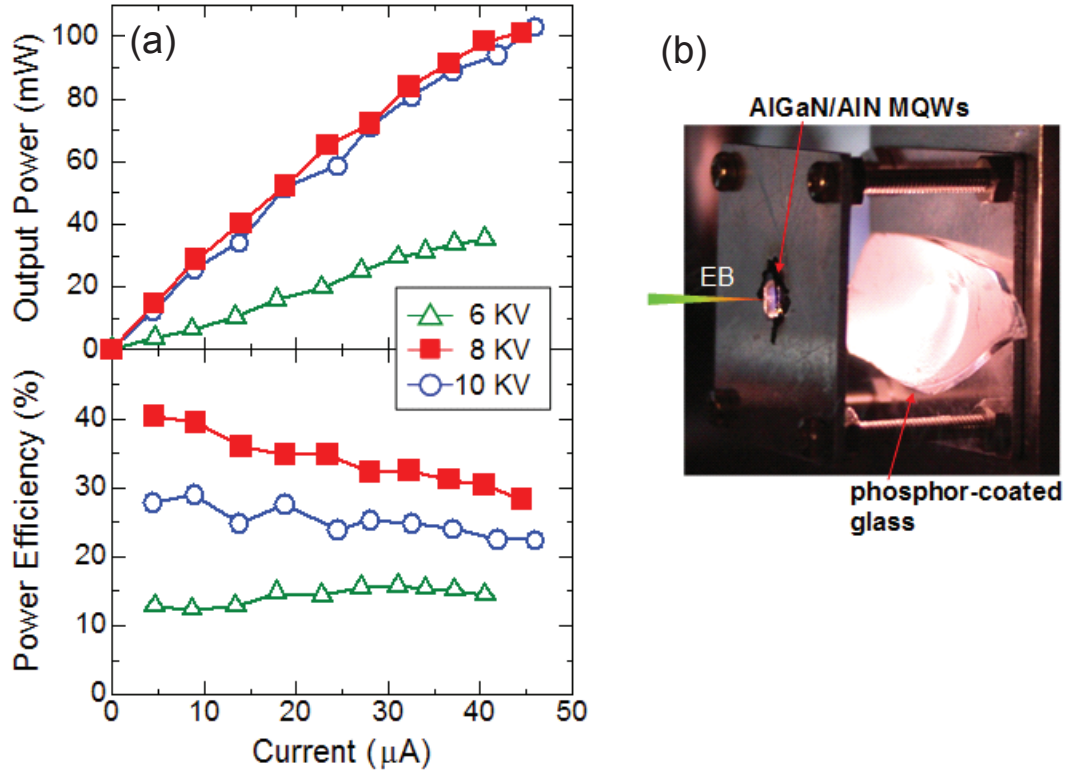


Figure 6.4: (a) P_{out} and PE as functions of irradiated current under different V_A . (b) Photograph showing a phosphor-coated glass excited by UV emission from our $\text{Al}_{0.69}\text{Ga}_{0.31}\text{N}/\text{AlN}$ MQW under 8 kV and 45 μA . All measurements were performed at RT. These figures are quoted from Ref. [13]

6.8 Summary

We used an EB pumping technique, and demonstrated an output of 100 mW and a record power efficiency of 40% from thin Al-rich AlGaIn/AlN QWs emitting at ~ 240 nm. This achievement is attributed to the optimization of both QW structures and EB conditions. It should be emphasized that the EB operating conditions are accessible using portable field-emission devices. Additionally, preliminary experiments showed that P_{out} did not decrease at all over a period of about an hour with $V_A = 6$ kV and $I = 35$ μA . Therefore, EB pumping may be a milestone in the path to realizing next-generation DUV light sources with great ecological and economic benefits.

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Chapter 7

Conclusions

7.1 Conclusions

In this thesis, the emission mechanisms of Al-rich AlGa_N/AlN QWs were presented. The conclusion of each chapter is presented as follow.

Chapter 2

We presented the fundamental optical properties in AlGa_N QWs and performed some calculations for Al_{*x*}Ga_{1-*x*}N. First, the well width dependence of potential fluctuations was quantified by solving the Schrödinger equations. As the well width becomes wider, the well width fluctuation and the statistically unavoidable alloy disorder effect are smaller, whereas the Al compositional fluctuation is wider. After that, the excitation power dependence of the peak shifts was calculated. Finally, Al compositional dependence of hole concentrations was calculated. The hole concentration of p-type Al-rich AlGa_N was very low due to the large acceptor activation energy. This result suggests that it is very difficult to fabricate the Al-rich AlGa_N-based LEDs with high EQEs for DUV region.

Chapter 3

The excition localization phenomena were presented for Al-rich AlGa_N/AlN QWs. From the temperature dependence of weak excitation PL measurements using a Xe₂^{*} excimer lamp and CL mapping measurements, it was found that the emission mechanisms were based on the two types of localization states. We identify that the experimentally observed two types of localization states, that is, shallow and deep localization states originate from the statistically unavoidable alloy disorder effect and 2 ML (± 1 ML) fluctuation of the well width, respectively. It is noteworthy that we obtained the same results about the origins of the localization states for the QWs with different well widths and Al compositions. For narrow QWs, many excitons migrated to deep localization states derived from 2 ML fluctuation and emitted brightly in those regions, due to the large density of deep localization states and the short PL lifetime. In addition to the emission from the near band edge, the emissions probably originating deep levels and local phase separation were observed by the temperature dependent CL mapping measurements.

Chapter 4

The emission mechanisms under increased excitation were discussed for the $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with different well widths. The well width dependence of emission mechanisms can be explained by the two types of localization states with the different densities of localization states and diffusion lengths. Moreover, the PL peak shift and its well-width dependence could reasonably be reproduced by considering BGR, B-M shift, and screening effect of internal electrical field. Among them, the major factor for the difference in the PL peak shift due to the well width was found to be the screening effect. To investigate the carrier dynamics, TRPL measurements for the Al-rich $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QWs with $L_w = 5$ nm were performed at 5.5 K. The fast and the slow lifetime components were observed under highly-excited conditions and were attributed to radiative recombination lifetimes of EHP and the EMB effect, respectively. Furthermore, the strong excitation conditions are very effective for the applications of DUV optical devices with high power and efficiency.

Chapter 5

We discussed the optical gain characteristics evaluated by the VSL method in Al-rich Al-GaN/AlN QWs at RT. Edge PL spectra were much narrower than surface spectrum and their intensities were increased exponentially as the excitation length was increased. In the result of well width dependence of VSL measurements in $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ MQWs, the largest optical gain of 140 cm^{-1} was obtained for the QW with $L_w = 5$ nm. Moreover, by comparing the conditions between with and without gain saturation, it was found that the redshift from L_s was caused by the gain consumption. For the first time, we experimentally demonstrated that the dominant polarization was changed from TE mode to TM mode as Al composition was increased. This result was derived from the switching of valence band ordering of strained AlGaIn/AlN QWs at a critical Al composition of ~ 0.8 .

Chapter 6

We presented an electron-beam pumping technique, demonstrating an output of 100 mW from the 8-period Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (1 nm)/AlN QWs emitting at ~ 240 nm in the condition of $V_A = 8$ kV and $I_E = 45 \mu\text{A}$. This achievement is attributed to the optimization of both QW structures and EB conditions, and may be a milestone in the path to realizing next-generation DUV light sources with great ecological and economic benefits.

7.2 Future Works

Through this study, a lot of new observations and aspects were revealed in optical properties of Al-rich AlGaIn/AlN QWs. However, several issues remain unsolved and should be clarified to understand the optical properties in more detail and realize the DUV optical devices with high emission efficiencies. These issues and their possible solutions are described below, in terms of optical properties and device applications.

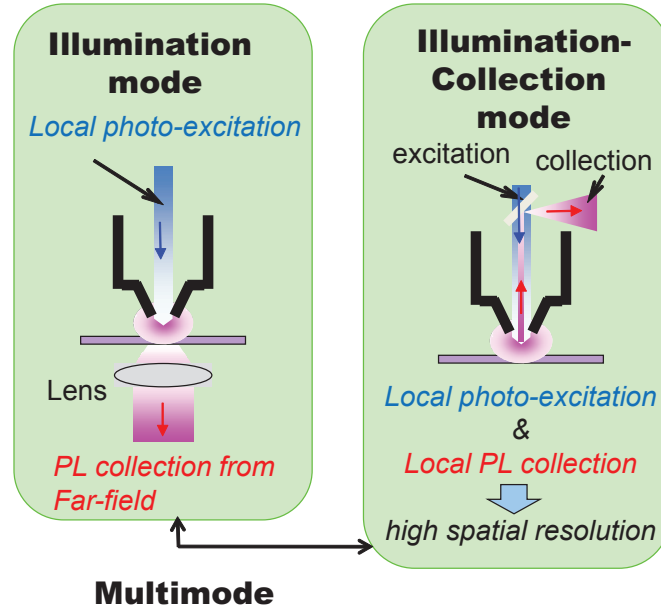


Figure 7.1: Schematic configurations of *I* mode and *I-C* mode. Multi-mode is the combination of *I* mode and *I-C* mode in SNOM measurements. This figure is quoted from Ref. [2].

7.2.1 Optical Properties

Scanning Near-field Optical Microscopy

In this study, the exciton dynamics were directly assessed by temperature dependent CL mapping measurements. Towards a better understanding of optical properties in Al-rich AlGa_N/AlN QWs, scanning near-field optical microscopy (SNOM) measurements are promising. General optical microscopes perform both photo-excitation and PL collection in the far-field through an objective lens. As a result, their spatial resolution is restricted by the diffraction limit. On the other hand, SNOM has a higher spatial resolution than the diffraction limit by detecting the near-field light. Figure 7.1 shows schematic configurations of the illumination mode (*I* mode) and the illumination-collection mode (*I-C* mode). In the *I* mode, photo-excitation is performed by near-field probe, and PL collection is performed by far field lens. The spatial resolution of the *I* mode is limited by the carrier diffusion length if it is larger than the aperture diameter. In the *I-C* mode, both photo-excitation and PL collection performed by the near-field probe. As a result, the PL peak positions directly reflect the potential energy beneath the probe aperture. Thus, this method realizes a high spatial resolution which is decided by a diameter of aperture. Furthermore, combining the *I*-mode and *I-C* mode (multi-mode), the information related to local carrier diffusion and/or radiative/nonradiative recombination processes can be obtained [1–4]. By these techniques, the optical properties in InGa_N/Ga_N QWs with various emission wavelengths [5] and planes such as (11 $\bar{2}$ 2) [6] and {20 $\bar{2}$ 1} [7] have been clarified. If SNOM measurements can be applied for the DUV region, more information regarding the carrier/exciton dynamics will be obtained in Al-rich AlGa_N/AlN QWs, which leads to a higher emission efficiencies.

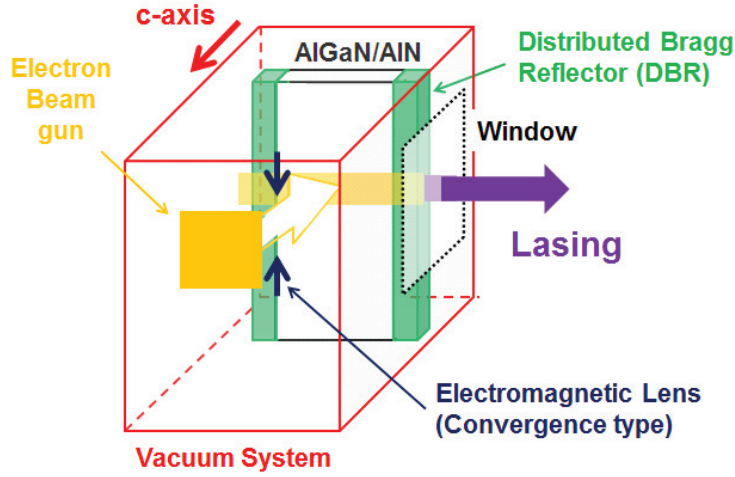


Figure 7.2: Handheld laser using AlGaIn/AlN QWs by EB pumping. Electrons emitted from a small EB gun are focused in the shape of stripe by a electromagnetic lens and irradiated onto the sample. To reduce the mirror loss, DBRs are deposited on the edge planes in AlGaIn/AlN QWs.

AlGaIn/AlN QWs Fabricated on High-Quality AlN Substrates

Recently, high quality AlN substrates with a threshold dislocation densities as low as $\sim 10^3 \text{ cm}^{-2}$ have been available [8]. Measuring Al-rich AlGaIn/AlN QWs fabricated on the high quality AlN substrates, optical properties can be precisely investigated. We have been already achieved high-quality *c*-plane and *r*-plane homoepitaxial AlN layer [9–11] and AlGaIn/AlN QWs [12,13]. Here, it has been theoretically predicted that the QCSE was drastically reduced in *r*-plane AlGaIn/AlN QWs. This means that the radiative recombination rates in *r*-plane AlGaIn/AlN QWs are larger than those in *c*-plane AlGaIn/AlN QWs. It is considered that the further information about the optical properties will be obtained by measuring the QWs with different planes.

7.2.2 Device Applications

Some groups have reported the DUV optical devices EB-pumped optical devices [14–18]. In this study, we have achieved one-order higher power efficiency than EQEs of current LEDs, using AlGaIn QWs by the EB pumping method. After our report related to EB-pumping [19], it has been demonstrated that EB pumped DUV optical devices with a output power of 20 mW and a power efficiency of $\sim 4\%$ [18]. In this way, EB-pumping has the possibility to be the main excitation method in particular for short wavelengths. In future studies, we should also try to fabricate handheld DUV optical devices with high efficiencies and high power DUV lamps by EB pumping. Furthermore, we believe that EB pumped AlGaIn based handheld lasers can be realized by fabricating distributed Bragg's reflectors to reduce the mirror loss. Fig. 7.2 shows schematic image of an EB-pumped DUV solid-state laser. Electrons emitted from a small EB gun are focused in the shape of stripe by a electromagnetic lens, irradiated onto the sample and achieve the lasing from the Al-rich AlGaIn/AlN QW. By applying this technique, we hope that EB-pumped vertical external cavity surface emitting lasers (VECSELs) will be also realized.

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Appendix A

Material Parameters

A.1 Material Parameters in AlN and GaN

In this section, the material parameters of GaN and AlN are introduced. Table A.1 lists the parameters in calculation. For $\text{Al}_x\text{Ga}_{1-x}\text{N}$, the parameters are obtained by the Vegard's law described in Eq. (2.20).

Table A.1: Material Parameters in the calculation

Parameters [unit]		AlN		GaN	
Lattice parameter [nm]	a	0.3112	[1]	0.3189	[1]
	c	0.4982	[1]	0.5185	[1]
Effective mass [m_0]	$m_e^{\parallel}$	0.32	[1]	0.21	[1]
	$m_e^{\perp}$	0.3	[1]	0.2	[1]
Elastic stiffness constant [GPa]	C_{13}	95	[2]	80	[3]
	C_{33}	402	[2]	387	[3]
Piezoelectric constant [C/m ²]	e_{31}	−0.58	[1]	−0.33	[1]
	e_{33}	1.55	[1]	0.65	[1]
Crystal field intercation [meV]	Δ_{cr}	−212	[4]	12.3	[5]
Spin-orbit interaction [meV]	Δ_{so}	18	[4]	15.6	[5]
Deformation potential [eV]	C_1	4.3	[4]	6.5	[5]
	C_2	11.5	[4]	11.2	[5]
	C_3	9.22	[4]	4.9	[5]
	C_4	−3.74	[4]	−5.0	[5]
Valence band parameters	A_1	−3.86	[1]	−7.21	[1]
	A_2	−0.25	[1]	−0.44	[1]
	A_3	3.58	[1]	6.68	[1]
	A_4	−1.32	[1]	−3.46	[1]
Dielectric constant	$\varepsilon_{r\parallel}$	9.32	[6]	10.4	[1]
	$\varepsilon_{r\perp}$	7.76	[6]	9.5	[1]
Spontaneous polarization [C/m ²]	P^{sp}	−0.040	[7]	−0.034	[1]

Here, superscripts $\parallel$ and $\perp$ represent the components parallel and perpendicular to c-axis, respectively.

A.2 How to Calculate Hole Effective Mass

Effective masses are calculated by [8,9],

$$\frac{m_0}{m_{\text{HH}}^{\parallel}} = -(A_1 + A_3), \quad (\text{A.1})$$

$$\frac{m_0}{m_{\text{LH}}^{\parallel}} = - \left[A_1 + \left(\frac{E_0^2 - \lambda_{\epsilon}}{E_0^2 - E_0^3} \right) A_3 \right], \quad (\text{A.2})$$

$$\frac{m_0}{m_{\text{CH}}^{\parallel}} = - \left[A_1 + \left(\frac{E_0^3 - \lambda_{\epsilon}}{E_0^3 - E_0^2} \right) A_3 \right], \quad (\text{A.3})$$

$$\frac{m_0}{m_{\text{HH}}^{\perp}} = -(A_2 + A_4), \quad (\text{A.4})$$

$$\frac{m_0}{m_{\text{LH}}^{\perp}} = - \left[A_2 + \left(\frac{E_0^2 - \lambda_{\epsilon}}{E_0^2 - E_0^3} \right) A_4 \right], \quad (\text{A.5})$$

$$\frac{m_0}{m_{\text{CH}}^{\perp}} = - \left[A_2 + \left(\frac{E_0^3 - \lambda_{\epsilon}}{E_0^3 - E_0^2} \right) A_4 \right]. \quad (\text{A.6})$$

where A_j ($j = 1, 2, 3, 4$) are valence band parameters, subscripts (HH, LH, CH) are the kind of valence band. In the case of AlN, we should change from HH to LH, from LH to CH, and from CH to HH, respectively.

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List of Publications

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1. **Takao Oto**, Ryan G. Banal, Ken Kataoka, Mitsuru Funato, and Yoichi Kawakami
 “100 mW deep ultraviolet emission from aluminum nitride based quantum wells pumped by an electron beam”
Nature Photonics **4**, 767 (2010).
2. Anna Kafar, Szymon Stańczyk, Grzegorz Targowski, **Takao Oto**, Irina Makarowa, Prezemek Wiśniewski, Tadeusz Suski, and Piotr Perlin
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3. **Takao Oto**, Ryan G. Banal, Mitsuru Funato, and Yoichi Kawakami
 “Optical Gain Characteristics in Al-rich AlGa_N/AlN Quantum Wells”
in preparation (2014).
4. **Takao Oto**, Ryan G. Banal, Yoshiya Iwata, David Gachet, Malik Benameur, Mitsuru Funato, and Yoichi Kawakami
 “Exciton Localization Characteristics in Al-rich AlGa_N/AlN Quantum Wells”
in preparation (2014).

Conference Papers

1. **Takao Oto**, Ryan G. Banal, Mitsuru Funato, and Yoichi Kawakami
 “Deep ultraviolet emission mechanisms in highly excited Al_{0.79}Ga_{0.21}N/AlN quantum wells”
Phys. Stat. Sol. (c) **7**, 1909 (2010).
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 “100 mW Deep Ultraviolet Emission from AlGa_N/AlN Quantum Wells by Electron Beam Pumping”
IEICE Technical Report **110**, 37 (2010) (in Japanese).

3. Yoshiya Iwata, **Takao Oto**, Akio Kaneta, Ryan G. Banal, Mitsuru Funato, and Yoichi Kawakami
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1. **Takao Oto**, Ryan G. Banal, Mitsuru Funato, and Yoichi Kawakami
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1. **Takao Oto**, Ryan G. Banal, Mitsuru Funato, and Yoichi Kawakami
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7. **(JSAP Paper Award)** **Takao Oto**, Ryan G. Banal, Ken Kataoka, Mitsuru Funato, and Yoichi Kawakami
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9. **(Invited)** **Takao Oto**, Ryan G. Banal, Ken Kataoka, Mitsuru Funato, and Yoichi Kawakami
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Patents

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