

**Fundamental Study on Carrier Recombination
Processes in AlGaN-related Materials
and their Structural Designs
toward Highly Efficient Deep-UV Emitters**

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Abstract

Sterilization techniques using deep-ultraviolet (DUV) light are commonly used to maintain the safety of air, water, food, and surgical instruments. Mercury lamps, for instance, are currently used to realize DUV luminescence at a wavelength of 253.7nm, which is effective for germicidal irradiation. Although DUV emitters have practical potential for various fields beyond sterilization (e.g., medical research and high-density optical data storage), current DUV sources have low efficiencies and contain toxic elements such as fluorine and mercury.

Recently, DUV light emitting devices based on AlGaIn quantum wells (QWs), which are promising candidates to replace current low efficient DUV sources, have been attracting great attentions. Although many AlGaIn-based light emitting diodes (LEDs) have recently been reported, the external quantum efficiency (EQE) is much lower ($\sim 10\%$) than that of blue LEDs based on InGaIn QWs. Additionally, laser diodes (LDs) oscillating at wavelengths less than 300 nm have yet to be reported. In order to achieve highly efficient LEDs and LDs, high internal quantum efficiency (IQE) and high light extraction efficiency (LEE), which are components of EQE, are indispensable.

In this thesis, we particularly focus on the improvement of IQE and LEE of AlGaIn QWs. For the former improvement, we propose the use of semipolar-plane QW to suppress the internal electric fields in QWs. Moreover, we identify the dominant nonradiative recombination paths in AlGaIn QWs, and the reduction method will be discussed. For the latter (LEE) improvement, optical polarizations in semipolar AlGaIn QWs are investigated, and we suggest a specific guideline for designing QW structures with high LEEs.

In Chapter 2, growth conditions for high quality semipolar AlN films and AlGaIn QWs are investigated using metalorganic vapor phase epitaxy (MOVPE) method. Through the careful observation of surface morphologies based on atomic force microscopy, we clarify that nucleation density control on the semipolar plane surface plays an important role in realizing an atomically smooth surface. We find that 500 Torr is the optimal reactor pressure for semipolar plane growth considering the growth rate and the nucleation density. Furthermore, the optical properties of high quality semipolar AlGaIn QWs are characterized by photoluminescence (PL) and cathodoluminescence (CL) measurements in comparison with conventional *c*-plane QW. The estimated internal electric fields in the semipolar *r*-plane and (11 $\bar{2}$ 2) QWs were less than one-third of that in the *c*-plane QW. The small internal electric fields in semipolar AlGaIn QWs significantly enhance the radiative recombination

probabilities and realize much stronger emissions compared to the conventional *c*-plane QWs. Furthermore, it is clarified that the potential fluctuations in semipolar AlGaIn QWs are also suppressed by the small internal electric fields.

In Chapter 3, dominant nonradiative recombination centers in AlGaIn-related materials are characterized using CL mapping measurements. From the temperature dependence of dark spot contrasts derived from TDs in CL mapping images, the impacts of point defects and threading dislocations (TDs) on IQE are investigated. In addition to the microscopic observation such as CL mappings, we perform macroscopic PL measurements and characterize the near band edge and deep level emissions. The combinational analysis identifies activation energies of the respective crystal defects, which are two types of point defects (PDs) and TDs, and we clarify that Al-vacancy related PDs predominantly degrade the emission efficiency at room temperature due to the high trap density. From the thermodynamic study on AlN epitaxy, we find that high reactor pressure and suppressed NH₃ flux lead to high equilibrium Al partial pressures, which may reduce Al-vacancy related PDs.

In Chapter 4, a novel critical thickness calculation model, which can reproduce the experimental results of AlGaIn heterostructures, is presented. Through the optical characterizations and observation of extraordinary growth surfaces, we point out the low sensitivity of X-ray diffraction measurements to lattice relaxations in AlGaIn heterostructures. Considering the unintentional off-angles, the severity of the critical thickness in (0001) AlGaIn/AlN heterostructures is highlighted. Moreover, the growth direction dependences of critical thickness and the primary slip system are discussed. The calculated critical thickness of semipolar AlGaIn QWs with 50°–55° off-angles, is the thickest in various growth planes. The results therefore indicate that semipolar *r*-plane and (11 $\bar{2}$ 2) QWs, which are realized in Chap. 2, are attractive growth planes in terms of the suppression of misfit dislocations in addition to the small internal electric fields.

In Chapter 5, optical polarization control for light extraction from semipolar AlGaIn/AlN QWs is described. The calculation results based on the $\mathbf{k} \cdot \mathbf{p}$ perturbation method and the experimental results by polarization PL measurements are compared, and appropriate material-parameter sets are investigated. The calculated results for out-of-plane polarization degree of semipolar *r*-plane AlGaIn/AlN QWs indicate that the *r*-plane AlGaIn QWs are very attractive structures to fabricate DUV LEDs with short wavelengths in terms of the LEE in addition to the high IQE because the *r*-plane QWs with narrow well widths (< 5.5 nm) can preserve out-of-plane polarization throughout the entire Al compositions in contrast to typical *c*-plane QWs. We also find that in-plane polarization of *r*-plane QWs can appropriately be controlled toward LDs by keeping the Al compositions more than 0.2. Furthermore, optical pumping measurements are performed for *r*-plane AlGaIn/AlN QWs, whose in-plane polarization degree are appropriately controlled, and the stimulated emissions at 250 nm from the semipolar AlGaIn QW is demonstrated for the first time.

Finally in Chapter 6, the obtained results are summarized, and some specific future prospects are discussed.

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Chapter 1

Introduction

1.1 Background of deep-UV light

Light, which is indispensable in modern human life, is a sort of electromagnetic waves, and is generally classified by wavelength. Visible light recognized by human eyes has wavelengths from 380 to 780 nm, whereas invisible lights with shorter and longer wavelengths than the visible spectral range are called as ultraviolet (UV) and infrared lights, respectively. UV lights are further divided into vacuum-UV (VUV: 10–200 nm), deep-UV (DUV: 200–300 nm), and near-UV (NUV: 300–380 nm) lights.¹

The most familiar light “sunlight” spans a wide spectral range from UV to infrared region [1] as shown in Fig. 1.1. However, the sunlight observed at the earth’s surface scarcely has the wavelength less than 300 nm because the earth’s ozone layer completely absorbs the light with wavelengths of 200–300 nm [2–4]. Therefore, DUV light does not exist at the earth’s surface in nature. Consequently, living things on the earth have never developed a tolerance for DUV radiation, and an artificial DUV light can work as a germicidal light. Figure 1.2 shows the wavelength dependence of relative germicidal effectiveness, and an emission at ~ 260 nm has maximum germicidal effectiveness. Sterilization techniques are commonly used to maintain the safety of air, water, food, and surgical instruments. Mercury lamps, for instance, are currently used to realize DUV luminescence at a wavelength of 253.7 nm.

Although DUV emitters have practical potential for various fields beyond sterilization (e.g., medical research and high-density optical data storage beyond Blu-ray discs), current DUV sources have very low efficiencies and contain toxic elements such as fluorine and mercury. In particular, the fabrication of devices with mercury and its compounds is determined to be limited by international treaty (Minamata Convention on Mercury) to protect human health and the environment from anthropogenic pollution [7]. To achieve benign and highly efficient DUV emitters, solid-state lighting devices based on semiconductors are

¹There are other classifications such as UV-A (315–380 nm), UV-B (280–315 nm), and UV-C (200–280 nm).

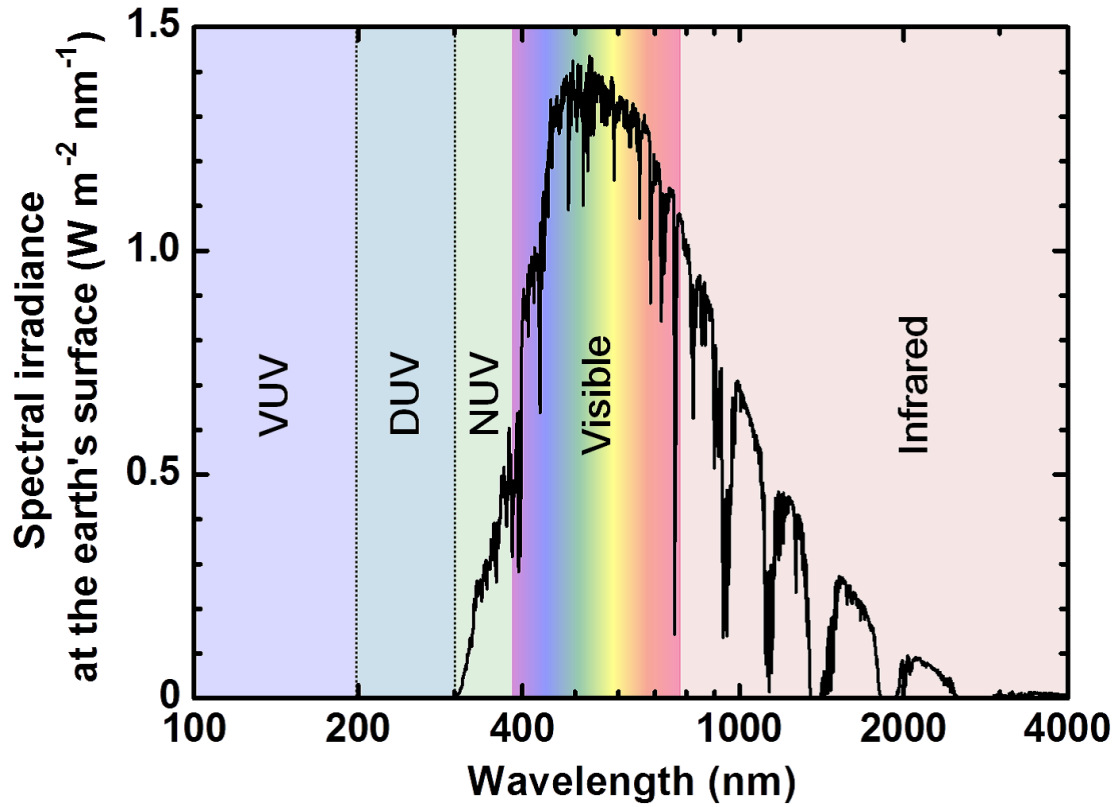


Figure 1.1: Sunlight spectrum observed at the earth's surface. The spectrum is taken from the data presented in Ref. [1].

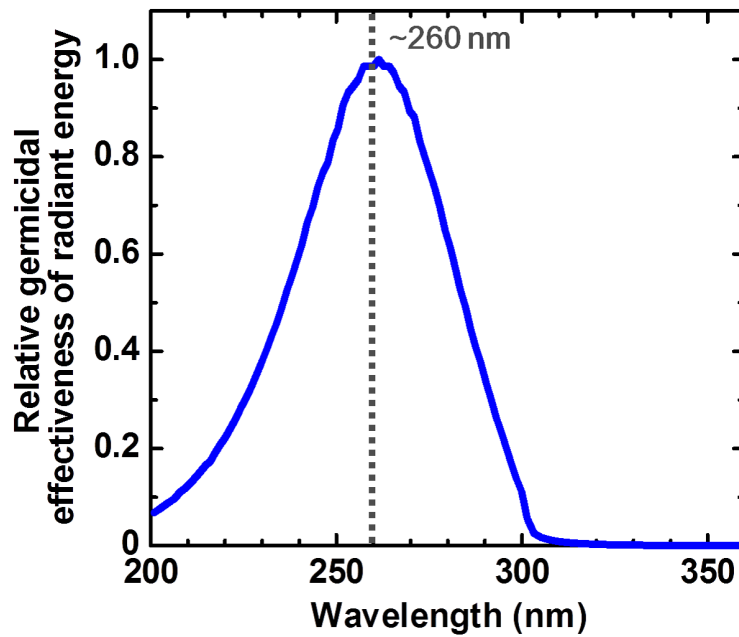


Figure 1.2: Wavelength dependence of relative germicidal effectiveness. The spectrum is taken from the data presented in Ref. [5, 6].

therefore required.

1.2 AlGaIn-based deep-UV emitters

Recently, group III-nitride semiconductors have attracted attentions for optical devices, because they are direct-transition semiconductors expected for highly efficient emissions and are compound semiconductors, which can realize arbitrary wavelengths by changing the molar fractions of their alloys. Furthermore, they can easily fabricate quantum well (QW) structures. The group III-nitride semiconductors mainly consist of aluminum nitride (AlN), gallium nitride (GaN), indium nitride (InN), and their alloys. The bandgap energies and the a -axis lattice constants of them are shown in Fig. 1.3. The bandgap energies of AlN, GaN, and InN at 0 K are 6.10, 3.51, and 0.69 eV, respectively, and according to the bandgaps, III-nitride semiconductors can cover a remarkably wide spectral range from DUV to infrared regions (200–1800 nm) [8]. In particular, InGaN and AlGaIn-based optical devices such as light emitting diodes (LEDs) and laser diodes (LDs) have been developed for visible and DUV emitters, respectively. The InGaN-based LEDs are now widely used in mobile phones, computer screens, and TVs in addition to general lightings. Due to such great contributions, Nobel Prize in Physics was awarded to Profs. Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura “for the invention of efficient blue light emitting diodes which has enabled bright and energy-saving white light sources” in 2014 [9].

Table 1.1 lists the key developments of AlGaIn-based optical devices. UV emission from a GaN/AlGaIn multiple-QW (MQW) structure was firstly investigated by photoluminescence measurements in 1990 [10], and J. Han *et al.* firstly demonstrated a GaN/AlGaIn MQW LED emitting at 354 nm in 1998 [11]. In 2001, A. Kahn *et al.* fabricated a UV-B LED emitting at 305 nm [12], and DUV LED emitting at 285 nm was firstly demonstrated by V. Adivarahan *et al.* in 2002 [13]. In 2006, Y. Taniyasu *et al.* reported the first AlN PIN (p-type/intrinsic/n-type) homojunction LED emitting at 210 nm [14], which is the theoretically lowest wavelength in III-nitride semiconductors. However, the reported external quantum efficiency (EQE) was only $\sim 10^{-6}\%$. In 2008, the first In-free AlGaIn MQW based UV LD oscillating at 342.3 nm was reported by H. Yoshida *et al.* [15].

Figure. 1.3 shows reported EQEs for InGaN, AlGaIn, and AlGaInP-based LEDs as a function of emission wavelength [14, 16–50]. Highly efficient red LEDs have been realized by AlGaInP-based LEDs, and nitride semiconductors have been mainly used for shorter wavelength LEDs. The EQEs of the InGaN-based LEDs are very high and that in blue region particularly exceeds 80% [46], whereas those of AlGaIn-based LEDs in DUV region are significantly low, which remain only $\sim 10\%$.

The threshold current density of LDs are shown in Fig. 1.5 as a function of oscillation wavelength [15, 51–87]. The threshold current density of nitride-based LDs are relatively high compared with that of II-VI and AlGaInP-based LDs. Although the minimum thresh-

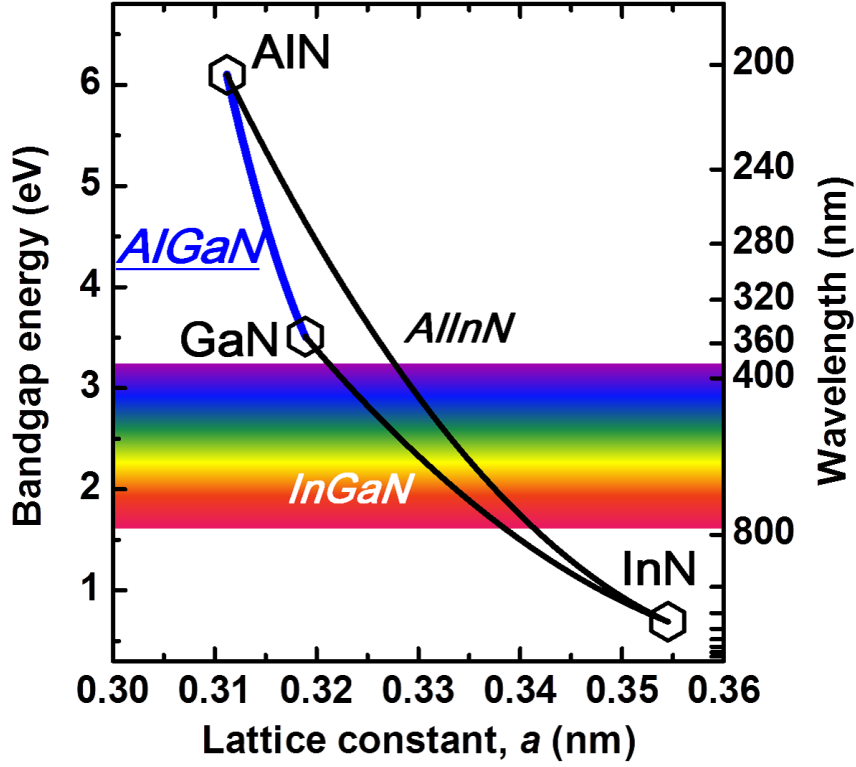


Figure 1.3: Bandgap energy and a -axis lattice constant of group III-nitride semiconductors.

Table 1.1: Key developments of AlGaInN-based optical devices.

Year	Key developments	Group
1990	GaN/AlGaIn MQW	A. Kahn <i>et al.</i> [10]
1998	GaN/AlGaIn MQW LED (354 nm)	J. Han <i>et al.</i> [11]
2001	UV-B LED (305 nm)	A. Kahn <i>et al.</i> [12]
2002	DUV LED (285 nm)	V. Adivarahan <i>et al.</i> [13]
2006	AlN-based LED (210 nm)	Y. Taniyasu <i>et al.</i> [14]
2008	In-free AlGaInN-based UV LD (342.3 nm)	H. Yoshida <i>et al.</i> [15]

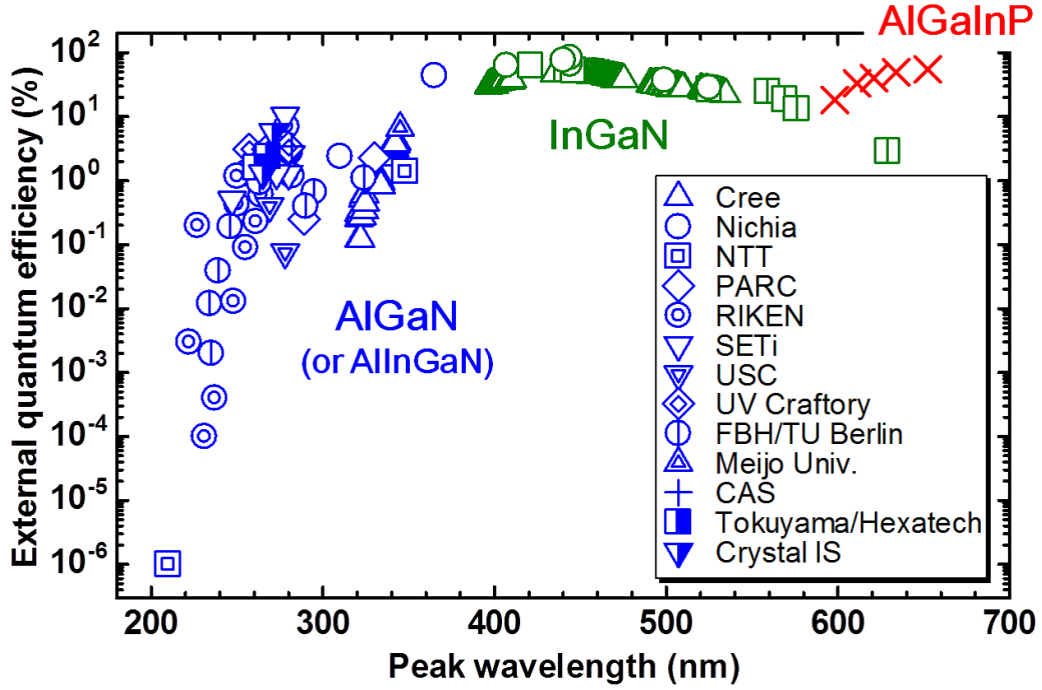


Figure 1.4: Emission wavelength dependence of EQEs for AlGaIn (or AlInGaIn) [14, 16–44], InGaIn [45–49], and AlGaInP-based LEDs [50].

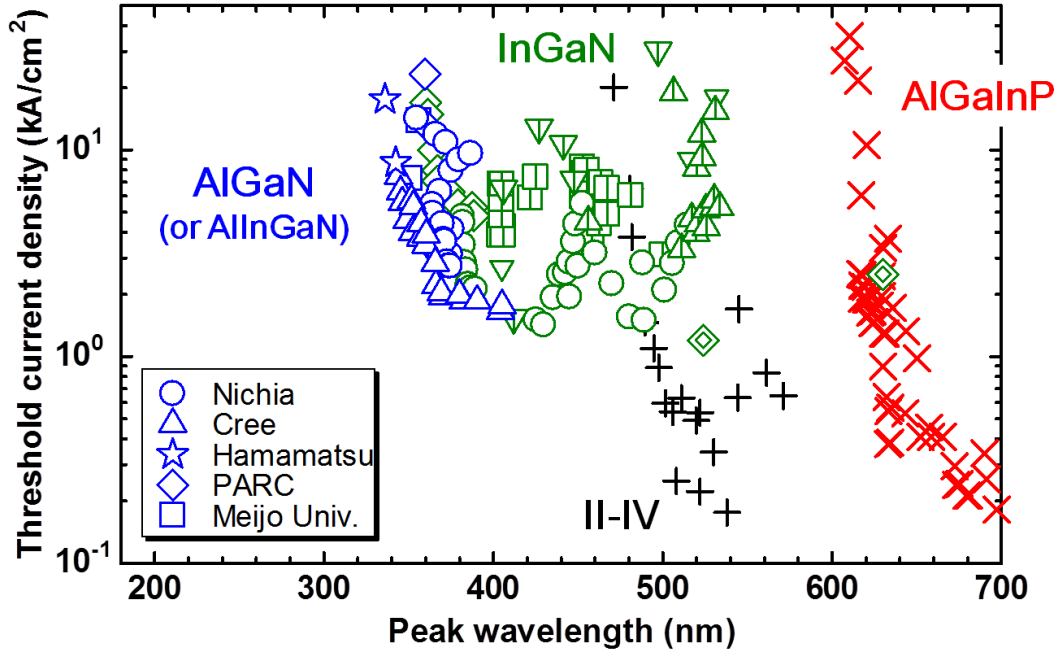


Figure 1.5: Oscillation wavelength dependence of threshold current density of AlGaIn (or AlInGaIn) [15, 51–58], InGaIn [59–80], II-VI semiconductors [81–86], and AlGaInP-based LEDs [87].

old current density of nitride semiconductors can be achieved at a wavelength ~ 405 nm for InGaN-based LD, it increases in the UV spectral range. In particular, LDs based on AlGaN QWs emitting at DUV region have yet to be achieved so far (Recently, AlGaN nanowire LD emitting at 239 nm was reported, but the oscillation is dominated by random lasing [88]), and we should therefore improve AlGaN-based optical device qualities to be highly efficient DUV emitters.

1.3 Toward highly efficient deep-UV emitters

In order to improve the performance of AlGaN-based DUV emitters, there are many factors to solve. The EQE (η_{EQE}) of optical devices is generally expressed as

$$\eta_{\text{EQE}} = \eta_{\text{IQE}} \times \eta_{\text{LEE}} \times \eta_{\text{CIE}}, \quad (1.1)$$

where η_{IQE} , η_{LEE} , and η_{CIE} mean internal quantum efficiency (IQE), light extraction efficiency (LEE), and carrier injection efficiency (CIE), respectively. Thus, Eq. (1.1) clearly indicates that higher IQE, LEE, and CIE directly lead to higher device performances. For example, though the p -type conductivity control is intrinsically difficult in AlN, better conductivity is required to improve CIE.

In addition, the optical polarization, which determines the light extraction, should be controlled for high LEE depending on each device structure. For LEDs, the emissions from active layers are generally obtained from the surfaces, whereas the cleaved planes (edge faces of samples) are used as cavity mirrors for LDs. Therefore, the optical polarizations, which lead to strong surface emissions and strong light extractions from cleaved planes, are desired for LEDs and LDs, respectively. Because the optical polarizations in AlGaN QWs strongly depend on the structures such as Al compositions, quantum confinement effects, and strains, appropriate structure designs are needed.

Furthermore, IQE enhancement is also indispensable for high EQE. In particular, the IQEs of AlGaN QWs are remarkably degraded under weak excitation conditions [89] (assuming LED operation conditions) and in the short wavelength regions (Al-rich conditions) [90, 91]. The IQE is written as

$$\eta_{\text{IQE}} = \frac{\tau_{\text{rad}}^{-1}}{\tau_{\text{rad}}^{-1} + \tau_{\text{nonrad}}^{-1}}, \quad (1.2)$$

where τ_{rad} and τ_{nonrad} are the carrier recombination lifetimes due to the radiative and non-radiative recombination processes, respectively. The reciprocals of the lifetimes mean the respective recombination probabilities, and a schematic image of the recombination paths are depicted in Fig. 1.6. Here, the radiative recombination path corresponds to the band-to-band transition. In the nonradiative recombination processes, on the other hand, the excited carriers are captured by some deep levels formed in the bandgap due to the crystal

defects such as dislocations and point defects. To achieve higher IQE, we should enhance the radiative recombination probability and should decrease the crystal defects. Then, we introduce some methods to realize the respective aims as follows.

1.3.1 Growth planes for QW structures

LEDs and LDs are generally based to QW structures for highly efficient emissions. In the case of AlGaIn QWs, the Ga-rich well layer is surrounded by Al-rich barrier layers which have larger energy bandgaps. However, the lattice parameters of AlN and those of GaN are quite different as shown in Fig. 1.3, and a large misfit strain should be induced in the pseudomorphically grown well layer (a -axis lattice mismatch is $\sim 2.4\%$). The lattice mismatch is much larger than that in other III-V semiconductor systems such as AlAs and GaAs (the lattice mismatch is only $\sim 0.14\%$ [92]). Consequently, the large misfit strains in AlGaIn QWs have some bad influences on the optical properties. One of the influences is the piezoelectric field.

The pseudomorphically grown AlGaIn well layer on AlN is compressively strained, and the strain induces piezoelectric polarization in addition to spontaneous polarization. When the polarizations cause the internal electric field along the growth direction, the wavefunctions of electrons and holes are spatially separated and the overlap integral is remarkably reduced in the well layer, as shown in Fig. 1.7 (a). The effect consequently decreases radiative recombination probability. Therefore, the suppression of the internal electric field can enhance the overlap integral of the wavefunctions as depicted in Fig. 1.7 (b), which improves IQE.

The magnitude of the induced internal electric field strongly depends on the growth plane. AlGaIn has a wurtzite structure and the basal plane (0001) is called as c -plane, which is a typical growth plane. Figure 1.8 shows various growth planes in wurtzite structures, which are roughly divided into three categories by the off-angles from the c -plane. The c -plane is also called as a polar plane, and planes perpendicular to the c -plane are called as nonpolar planes. All other planes are defined as semipolar planes, and QWs fabricated on semipolar and nonpolar planes can effectively suppress the internal electric fields.

The crystal orientation effects on internal electric fields are shown in Fig. 1.9. (The detailed calculation method [93] will be discussed in Chap. 2.) The calculated internal electric fields in AlGaIn/AlN QWs indicate that the internal electric field is the largest in the c -plane QW and decreases in the QWs with larger off-angles. For nonpolar plane QWs, the internal electric fields equal to zero. Thus, semipolar and nonpolar plane QWs are very attractive for highly efficient DUV emitters, but the crystal growth techniques have yet to be matured due to the different growth conditions from the conventional c -plane growth. As a consequence, current semipolar (and nonpolar) AlGaIn films and QWs have rough surfaces (or interfaces) and stacking faults in addition to a large number of threading dislocations (TDs) [94–99], and the crystal qualities are insufficient to achieve high IQEs. Therefore,

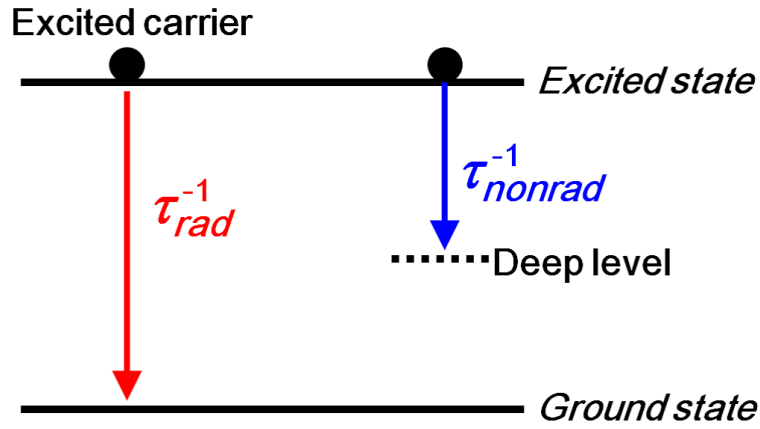


Figure 1.6: Schematic image of radiative and nonradiative recombination paths. Radiative recombination path corresponds to the band-to-band transition, whereas nonradiative recombination processes are mediated through deep levels in the bandgap formed by the crystal defects such as dislocations and point defects.

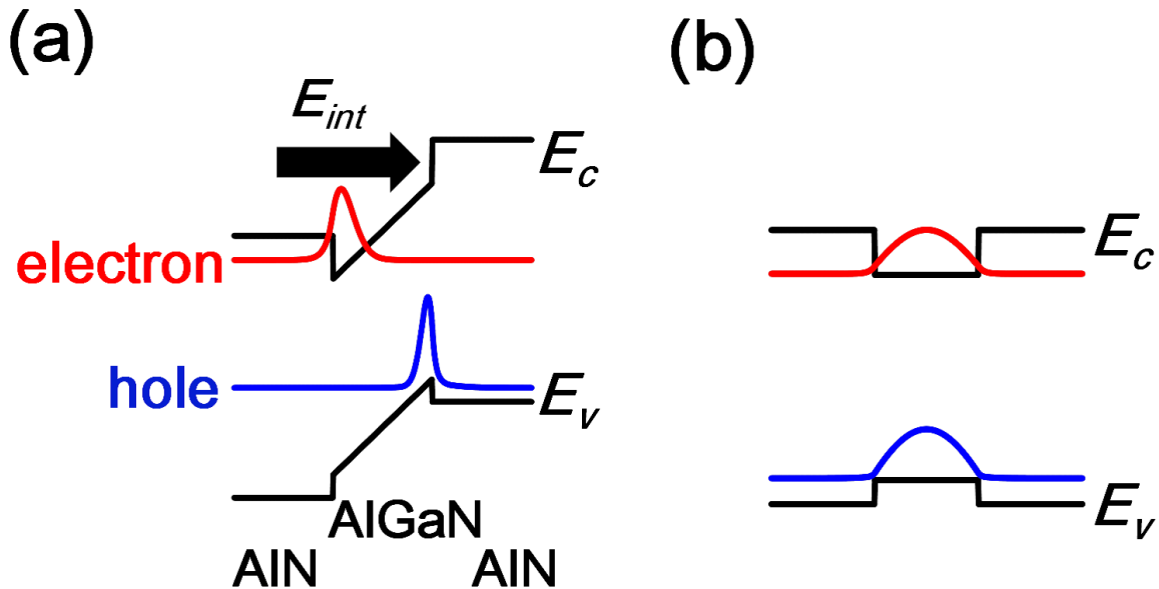


Figure 1.7: Wavefunctions of electrons and holes in the AlGaIn well layer when the internal electric field is (a) non-zero and (b) zero.

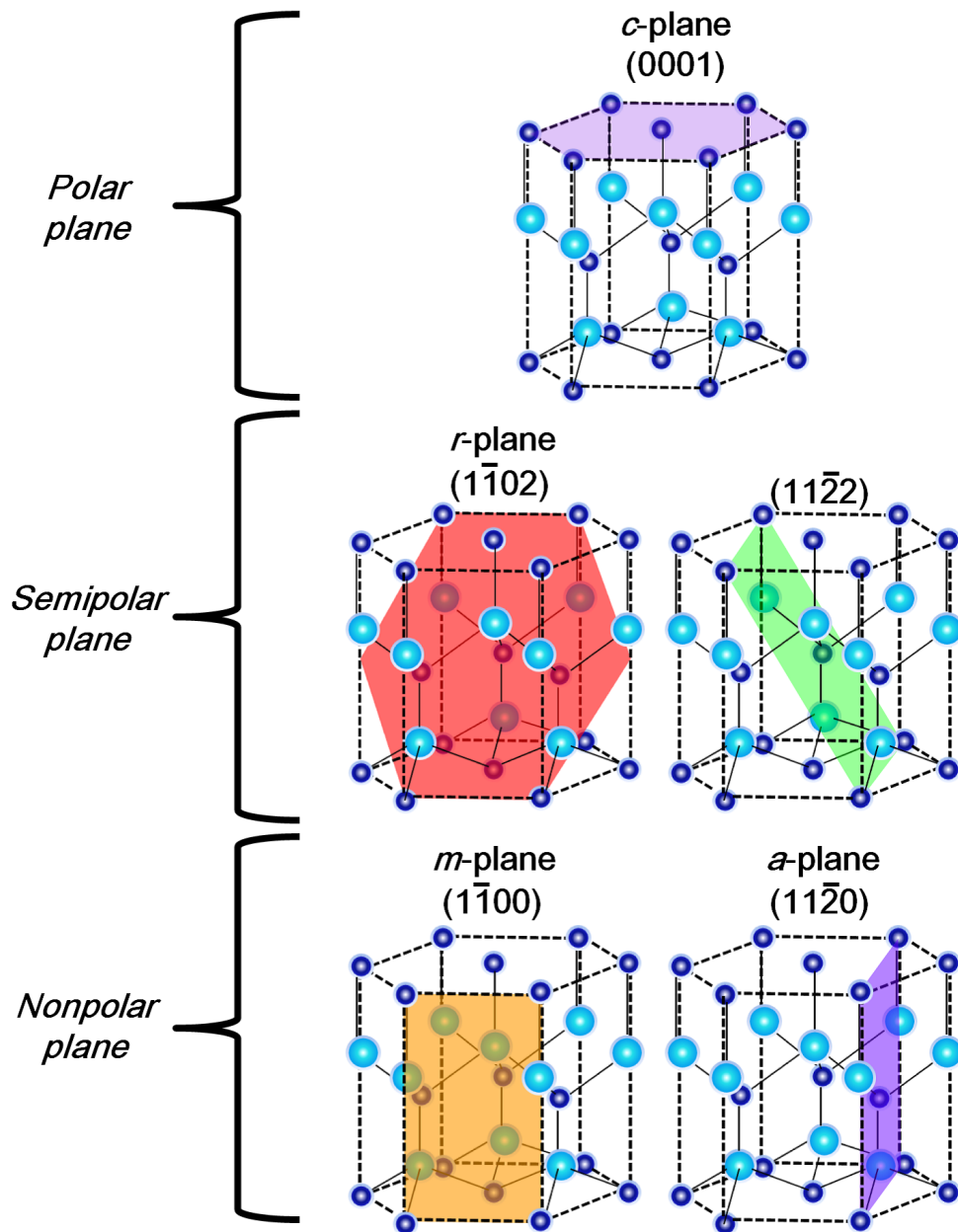


Figure 1.8: Various growth planes in wurtzite structures.

the clarification of the optimal growth condition for high quality semipolar AlGaIn QWs is desired.

1.3.2 Defects in AlGaIn crystals

III-nitride semiconductors typically have high density of TDs (10^9 – 10^{10} cm $^{-2}$) because they are heteroepitaxially grown on sapphire substrates in many cases. Thus, a lot of efforts have been made to reduce TD density (TDD) in AlGaIn films. Recently, high quality AlN substrates have been developed [100], and we have also realized high quality *c*-plane AlN homoepitaxial films with a very low TDD $< 10^5$ cm $^{-2}$ [101]. Furthermore, several DUV LEDs based on AlGaIn QWs have been fabricated on AlN substrates [30, 34, 35, 41]. However, in spite of such low TDDs, the AlGaIn-based LEDs fabricated on AlN substrates still have very low EQE (only several percents). According to the results, some other defects in AlGaIn crystals such as point defects should be also considered as nonradiative recombination centers. In particular, the theoretically calculated formation energies of Al vacancies and their complex defects in n-type AlN films are remarkably low compared with simple substitutional impurity defects [102–104]. However, the impacts of these vacancy-related point defects on optical properties have yet to be clarified.

In addition to TDs and point defects, we have to take the misfit dislocations (MDs) into account in the case of strained QW structures. As we mentioned above, the pseudomorphically grown AlGaIn well layers are compressively strained due to the large lattice mismatch with respect to the barrier layers. Figure 1.10 shows the schematic image of the MD generation. An epitaxial layer can be pseudomorphically grown on a substrate when the epilayer thickness (h) is thinner than a certain critical thickness (h_c), whereas MDs are generated at the interface between the epilayer and the substrate in the case of $h \geq h_c$. Similarly in QW structures, MDs are generated when the well layer thickness exceeds the critical thickness. Because the MDs may significantly degrade the IQE, we have to appropriately design the QW structures considering the critical thickness in order to avoid the MD generations. However, it has been reported that AlGaIn films with thicknesses exceeding the calculated critical thickness by more than an order of magnitude are pseudomorphically grown on AlN substrates [105], and the mechanism of such phenomena has not yet to be clear. For appropriate designs of AlGaIn QWs, the comprehensive understanding for critical thickness is required.

1.4 Aims and outline of this study

As we described in Sec. 1.3, IQE, LEE, and CIE should be improved for high performances of AlGaIn-based DUV emitters. In this study, we particularly focus on the improvement of IQE and LEE of AlGaIn QWs. For the former improvement, we propose the use of semipolar plane growth to suppress the internal electric fields in AlGaIn QWs. Furthermore, the

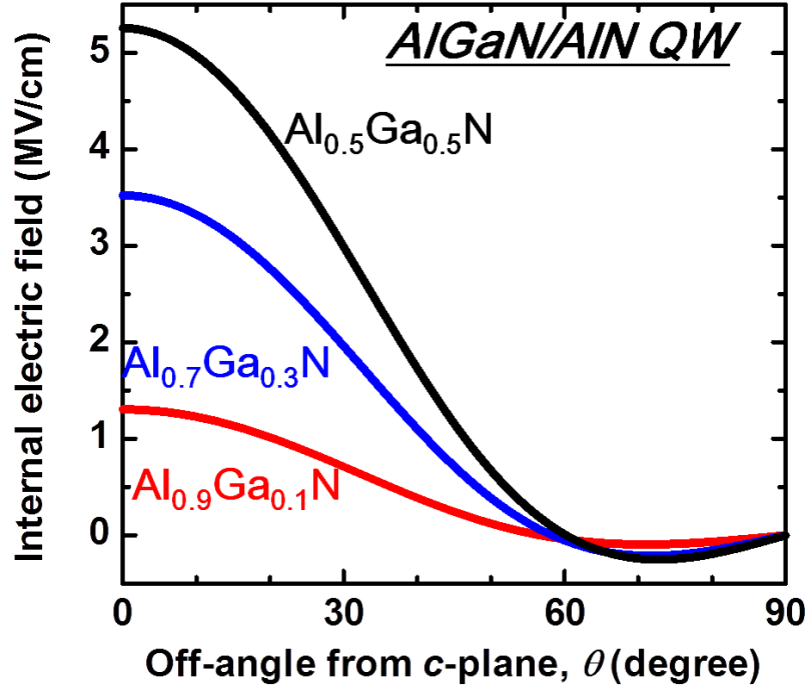


Figure 1.9: Growth orientation effects on internal electric fields along the growth direction in AlGaIn/AlN QWs.

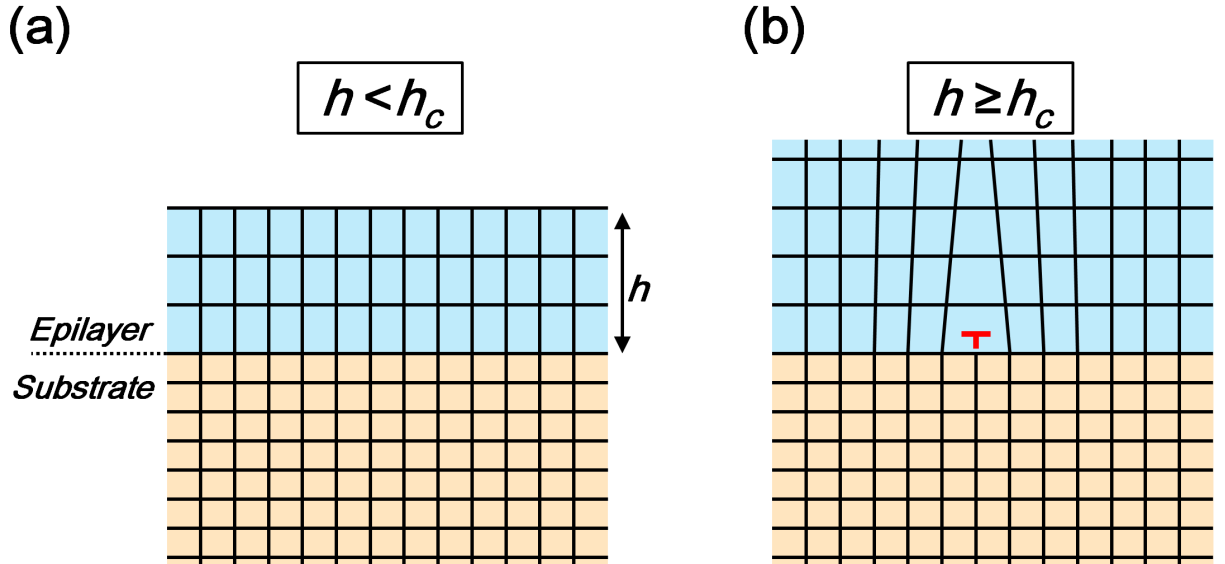


Figure 1.10: Schematic images of the MD generation. (a) Epilayer is pseudomorphically grown on a substrate when the epilayer thickness (h) is thinner than critical thickness (h_c). (b) A MD is generated at the interface between epilayer and substrate when the epilayer thickness exceeds the critical thickness.

impacts of defects in AlGaIn-related materials on the emission intensities are investigated to identify the dominant nonradiative recombination paths. For the latter (LEE) improvement, the optical polarizations in semipolar AlGaIn QWs are investigated, and we suggest a specific guideline to appropriately design the QW structures.

In Chapter 2, growth conditions for high quality semipolar AlN films and AlGaIn QWs are investigated using a metalorganic vapor phase epitaxy method. Through the careful observation of the surface morphologies by atomic force microscopy, we prove that nucleation-density control on semipolar plane surfaces plays an important role in realizing an atomically smooth growth surface. Furthermore, the optical properties of fabricated high quality semipolar AlGaIn QWs are characterized by photoluminescence (PL) and cathodoluminescence (CL) measurements in comparison with the conventional *c*-plane QWs. The effects of the internal electric fields on the emission intensities, recombination lifetimes, energy fluctuations are discussed.

In Chapter 3, the dominant nonradiative recombination centers in AlGaIn-related materials are characterized using CL mapping measurements. From the temperature dependence of dark spot contrasts derived from TDs in CL mapping images, the impacts of point defects and TDs on IQE are investigated. In addition to the microscopic observation of such as CL mappings, we perform macroscopic PL measurements and characterize the near band edge and deep level emissions. The combinational analysis identifies some important parameters such as activation energies of the respective crystal defects, and we suggest a specific guideline for high IQE. Furthermore, from the thermodynamic study on AlN epitaxy, we discuss the impacts of the growth conditions on point defect density, and propose the optimal growth condition to reduce point defects while keeping the smooth surfaces.

In Chapter 4, a novel calculation model of critical thickness, which can reproduce the experimental results of AlGaIn heterostructures, is presented. Through the optical characterizations and observation of extraordinary growth surfaces, we point out the low sensitivity of X-ray diffraction measurement to the lattice relaxations in AlGaIn heterostructures. We demonstrate the critical thickness in (0001) AlGaIn/AlN heterostructures is considerably thinner than expected. Moreover, the growth direction dependences of critical thickness and the primary slip system are discussed. Based on our calculation model, we demonstrate a novel AlGaIn QW structures, where lattice relaxation positions are appropriately controlled to suppress the MD generations in the well layers, toward highly efficient DUV emissions.

In Chapter 5, the optical polarization control for light extraction from semipolar AlGaIn/AlN QW is described. The calculation results based on the $\mathbf{k} \cdot \mathbf{p}$ perturbation method and the experimental results by polarization PL measurements are compared, and appropriate material-parameter sets of the effective mass parameters for the valence bands and the deformation potentials are investigated. Optical pumping measurements are performed for a semipolar ($\bar{1}\bar{1}02$) AlGaIn/AlN MQW whose in-plane polarization is appropriately controlled, and the stimulated emissions from semipolar AlGaIn QWs are demonstrated for the

first time.

Finally in Chapter 6, the obtained results are summarized, and some future prospects are discussed.

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Chapter 2

Enhanced radiative recombination probabilities in semipolar AlGa_N/AlN QWs

2.1 Introduction

As we mentioned in Chap. 1, current DUV light sources use toxic elements and have a low efficiency. Although AlGa_N QWs are promising candidates to realize harmless and highly efficient DUV light emitters, their EQEs remain $\sim 10\%$ [1–5], unlike highly efficient blue LEDs based on InGa_N QWs [6]. Additionally, AlGa_N-based LDs oscillating at wavelengths less than 300 nm have yet to be reported. In order to achieve highly efficient LEDs and LDs, high IQE, which is a component of EQE, is indispensable. However, the IQE of current AlGa_N QWs is drastically degraded at short wavelengths [7, 8] and under weak excitation conditions [9]. Because IQE is expressed by radiative and nonradiative recombination lifetimes of carriers, the control of them is crucial for high IQE QWs. In particular, shorter radiative recombination lifetimes can enhance the IQE independently of the defect density in the crystals.

Because most QW structures are grown along the [0001] *c*-axis, they inevitably suffer from large spontaneous and piezoelectric polarization fields, which decrease the radiative recombination probability. To enhance radiative recombination probability for high IQE, nonpolar or semipolar plane AlGa_N QWs are promising because they can suppress the internal electric fields in the well layers. In fact, semipolar InGa_N visible QWs with short radiative recombination lifetimes have been reported [10, 11]. Although some groups have reported non-*c*-plane AlN or AlGa_N epitaxial films (QWs), the surface flatness and the interface abruptness are insufficient to achieve highly efficient emissions [12–17]. In addition, the basal plane stacking faults can be introduced in contrast to the conventional (0001) growth, and they also degrade the IQE [13].

We consider that there are two reasons why high-quality semipolar or nonpolar films and

QWs have yet to be fabricated. One is that these structures are heteroepitaxially grown on foreign substrates such as *r*- or *m*-plane sapphire and semipolar ZnO substrates [12–16]. The other is that the optimal growth conditions differ between *c*-plane and non-*c*-plane growths due to differences in dangling bonds, surface structure, etc. Considering the difficulties observed for homoepitaxy on *m*-plane AlN substrates [17], the latter reason (growth condition) seems crucial.

In this chapter, we fabricate high-quality semipolar AlGa_N/AlN QWs on various semipolar AlN substrates using the metalorganic vapor phase epitaxy (MOVPE) method by adjusting the growth conditions. Furthermore, the optical properties of fabricated semipolar QWs are investigated, and we experimentally demonstrate the superior optical properties compared with those of the conventional (0001) AlGa_N QWs.

2.2 MOVPE growth machine

All of the epitaxial films and QWs were fabricated by the MOVPE method in this study. MOVPE is one of the chemical vapor deposition processes used for crystal growth, and metalorganic compounds are used as precursors. The metalorganics and other gases injected into a reactor chemically react with each other on a heated substrate, and the reaction promotes the crystal growth of epitaxial layers on the substrate. The reactions generally take place at moderate pressures (10–760 Torr) and do not require ultra-high vacuum systems in contrast to molecular beam epitaxy. The MOVPE method can be adopted for large-scale epitaxy and is preferable for the manufacture of practical devices. Moreover, abrupt heterointerfaces such as QWs and p-n junctions can be fabricated by changing the gas fluxes, growth temperatures, and reactor pressures with relative ease.

For the epitaxy of AlGa_N crystals, trimethylaluminum [(CH₃)₃Al: TMA], trimethylgallium [(CH₃)₃Ga: TMG], and triethylgallium [(C₂H₅)₃Ga: TEG] were used as metalorganic sources in this thesis. H₂ gas was used as the carrier gas to transfer the metalorganic sources into a reactor. In addition, ammonia (NH₃) was used as a precursor for N. The chemical reaction in AlN growth can be expressed as

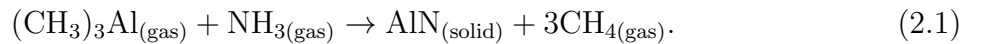


Figure 2.1 shows the schematic image of the MOVPE growth machine used in this study. H₂ gas was purified by a palladium hydrogen purifier, and all the gas fluxes were adjusted by mass flow controllers (MFCs). The metalorganic precursors were kept in bubbler cylinders, and the bubbling temperatures were controlled by thermostatic baths. NH₃ and metalorganic precursors were carried by separate lines and were mixed within the reactor. Reactor pressure was adjusted by a rotary pump, and the exhaust gases were released into atmosphere through a scrubber. The susceptor was resistively heated from room temperature to ~1300°C. The reactor is made of quartz and is a vertical type. To

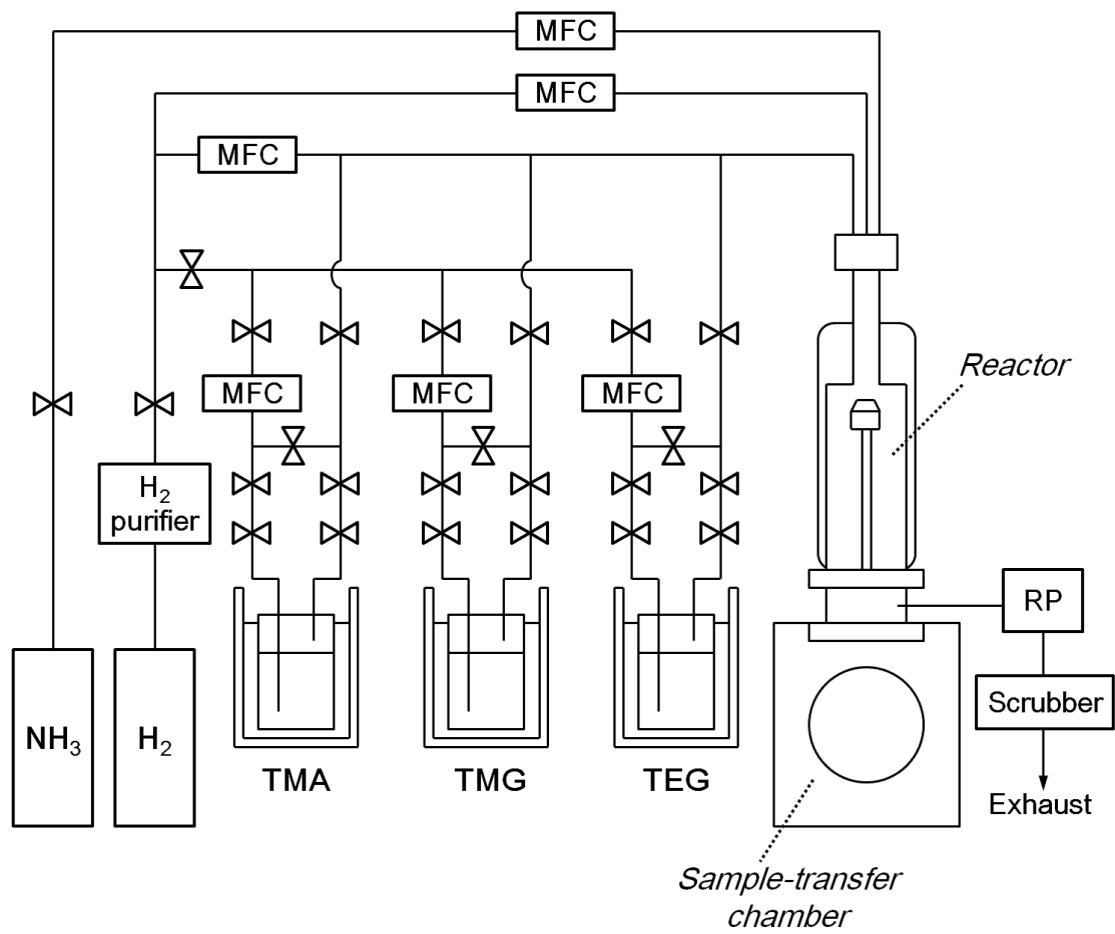


Figure 2.1: Schematic image of the metalorganic vapor phase epitaxy (MOVPE) growth machine used in this study.

suppress desorption from the reactor wall, a cold-type reactor was adopted.

2.3 Experimental procedures

In this study, AlN and AlGaIn QWs were grown on nominally on-axis (0001) (*c*-plane), 15° off surface,¹ ($1\bar{1}02$) (*r*-plane), and ($11\bar{2}2$). *r*-Plane and ($11\bar{2}2$) are 42.75° and 58.01° inclined from the *c*-plane, respectively. All the samples were grown on AlN substrates prepared by physical vapor transport methods. The *c*-plane (*r*-plane) AlN substrates were obtained from AlN bulk crystals grown on *c*-plane (*r*-plane [18]) templates. The other semipolar AlN substrates were given by slicing bulk crystals grown on *c*-plane templates. Prior to epitaxy, the substrates were wet etched in a 3:1 $\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4$ mixture for 10 min at 90°C in order to remove the aluminum hydroxide layer formed on the surface [19, 20]. Wet etched substrates were then rinsed in deionized water for 15 min, dried with flowing nitrogen, and transferred into a MOVPE reactor.

Figure 2.2 shows the growth sequence of AlGaIn/AlN QWs in this study. The temperature was increased to 1215°C under an NH_3 atmosphere, and the substrates were annealed at 76 Torr for 15 min. TMA, TMG, and NH_3 were used as precursors for Al, Ga, and N, respectively. AlN epitaxial layers were grown at $1150\text{--}1200^\circ\text{C}$ with V/III ratios of 217–651 in H_2 diluent with 2 slm (standard litre per minute), and the reactor pressures were adjusted from 76 to 608 Torr by a rotary pump. When we grow QW structures, AlGaIn/AlN QWs were subsequently fabricated on the AlN films at lower temperatures for promoting Ga incorporation.

The surface morphologies of AlN films and AlGaIn/AlN QWs were characterized by atomic force microscopy (AFM) in the tapping mode. The structural properties and Al compositions of well layers were assessed by cross-sectional transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements. Carbon, oxygen, and silicon impurities in AlN films were assessed by secondary ion mass spectrometry (SIMS) using Cs^+ as a primary ion at an acceleration voltage of 15 kV.

To characterize the optical properties of AlN homoepitaxial films, photoluminescence (PL) spectroscopy was performed. The excitation source was a pulsed ArF excimer laser (193 nm) with a repetition frequency of 25 Hz and a pulse duration of 4 ns. Semipolar AlN films were excited at angle of an 60° with the surface normal, and the PL signals were detected from the surface normal. For *c*-plane AlN films, the excitation laser is incident to the surface normal, and PL signal was detected 60° from the surface normal. The PL was focused on the entrance of a 50-cm monochromator and the detection was ensured by a liquid- N_2 -cooled CCD camera.

The optical properties of the *c*-plane and semipolar AlGaIn QWs were compared using time-integrated and time-resolved photoluminescence (TRPL) spectroscopy where the ex-

¹(0001) with a tilt of 15° toward $\langle 11\bar{2}0 \rangle$.

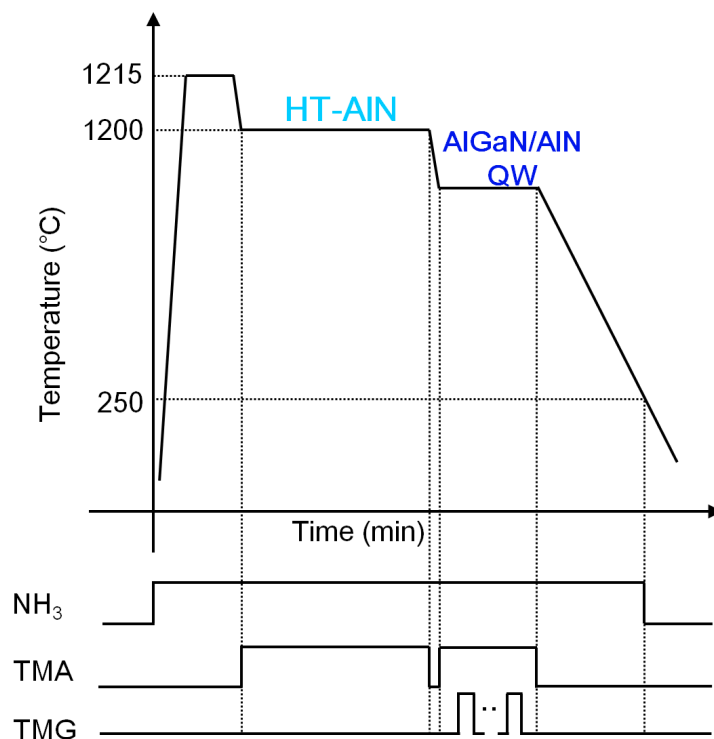


Figure 2.2: Growth sequence of AlGaIn/AlIn QWs in this study. Prior to the growth, AlIn substrates were annealed at 1215°C (76 Torr for 15 min) under an NH_3 atmosphere. TMA, TMG, and NH_3 were used as precursors for Al, Ga, and N, respectively.

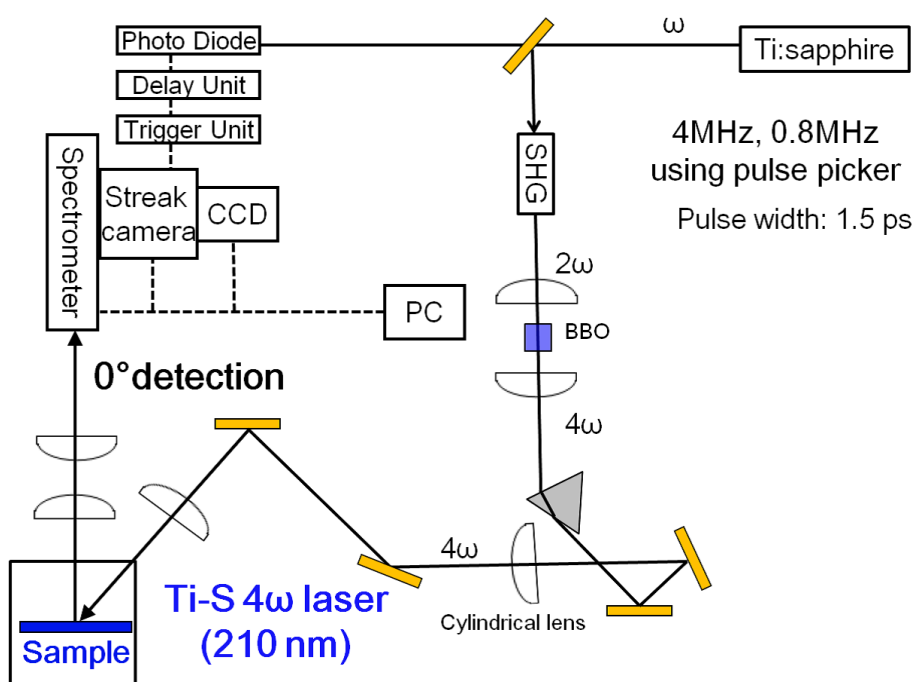


Figure 2.3: TRPL spectroscopy setup for the characterization of the optical properties of *c*-plane and semipolar QWs.

citation pulse light source was a Ti:Al₂O₃ fourth-harmonic generation laser with a pulse repetition rate and width of 4 MHz (or 0.8 MHz) and 1.5 ps, respectively. The TRPL spectroscopy setup was shown in Fig. 2.3. To selectively excite the AlGaIn QWs, the excitation wavelength was adjusted to 210 nm. The estimated initial carrier density was $0.95\text{--}5.0 \times 10^{14} \text{ cm}^{-3}$, which is sufficiently low to barely screen the internal electric fields. PL at ~ 6.5 K was detected by a streak camera.

Cathodoluminescence (CL) mapping was performed to characterize the energy fluctuations in AlGaIn/AlN QWs in the temperature range between 9 and 293 K. The acceleration voltage of electron beam for CL measurements was 5 kV.

2.4 Crystal growth of semipolar AlN

Prior to the growth of semipolar AlGaIn/AlN QWs, high quality semipolar AlN films with atomically smooth surfaces are required as underlying layers of the QWs. Then, we optimize the growth condition for semipolar AlN homoepitaxial films. For the simplicity, we mainly focus on *r*-plane AlN growth as a representative of the various semipolar planes in the following discussions, and the difference from conventional *c*-plane growth will be also discussed.

2.4.1 Semipolar AlN surface grown by conventional condition

c-Plane AlN films were grown at 1200°C for 20 min with a V/III ratio of 217. The reactor pressure was initially adjusted to 76 Torr, and TMA and NH₃ were supplied with 4.11 and 893 $\mu\text{mol/min}$, respectively. The growth condition is the same as the condition optimized for 600-nm-thick *c*-plane AlN heteroepitaxial films on sapphire substrates [21]. We call the condition as “standard growth condition” for the following discussions. We firstly adopted the standard growth condition for *r*-plane AlN homoepitaxial growth, and ~ 600 -nm-thick epilayer was obtained.

The typical surface morphologies of the grown *c*- and *r*-plane AlN films assessed by AFM are shown in Fig. 2.4. In the case of the *c*-plane AlN, we can clearly observe the atomically smooth surface with a step-and-terrace structure where the step height is one mono-molecular layer (ML). For the *r*-plane AlN film, on the other hand, high density of pits ($7\text{--}9 \times 10^7 \text{ cm}^{-2}$) are generated on the surface. The root mean square (RMS) of the surface roughness is 59.8 nm, which is too rough to be used as underlying layers of several nanometer-thick QWs. The results clearly indicate that the optimal growth condition of semipolar AlN epitaxial layers is quite different from that of *c*-plane AlN.

To investigate the origin of pits generated on the *r*-plane AlN surface, cross sectional TEM image was characterized. Figure 2.5 shows the cross sectional TEM bright field image of an ~ 80 -nm-thick *r*-plane AlN film in the vicinity a pit. Under the surface pit, we can confirm a defect-like area marked by an arrow in Fig. 2.5. The defect-like area,

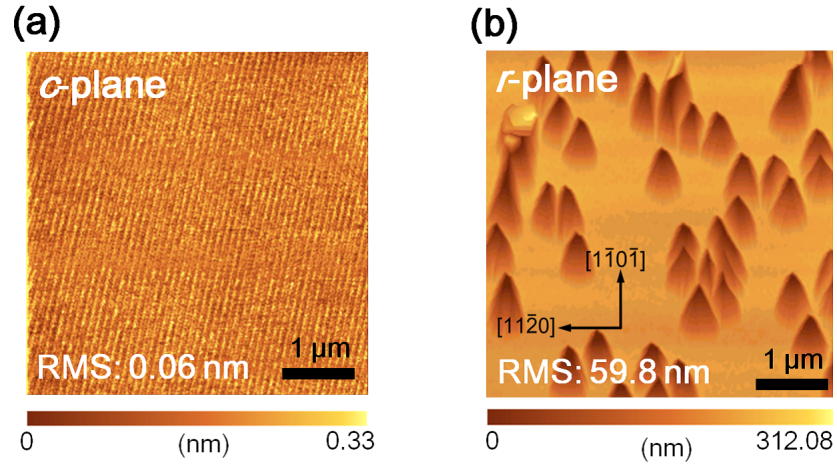


Figure 2.4: Surface morphologies assessed by AFM for (a) *c*- and (b) *r*-plane AlN films grown under the standard growth condition (1200°C, 76 Torr, and V/III ratio of 217) for *c*-plane heteroepitaxy.

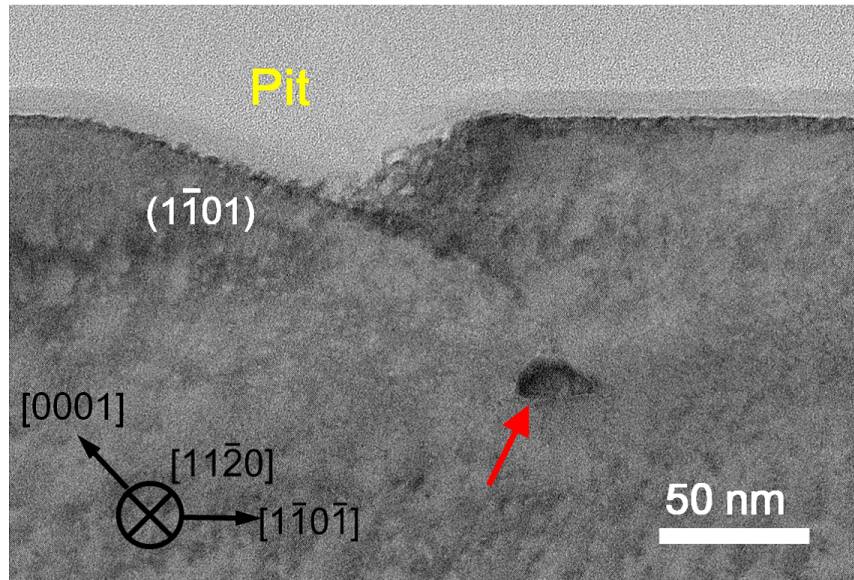


Figure 2.5: Cross sectional bright field TEM image of an *r*-plane AlN film in the vicinity a pit. Defect-like area marked by an arrow is observed. It might be an inversion domain caused by the unintentional low temperature annealing during increasing temperature. In the pit, $\{1\bar{1}01\}$ is formed as a stable facet.

where crystalline structure is disordered, is not propagated from the substrate, and we conclude that it is introduced in the epilayer at the initial growth stage. Although the origin of the defect has not been identified, we consider that it might be an inversion domain derived from the partial etchings of the substrate surface. The etchings should be caused by the unintentional low temperature annealing during increasing temperature because we confirmed that the high temperature annealing time at 1215°C and the temperature variations ($\geq 1200^\circ\text{C}$) hardly affect the pit density. Furthermore, from the shape of a pit, it was clarified that $\{1\bar{1}01\}$ is formed in the pit as a stable facet.

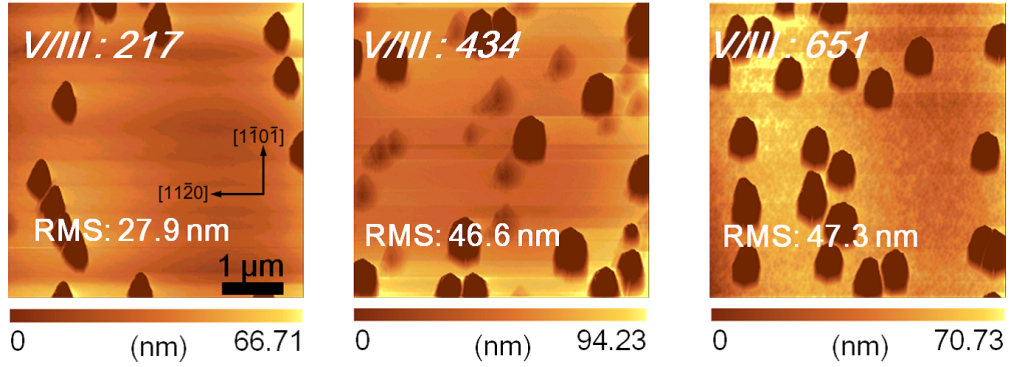
2.4.2 Growth condition dependence of pit density in semipolar AlN

Subsequently, we investigated the density of pits generated on *r*-plane AlN films while changing the growth conditions. Initially, the V/III ratio was varied for *r*-plane AlN growth, adjusting the NH_3 flux from 8.18 to 24.5 $\mu\text{mol}/\text{min}$. The other conditions except for the V/III ratio were the same as the standard growth conditions. Figure 2.6(a) shows the AFM images of the *r*-plane AlN films when V/III ratio is ranged from 217 to 651 by changing the NH_3 fluxes. For all of the samples, a lot of pits are invariably observed on the surfaces and the pits also degrade the surface flatnesses.

The V/III ratio dependence of the pit density is shown in Fig. 2.6(b). In addition to the above samples, a sample grown with a V/III ratio 434 by reducing TMA flux to 2.06 $\mu\text{mol}/\text{min}$ is also depicted. To compensate for the slower growth rate due to the TMA reduction, the growth duration was twice as long as that of the standard condition, resulting in the same thickness. Furthermore, a sample grown at 1150°C (the other conditions are the same as the standard growth conditions) is also plotted in Fig. 2.6(b). In any cases, the pit density is almost the same, and the pit density is found to be independent of V/III ratio and growth temperature.

Then, the reactor pressure dependence of the surface morphologies were investigated. Only the reactor pressure was controlled in the ranges of 76–500 Torr by adjusting the throughput of the rotary pump, and the surface morphologies of the grown samples were characterized. Figure 2.7 shows the AFM images of the *c*- and *r*-plane AlN films grown at various reactor pressures. For the *r*-plane AlN films, the pit density drastically decreases with an increase of the reactor pressure, and these pits are completely eliminated (less than $2.5 \times 10^5 \text{ cm}^{-2}$ at most) in the sample grown at 500 Torr. As a consequence of the pit elimination, the RMS of surface roughness is 0.19 nm, which well agrees with the interplanar spacing of *r*-plane (0.18 nm), and it means that a high quality semipolar *r*-plane AlN film with an atomically smooth surface is achieved. On the contrary, the high pressure growth causes a rough surface for *c*-plane AlN as shown in Fig. 2.7. This may be because the migration of Al adatoms is suppressed by the high reactor pressure. These findings clearly indicate that there are the appropriate growth pressures for the respective growth planes,

(a)



(b)

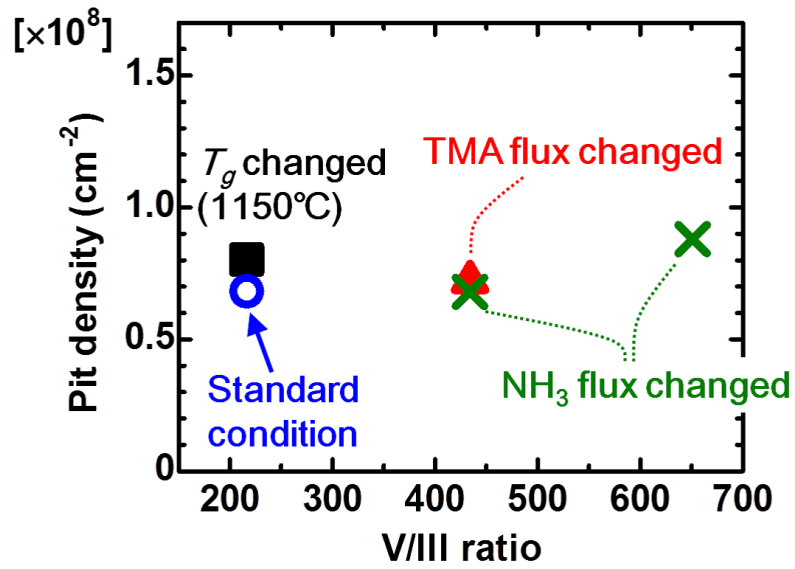


Figure 2.6: (a) AFM images of *r*-plane AlN films when V/III ratio is varied from 217 to 651 by changing the NH₃ fluxes. (b) V/III ratio dependence of pit density on the *r*-plane AlN surfaces.

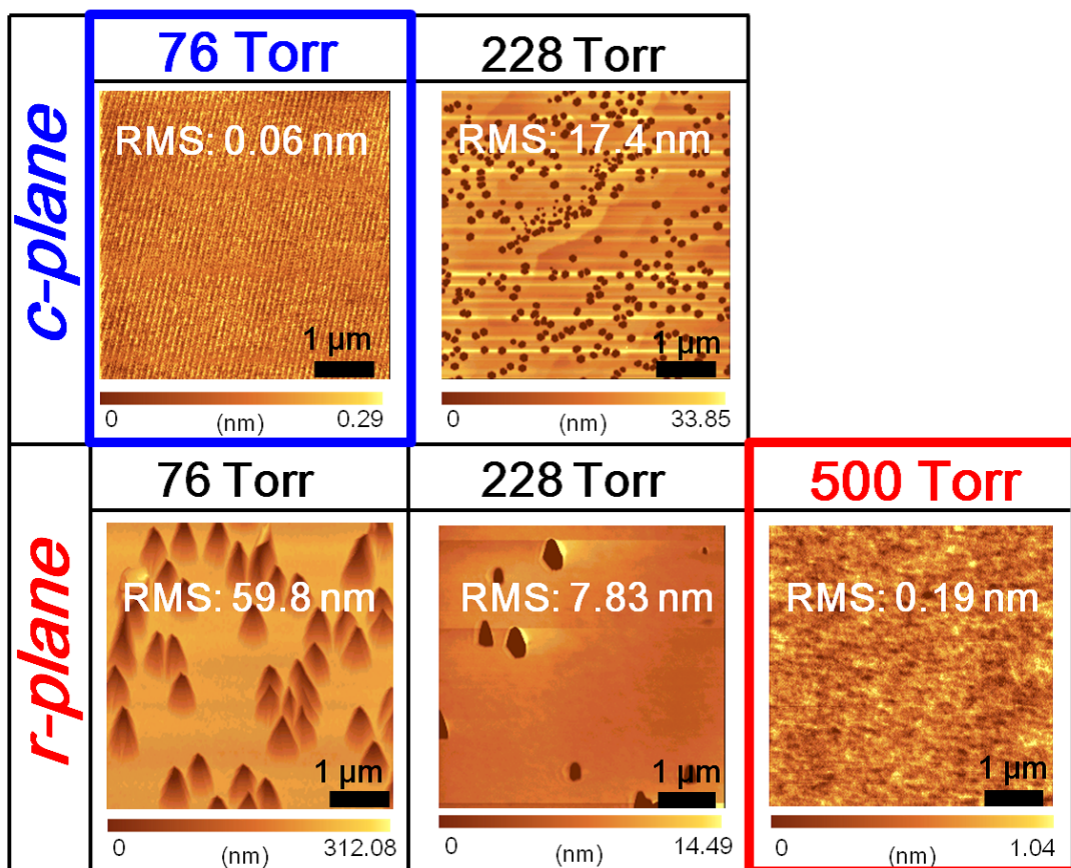


Figure 2.7: AFM images of the *c*- and *r*-plane AlN films grown at various reactor pressures.

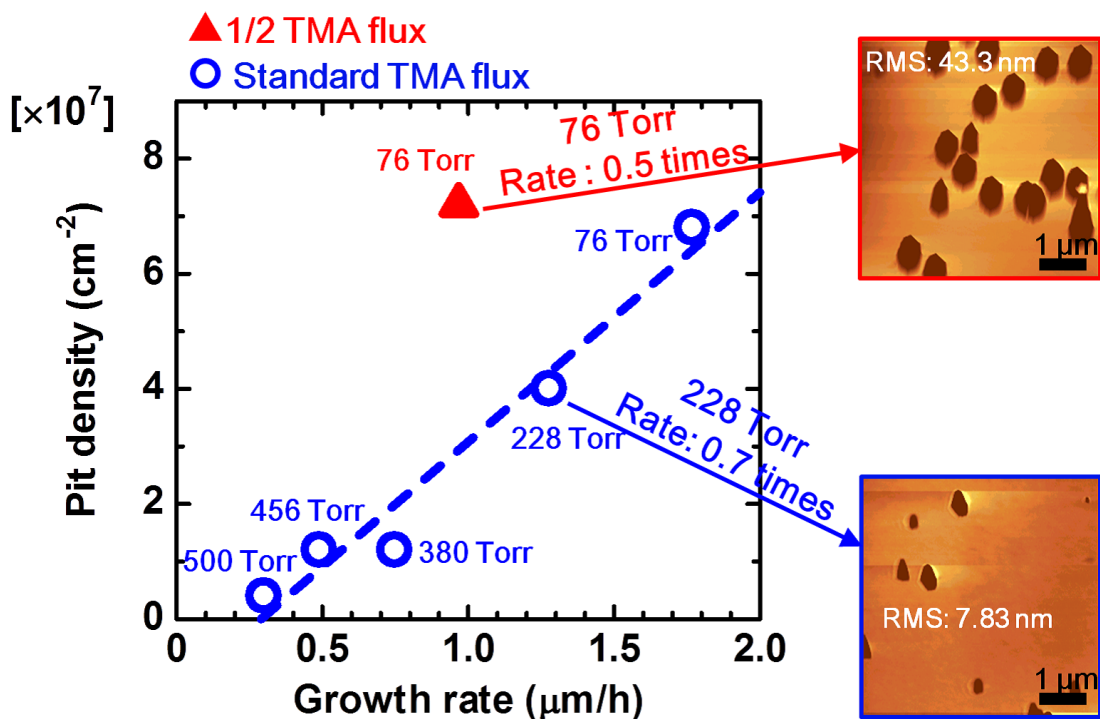


Figure 2.8: Growth rate dependence of the pit density for *r*-plane AlN films. Though the sample grown with the half TMA flux has the half growth rate (triangle), the pit density was almost the same as that of *r*-plane AlN grown by the standard growth condition.

and higher pressure growth is effective to achieve high quality *r*-plane AlN films.

2.4.3 Pit elimination mechanism

In order to clarify the reason why the pits are eliminated by high pressure growth, we investigated the growth rate dependence of the pit density at first. In general, high pressure growth of AlN causes low growth rate due to the parasitic reaction [22, 23], which is the pre-reaction between TMA and NH_3 . This reaction is more significant in AlN growth than GaN growth because the binding energy between Al and N is relatively large compared with that between Ga and N. Although the parasitic reaction often forms the particles on the growth surfaces [24], such particles cannot be observed in our case as shown in Fig. 2.7. This may be because we use lower V/III ratios than typical values and excess pre-reactions are suppressed.

Figure 2.8 shows the growth rate dependence of the pit density for *r*-plane AlN films. In fact, we can confirm that higher reactor pressures decrease the growth rates due to the parasitic reactions. Although the pits are seemingly reduced with decreasing the growth rates, it is not clear whether the slower growth rates themselves are the reason for the pit reduction or not. To precisely investigate the effect of the low growth rate, an AlN film was grown with a half growth rate at conventional reactor pressure 76 Torr. The low growth rate was realized by reducing the TMA flux to half. Though the sample grown with the half TMA flux has the half growth rate, the pit density was almost the same as that on the *r*-plane AlN surface grown by the standard growth condition. It clearly indicates that the lower growth rate is not an essential factor for the pit elimination in high pressure growth.

To further investigate the mechanism of pit elimination, we characterized the epilayer thickness dependence of the pit density. The epilayer thickness of the *r*-plane was varied from 0 to 1200 nm by changing the growth time.

Figures 2.9 and 2.10 show the AFM images of the *r*-plane AlN films with various epilayer thicknesses grown at 76 and 500 Torr, respectively. Here, the AFM image of 0-nm-thick epilayer means the substrate surface just after the NH_3 annealing at 1215°C for 15 min (before growth). We cannot confirm any significant roughening on the substrate surface just after the annealing, whereas the thin epilayers have small pits regardless of the reactor pressures. Moreover, it was clarified that these pits get larger with increasing the epilayer thickness without changing the structural shapes. The pit density increases with epilayer thickness for thin epilayers ($< \sim 50$ nm) but is reduced for thicker films grown at both reactor pressures.

The epilayer thickness dependence of the pit density and the area of a pit are shown in Fig. 2.11. For both *r*-plane AlN films grown at 76 and 500 Torr, the pit density has almost the same maximum values ($\sim 1.2 \times 10^8 \text{ cm}^{-2}$) at ~ 50 nm. Furthermore, the area per pit (S_{pit}) gets larger as a quadratic function of epilayer thickness regardless of the growth pressures. This is because the pit depths proportionally get deeper with increasing epilayer

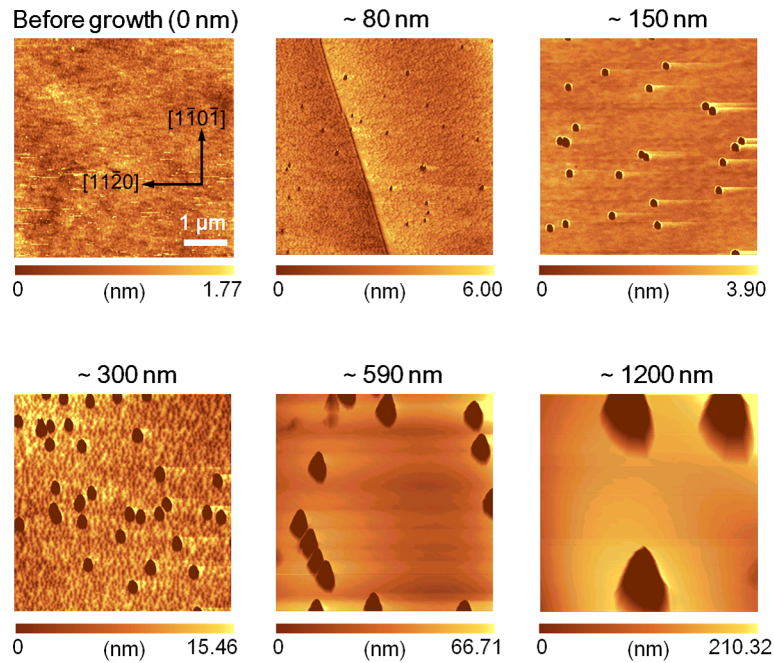
76 Torr

Figure 2.9: AFM images of *r*-plane AlN films with various epilayer thicknesses grown at 76 Torr. AFM image of 0-nm-thick epilayer means the substrate surface just after the NH₃ annealing at 1215°C for 15 min (before growth).

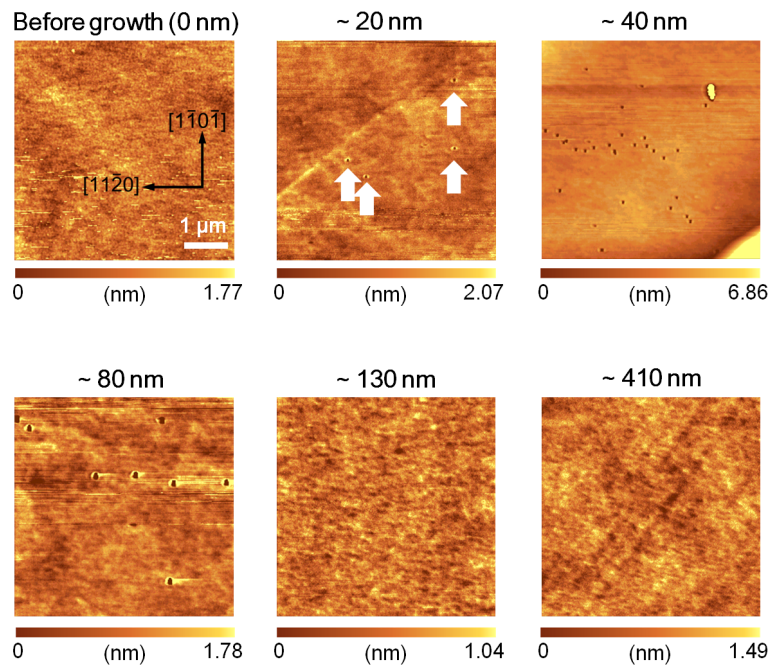
500 Torr

Figure 2.10: AFM images of *r*-plane AlN films with various epilayer thicknesses grown at 500 Torr. AFM image of 0-nm-thick epilayer means the substrate surface just after the NH₃ annealing at 1215°C for 15 min (before growth).

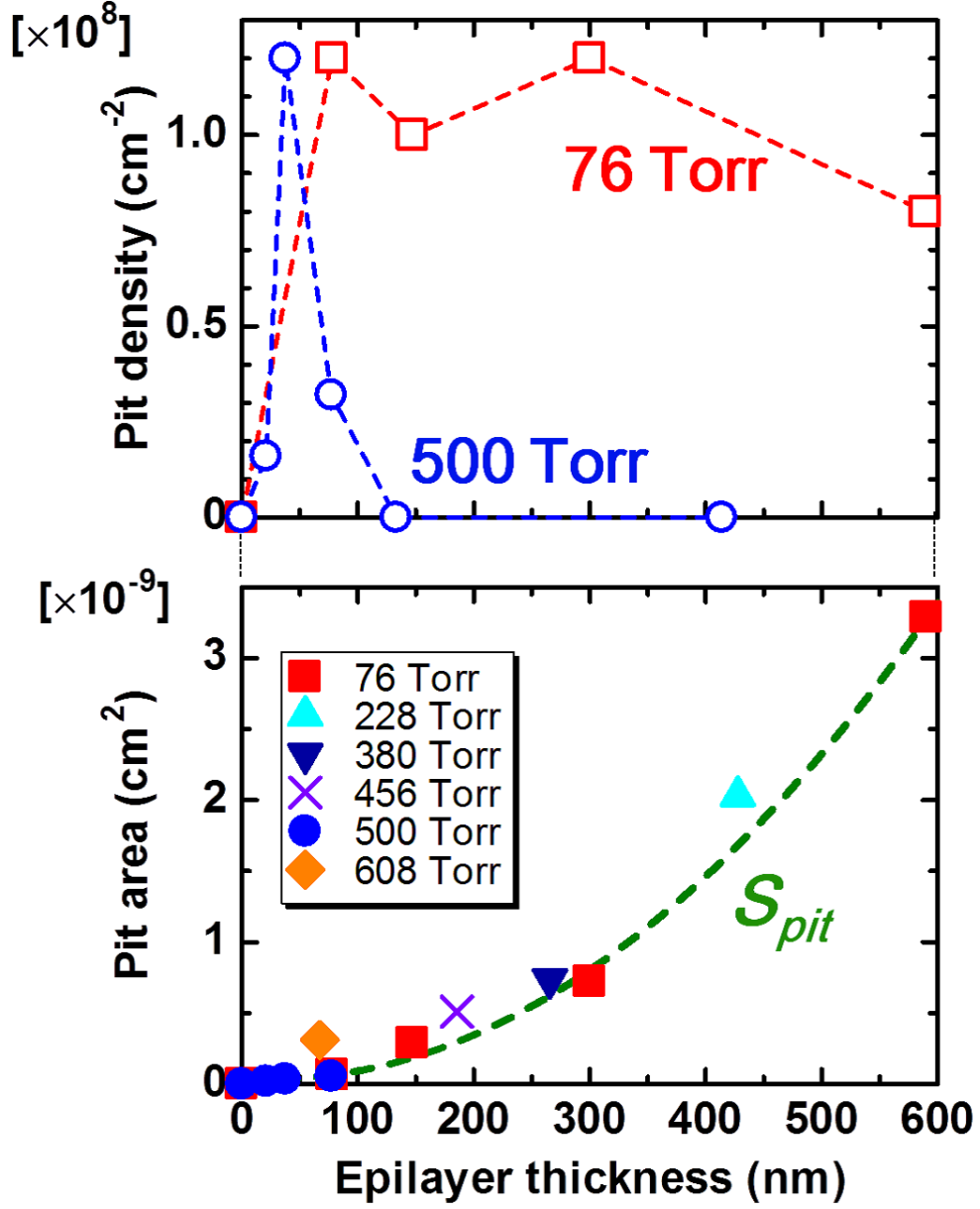


Figure 2.11: Epilayer thickness dependences of the pit density and the area of a pit. The pit density in the sample grown at 500 Torr is drastically reduced for thicker epilayers and approaches zero at ~ 200 nm, whereas that in the sample grown at 76 Torr quite slowly decreases. The pit area (S_{pit}) gets larger as a quadratic function of epilayer thickness regardless of the growth pressures.

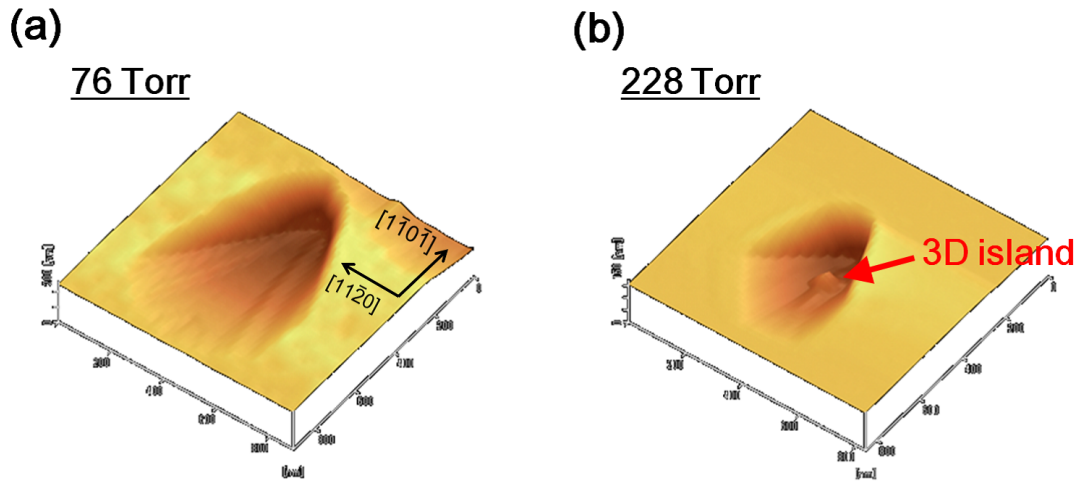


Figure 2.12: Bird's eye views of AFM images in the vicinity of the pits for the samples grown at (a) 76 Torr and (b) 228 Torr. In (b), a 3D AlN growth island can be observed inside the residual pit.

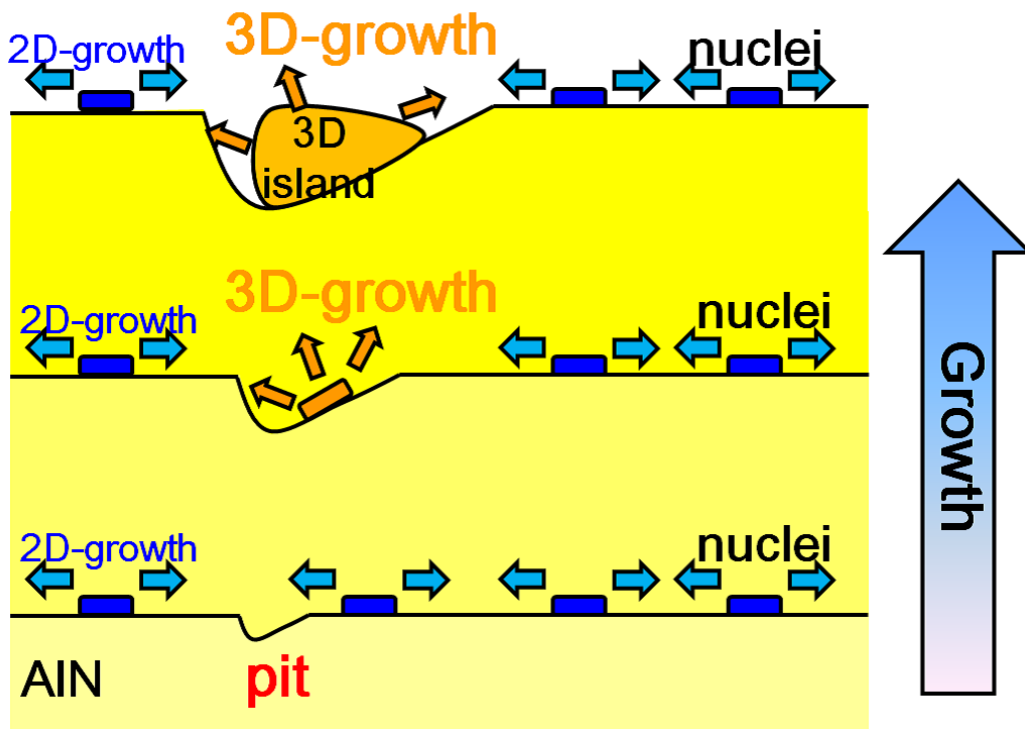


Figure 2.13: Schematic image of a growth process under the high reactor pressure. The image is based on the hypothesis that nuclei generated in pits three-dimensionally expand and bury the pits.

thickness while keeping the stable $\{1\bar{1}01\}$ facets.

The pit density in the sample grown at 500 Torr is drastically reduced for thicker epilayers and approaches zero at ~ 200 nm, whereas that in the sample grown at 76 Torr quite slowly decreases. We consider that the difference of the pit density behaviors should be affected by the growth kinetics variation depending on the reactor pressures. Figures 2.12(a) and (b) show the bird's eye views of AFM images in the vicinity of the pits for the samples grown at 76 and 228 Torr, respectively. 3D AlN growth islands can be observed inside the several residual pits when the samples are grown at high reactor pressures as marked in Fig. 2.12(b). Then, we consider that nuclei may easily be generated in pits due to higher reactor pressures and their three-dimensional expansion buries the pits.

The schematic image of a growth process based on the hypothesis is shown in Fig. 2.13. In the initial growth stage, nuclei are hardly generated inside pits because the pit area is very small for a thin epilayer as shown in Fig. 2.11. As the growth proceeds, pits get larger and nuclei are generated inside pits. Because there may be a lot of kinks in pits due to the complicated structures, the generated nuclei three-dimensionally grow and bury the pits. Note that nuclei outside pits should two-dimensionally expand and the growth rate should be slower than three-dimensional growth of nuclei inside pits considering the atomically smooth surface observed after the pit elimination.

2.4.4 Calculation model for pit elimination process

Based on the hypothesis that nucleation inside pits leads to pit elimination, we propose a calculation model to further investigate the effect of the nucleation on pit elimination at various reactor pressures.

Here, we define nucleation density (N_{nuc}) as a surface nuclei density generated per unit thickness. Therefore, for the epitaxy of extremely thin thickness Δt , $N_{\text{nuc}}\Delta t$ means the so-called surface density of nucleation sites observed from the normal of the surface. Then, the number of nuclei in a pit is expressed as $S_{\text{pit}}N_{\text{nuc}}\Delta t$, where S_{pit} is an area of a pit obtained in Fig. 2.11. Assuming that a pit is instantly buried when one nucleus is generated in the pit, $S_{\text{pit}}N_{\text{nuc}}\Delta t$ can be reconsidered as the pit-elimination probability.² At a certain epilayer thickness t , the density of pits that will be eliminated during the next epitaxy of Δt can be described as $n_{\text{pit}}(S_{\text{pit}}N_{\text{nuc}}\Delta t)$, where n_{pit} is the current pit density. Thus, the pit density variation during the epitaxy from t to $t + \Delta t$ can be expressed as

$$n_{\text{pit}}(t + \Delta t) - n_{\text{pit}}(t) = -n_{\text{pit}}(t)S_{\text{pit}}(t)N_{\text{nuc}}\Delta t. \quad (2.2)$$

When $\Delta t \rightarrow 0$, we can rewrite Eq. (2.2) as

$$\frac{dn_{\text{pit}}(t)}{dt} = -n_{\text{pit}}(t)S_{\text{pit}}(t)N_{\text{nuc}}. \quad (2.3)$$

²When $S_{\text{pit}}N_{\text{nuc}}\Delta t$ reaches 0.5, 50% of pits may include nuclei and will be eliminated.

By solving the differential equation, we obtain

$$n_{\text{pit}}(t) = n_0 \exp \left[-N_{\text{nuc}} \int_0^t S_{\text{pit}}(t) dt \right], \quad (2.4)$$

where n_0 is the maximum pit density ($1.2 \times 10^8 \text{ cm}^{-2}$) given in Fig. 2.11. Equation (2.4) explains the pit-decreasing process with respect to the epilayer thickness. Then, we fitted the experimental results of pit-decreasing processes at various growth pressures based on Eq. (2.4) using N_{nuc} as a fitting parameter. The obtained fitted curves are depicted as broken lines in Fig. 2.14, and they well fitted the experimental results plotted in the figure. The nucleation densities N_{nuc} given by the fittings are plotted in Fig. 2.15 as a function of the reactor pressure. Figure 2.15 indicates that the nucleation density exponentially increases with respect to the reactor pressure, and this qualitatively agrees with the fact that migration length of Al adatoms gets shorter with increasing growth pressure. The moderate suppression of Al migrations realized a pit-free and atomically smooth surface for r -plane AlN film. In Fig. 2.15, the exponentially fitted line is depicted as a solid line.

The high nucleation density due to high pressure growth can generate nuclei even in small pits. In other words, high pressure growth can eliminate pits with thin epilayer thickness, and it corresponds to the experimental results as shown in Fig. 2.11. Here, we define the threshold pit density n_{th} as a criterion of pit elimination. When the pit density n_{pit} is less than n_{th} , we assume that pits are eliminated. From the definition and Eq. (2.4), the following equation is obtained,

$$\int_0^{h_e} S_{\text{pit}}(t) dt = \frac{1}{N_{\text{nuc}}} \ln \left(\frac{n_0}{n_{\text{th}}} \right), \quad (2.5)$$

where h_e is the epilayer thickness required for pit elimination. Here, we set n_{th} as $1.0 \times 10^6 \text{ cm}^{-2}$ and use N_{nuc} obtained from Fig. 2.15 to calculate h_e using Eq. (2.5). The obtained h_e is shown in Fig. 2.16 as a function of the reactor pressure. The plotted h_e and a calculated solid line make use of N_{nuc} depicted as the plots and the exponentially fitted line in Fig. 2.15, respectively. We found that the thickness required for pit-elimination is exponentially reduced for higher growth pressures due to the impact of high nucleation density. On the other hand, the growth rate linearly decreases with an increase of pressure due to the parasitic reaction as additionally shown in Fig. 2.16. These findings indicate that the optimal growth pressure exists to achieve high quality r -plane AlN keeping the growth rate.

2.4.5 Optimal growth pressure for pit elimination

Here, we try to derive the optimal growth pressure for pit elimination considering the growth rate and nucleation density. The growth time for pit elimination (τ_{pit}) can be expressed as

$$\tau_{\text{pit}} = \frac{h_e}{R_g}, \quad (2.6)$$

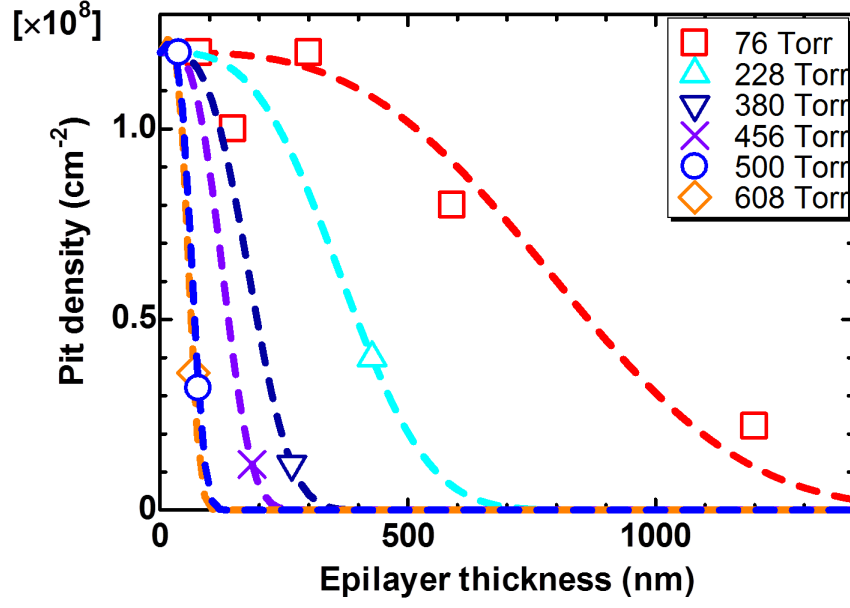


Figure 2.14: Fitting results of the experimentally obtained pit-decreasing processes based on Eq. (2.4) using N_{nuc} as a fitting parameter. The obtained fitted curves are depicted as broken lines, which well fitted the experimental results.

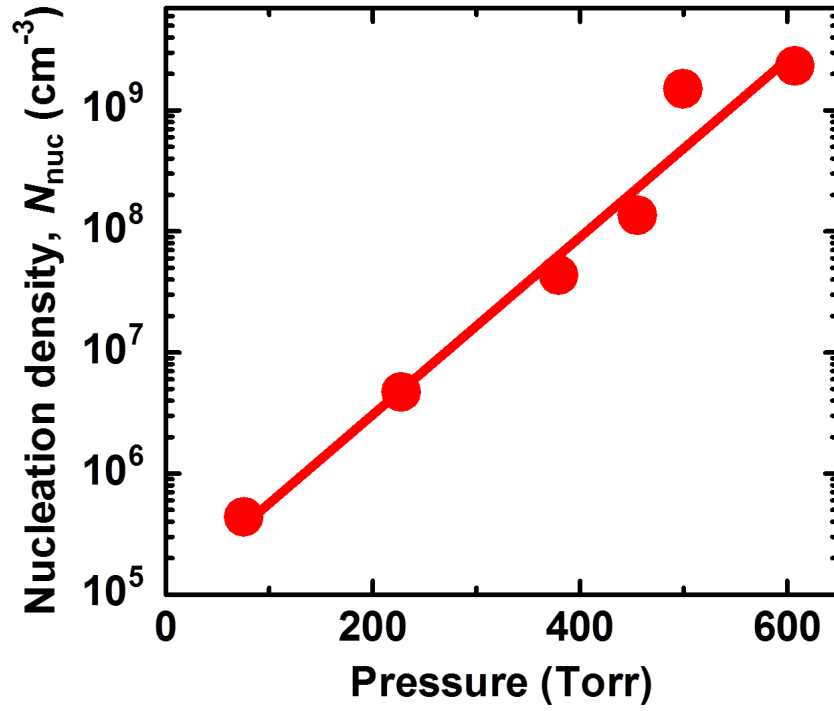


Figure 2.15: Nucleation densities N_{nuc} given by the fittings based on Eq. (2.4) are plotted as a function of the reactor pressure. Exponentially fitted line is depicted as a solid line.

where R_g means the growth rate, which is given by the linearly approximated line shown in Fig. 2.16. The reactor pressure dependence of τ_{pit} given by Eq. (2.6) is depicted in Fig. 2.17. The plots and a solid line in Fig. 2.17 are depicted by using h_e shown as the plots and the calculated solid line in Fig. 2.16, respectively. The result in Fig. 2.17 indicates that τ_{pit} on the lower pressure side is limited by the low nucleation density and that on the high pressure side is limited by the low growth rate due to the parasitic reaction. Thus, we conclude that ~ 500 Torr is the optimal growth pressure to effectively eliminate pits in r -plane AlN films.

Subsequently, we discuss the limitation to achieve atomically smooth surfaces after the pit elimination. Although a long time growth at low reactor pressure is also seemingly effective to eliminate pits, we experimentally confirmed that the actual epilayer surfaces grown by such conditions were heavily roughened. This may be because the pit density is reduced as growth proceeds, whereas the pit area gets larger. The surface occupancy rate (R_{oc}) of the pit region can be expressed as

$$R_{\text{oc}} = S_{\text{pit}} \cdot n_{\text{pit}}. \quad (2.7)$$

The epilayer thickness dependences of the calculated surface occupancy rates (10–90%) are depicted as solid lines in Fig. 2.18. Note that the calculated lines are independent of growth pressures because S_{pit} is a function of epilayer thickness regardless of the reactor pressures as described in Fig. 2.11. For the discussion, the pit reduction processes (shown in Fig. 2.14) are also depicted in Fig. 2.18. In addition, the surface morphology of a 1200-nm-thick r -plane AlN film grown at 76 Torr is also shown in Fig. 2.18. The sample is marked by the arrow in Fig. 2.18, and the pit density is actually reduced to be $\sim 2.2 \times 10^7 \text{ cm}^{-2}$. Though the AFM image was assessed at a seemingly pit-free area, the surface is remarkably roughened. We consider that the surface roughening is caused by the high surface occupancy rate of the pit region. During the pit-reduction process, the 1200-nm-thick sample grown at 76 Torr went through the high R_{oc} region. In such a case, the three-dimensional growth inside pits may become more dominant compared with the two-dimensional growth outside pits. As a consequence, smooth surface cannot be achieved after the pit reduction. From the experimental and calculation results, the threshold surface occupancy rate of the pit region is estimated to be 30% at most, and we should keep $R_{\text{oc}} < 30\%$ during the r -plane AlN growth. Therefore, high pressure growth is also effective to achieve smooth surfaces because such growth condition does not go through high R_{oc} region as shown in Fig. 2.18.

2.4.6 Surface morphology of 15° off and $(11\bar{2}2)$ AlN

As we described above, high pressure growth is effective to achieve smooth surface for r -plane AlN homoepitaxy. Here, we investigated the surface morphologies of 15° off and $(11\bar{2}2)$ AlN homoepitaxial films. For the growth, we used the same growth conditions except for reactor pressures as the standard growth condition.

Figures 2.19(a) and (b) show the AFM images of 15° off AlN films grown at 76 and 500

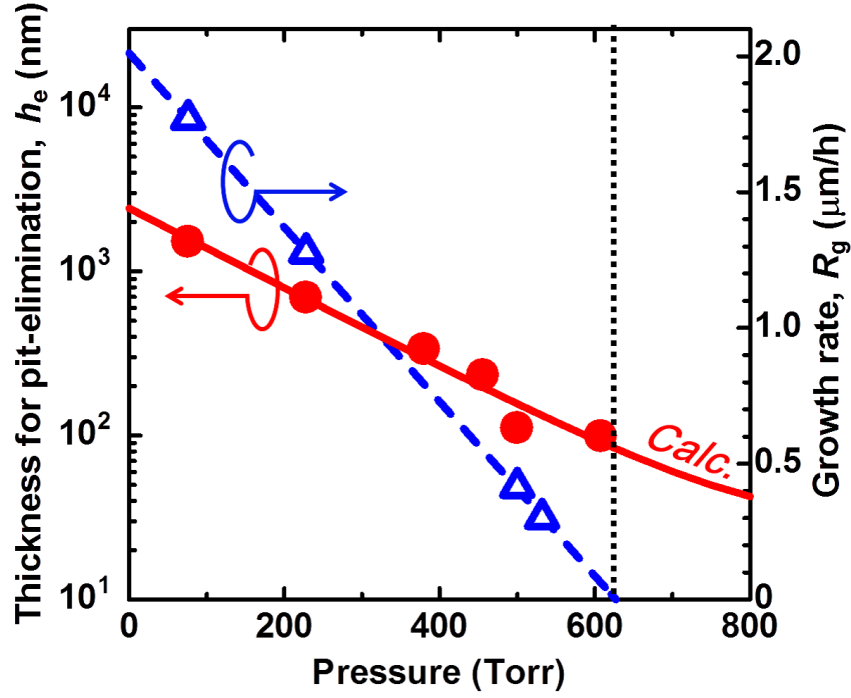


Figure 2.16: Reactor pressure dependence of the epilayer thickness required for pit elimination (h_e) given by Eq. (2.5) and growth rates of r -AlN films. Plotted h_e and a solid line make use of N_{nuc} depicted as the plots and the exponentially fitted line in Fig 2.15, respectively. A broken line for the growth rate is obtained by linear approximation.

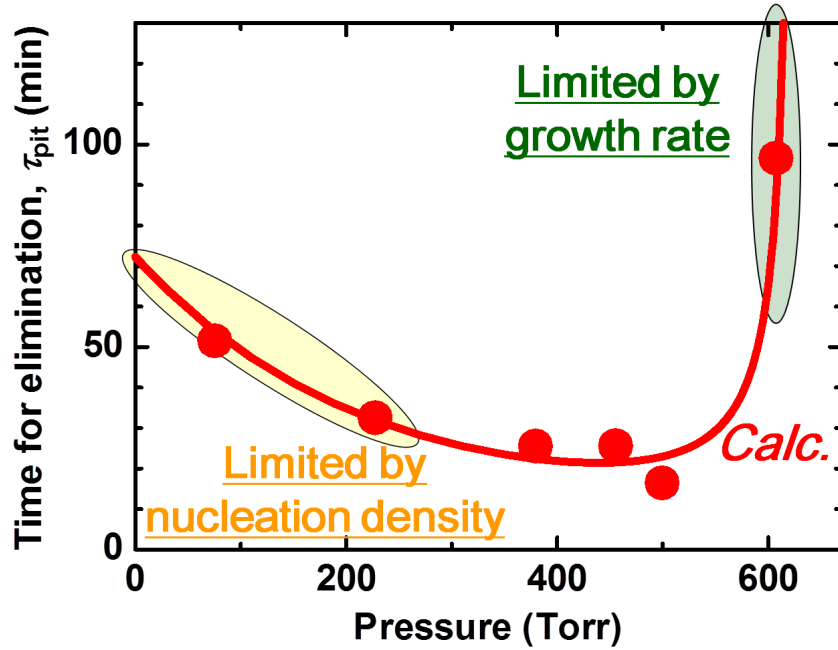


Figure 2.17: Reactor pressure dependence of τ_{pit} given by Eq. (2.6). Plots and a calculated solid line are depicted by using h_e shown as the plots and the calculated solid line in Fig 2.16, respectively.

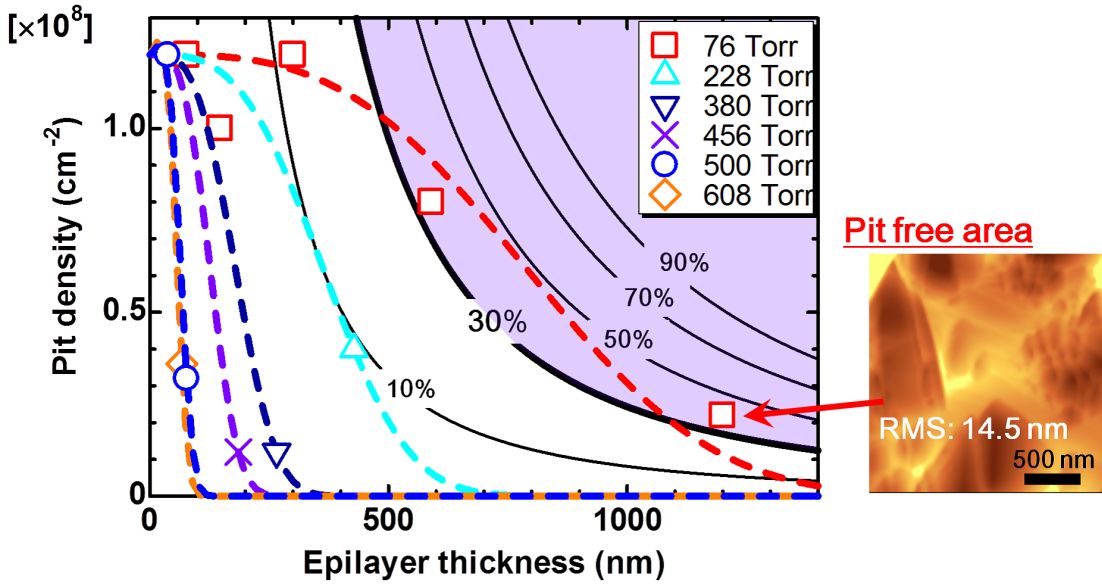


Figure 2.18: Epilayer thickness dependences of surface occupancy rates (R_{oc}) of pit region calculated by Eq. (2.7) are depicted as solid lines. In addition, the surface morphology of 1200-nm-thick r -plane AlN film grown at 76 Torr is also shown.

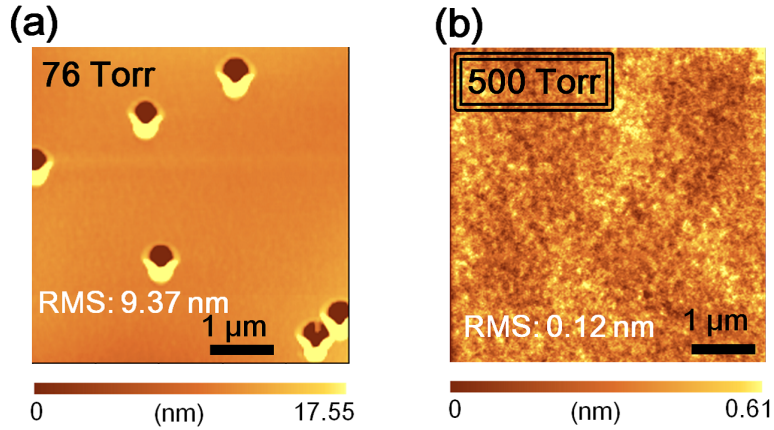


Figure 2.19: Surface morphologies of 15° off AlN grown at (a) 76 and (b) 500 Torr.

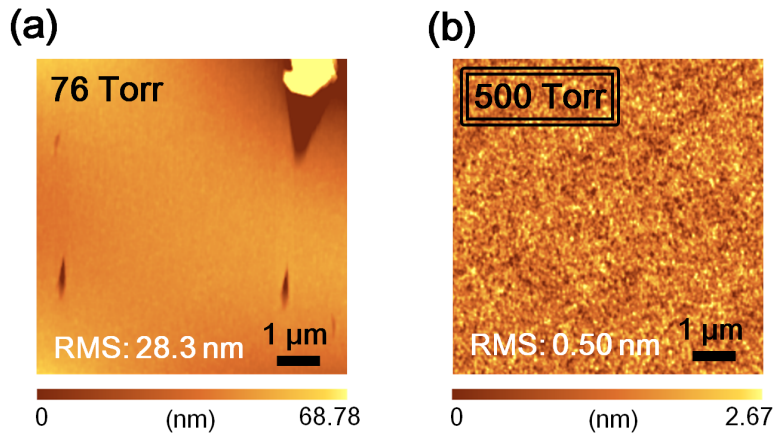


Figure 2.20: Surface morphologies of $(11\bar{2}\bar{2})$ AlN grown at (a) 76 and (b) 500 Torr.

Torr, respectively. Similar to the r -plane AlN epilayer surface, pits are generated on the 15° off AlN surface grown at conventional 76 Torr, whereas the pits are eliminated by 500 Torr growth. We consider that the results originate from the same pit-elimination mechanism as in r -plane AlN homoepitaxy. As a consequence, we can also achieve atomically smooth surface of 15° off AlN (RMS: 0.12 nm) by 500 Torr growth. Although the generated pit density for 76-Torr-grown sample is different from that in r -plane AlN, this may be caused by the surface etching difference due to the crystal orientation variation.

Figures 2.20(a) and (b) show the AFM images of $(11\bar{2}2)$ AlN films grown at 76 and 500 Torr, respectively. $(11\bar{2}2)$ AlN grown at 76 Torr also has a certain number of pits as well as the other semipolar plane AlN films. In the vicinity of the large pits on $(11\bar{2}2)$ AlN surface, spiral hillocks are observed in addition to pits. Although there is no experimental evidence, it is speculated that the large pits may be related to the screw dislocations propagating from substrates. The RMS of surface roughness is 28.3 nm in 76-Torr-grown sample due to the large pits and spiral hillocks, whereas the surface defect elimination and the smooth surface (RMS: 0.50 nm) are realized by 500 Torr growth. Though the $(11\bar{2}2)$ surface flatness is a little worse than the other semipolar plane surfaces, the flatness is sufficient to fabricate QW structures.

2.5 Crystal quality of semipolar AlN epitaxial films

2.5.1 Impurity concentrations

As we discussed above, we clarified the optimal growth condition for semipolar AlN films and achieved atomically smooth surfaces, which are comparable to the conventional c -plane AlN surfaces. Then, we investigated the impurities in the grown semipolar AlN films by SIMS measurements.

Here, 1- μm -thick c -plane and 600-nm-thick r -plane AlN films were grown at 76 and 470 Torr, respectively (There is no scientific reason for the difference between 470 and 500 Torr for the growth of the r -plane AlN film, but this is due to the growth machine condition). Carbon, oxygen, and silicon impurities in these AlN films were assessed.

Figures 2.21(a) and (b) shows the SIMS depth profiles of c - and r -plane AlN films, respectively. In the c -plane AlN epilayer, silicon and carbon concentrations were below the detection limits ($< 1.0 \times 10^{16}$ and $< 4.5 \times 10^{16} \text{ cm}^{-2}$, respectively), and oxygen concentration was near the detection limit ($\leq 1.1 \times 10^{17} \text{ cm}^{-2}$). In the r -plane AlN epilayer, carbon impurity was below the detection limit ($< 2.0 \times 10^{16} \text{ cm}^{-2}$), whereas detected silicon and oxygen impurities were 2.4×10^{17} and $2.0 \times 10^{17} \text{ cm}^{-2}$, respectively. These results indicate that silicon and oxygen impurities were a little more incorporated in the r -plane AlN film than in the c -plane AlN. This may be because r -plane AlN films were affected by the desorption reaction of the quartz (SiO_2) reactor due to the high pressure growth. Thus, we predict that the other semipolar AlN films also include silicon and oxygen impurities as

well as the r -plane AlN film. To suppress the desorption reaction of the quartz reactor, we should improve the growth machine.

2.5.2 PL studies

2.5.2.1 Near band edge emission

Subsequently, we perform PL measurements at 9.5 K for the grown AlN films to characterize the crystal qualities in terms of the optical properties. The samples were grown at 76 and 500 Torr for c -plane and semipolar plane AlN, respectively.

Figure 2.22 shows the PL spectra near the band edges of the homoepitaxial AlN films acquired at 9.5 K. The excitation light source was an ArF excimer laser. Several sharp peaks are observed from each AlN film, and we call them as FX, α , X, and Si⁰X from higher to lower energies for the following discussions in this study. From the thermal behaviors and the optical polarization, the origin of the FX peaks is assigned as a free exciton with Γ_1 [25, 26]. The origin of the α peaks is suggested to be as the donor-bound exciton of the FX peak [25], and that of the Si⁰X peaks is assigned as silicon donor-bound exciton of the FX peak [27]. Furthermore, the origin of the X peaks is assigned as a free exciton with an irreducible representation of Γ_5 [25].

The PL peak positions for the respective AlN films are summarized in Tab. 2.1, where FXⁿ⁼² peak means the first excited state of the free A excitons [26]. Considering the spectral resolution at the observed wavelength (~ 1 meV), we found that the respective energy positions in all the samples almost completely correspond to each other. The result indicates that the semipolar AlN epilayers as well as the c -plane AlN homoepitaxial film scarcely involve the strains. Furthermore, Si⁰X peaks show the remarkably narrow line widths of ~ 1 – 2 meV after fitting the profiles with a Lorentzian function. Thus, these findings clarified that semipolar AlN films have very high crystalline qualities in terms of optical properties in addition to the structural perspective as we mentioned above. On the other hand, the Si⁰X peaks in semipolar AlN films are much stronger than that in the c -plane AlN film as shown in Fig. 2.22 most likely due to the higher concentrations of silicon impurities revealed by SIMS in Fig. 2.21.

Although the intensity correlations among the observed PL peaks were changed by the samples in Fig. 2.22, the main reason for the results may not be the crystalline quality difference (except for Si⁰X) but the optical polarization difference of the respective PL peaks. The luminescence peaks of FX and X are polarized parallel and perpendicular to the c -axis ($\mathbf{E}||c$ and $\mathbf{E}\perp c$), respectively [25, 26], where $\mathbf{E}$ is the electric field vector of emitted light. For the semipolar plane AlN films, the PL signals were detected at the surface normal. Therefore, the emissions from the semipolar AlN with larger off-angles [15° off $< r$ -plane $< (11\bar{2}2)$] should weaken the PL peaks with $\mathbf{E}\perp c$ and enhance those with $\mathbf{E}||c$. In fact, the X peaks relatively get weaker with increasing off-angles for semipolar AlN films. Moreover, the previous works have clarified that the α peaks have the polarization $\mathbf{E}||c$ [25, 26], and

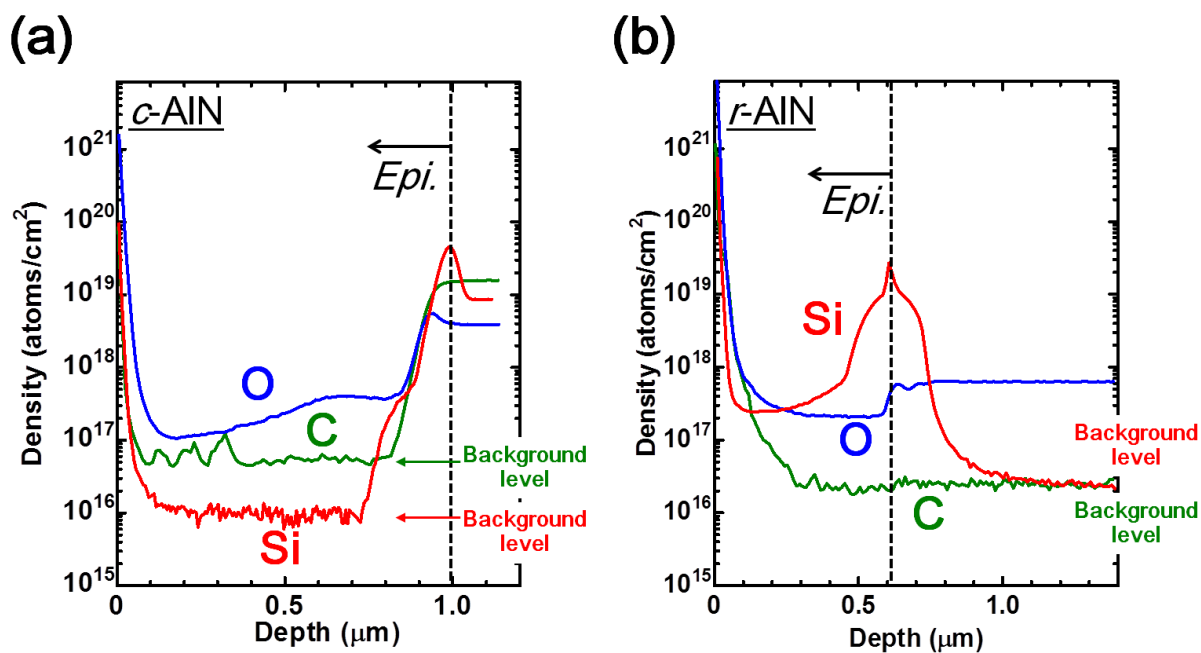


Figure 2.21: SIMS depth profiles of (a) *c*-plane and (b) *r*-plane AlN films.

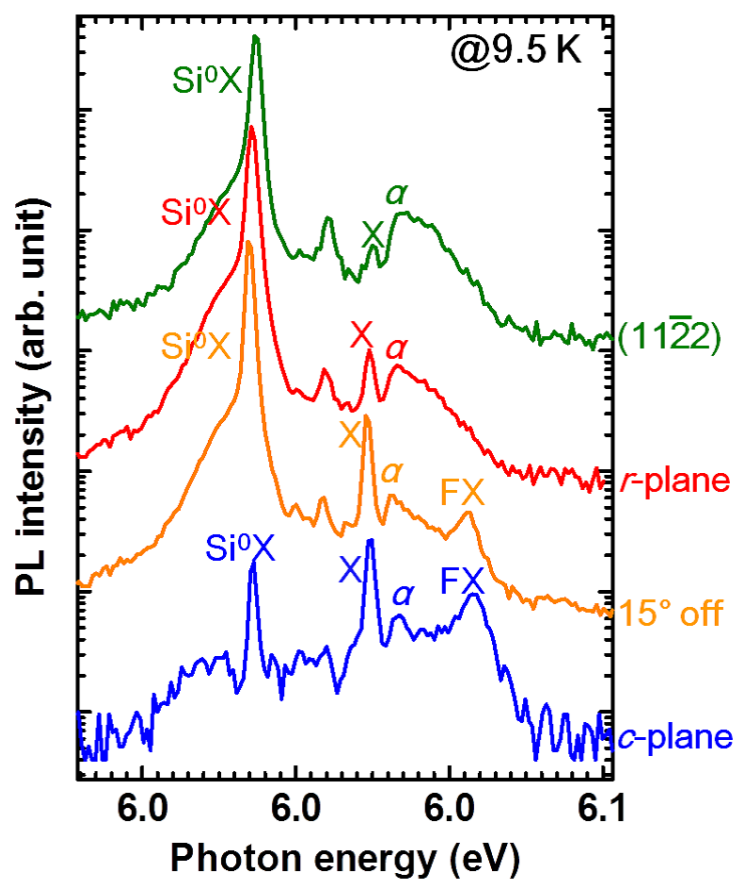


Figure 2.22: PL spectra near the band edges of homoepitaxial AlN films acquired at 9.5 K.

we actually found that the peaks get stronger for larger off-angle samples. However, the reason why the intensity of α peaks in the r -plane and (11 $\bar{2}2$) AlN overcomes that of the FX peaks so that the FX peaks cannot be observed is not clear, and further analyses for the origin of α peaks are needed.

2.5.2.2 Deep level emission

In addition to the near band edge emissions, we characterized the deep level emissions. Figure 2.23 shows the normalized PL spectra of the r -plane AlN epilayer and the substrate at 9.5 K. Although the deep level emissions peaking at 3.0 and 4.3 eV are mainly observed in both samples, the relative intensity of these emissions are well suppressed by more than two orders of magnitude in the epitaxial film.

The emission around 3.0 eV cannot be well separated and it seems to involve various components, whereas the origin of the emission at 4.3 eV has often been ascribed to defects related to carbon impurities [28]. However, it is uncertain whether or not this is the case in our samples because we confirmed that the carbon impurities in our samples are below the detection limit by SIMS even in the r -plane AlN substrate as shown in Fig. 2.21(b). Though the origins of the deep level emissions are not clear, we found that the density of some defects related to the emissions are significantly reduced in the r -plane AlN epitaxial film compared with the substrate. The result also supports that high quality semipolar AlN films were realized by high pressure growth.

2.6 Crystal growth of AlGa_N/AlN QWs

2.6.1 Surface morphology and QW interface

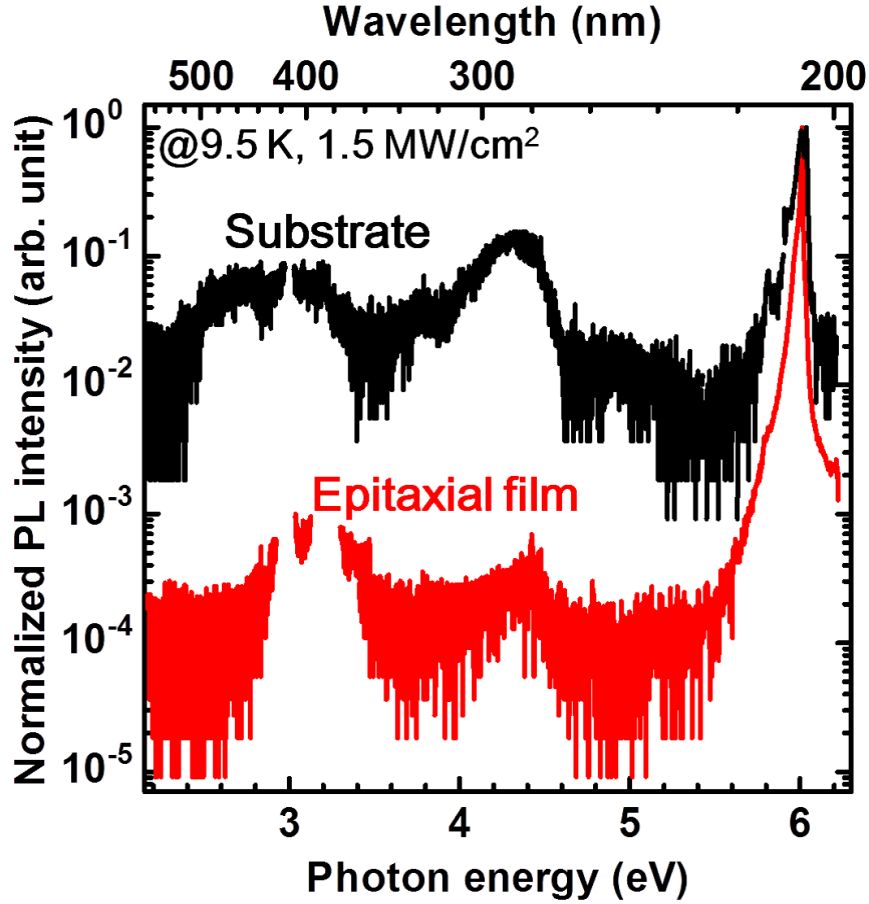
As we described above, the growth conditions for semipolar AlN films were optimized. Herein, we demonstrate semipolar AlGa_N/AlN QW structures on the high quality AlN films.

AlGa_N/AlN QWs were fabricated on c -plane, 15° off, r -plane, and (11 $\bar{2}2$) AlN substrates by the growth sequence shown in Fig. 2.2. Throughout the growth processes from AlN epitaxy to fabrication of AlGa_N/AlN QWs, we used 76 and 500 Torr as the reactor pressures, which are optimized for AlN films, for c -plane and semipolar-plane QW growth, respectively. For the growth of AlGa_N QWs, TMG fluxes were adjusted to be 8.18 and 16.36 $\mu\text{mol/min}$ for the c -plane and semipolar-plane QWs, respectively. The additional controls of Al compositions in AlGa_N QWs were performed by growth temperatures.

Figures 2.24(a) and (b) show the surface morphology and the symmetric (0002) XRD 2θ - ω scan of a c -plane AlGa_N/AlN QW, respectively. Steps with 1 ML height and atomically flat terraces are present, similar to the c -plane AlN surface. The RMS of the surface roughness is 0.12 nm. The clear satellite peaks in Fig. 2.24(b) confirm the high structural

Table 2.1: Energy positions of the observed PL peaks for various plane AlN films.

Levels (assignments)	<i>c</i> -plane (eV)	15° off (eV)	<i>r</i> -plane (eV)	(1122) (eV)
FX ⁿ⁼²	6.0824	6.0812	6.0822	6.0826
FX	6.0430	6.0423	—	—
α	6.0335	6.0323	6.0332	6.0336
X	6.0294	6.0291	6.0296	6.0300
Si ⁰ X	6.0145	6.0137	6.0142	6.0146

**Figure 2.23:** Normalized PL spectra of the *r*-plane AlN epilayer and the substrate at 9.5 K.

quality of the AlGa_N/AlN QW interfaces. From the XRD 2θ - ω scan, the estimated Al composition x of the Al _{x} Ga_{1- x} N layer is 0.8.

Subsequently, the typical surface morphologies of semipolar AlGa_N/AlN QWs are shown in Figs. 2.25. Similarly, we can confirm that quite smooth surfaces are maintained for all of the samples during the QW growths without any pit regenerations. The RMS of surface roughness of each semipolar QW is less than 1 nm, which is sufficiently smooth for typical QW structures (in most cases, well widths > 1 nm). In particular, we obtained atomically smooth surfaces for 15° off and r -plane QWs, where the surface RMS roughness is equivalent to or less than the lattice spacing of each plane.

To characterize the QW interfaces of the semipolar AlGa_N/AlN QWs, cross sectional TEM images were acquired for the r -plane and (11 $\bar{2}2$) QWs as shown in Figs. 2.26(a) and (b), respectively. The abrupt QW interfaces were observed in both QWs, and it clearly indicates that the growth pressure optimization for underlying AlN films plays an important role to achieve such high quality semipolar AlGa_N/AlN QWs.

2.6.2 Ga incorporation

Here, we discuss the control of Ga incorporation in semipolar AlGa_N/AlN QWs focusing on r -plane QWs. In general, Al compositions of AlGa_N QWs decrease with increasing the growth temperatures [8], and the control is very easy for the conventional c -plane AlGa_N QWs. However, crystallographic orientations may strongly affect the Ga incorporations into AlGa_N alloys. For example, in molecular beam epitaxy, a large difference in the Ga incorporation between (1 $\bar{1}00$) and (11 $\bar{2}0$) has been reported, and in that case, Ga is hardly incorporated in (11 $\bar{2}0$) layers [29]. Furthermore, the c -plane AlGa_N surface has a step and terrace structure in contrast to the semipolar AlGa_N surfaces as shown in Figs. 2.24 and 2.25. The surface difference between c -plane and semipolar plane AlGa_N may alter the Al composition. In addition, the high pressure growth for semipolar AlGa_N QWs also affects the Ga incorporations due to the parasitic reactions as we described above. Therefore, we investigated the Ga incorporation in our semipolar AlGa_N QWs with particular focus on r -plane QWs.

We fabricated r -plane AlGa_N/AlN QWs on AlN layers only varying growth temperatures from 1000 to 1200°C. Figure 2.27 shows the growth temperature dependence of Al compositions in the r -plane AlGa_N/AlN QWs and the growth rates of AlN barrier layers. The Al compositions were estimated by X-ray diffraction measurements. Even though the gas flow rates were constant, we could easily adjust the Al composition from 0.2 to 0.9. Because AlN (Ga_N) can be grown without supplying TMG (TMA), we found that semipolar AlGa_N layers with arbitrary Al compositions from 0 to 1 can be obtained by the growth temperature control, similar to the conventional c -plane QWs. On the other hand, the slope on the graph is drastically changed between 1050 and 1100°C, and the amount of increase for Al compositions is suppressed at higher growth temperatures. We consider

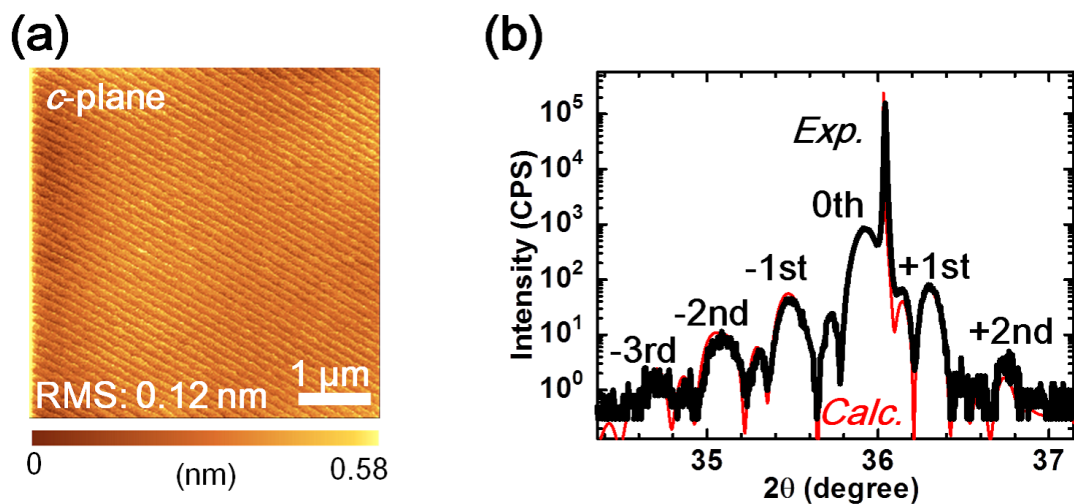


Figure 2.24: (a) Surface morphology assessed by AFM and (b) symmetric (0002) XRD 2θ - ω scan of a *c*-plane AlGa_N/AlN QW.

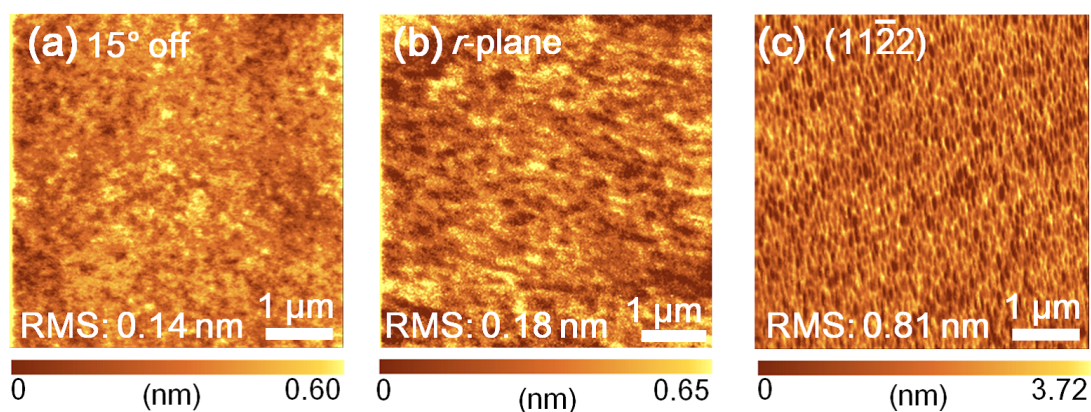


Figure 2.25: Typical surface morphologies of (a) 15° off, (b) *r*-plane, and (c) (11 $\bar{2}2$) AlGa_N/AlN QWs.

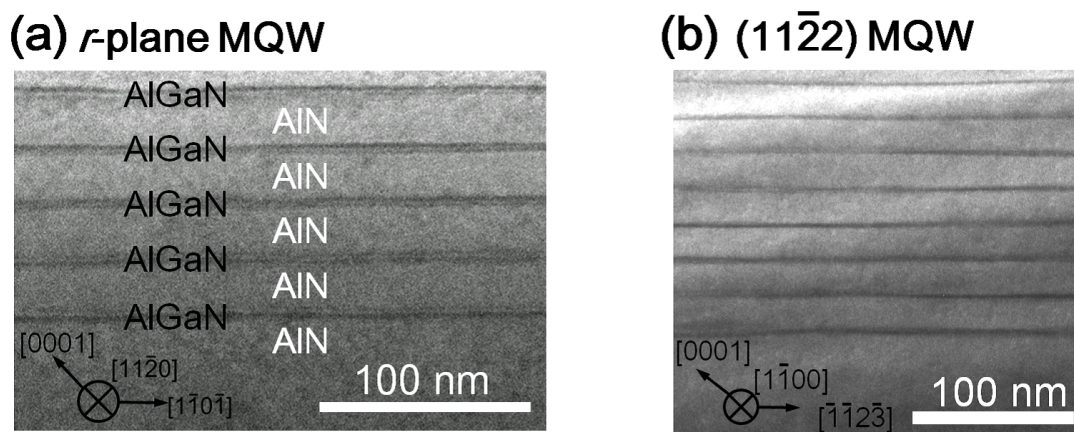


Figure 2.26: Cross sectional TEM bright field images of semipolar *r*-plane and (11 $\bar{2}2$) AlGa_N/AlN MQWs.

that the slope variation is caused by the parasitic reaction between TMA and NH₃. From the Fig. 2.27, we can confirm that the growth rate of AlN layers decreases with an increase of temperature due to the stronger parasitic reactions, which corresponds to the tendency in the previous work [22]. However, the growth rate of AlN is almost unchanged at the temperature below 1050°C. The result means that the temperature below 1050°C is low enough to avoid the pre-reactions between TMA and NH₃. Therefore, in the growth of “AlGa_{0.2}N”, Al incorporations are not impeded below 1050°C but impeded above 1050°C. On the other hand, Ga incorporations are also prevented by higher growth temperatures. As a consequence, Al compositions at temperatures below 1050°C are dominated by the decrease of Ga incorporations, whereas those above 1050°C are determined by the difference of Ga and Al incorporation decreases. These findings well explain the slope variation for Al compositions in Fig. 2.27.

Figure 2.28 shows the PL spectra of the fabricated *r*-plane AlGa_{0.2}N/AlN QWs (well width: 1–2 nm). The PL measurements were performed at room temperature using an ArF excimer laser as an excitation source. We can clearly observe the strong near band edge emissions at wavelengths of 220–280 nm, which indicates that the Ga incorporation can be controlled while keeping the crystal qualities. Therefore, we can easily adjust the wavelength in almost the whole DUV ranges for semipolar AlGa_{0.2}N QWs.

2.7 Effects of internal electric fields

2.7.1 Internal electric fields in polar and semipolar QWs

To compare the optical properties between the fabricated high quality *c*-plane and semipolar QWs, PL measurements were performed at 6.5 K for the Al_{0.8}Ga_{0.2}N/AlN QWs on various crystal planes. AlGa_{0.2}N well layers were selectively excited by a Ti:sapphire fourth harmonic generation laser (wavelength: 210 nm). The generated initial carrier density was less than $5 \times 10^{14} \text{ cm}^{-3}$, which corresponded to a so-called weak excitation condition.

Figure 2.29 shows the PL spectra of the *c*-plane and semipolar Al_{0.8}Ga_{0.2}N/AlN QWs with about 4.5-nm-thick wells. It was clarified that all of the semipolar QWs have much narrower emission line widths than the *c*-plane QW. As a consequence, LO phonon replicas can be clearly resolved in the PL spectra of many of the semipolar QWs, unlike *c*-plane QWs. In most cases of the *c*-plane QWs, micro-PL measurements, which have a much higher spatial resolution than normal macro-PL measurements, are necessary for clearly observing the LO phonon replicas [30, 31]. The LO phonon energies of the semipolar Al_{0.8}Ga_{0.2}N/AlN QWs were determined by Gaussian fittings to be $\sim 105 \text{ meV}$, which are close to the energy calculated by Vegard’s law (106 meV) using the LO phonon energies of AlN (110 meV) and GaN (90 meV) [32]. In addition, the LO phonon energy is also comparable to the experimental estimation from the *c*-plane Al_{0.8}Ga_{0.2}N/AlN QW emission using micro-PL measurements (104 meV) [30, 31].

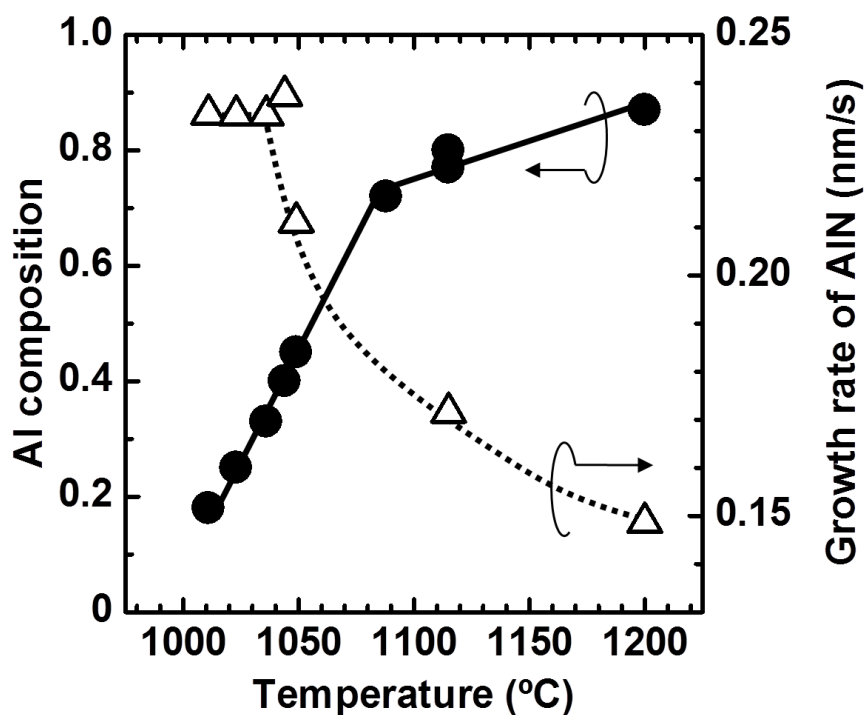


Figure 2.27: Growth temperature dependence of Al compositions in *r*-plane AlGaIn/AlN QWs and growth rates of AlN layers.

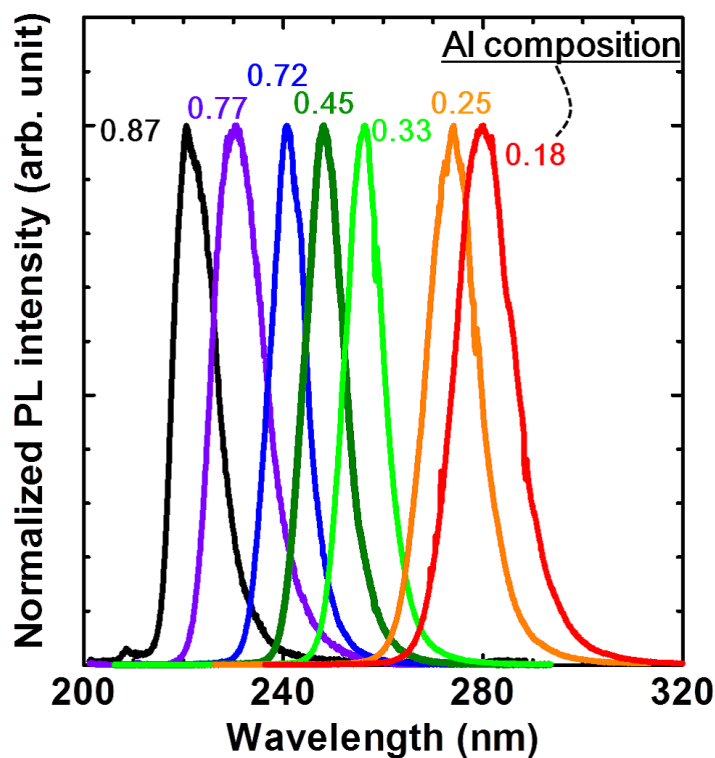


Figure 2.28: PL spectra of the fabricated *r*-plane AlGaIn/AlN QWs (well width: 1–2 nm). The PL measurements were performed at room temperature using an ArF excimer laser as an excitation source.

Figure 2.30 plots the well-width dependence of the PL peak energies of the c -plane, r -plane, and (11 $\bar{2}2$) Al_{0.8}Ga_{0.2}N/AlN QWs. The solid lines show the calculation results when the internal electric field is 2.3, 0.70, or 0.20 MV/cm. Because the internal electric field dominates the linear change in the transition energy of wide QW due to the well width, fairly good agreements in the slopes of the experiments and calculations indicate that the internal electric fields in c -plane, r -plane, and (11 $\bar{2}2$) Al_{0.8}Ga_{0.2}N/AlN QWs are 2.3, 0.70, and 0.20 MV/cm, respectively. Hence, we experimentally confirmed that the internal electric fields in the semipolar QWs are less than one-third of those in the (0001) QWs.

Then, we will compare the experimentally estimated internal electric fields with the calculated results. Here, we define the orthogonal coordinate systems (x, y, z) and (x', y', z') for the following discussions. The (x, y, z) coordinate is defined for wurtzite structure. The x and y axes are in (0001), whereas the z axis corresponds to the c -axis. On the other hand, (x', y', z') coordinate is defined for an arbitrary growth plane. The z' axis is parallel to the growth direction inclined from the z axis with the angle θ . The x' and y' axes are on the growth plane, and the y' axis is the same as the y axis.

The correlation between piezoelectric polarization ($\mathbf{P}^{\text{pz}}$) and strains for the wurtzite structure is expressed as [33, 34]

$$\mathbf{P}^{\text{pz}} = \begin{pmatrix} P_x^{\text{pz}} \\ P_y^{\text{pz}} \\ P_z^{\text{pz}} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xz} \\ 2\epsilon_{xy} \end{pmatrix}, \quad (2.8)$$

where e_{ij} and ϵ_{ij} are piezoelectric constant tensor and strain tensor,³ respectively. The piezoelectric polarization for the (x', y', z') coordinate can be obtained using a rotation matrix

$$\mathbf{U} = \begin{pmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix}. \quad (2.9)$$

Using Eqs. (2.8) and (2.9), the rotated piezoelectric polarization is given by

$$\begin{pmatrix} P_{x'}^{\text{pz}} \\ P_{y'}^{\text{pz}} \\ P_{z'}^{\text{pz}} \end{pmatrix} = \mathbf{U} \mathbf{P}^{\text{pz}}. \quad (2.10)$$

As a consequence, we obtain each component of piezoelectric polarization as

³The expression of strain tensor will be discussed in Chap. 4.

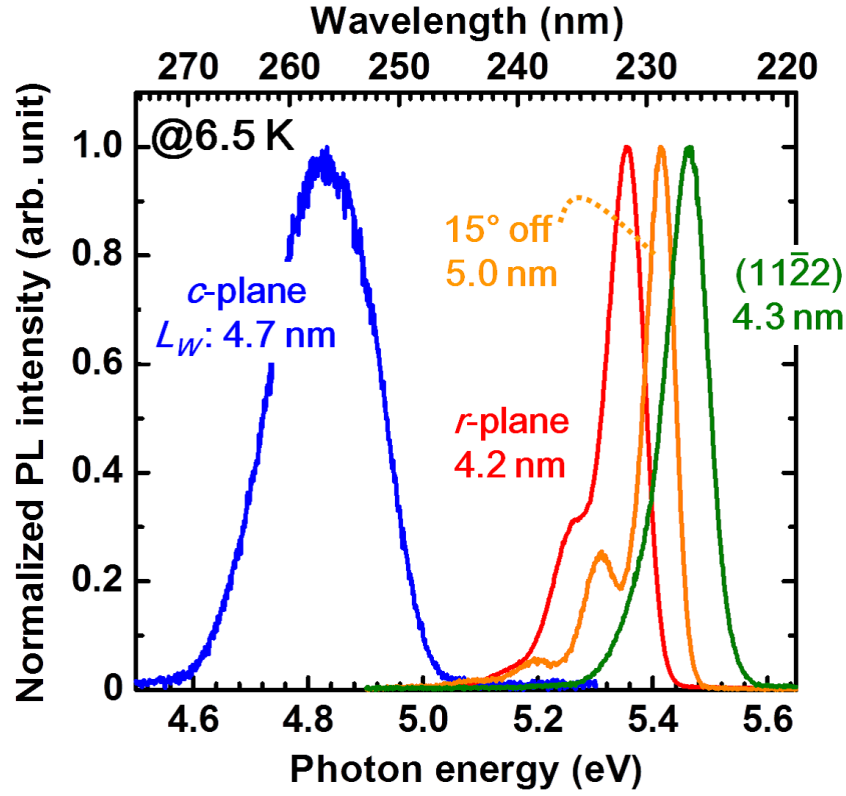


Figure 2.29: PL spectra at 6.5 K of the c -plane and semipolar $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs with about 4.5-nm-thick wells.

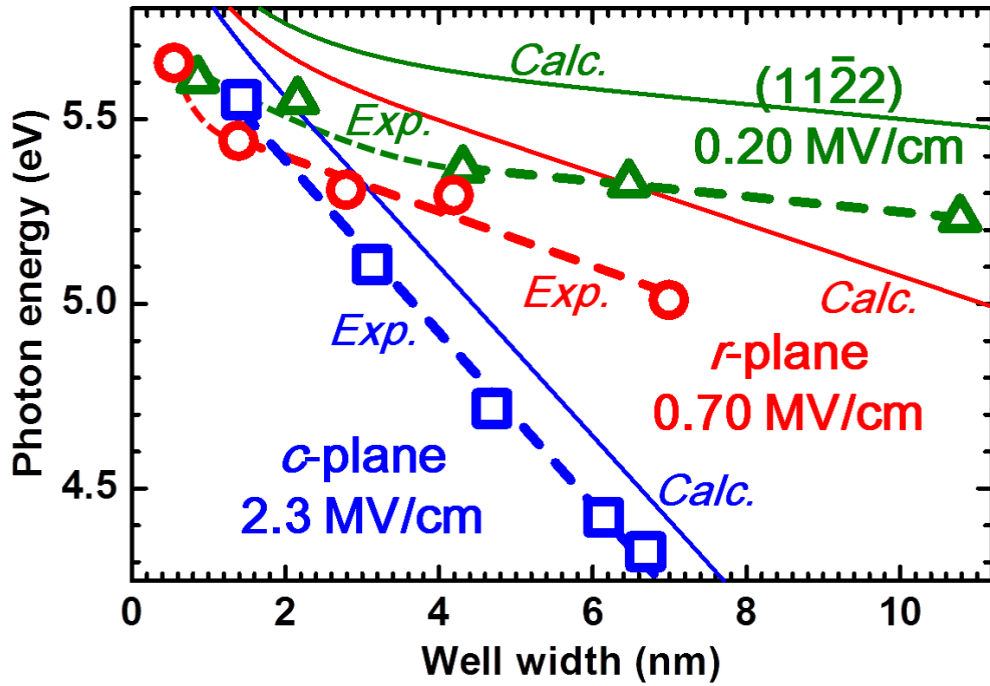


Figure 2.30: Well-width dependence of the PL peak energy of the c -plane, r -plane, and $(11\bar{2}2)$ $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs are plotted. The solid lines show the calculation results when the internal electric field is 2.3, 0.70, or 0.20 MV/cm.

$$P_{x'}^{\text{pz}} = e_{15}\epsilon_{xz} \cos \theta - [e_{31}(\epsilon_{xx} + \epsilon_{yy}) + e_{33}\epsilon_{zz}] \sin \theta, \quad (2.11)$$

$$P_{y'}^{\text{pz}} = 0, \quad (2.12)$$

$$P_{z'}^{\text{pz}} = e_{15}\epsilon_{xz} \sin \theta + [e_{31}(\epsilon_{xx} + \epsilon_{yy}) + e_{33}\epsilon_{zz}] \cos \theta. \quad (2.13)$$

Similarly, each component of the spontaneous polarization (P^{sp}) in (x', y', z') coordinate system is also expressed as

$$P_{x'}^{\text{sp}} = -P^{\text{sp}} \sin \theta, \quad (2.14)$$

$$P_{y'}^{\text{sp}} = 0, \quad (2.15)$$

$$P_{z'}^{\text{sp}} = P^{\text{sp}} \cos \theta. \quad (2.16)$$

Combining Eqs. (2.11)–(2.16), we can obtain the total polarization along i' direction as

$$P_{i'} = P_{i'}^{\text{pz}} + P_{i'}^{\text{sp}}. \quad (2.17)$$

The polarization $P_{i'}$ lead to an electric field $E_{i'}$ given by

$$D_{i'} = \epsilon_{i'j'}^{\text{p}} E_{j'} + P_{i'}, \quad (2.18)$$

where $D_{i'}$ and $\epsilon_{i'j'}^{\text{p}}$ are the electric displacement and permittivity tensor, respectively. $\epsilon_{i'j'}^{\text{p}}$ is given by

$$\begin{aligned} \epsilon_{i'j'}^{\text{p}} &= \mathbf{U} \epsilon_{ij}^{\text{p}} \mathbf{U}^{-1} \\ &= \begin{pmatrix} \epsilon_{x'x'}^{\text{p}} & 0 & \epsilon_{x'z'}^{\text{p}} \\ 0 & \epsilon_{\perp}^{\text{p}} & 0 \\ \epsilon_{x'z'}^{\text{p}} & 0 & \epsilon_{z'z'}^{\text{p}} \end{pmatrix}, \end{aligned} \quad (2.19)$$

where ϵ_{ij}^{p} is expressed as

$$\epsilon_{ij}^{\text{p}} = \begin{pmatrix} \epsilon_{\perp}^{\text{p}} & 0 & 0 \\ 0 & \epsilon_{\perp}^{\text{p}} & 0 \\ 0 & 0 & \epsilon_{\parallel}^{\text{p}} \end{pmatrix}. \quad (2.20)$$

Here, $\epsilon_{\perp}^{\text{p}}$ and $\epsilon_{\parallel}^{\text{p}}$ are permittivities perpendicular and parallel to the c -axis direction, respectively. From Eqs. (2.19) and (2.20), we obtain each component of $\epsilon_{i'j'}^{\text{p}}$ as

$$\varepsilon_{x'x'}^p = \varepsilon_{\perp}^p \cos^2 \theta + \varepsilon_{\parallel}^p \sin^2 \theta, \quad (2.21)$$

$$\varepsilon_{z'z'}^p = \varepsilon_{\perp}^p \sin^2 \theta + \varepsilon_{\parallel}^p \cos^2 \theta, \quad (2.22)$$

$$\varepsilon_{x'z'}^p = \left(\varepsilon_{\perp}^p - \varepsilon_{\parallel}^p \right) \sin \theta \cos \theta. \quad (2.23)$$

Thus, we obtain the following equations related to the electric displacement $D_{i'}$,

$$D_{x'} = \varepsilon_{x'x'}^p E_{x'} + \varepsilon_{x'z'}^p E_{z'} + P_{x'}, \quad (2.24)$$

$$D_{y'} = \varepsilon_{\perp}^p E_{y'}, \quad (2.25)$$

$$D_{z'} = \varepsilon_{x'z'}^p E_{x'} + \varepsilon_{z'z'}^p E_{z'} + P_{z'}. \quad (2.26)$$

Considering the continuity of the electric displacement $D_{z'}$ and the periodic boundary condition between the well and barrier layers, we can obtain the internal electric fields ($E_{z'}$) along the z' axis in well ($E_{\text{int}}^{\text{well}}$) and barrier layers ($E_{\text{int}}^{\text{bar}}$). Using the thickness of well and barrier layers (L_w and L_b , respectively), the internal electric fields are given by

$$E_{\text{int}}^{\text{well}} = \frac{P'_{z',\text{bar}} - P'_{z',\text{well}}}{\varepsilon_{z',\text{well}}'^p + \varepsilon_{z',\text{bar}}'^p (L_w/L_b)}, \quad (2.27)$$

$$E_{\text{int}}^{\text{bar}} = -\frac{L_w}{L_b} E_{\text{int}}^{\text{well}}, \quad (2.28)$$

where $P'_{z'}$ and $\varepsilon_{z'}'^p$ are expressed as

$$P'_{z'} = P_{z'} - \frac{\varepsilon_{x'z'}^p}{\varepsilon_{x'x'}^p} P_{x'}, \quad (2.29)$$

$$\varepsilon_{z'}'^p = \varepsilon_{z'z'}^p - \frac{(\varepsilon_{x'z'}^p)^2}{\varepsilon_{x'x'}^p}. \quad (2.30)$$

In the case of SQW structures or sufficiently narrow QWs with respect to barrier layers, we can consider $L_b \rightarrow \infty$, and Eqs. (2.27) and (2.28) are rewritten as

$$E_{\text{int}}^{\text{well}} = \frac{P'_{z',\text{bar}} - P'_{z',\text{well}}}{\varepsilon_{z',\text{well}}'^p}, \quad (2.31)$$

$$E_{\text{int}}^{\text{bar}} = 0. \quad (2.32)$$

Thus, we can calculate the internal electric field in a well layer using Eq. (2.27) or (2.31).

In the calculation, all parameters of AlGa_{0.8}N except for the spontaneous polarization (P^{sp}) are obtained by linear interpolations between the parameters of AlN and GaN. For the spontaneous polarization, -0.090 and -0.034 C/m² have been suggested for AlN and GaN, respectively, and -0.021 C/m² is suggested as a bowing parameter ($P_{\text{bow}}^{\text{sp}}$) for AlGa_{0.8}N alloys [35].

Figure 2.31 shows the off-angle dependence of internal electric fields in Al_{0.8}Ga_{0.2}N/AlN QWs. The experimentally determined $E_{\text{int}}^{\text{well}}$ for the c -plane and semipolar plane Al_{0.8}Ga_{0.2}N/AlN QWs are plotted⁴ in the figure, and the calculated result is depicted as a solid line. We found that the calculated result almost completely reproduces the experimental results. Therefore, we use the calculated internal electric fields for the following discussions including other chapters.

2.7.2 Radiative recombination lifetimes of semipolar AlGa_{0.8}N QWs

To elucidate the effect of internal electric fields on the radiative recombination processes, TRPL measurements were performed for the fabricated QWs. Figure 2.32 shows the TRPL decays near the PL peak energy of c -plane, 15° off, r -plane, and (11 $\bar{2}2$) Al_{0.8}Ga_{0.2}N/AlN QWs with about 4.5-nm-thick wells. The measurements were performed at 6.0 K to suppress non-radiative recombination processes. Because the decay curves look like a single exponential type for the c -plane QW and a double exponential type for the semipolar-plane QWs, we fitted the results using

$$I_{\text{TRPL}} = A \exp\left(-\frac{t}{\tau}\right), \quad (2.33)$$

$$I_{\text{TRPL}} = A_{\text{fast}} \exp\left(-\frac{t}{\tau_{\text{fast}}}\right) + A_{\text{slow}} \exp\left(-\frac{t}{\tau_{\text{slow}}}\right), \quad (2.34)$$

respectively. Here, τ is the lifetime obtained by the single exponential fit, and τ_{fast} and τ_{slow} are the fast and slow lifetimes obtained by the double exponential fit, respectively. The A , A_{fast} , and A_{slow} are the coefficients for the respective lifetimes.

At first, we focus on the lifetimes of the c -plane and r -plane QWs for the simplicity. The carrier recombination lifetime τ in the c -plane QW estimated by the fitting is 277 ns, whereas the τ_{fast} and τ_{slow} for the r -plane QW are 3.50 and 24.0 ns, respectively. The internal electric fields should affect the optical transition in QWs with wider well widths more, causing longer radiative recombination lifetimes. In fact, τ_{fast} in the r -plane QW becomes longer for wider QWs, and the same trend is observed for c -plane QWs. These results indicate that τ_{fast} in the r -plane QW and τ in the c -plane QW are predominantly influenced by radiative recombination.

⁴Although nonpolar plane QW was not fabricated, the $E_{\text{int}}^{\text{well}}$ theoretically equals to zero. In addition, the actual miscut (5.8°) is considered for the plot of the (11 $\bar{2}2$) QW.

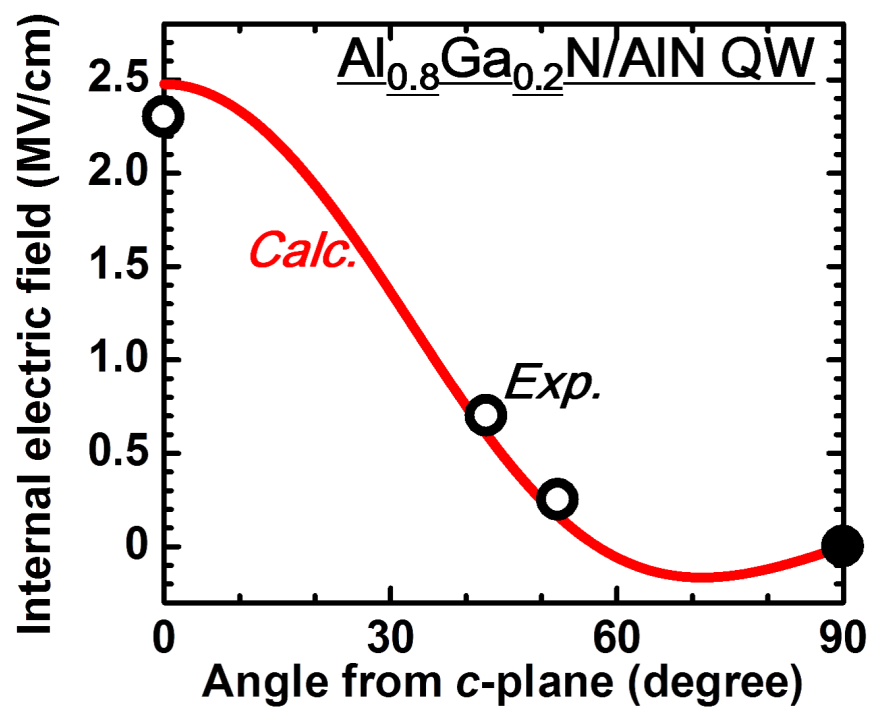


Figure 2.31: Off-angle dependence of internal electric fields in $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs. The experimentally determined $E_{\text{int}}^{\text{well}}$ for c -plane and semipolar plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs are plotted in the figure, and the calculated result is depicted as a solid line.

In the same way as the r -plane QW, we consider that the τ_{fast} in 15° off and $(11\bar{2}2)$ QWs are dominated by radiative recombination processes, and the estimated lifetimes are 6.85 and 0.54 ns, respectively. Therefore, these results clearly indicate that the radiative recombination lifetimes in the semipolar QWs are much shorter than that in the c -plane QW due to the small internal electric fields.

The square of the overlap integral between the electron and hole wave functions is proportional to the reciprocal of radiative recombination lifetime. That is, $\tau_{\text{rad}}^{-1} = F^2/A_i$, where F is the aforementioned overlap integral, and A_i is a constant. To strengthen our hypothesis that τ_{fast} and τ are predominantly affected by radiative recombination, we calculated the squares of overlap integrals for c -plane, r -plane, and $(11\bar{2}2)$ QWs using the internal electric fields of 0.30, 0.70, and 2.3 MV/cm, respectively. Figure 2.33 shows the calculated results as the broken lines. In addition, the reciprocals of τ_{fast} and τ in the $(11\bar{2}2)$, r -plane, and c -plane QWs multiplied by A_i are plotted, where $A_{(11\bar{2}2)}$, A_r , and A_c are 0.36, 0.88, and 3.4, respectively. The agreement in these results also support that τ_{fast} and τ are due to the radiative recombination. Although there is a slight difference (0.10 MV/cm) of the estimated internal electric fields in $(11\bar{2}2)$ QWs from Fig. 2.30, we think that it is within an error range of the estimation. Then, we estimated the internal electric field in $(11\bar{2}2)$ QWs to be averaged 0.25 MV/cm and the value was actually plotted in Fig. 2.31. Therefore, the radiative recombination lifetimes in the semipolar QWs are one hundred times shorter than that of the c -plane QW due to the small internal electric fields. The variation in A_i may be ascribed to the difference in the crystallographic angle dependent band structures.

2.7.3 Enhanced emission intensity in semipolar AlGa_N QWs

Figure 2.34 shows temperature dependence of the integrated PL intensity of c -plane, 15° off, r -plane, and $(11\bar{2}2)$ Al_{0.8}Ga_{0.2}N/AlN QWs with about 1.5-nm-thick wells under a weak excitation condition. The semipolar QW emissions were much stronger than the c -plane QW emissions throughout the entire temperature region. The intensity difference was more pronounced at higher temperatures, and the r -plane and $(11\bar{2}2)$ QW emissions were more than two orders of magnitude stronger than the c -plane QW emission at room temperature. The relatively weak emission intensity of the 15° off QW compared with those from the other semipolar-plane QWs is likely due to the smaller off-angle, which induces the slightly larger internal electric field and elongates τ_{fast} (see Figs. 2.31 and 2.32).

Although the IQE of all of the QWs seemed low, we confirmed that a similar weak excitation condition adopted in this study also remarkably degraded the IQE of QWs on c -plane sapphire substrates to $\sim 1\%$ or less. Hence, we experimentally demonstrated that the short radiative recombination lifetimes in semipolar QWs brought stronger emissions which should be a consequence of greatly improved IQE. However, the IQE is only $\sim 5\%$ at most under weak excitation conditions even for semipolar QWs. Thus, we should also investigate the suppression of nonradiative recombination processes for higher IQE, which

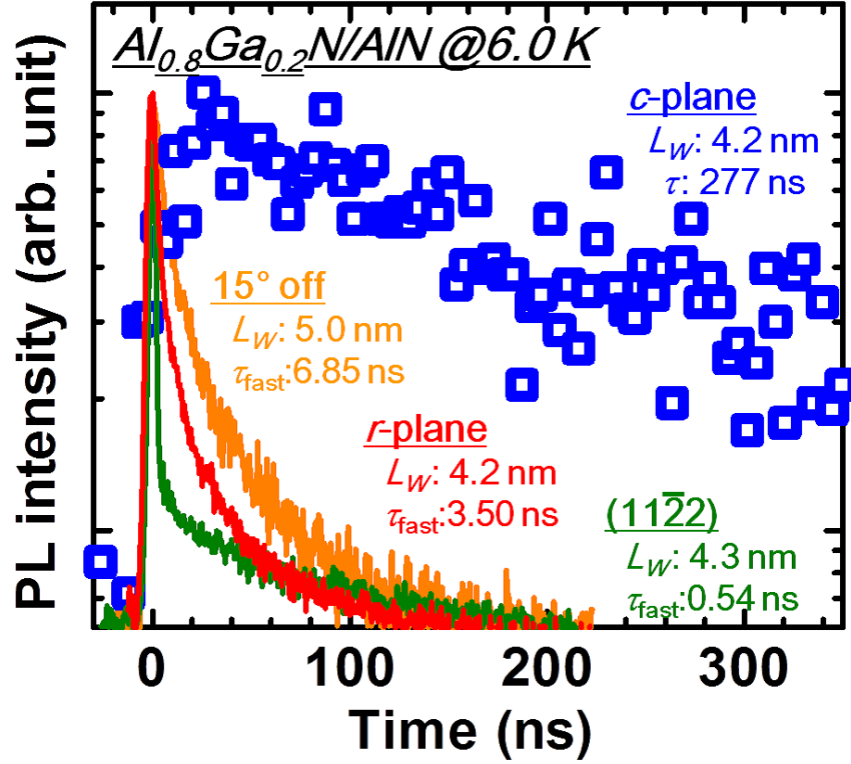


Figure 2.32: TRPL decays near the PL peak energy of *c*-plane, 15° off, *r*-plane, and (11̄2̄2) $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs with about 4.5-nm-thick wells at 6.0 K.

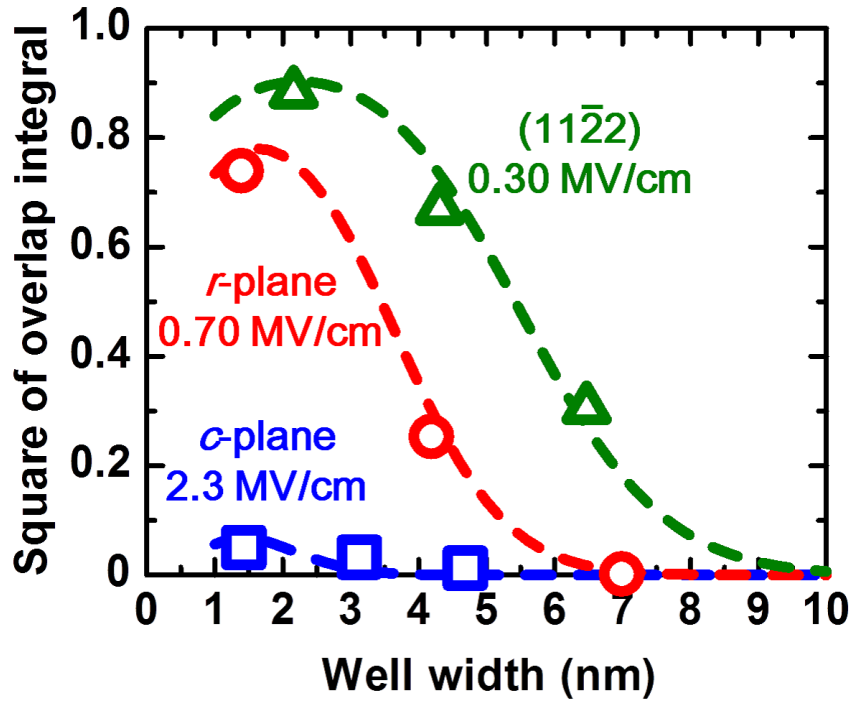


Figure 2.33: Broken lines indicate the calculated squares of the overlap integrals in (11̄2̄2), *r*-plane *c*-plane QWs using the internal electric fields of 0.30, 0.70, and 2.3 MV/cm. Reciprocals of τ_{fast} and τ in the (11̄2̄2), *r*-plane, and *c*-plane QWs multiplied by A_i are also plotted where $A_{(11̄2̄2)}$, A_r , and A_c are 0.36, 0.88, and 3.4, respectively.

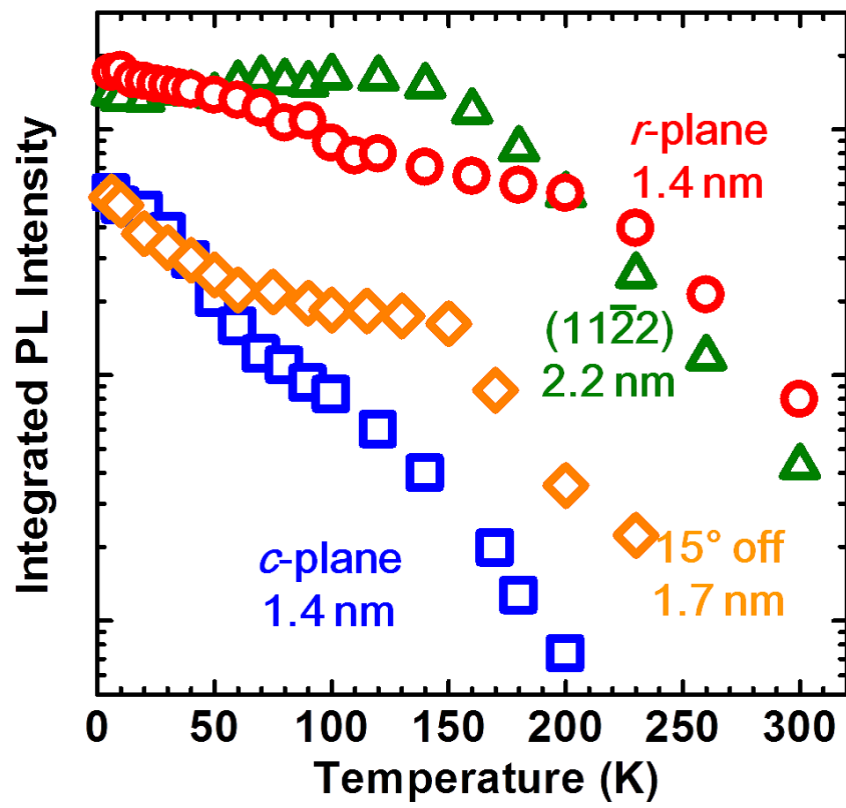


Figure 2.34: Temperature dependences of the integrated PL intensities of *c*-plane, 15° off, *r*-plane, and (11 $\bar{2}$ 2) Al_{0.8}Ga_{0.2}N/AlN QWs with about 1.5-nm-thick wells under a weak excitation condition.

will be discussed in Chap. 3.

2.7.4 Potential fluctuations

2.7.4.1 Macroscopic PL measurements

As we mentioned above, the semipolar plane AlGa_{0.8}N/AlN QWs have narrower emission line widths than the *c*-plane QWs (see Fig. 2.29). Figure 2.35, which shows the well-width dependence of the full-widths at half maximums (FWHMs) of the Al_{0.8}Ga_{0.2}N/AlN QW emissions at 6.5 K, quantitatively indicates that the FWHMs of the semipolar-plane QW emissions are narrower than those of the *c*-plane QW emissions throughout the entire well-width region. These differences are more pronounced for wider well widths. It is noteworthy that the FWHMs of the emissions from *c*-plane QWs on AlN substrates are approximately the same as those fabricated on sapphire substrates. The result indicates that the wide line widths of *c*-plane QW emissions may reflect the intrinsic properties.

To clarify the reason for the narrower line widths of semipolar AlGa_{0.8}N/AlN QWs, we subsequently discuss the correlation between internal electric fields and potential fluctuations. Multiple factors such as the well-width fluctuations, Al composition fluctuations, and the statistically unavoidable alloy disorder [36, 37] can induce the energy fluctuations of the QW emissions. Here, we concentrate on two major factors, which are the well width and Al composition fluctuations, and we discuss such fluctuations focusing on the comparison between *c*- and *r*-plane QWs for the simplicity.

Figure 2.36(b) shows the calculated well-width dependence of the energy fluctuations for Al_{0.8}Ga_{0.2}N/AlN QWs where the Al composition and well-width fluctuations are expressed as Δx_i and ΔL_i , respectively (i is *c* or *r* for *c*- or *r*-plane QWs, respectively). ΔL_i should be greater than ± 1 ML fluctuation in the QW structures because the crystal growth always proceeds with 2D or 3D islands (≥ 1 ML height) on top of the growth surface. Thus, we calculated the energy fluctuations assuming that ΔL_i is ± 1 ML and Δx_i is $\pm 1\%$. In Fig. 2.36(b), the broken, dashed-dotted, and solid lines denote the energy fluctuations due to the ΔL_i , Δx_i , and their total, respectively. In the calculations, the internal electric fields are the same as the experimentally estimated values in Fig. 2.30. The calculated total energy fluctuation of the *r*-plane QWs is much smaller than that of the *c*-plane QWs even though ΔL_i and Δx_i are the same, because both fluctuation components increase as the internal electric field increases.⁵ Consequently, semipolar QWs, which can suppress the internal electric field, realize much narrower emission line widths than *c*-plane QWs, in principle. In addition, because 1 MLs for *c*-plane and *r*-plane AlGa_{0.8}N (AlN) are about 0.25 and 0.18 nm, respectively, the well width fluctuations are also suppressed for the *r*-plane QWs.

The experimentally obtained FWHMs of *c*-plane and *r*-plane QW emissions are plotted in Fig. 2.36(a), and the solid lines in the figure are the same as the calculated solid

⁵To be exact, the energy fluctuation due to Δx_i is proportional to $\partial E_{\text{int}}^{\text{well}} / \partial x$, where x is Al composition.

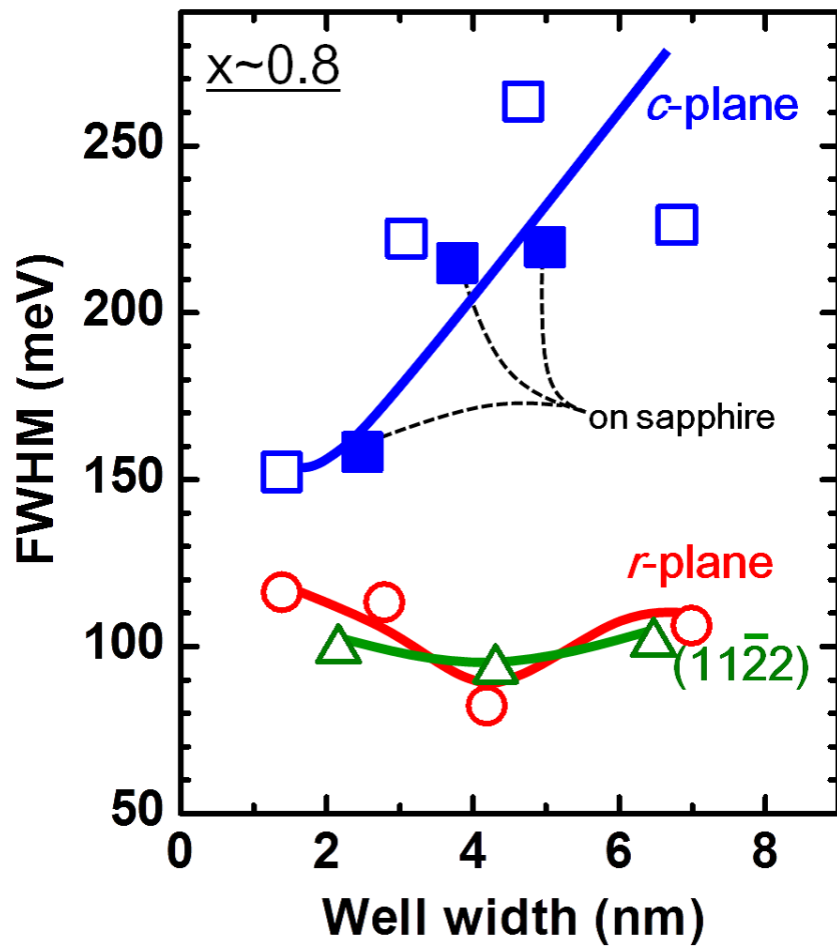


Figure 2.35: Well-width dependence of the FWHMs of the c -plane, r -plane, and $(11\bar{2}2)$ Al_{0.8}Ga_{0.2}N/AlN QW emissions at 6.5 K. The solid curves are to guide the eyes.

lines in Fig. 2.36(b). The magnitudes and the trends of the calculated total energy fluctuations almost completely agree with the experimental results. Because we consider only two representative factors as energy fluctuations here, we suppose that the Al composition fluctuations are at most $\pm 1\%$. It is noteworthy that InGaN QWs do not exhibit a specific correlation between energy fluctuations and internal electric fields [38], whereas AlGaN QWs do so similar to another material system [39].

2.7.4.2 Microscopic CL measurements

In addition to the macroscopic PL analyses, CL mapping measurements were performed to investigate microscopic fluctuations of transition energy and emission intensity. Figures 2.37(a) and (b) show the maps of the CL peak wavelength for a *c*-plane $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ QW on sapphire substrate (L_w : 2.5 nm) at 18 K taken from Ref. [30, 40] and an *r*-plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW (L_w : 1.4 nm) at 9 K, respectively. We calculated the potential fluctuations for the both QWs from the wavelength distributions in the CL maps. The fluctuations of the *c*-plane and *r*-plane QWs estimated from the spectral ranges in the CL maps are 135 and 65.4 meV, respectively. It clearly indicates that the energy fluctuation in the *r*-plane AlGaN QW is also remarkably suppressed due to the small internal electric field from the microscopic perspective. Note that the difference in the substrates (AlN or sapphire) seems not to affect the fluctuation, as suggested in Fig. 2.35.

Subsequently, we also investigated the fluctuations for the *r*-plane AlGaN QW at room temperature. Figure 2.38(a) and (b) show the maps of the peak wavelength and CL intensity for the *r*-plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW at 300 K. It was clarified that the *r*-plane AlGaN QW emission has extremely high homogeneities in terms of both intensity distribution and energy fluctuation. Figure 2.39 shows temperature dependences of the obtained energy fluctuations and CL intensity fluctuations for the *c*-plane $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N}/\text{AlN}$ and the *r*-plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs. Here, the CL intensity fluctuations are defined as the ratio of the maximum intensity to minimum intensity. The plots about the *c*-plane QW are recalculated from the CL mapping results in Ref. [30, 40], where the CL measurements were performed for a similar scale area. The emission-intensity fluctuations and the energy fluctuations in the *r*-plane QW are about half of those in the *c*-plane QW throughout the entire temperature region. These results are also derived from the small internal electric field. Therefore, in addition to the strong emission intensities, semipolar AlGaN QWs are quite attractive structures for DUV LDs than *c*-plane QWs because narrow emission line widths due to the well suppressed potential fluctuations are desirable for the low threshold current density of LDs.

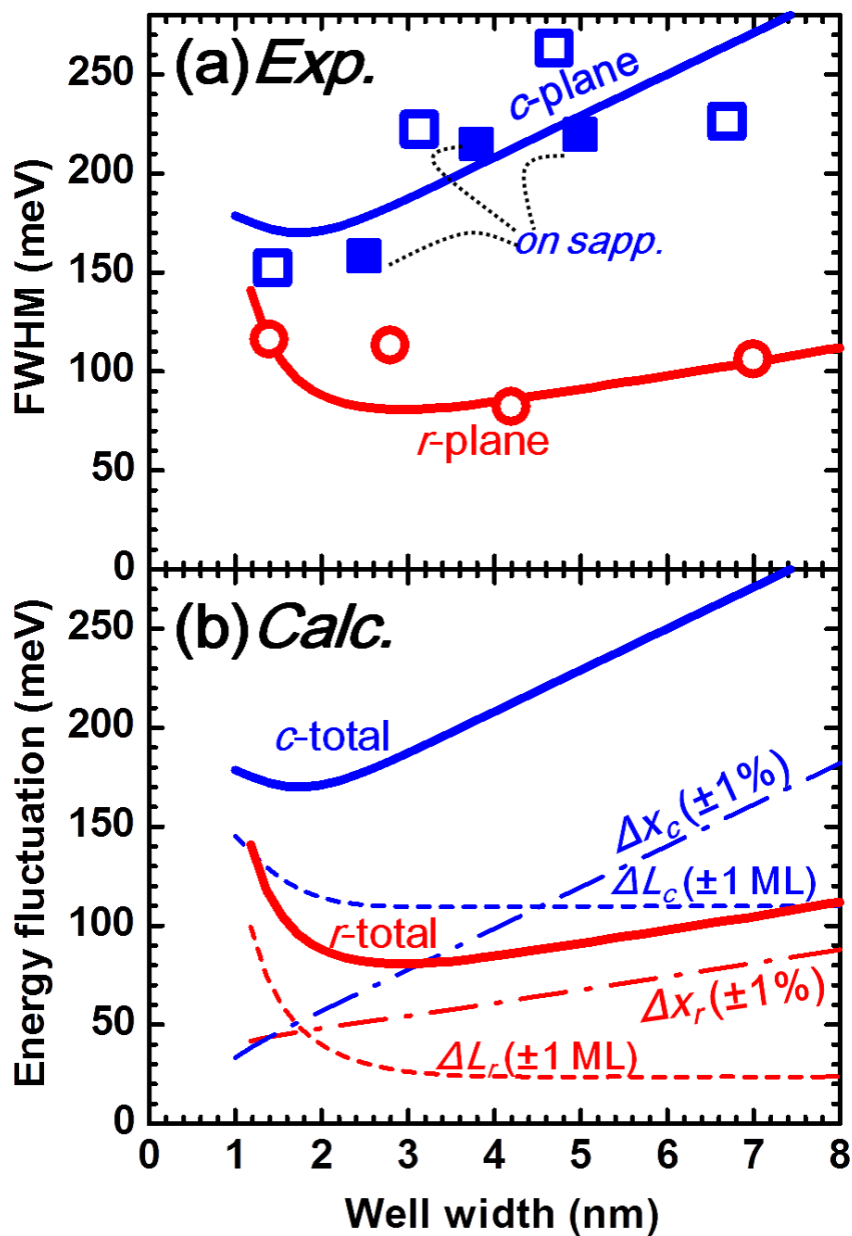


Figure 2.36: (a) Experimentally obtained FWHMs of *c*-plane and *r*-plane QW emissions are plotted, and solid lines correspond to the calculated solid lines in (b). (b) Calculated well-width dependence of the energy fluctuations for Al_{0.8}Ga_{0.2}N/AlN QWs. Broken, dashed-dotted, and solid lines denote energy fluctuations due to well-width fluctuations (± 1 ML), Al-composition fluctuations ($\pm 1\%$), and their total, respectively.

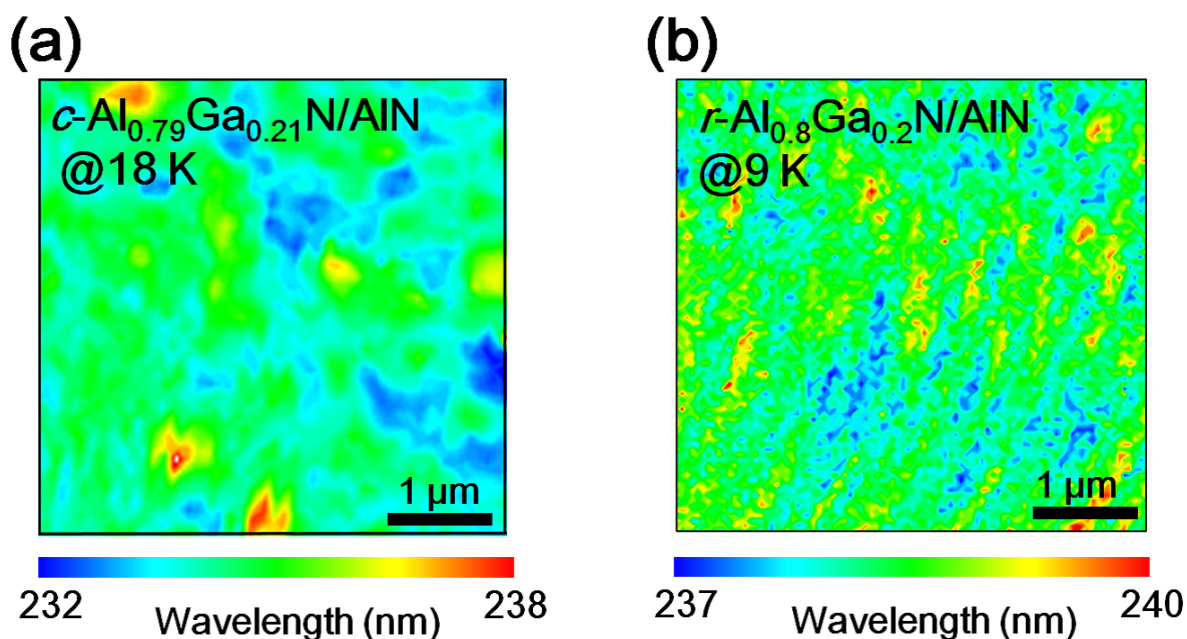


Figure 2.37: Maps of the CL peak wavelength for a c -plane $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N/AlN}$ QW on sapphire substrate (L_w : 2.5 nm) at 18 K taken from Ref. [30, 40] and an r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N/AlN}$ QW (L_w : 1.4 nm) at 9 K.

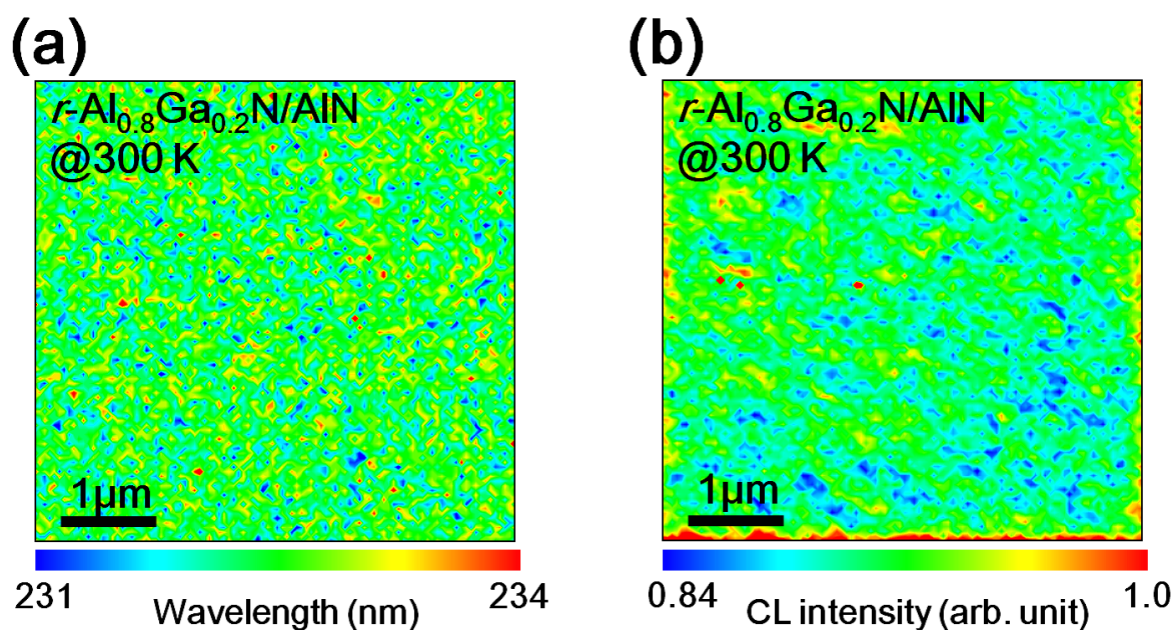


Figure 2.38: Maps of the (a) peak wavelength and (b) CL intensity for the r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N/AlN}$ QW at 300 K.

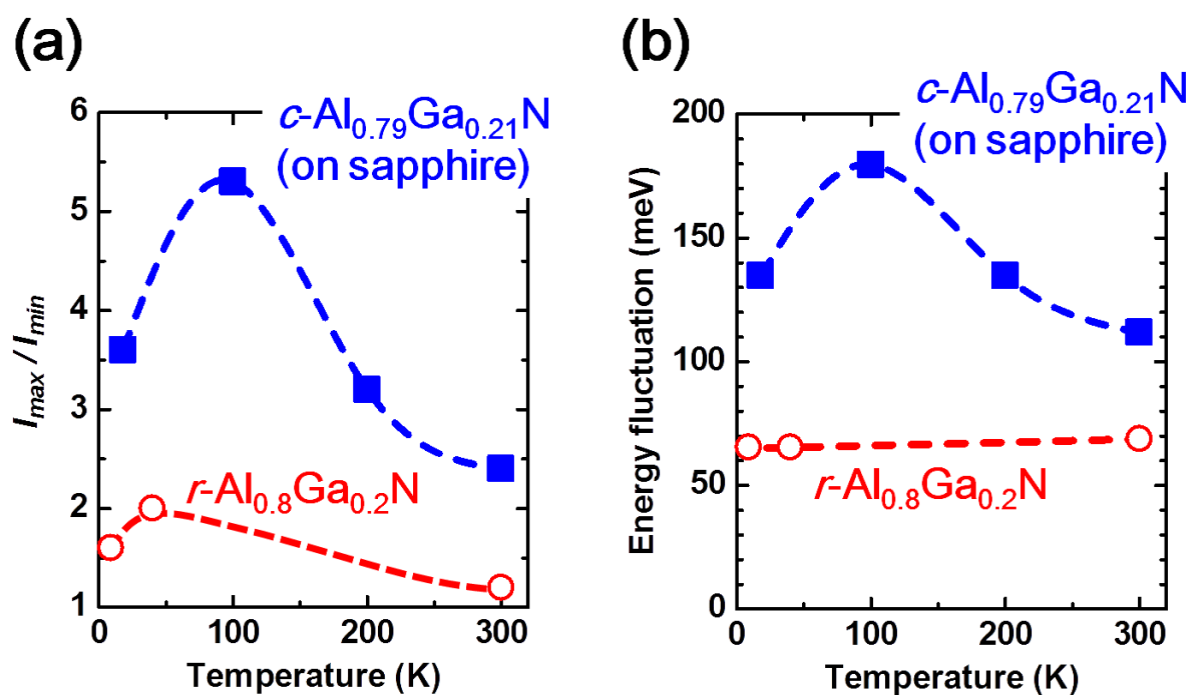


Figure 2.39: Temperature dependences of the obtained CL intensity fluctuations and energy fluctuations for the c -plane Al_{0.79}Ga_{0.21}N/AlN and the r -plane Al_{0.8}Ga_{0.2}N/AlN QWs. The plots about the c -plane QW are recalculated from the CL mapping results in Ref. [30, 40], where the CL measurements were performed for a similar scale area.

2.8 Summary

In this chapter, semipolar AlN homoepitaxial films and AlGa_N/AlN QWs were fabricated on 15° off, *r*-plane, (11 $\bar{2}$ 2) AlN substrates. For the growth of AlN on *c*-plane substrates, low pressure growth is generally preferred in order to decrease parasitic reactions between TMA and NH₃. On the other hand, for the homoepitaxy on semipolar AlN substrates, it was clarified that low pressure growth causes a lot of pits on the surfaces, whereas higher pressure growth drastically decreases the pit density without degrading the flatness. Then, to clarify the mechanism of pit-elimination, semipolar AlN homoepitaxy was demonstrated at various growth pressures in the range of 76 to 608 Torr. From the experiments, we found that higher pressure growth leads to a higher nucleation density and this is the reason why pit-elimination occurs in high pressure growth. Particularly, 500 Torr is the optimal reactor pressure for the elimination of pits, and high quality semipolar AlN homoepitaxial films with atomically smooth surfaces were obtained. The strong near band edge emissions with narrow line widths and the suppressed deep level emissions were confirmed from the semipolar AlN films. Moreover, it was clarified that high quality semipolar AlGa_N/AlN QWs with atomically smooth surfaces and abrupt interfaces were also obtained by 500 Torr growth.

The high quality semipolar AlGa_N/AlN QWs enable us to investigate their fundamental optical properties. From the well-width dependence of the PL peak energy, the internal electric fields are estimated for *c*-plane and semipolar-plane QWs. As a consequence, we experimentally confirmed that the internal electric fields in semipolar AlGa_N QWs with large off-angles are remarkably suppressed, and the estimated internal electric fields well agree with the calculation results.

Additionally, we investigated the impacts of internal electric fields on carrier recombination lifetimes and emission intensities. We clarified that the small internal electric fields in semipolar-plane QWs enhance the radiative recombination probabilities and realize much stronger emissions compared to the conventional *c*-plane QWs. Furthermore, it was clarified that the potential fluctuations in semipolar AlGa_N QWs are also suppressed by the small internal electric fields.

Therefore, we experimentally confirmed that the semipolar AlGa_N QWs have a lot of optical superiorities over the conventional *c*-plane QWs. However, the IQE of the semipolar QW remains only ~5% at most under a weak excitation condition. Thus, we have to investigate reduction methods of dominant nonradiative recombination centers in AlGa_N QWs in addition to the high radiative recombination probabilities in semipolar QWs.

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Chapter 3

Dominant nonradiative recombination centers in AlGaIn-related structures

3.1 Introduction

In spite of extensive studies on $\text{Al}_x\text{Ga}_{1-x}\text{N}$ -based LEDs [1–4], their EQE is considerably low ($\sim 10\%$) [5] in contrast to that of InGaIn-based blue LEDs ($> 80\%$) [6]. Particularly, the IQE of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs is remarkably degraded under weak excitation conditions [7] and in the short wavelength regions (Al-rich conditions) [8, 9]. To improve the IQE of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs, two different simple ideas are generally proposed. One is enhancement of radiative recombination probabilities, and the other is reduction of nonradiative recombination processes. We have already demonstrated a former solution via suppression of internal electric fields using semipolar-plane QWs, and achieved much stronger emissions compared with the conventional c -plane QWs, as described in Chap. 2. However, the IQE of the semipolar $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs remains only $\sim 5\%$ at most under a weak excitation condition. Thus, we have to clarify and reduce the dominant nonradiative recombination centers in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs in addition to the high radiative recombination probabilities in semipolar-plane QWs.

Current $\text{Al}_x\text{Ga}_{1-x}\text{N}$ crystals involve many lattice defects which generate deep levels in their bandgaps and act as nonradiative recombination centers. Furthermore, such deep levels may also degrade the CIE due to the enhancement of carrier recombination in the barrier layers. Although deep levels thus dominate the performances of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ -based devices, their natures such as activation energies, capture cross sections, and trap densities have yet to be comprehensively understood. For example, even defects which dominantly affect the efficiency degradation are unknown. Many efforts have been made to reduce threading dislocations (TDs) as representative lattice defects [10–13], and high quality homoepitaxial films or QWs have been recently grown on AlN bulk substrates with low TD density (TDD: $< 10^5 \text{ cm}^{-2}$) [14, 15]. In spite of such low TDDs, the IQE under weak excitation condition remains low ($< 1\%$), and it is almost the same as that of QWs on sapphire substrates with high TDDs ($\sim 10^9\text{--}10^{10} \text{ cm}^{-2}$). This indicates that TDs may not act as dominant

nonradiative recombination centers. In fact, S. F. Chichibu *et al.* have suggested the impacts of the point defects (PDs) in AlN [16, 17].

In this chapter, we clarify the correlations between nonradiative recombination lifetimes and the activation energies of various lattice defects. Furthermore, we discuss the temperature variations of the dominant nonradiative recombination paths in AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ structures and identify the lifetime-killing defect at each temperature.

3.2 Experimental procedures

AlN epitaxial films and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ /AlN QWs were grown on AlN bulk substrates using MOVPE method. The substrates were prepared by physical vapor transport method and have (0001) (*c*-plane) or semipolar ($1\bar{1}02$) (*r*-plane) surfaces. Both of the *c*-plane and *r*-plane surfaces used in this chapter were obtained by being sliced with different angles from bulk AlN ingots grown on *r*-plane. Thus, their crystalline qualities were nominally almost the same, and the TDD of the substrates observed by plan-view transmission electron microscopy was about $5 \times 10^7 - 1 \times 10^8 \text{ cm}^{-2}$. The surface treatments of the substrates prior to the epitaxy and the detail growth conditions were described in Chap. 2. One remarkable difference between the *c*-plane and *r*-plane growths was the optimized reactor pressure, which was higher for the *r*-plane growth (500 Torr) than for the *c*-plane growth (76 Torr). The thickness of *c*-plane (*r*-plane) AlN epitaxial film was about 1 μm (400 nm), and the well and the barrier layer thicknesses of the fabricated $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}$ /AlN 3QWs were about 1.5 nm and 15 nm, respectively. The AlN homoepitaxial films and the QWs had very high structural quality with atomically smooth surfaces and abrupt interfaces as described in Chap. 2.

Temperature dependent cathodoluminescence (CL) mapping was performed to characterize the carrier recombination processes in the AlN films and $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}$ /AlN QWs in the temperature range between 9 and 293 K. The acceleration voltage of an electron beam for scanning electron microscopy (SEM) and CL measurements was 5 kV, which enabled us to obtain CL signals only from the epilayers. To precisely estimate the emission intensity without influences of carbon deposition and charge-up due to the electron beam irradiation, temperature dependent photoluminescence (PL) measurements were also performed. The excitation light source was a pulsed ArF excimer laser (193 nm) with a repetition frequency of 25 Hz and a pulse duration of 4 ns. The time-averaged excitation power density ranged from 110 to 910 kW/cm².

3.3 Impact of TDs on efficiency degradation

3.3.1 CL mapping

Because a part of the excited carriers are captured by nonradiative recombination centers, we often observe the emission intensity reductions near extended defects such as TDs and stacking faults. This is the reason why extended defects are generally observed as dark spots or dark areas in CL (or PL) mapping images, and Fig. 3.1(a) illustrates such a situation. Assuming the isotropic carrier diffusion, the emission intensity $I(r)$ in the vicinity of a TD is written by

$$I(r) = I_0 - I_D \exp\left(-\frac{r}{L_{\text{eff}}}\right), \quad (3.1)$$

where r is the distance from a TD, I_0 and I_D are the emission intensity far from TDs and the intensity reduction just at TDs, respectively, and L_{eff} is carrier diffusion length. Then, we can define the contrast of a dark spot due to a TD as

$$C_{\text{max}} = \frac{I_D}{I_0}. \quad (3.2)$$

On the other hand, when PDs are more dominant nonradiative centers than TDs, even near the TDs, dark spots cannot be observed as shown in Fig. 3.1(b) because most excited carriers are captured by PDs, which are uniformly formed in crystals, before reducing TDs. Note that dark spots hardly appear even when radiative recombination is the most dominant recombination process because most excited carriers are radiatively recombined before reaching TDs in such a case. These considerations reveal that the impact of TDs strongly depends on other recombination paths, and the detailed characterization of the dark spots using CL mapping measurements is very useful to identify the dominant recombination path.

Figure 3.2 shows the CL mapping images of each sample and the SEM image of the r -plane AlN at 60 K (at the same place as the CL image of r -plane AlN at 60 K). All CL mapping measurements were performed at structurally featureless areas, of which Fig. 3.2(a) shows an example. In the CL maps, we can clearly observe the dark spots at low temperatures for the c - and r -plane AlN films, but the dark spot contrasts are drastically weakened at room temperatures. Because the densities of the dark spots are comparable to the TDDs in the AlN substrates confirmed by plan-view transmission electron microscopy, the dark spots are attributed to TDs. On the other hand, no dark spots are observed in the CL images of r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs in the entire temperature regions, and we confirmed that the same tendency also occurs in c -plane Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs (data not shown). These results indicate that temperatures and the sample structures change the dominant recombination paths.

To elucidate the carrier recombination processes in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ -related structures, the

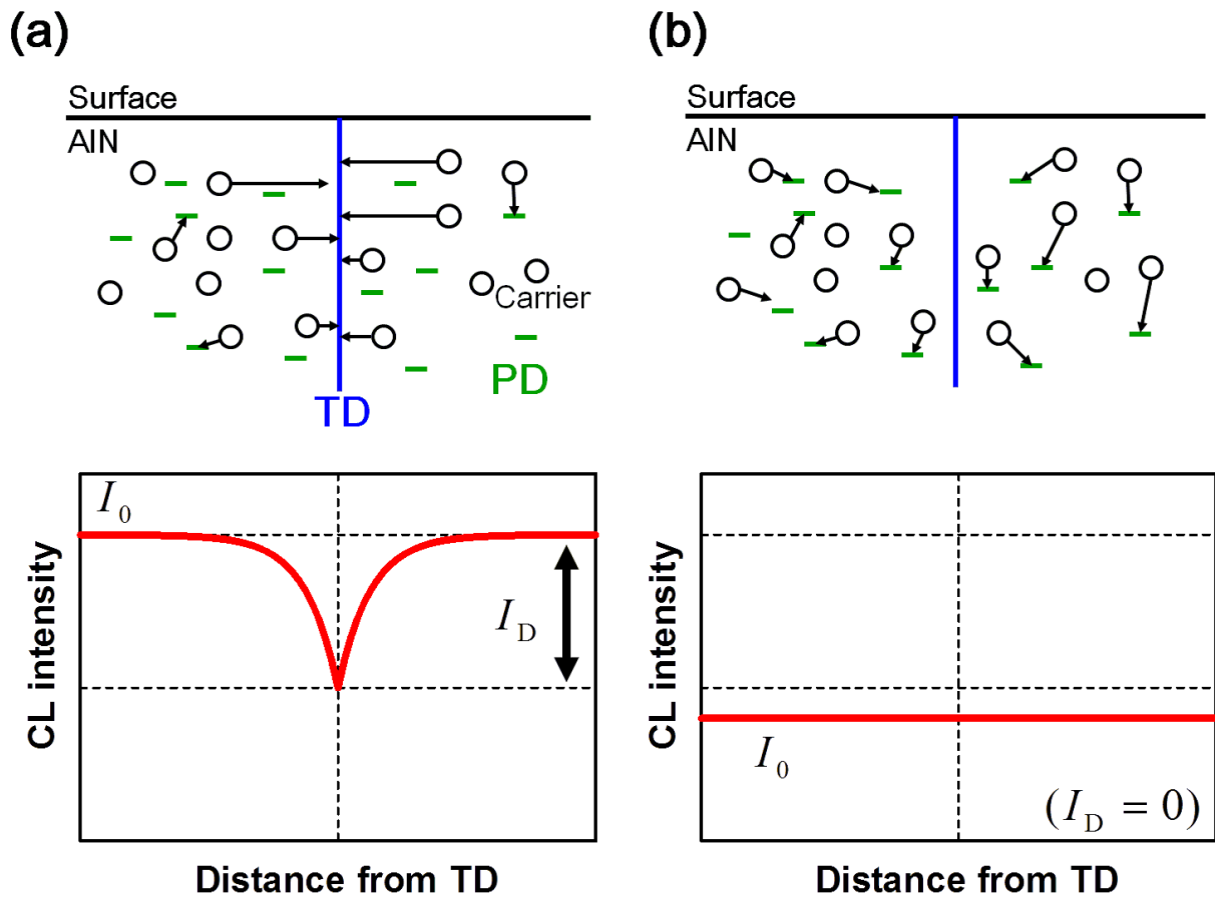


Figure 3.1: Schematic images of the carrier recombination processes and the resultant variation of the emission intensity near a TD in the cases that dominant recombination centers are (a) TDs and (b) PDs.

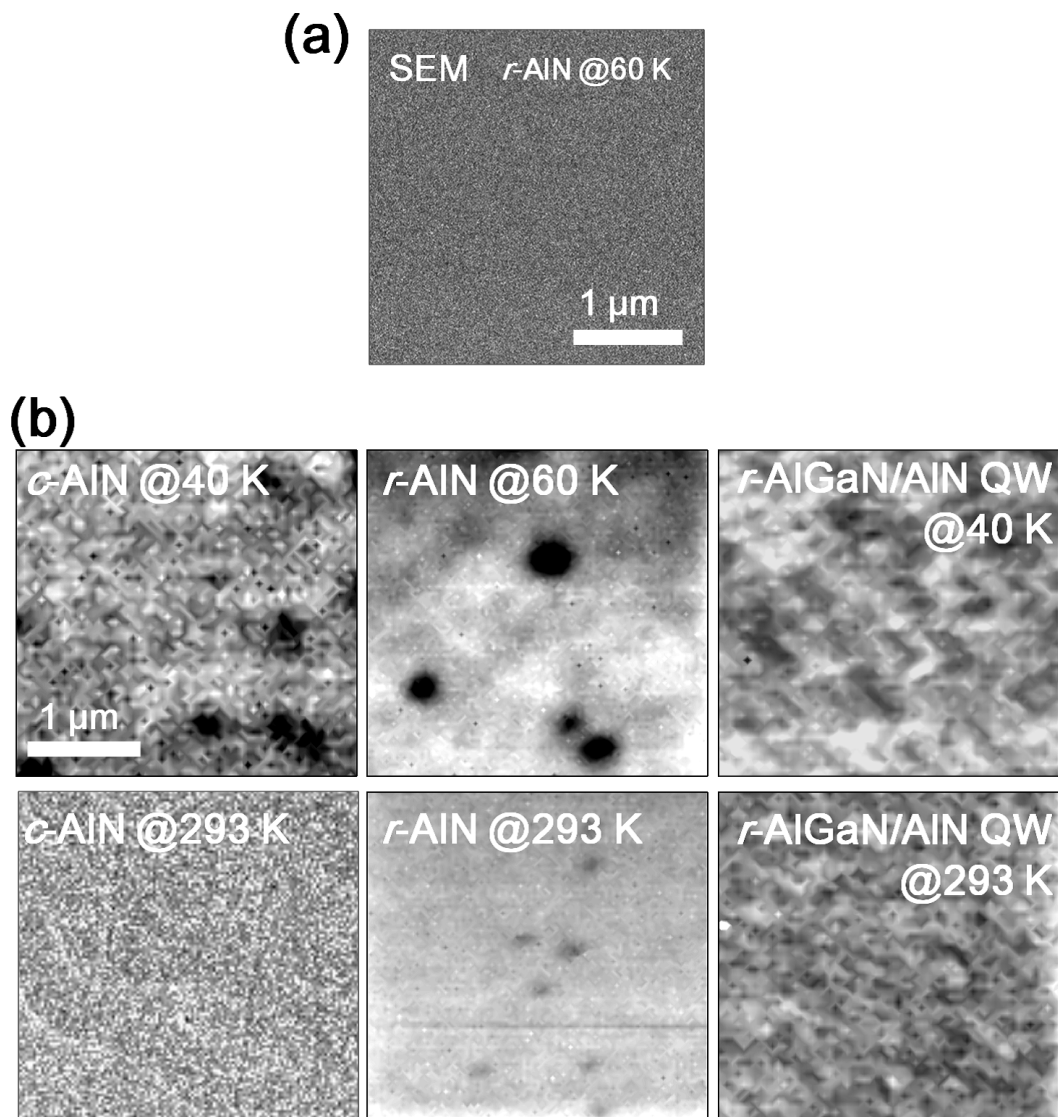


Figure 3.2: (a) SEM image of the r -plane AlN surface. (b) CL mapping images of AlN films and an r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW at low temperatures and room temperatures. Measured area is $3 \mu\text{m}^2$ for all the images. For the r -plane AlN, the SEM image and CL image at 60 K were taken at the same position.

contrast variations in the vicinity of the dark spots of the r -plane AlN were carefully analyzed at various temperatures as shown in Figs. 3.3(a) and (b). The line profiles of the CL intensity across the TDs were well fitted with Eq. (3.1), and Fig. 3.3(b) shows a representative example of the analyses for the r -plane AlN film. The experimental profiles quantifies the temperature dependence of the carrier diffusion lengths (L_{eff}) and the dark spot contrasts (C_{max}) as shown in Fig. 3.4 and Fig. 3.5, respectively. Note that the carrier diffusion lengths could not be determined for the c -plane AlN at high temperatures and for the QWs at any temperatures because dark spots were not observed in the CL mapping images.

3.3.2 Diffusion length, L_{eff}

At first, the carrier diffusion length L_{eff} is discussed. Figure 3.4 plots the determined L_{eff} in the c - and r -plane AlN films. The carrier diffusion lengths in the AlN epilayers have certain maximum values and are shortened by elevating temperature. The diffusion length L_{eff} can generally be written as

$$L_{\text{eff}} = \sqrt{D_{\text{diff}} \cdot \tau_{\text{eff}}} = \sqrt{\frac{\mu k_{\text{B}} T}{e} \cdot \tau_{\text{eff}}}, \quad (3.3)$$

where D_{diff} is diffusion coefficient, which can be rewritten by Einstein's relation using carrier mobility μ , Boltzmann constant k_{B} , temperature T , and elementary electric charge e . τ_{eff} is the effective carrier recombination lifetime in the areas far from TDs, and is defined as

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{p}}}, \quad (3.4)$$

where τ_{rad} is the radiative recombination lifetime and τ_{p} is the nonradiative recombination lifetime due to PDs.

Here, we describe the interpretation for the mobility and the carrier recombination lifetime of AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ in this study. Electrons and holes in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ -related structures are basically bound into pair states (excitons) even at room temperature due to the large binding energies. The diffusion coefficient of the excitons may be limited by holes which are much heavier than electrons. In addition, nonradiative recombination lifetimes of excitons should be determined by those of minority carriers because nonradiative recombination centers are occupied with majority carriers in many cases. In this study, we consider that the diffusion coefficients and the nonradiative recombination lifetimes in our un-doped, n^- -type $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples are mainly determined by holes' characteristics.

It has been reported that the hole mobility in AlN is proportional to $T^{-1.5}$ in the high temperature region due to the phonon scattering [18]. Therefore, $\sqrt{D_{\text{diff}}} \propto T^{-0.25}$ is predicted from the Einstein's relation. Experimentally, on the other hand, because the temperature induced decreases of L_{eff} in the r -plane and c -plane AlN films (Fig. 3.4) are well reproduced with $T^{-0.65}$ and $T^{-1.7}$, respectively, they are likely dominated not by μ (D_{diff})

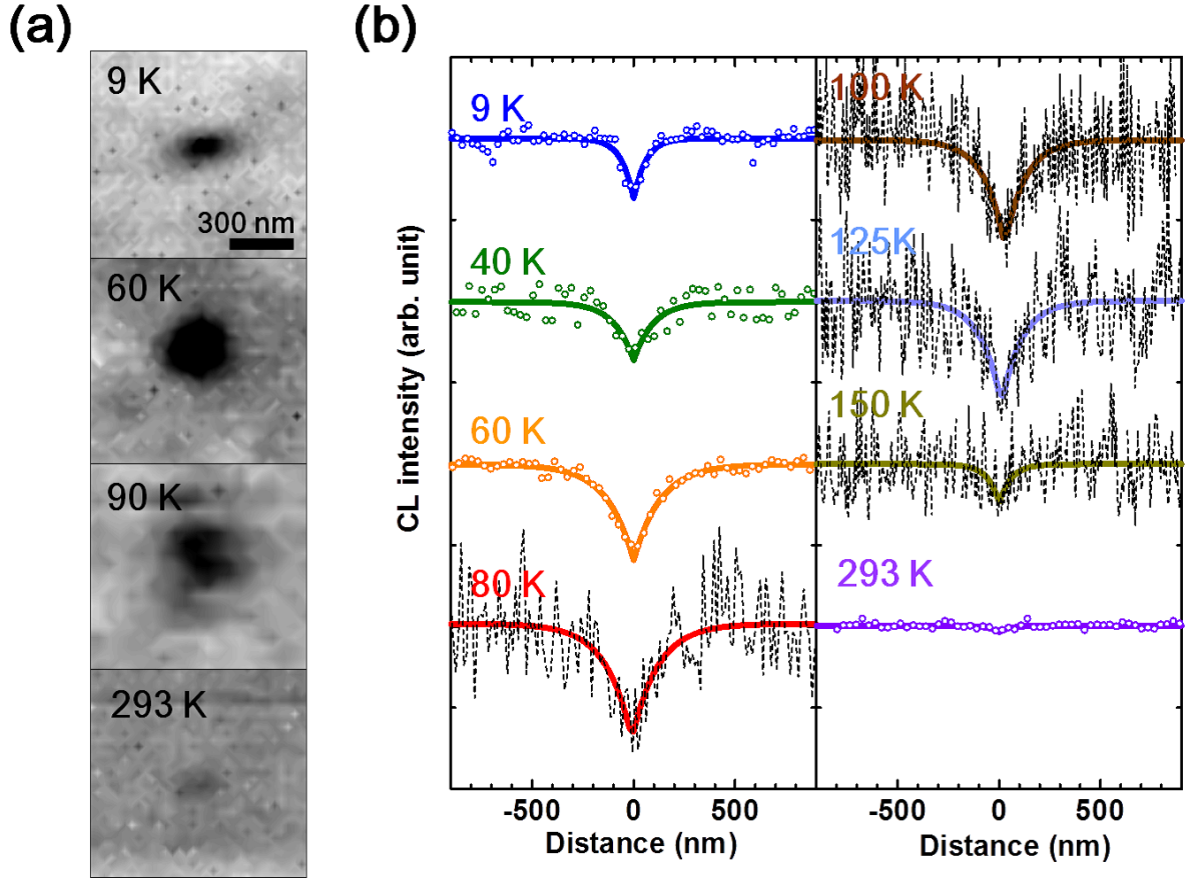


Figure 3.3: (a) Temperature dependence of the dark spot contrasts in the vicinity of TDs of the r -plane AlN. (b) Symbols and dotted lines are the experimental CL intensity profiles across TDs in the r -plane AlN at various temperatures. (The manners of data plots were appropriately selected to clearly show the tendency of the contrast variation.) Solid lines show results of fitting with Eq. (3.1).

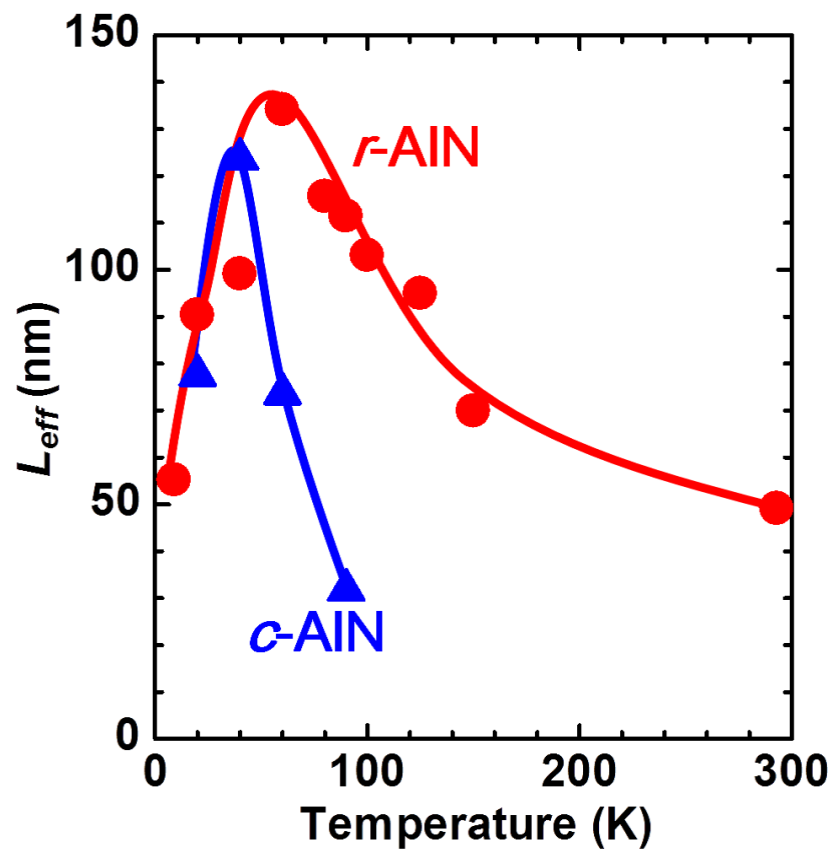


Figure 3.4: Temperature dependences of the carrier diffusion lengths in the *c*-plane and *r*-plane AlN films. The solid curves are to guide the eyes.

but by τ_{eff} . In other words, τ_{eff} should decrease with increasing of temperature. This finding along with Eq. (3.3) tells us that τ_p dominates the L_{eff} shortenings at higher temperatures because τ_{rad} in films are theoretically proportional to $T^{+1.5}$. The shorter L_{eff} in the c -plane AlN indicates that the c -plane AlN film has more PDs (shorter τ_p) than the r -plane AlN film. The different density of PDs may be caused by the different growth conditions, and the detailed reason will be discussed in Sec. 3.6.

3.3.3 Dark spot contrast, C_{max}

Secondly, we discuss the contrast C_{max} of dark spots. Figure 3.5 shows the temperature dependence of the dark spot contrasts in the AlN films and the r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs. For the AlN films, the dark spots were clearly observed at low temperatures (9–60 K), but their contrasts were drastically decreased (or eliminated) with an increase of temperature as shown in Fig. 3.3. Therefore, temperature dependences of C_{max} also have the maxima like L_{eff} as shown in Fig. 3.5. This result indicates that the impacts of PDs get larger with elevating temperatures in such a way that the change from Fig. 3.1(a) to Fig. 3.1(b) shows. On the other hand, we cannot observe any dark spots in the CL image of the c - and r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs in the whole temperature regions. The tendencies of the contrasts in films and QWs will be discussed in detail in Sec. 3.5, which suggests that the emission intensities from QWs are less affected by TDs than those of AlN films.

3.3.4 Macroscopic impacts of nonradiative recombination centers on efficiency degradation

The temperature dependences of L_{eff} and C_{max} enable us to estimate the efficiency degradation by TDs at various temperatures. The total intensity loss caused by one TD can be written as

$$\begin{aligned} i_{\text{Dtotal}} &= \int_0^\infty \int_0^{2\pi} \left[I_{\text{D}} \exp\left(-\frac{r}{L}\right) \right] r d\theta dr \\ &= 2\pi L^2 I_{\text{D}}, \end{aligned} \quad (3.5)$$

where L is the carrier diffusion length considering the macroscopic impacts of TDs and PDs as described below. (When the dark spots are well isolated each other and TDs do not affect the carrier diffusion length, L equals to L_{eff} .) L is expressed by

$$L^2 = D_{\text{diff}} \cdot \tau_{\text{totalarea}}, \quad (3.6)$$

where $\tau_{\text{totalarea}}$ is the macroscopic recombination lifetime determined by

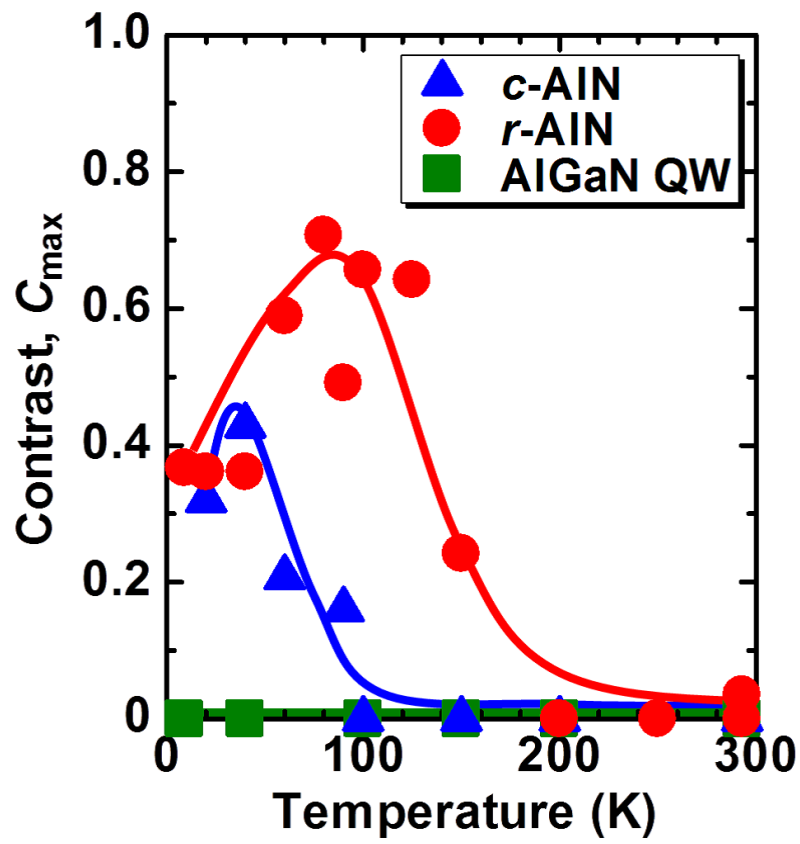


Figure 3.5: Temperature dependences of the dark spot contrasts in the AlN films and the r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW. The solid curves are to guide the eyes.

$$\begin{aligned}
\frac{1}{\tau_{\text{total_area}}} &= \frac{1}{\tau_{\text{dis_area}}} + \frac{1}{\tau_{\text{eff}}} \\
&= \frac{1}{\tau_{\text{dis_area}}} + \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{p}}}.
\end{aligned} \tag{3.7}$$

Here, $\tau_{\text{dis_area}}$ means the macroscopically averaged nonradiative recombination lifetime due to TDs. Moreover, the correlation between IQE (η_{IQE}) and $\tau_{\text{total_area}}$ is described by

$$\begin{aligned}
\eta_{\text{IQE}} &= \frac{\tau_{\text{rad}}^{-1}}{\tau_{\text{dis_area}}^{-1} + \tau_{\text{eff}}^{-1}} \\
&= \frac{\tau_{\text{total_area}}}{\tau_{\text{rad}}}.
\end{aligned} \tag{3.8}$$

Equations (3.6) and (3.8) lead to $L^2 \propto \tau_{\text{total_area}} \propto \eta_{\text{IQE}}$, and we can rewrite L^2 as

$$L^2 = A \cdot \eta_{\text{IQE}}, \tag{3.9}$$

where A is a proportionality coefficient.

In areas thoroughly away from the dark spots due to TDs, the effective efficiency η_{eff} can be written by

$$\eta_{\text{eff}} = \frac{\tau_{\text{rad}}^{-1}}{\tau_{\text{rad}}^{-1} + \tau_{\text{p}}^{-1}} = \frac{\tau_{\text{eff}}}{\tau_{\text{rad}}}. \tag{3.10}$$

When TDs barely impact on the macroscopic emission efficiency and carrier diffusion length, η_{IQE} and L equal to η_{eff} and L_{eff} , respectively. Therefore, A can be written as $L_{\text{eff}}^2/\eta_{\text{eff}}$, and we obtain

$$L^2 = \frac{L_{\text{eff}}^2}{\eta_{\text{eff}}} \cdot \eta_{\text{IQE}}. \tag{3.11}$$

With a definition I_{max} as the emission intensity for 100% IQE, I_0 and I_{D} are written as

$$I_0 = \eta_{\text{eff}} \cdot I_{\text{max}}, \tag{3.12}$$

and

$$\begin{aligned}
I_{\text{D}} &= I_0 C_{\text{max}} \\
&= \eta_{\text{eff}} \cdot I_{\text{max}} C_{\text{max}},
\end{aligned} \tag{3.13}$$

respectively. Note that I_0 , I_{D} , and I_{max} are the emission intensities per unit area. Moreover,

we can describe the IQE using Eqs. (3.5), (3.12), and (3.13) as

$$\begin{aligned}\eta_{\text{IQE}} &= \frac{I_0 \cdot S - i_{\text{Dtotal}}(T_{\text{D}} \cdot S)}{I_{\text{max}} \cdot S} \\ &= \eta_{\text{eff}} \cdot (1 - 2\pi L^2 C_{\text{max}} T_{\text{D}}),\end{aligned}\tag{3.14}$$

where T_{D} is TDD and S is the area of the measured region. Here, η_{IQE} is rewritten as

$$\eta_{\text{IQE}} = \eta_{\text{eff}} \cdot \eta_{\text{TD}},\tag{3.15}$$

where η_{TD} is the efficiency with respect to η_{eff} and represents the impacts of TDs. ($\eta_{\text{TD}} = 100\%$ means that IQE is completely determined by PDs.) Then, from Eqs. (3.11), (3.14), and (3.15), we have

$$\begin{aligned}\eta_{\text{TD}} &= 1 - 2\pi L^2 C_{\text{max}} T_{\text{D}} \\ &= \frac{1}{1 + 2\pi L_{\text{eff}}^2 C_{\text{max}} T_{\text{D}}}.\end{aligned}\tag{3.16}$$

Using the experimentally determined L_{eff} (Fig. 3.4) and C_{max} (Fig. 3.5), η_{TD} values for the r -plane AlN film at certain temperatures were calculated as functions of T_{D} , and the results are shown in Fig. 3.6. Temperatures strongly affect the impacts of TDs.

To more quantitatively characterize the emission efficiency degradations due to TDs, we defined $\text{TDD}_{\text{threshold}}$ as the lowest limit of TDD which degrades emission efficiency, as shown in Fig. 3.6. Figure 3.7 indicates the estimated $\text{TDD}_{\text{threshold}}$ for the r - and c -plane AlN as functions of temperature. The IQE of the r -plane AlN film at room temperature is dominated by PDs when $\text{TDD} < 2.6 \times 10^{10} \text{ cm}^{-2}$. Because the c -plane AlN film has more PDs and $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs are less affected by TDs as described above, $\text{TDD}_{\text{threshold}}$ are higher than those for the r -plane AlN film. Therefore, from the macroscopic point of view, TDs scarcely act as major nonradiative recombination centers at room temperature as long as TDD is less than $2.6 \times 10^{10} \text{ cm}^{-2}$ even if AlN epitaxial films or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs are heteroepitaxially grown. In fact, heteroepitaxial AlN films on sapphire substrates with $\text{TDD} < 5 \times 10^9 \text{ cm}^{-2}$ have recently been reported [19–21]. Considering the reported TDDs of AlN films, the results clearly indicate that the most effective method to improve the IQE in current Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ -related structures is not a reduction of TDs but that of PDs.

It is noteworthy that the dark spots due to TDs are observed in the c - and r -plane AlN films at low temperatures though TDDs are less than $\text{TDD}_{\text{threshold}}$ at any temperatures as shown in Fig. 3.7. This means that although TDs can act nonradiative recombination centers, the influence is microscopically limited in the vicinity of TDs, and the macroscopic efficiency is predominantly determined by PDs over the entire temperature range.

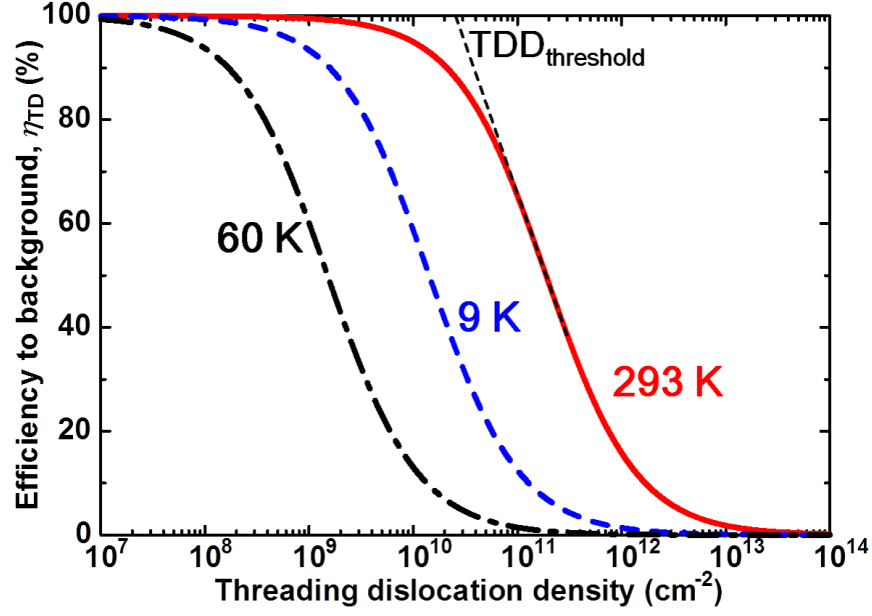


Figure 3.6: Efficiency degradation due to TDs (η_{TD}) in the r -plane AlN film. Broken, dash-dotted, and solid lines are the calculated results for 9, 60, and 293 K, respectively.

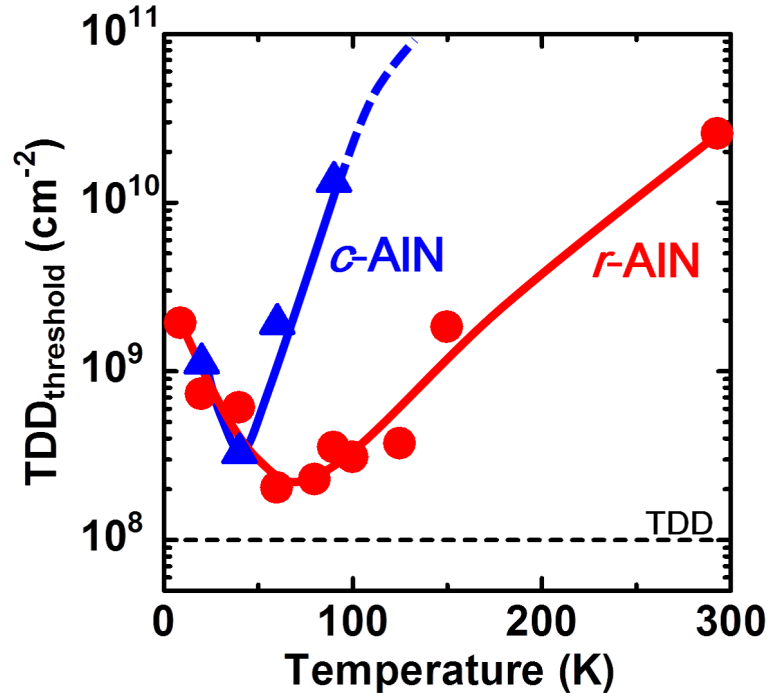


Figure 3.7: Threshold TDDs defined as the lowest limits which degrade the IQE in the c -plane and r -plane AlN films.

As described above, $\text{TDD}_{\text{threshold}}$ is an index of the impact of TDs on efficiency degradation. However, it strongly depends on many factors such as temperature, point defect density, sample structure, and alloy composition, because they affect the carrier diffusion length (L_{eff}). To more simplify and generalize the discussion, the correlation between L_{eff} and $\text{TDD}_{\text{threshold}}$ is calculated using Eq. (3.16). The effects due to the aforementioned many factors are all included in L_{eff} . Figure 3.8 shows the $\text{TDD}_{\text{threshold}}$ as a function of L_{eff} using C_{max} as a parameter. Here, the larger C_{max} cause greater impacts of TDs on efficiency degradation [Eq. (3.16)], and lead to lower $\text{TDD}_{\text{threshold}}$. The calculated $\text{TDD}_{\text{threshold}}$ with $C_{\text{max}} = 1.0$ indicates the theoretical lowest limit of TDD which affects the IQE, regardless of materials and structures. Therefore, PDs are absolutely dominant nonradiative recombination centers in the shaded region of Fig. 3.8.

The reported hole diffusion lengths of GaN and Ga-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films are several hundred nanometers [22–24], and they seem to be approaching the intrinsic material properties. If the hole diffusion lengths of un-doped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ related structures are also limited within $\sim 1 \mu\text{m}$ due to the intrinsic characteristics (radiative recombination processes), the reduction of TDDs less than 10^6 cm^{-2} does not improve the IQE, regardless of the PD density.

3.4 PL studies for determining the activation energies of PDs

3.4.1 Near band edge emission

Here, to clarify the correlation between the near band edge emission (NBE) intensity and the carrier recombination lifetimes, we consider a rate equation for excited carriers (excitons). The rate equation is generally expressed as

$$\frac{d\Delta p}{dt} = g - \frac{\Delta p}{\tau_{\text{totalarea}}}, \quad (3.17)$$

where Δp and g are the excess carrier density and the carrier generation rate, respectively. The left side of Eq. (3.17) equals to zero under the equilibrium conditions, and we obtain

$$\begin{aligned} \frac{\Delta p}{\tau_{\text{rad}}} &= \frac{\tau_{\text{totalarea}}}{\tau_{\text{rad}}} \cdot g \\ &= \eta_{\text{IQE}} \cdot g. \end{aligned} \quad (3.18)$$

Meanwhile, because $\Delta p/\tau_{\text{rad}}$ is proportional to the NBE emission intensity $I_{\text{NBE}}(T)$, it is written by

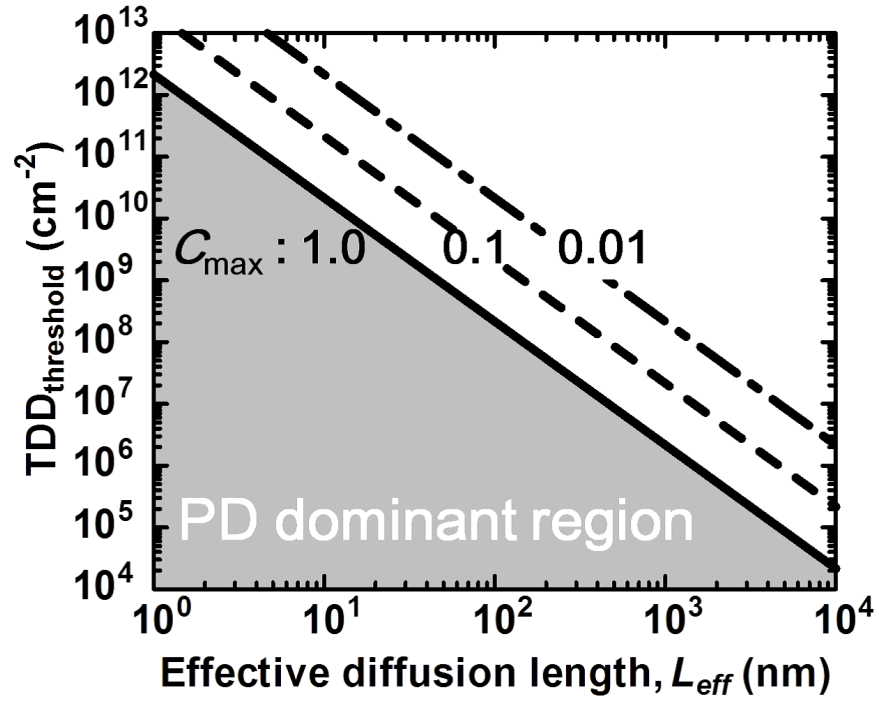


Figure 3.8: Correlation between the carrier diffusion length and $TDD_{threshold}$. The solid line is the theoretical lowest limit of TDD which affects the IQE, regardless of materials and structures.

$$I_{\text{NBE}}(T) = \eta_{\text{IQE}} \cdot I_{\text{max}} S. \quad (3.19)$$

where S is the measured area used in Eq. (3.14). When TDs are absent, η_{IQE} equals to η_{eff} , and Eq. (3.12) is derived from Eq. (3.19).

In this study, we consider that the nonradiative recombination centers trap carriers through the multiphonon emissions (MPEs).

In the MPE processes, nonradiative recombination paths are explained by configuration coordinate diagrams [25], and the capture cross section of each defect is written by

$$\sigma_i(T) = \sigma_{0i} \exp\left(-\frac{E_{ai}}{k_{\text{B}}T}\right), \quad (3.20)$$

where σ_{0i} is capture cross section at $T \rightarrow \infty$ and E_{ai} is the activation energy as shown in Fig. 3.9 (i is d or p for TDs or PDs, respectively). Then, the nonradiative recombination lifetime due to each defect can be described as

$$\begin{aligned} \tau_{\text{nonrad}} &= \frac{1}{v_{\text{th}} N_{ti} \sigma_i(T)} \\ &= \frac{1}{\sqrt{\frac{3k_{\text{B}}T}{m^*}} N_{ti} \sigma_{0i} \exp\left(-\frac{E_{ai}}{k_{\text{B}}T}\right)}, \end{aligned} \quad (3.21)$$

where m^* is the effective mass of carriers, v_{th} is thermal velocity of carriers ($= \sqrt{3k_{\text{B}}T/m^*}$), and N_{ti} is the trap density of each defect. Moreover, the radiative recombination lifetime is expressed by

$$\tau_{\text{rad}} = \alpha T^\gamma, \quad (3.22)$$

where α and γ is constant depending on the dimension of carrier confinement ($\gamma = 3/2$ or 1 for bulk or QW, respectively) [26, 27]. From Eqs. (3.12), (3.21), and (3.22), temperature dependence of I_0 can be written as

$$\begin{aligned} I_0(T) &= \eta_{\text{eff}} \cdot I_{\text{max}} \\ &= \frac{\tau_{\text{rad}}^{-1}}{\tau_{\text{rad}}^{-1} + \tau_{\text{p}}^{-1}} \cdot I_{\text{max}} \\ &= \frac{I_{\text{max}}}{1 + \alpha T^\gamma \sqrt{\frac{3k_{\text{B}}T}{m^*}} \sum_{s=1}^n N_{tps} \sigma_{0ps} \exp\left(-\frac{E_{aps}}{k_{\text{B}}T}\right)}. \end{aligned} \quad (3.23)$$

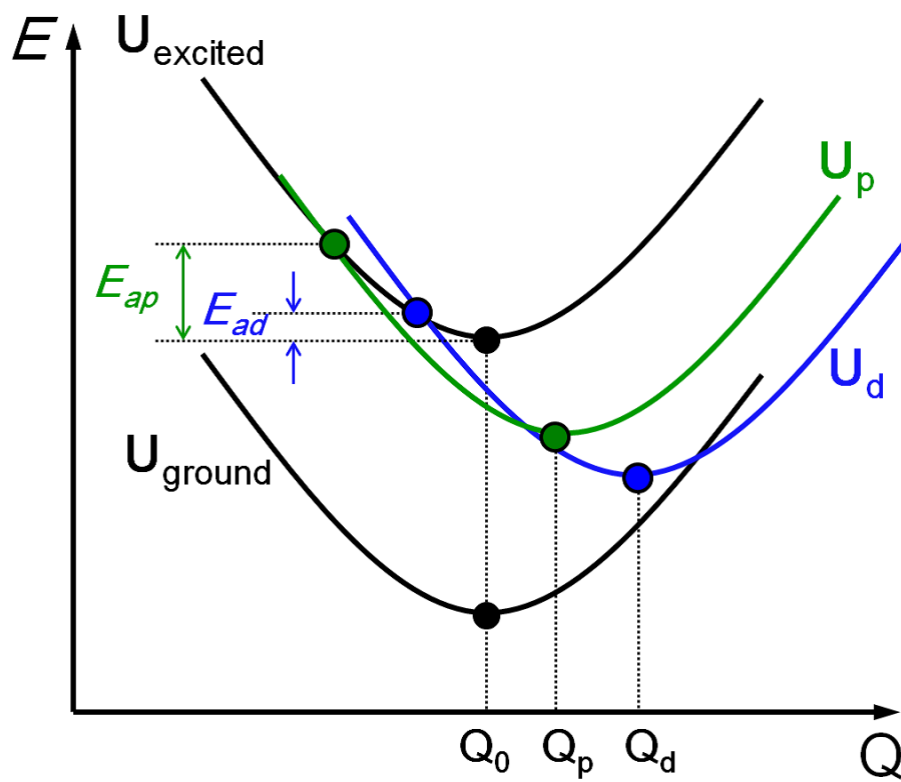


Figure 3.9: Configuration coordinate diagram of MPE process assuming TDs and PDs as different nonradiative recombination paths.

Here, to reproduce the experimental results show below, multiple types of PDs are assumed (the number of the types is n), and TDs are neglected due to the following reason. As shown in Fig. 3.7, from the macroscopic point of view, TDDs in our samples are low enough to hardly affect the emission efficiency degradation in the whole temperature regions. Therefore, thermal quenching in our samples observed by the macroscopic measurements is ascribed to only PDs, and we can express the emission intensity $I_{\text{NBE}}(T) \approx I_0(T)S$.

We perform macroscopic PL measurement for the r -plane AlN homoepitaxial film. The PL spectra at low temperature and room temperature are shown in Fig. 3.10. In addition to the NBE emissions, deep level emissions are observed. The peak intensity (and the integrated intensity) of the NBE emission is much stronger than those of the deep level emissions at any temperatures.

The temperature dependences of the integrated PL intensities of NBE emissions under various excitation powers are plotted in Fig. 3.11. Under any excitation conditions, two different types of thermal quenching are observed at 10–200 K and 200–300 K. The two step thermal quenching is also observed in the c -plane AlN film. These results indicate that two types of PDs with different activation energies E_{ap1} and E_{ap2} dominantly act as nonradiative recombination centers in Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ related structures. Then, assuming $n = 2$ in Eq. (3.23), $I_{\text{NBE}}(T)$ is expressed as

$$I_{\text{NBE}}(T) = \frac{I_{\text{max}}S}{1 + \alpha T^\gamma \sqrt{\frac{3k_{\text{B}}T}{m^*}} \left[N_{tp1}\sigma_{0p1} \exp\left(-\frac{E_{ap1}}{k_{\text{B}}T}\right) + N_{tp2}\sigma_{0p2} \exp\left(-\frac{E_{ap2}}{k_{\text{B}}T}\right) \right]} \quad (3.24)$$

$$\approx \frac{I_{\text{max}}S}{1 + a \exp\left(-\frac{E_{ap1}}{k_{\text{B}}T}\right) + b \exp\left(-\frac{E_{ap2}}{k_{\text{B}}T}\right)}, \quad (3.25)$$

where a and b are approximated to be constants. Although Eq. (3.24) is more strict, Eq. (3.25) is often used for estimation of activation energies because the exponential term varies more significantly than the $T^{\gamma+\frac{1}{2}}$ term due to temperature. The PDs which cause the first (at 10–200 K) and the second (at 200–300 K) thermal quenching are referred to P1 and P2, respectively. The thermal quenching due to those PDs is well fitted by Eq. (3.25) and the fitting results are shown as solid lines in Fig. 3.11. The estimated activation energies of P1 and P2 are $E_{ap1} \sim 10$ meV and $E_{ap2} \sim 130$ meV, regardless of the excitation powers. However, the stronger excitation conditions lead to weaker thermal quenching, which is due to the occupation of P1 and P2 by photo-excited carriers [7]. Note that both of the estimated activation energies are considerably different from the exciton binding energy of AlN (53.7 meV) [28]. This result indicates that the thermal quenching is mainly caused not by exciton ionization but by PDs' activations.

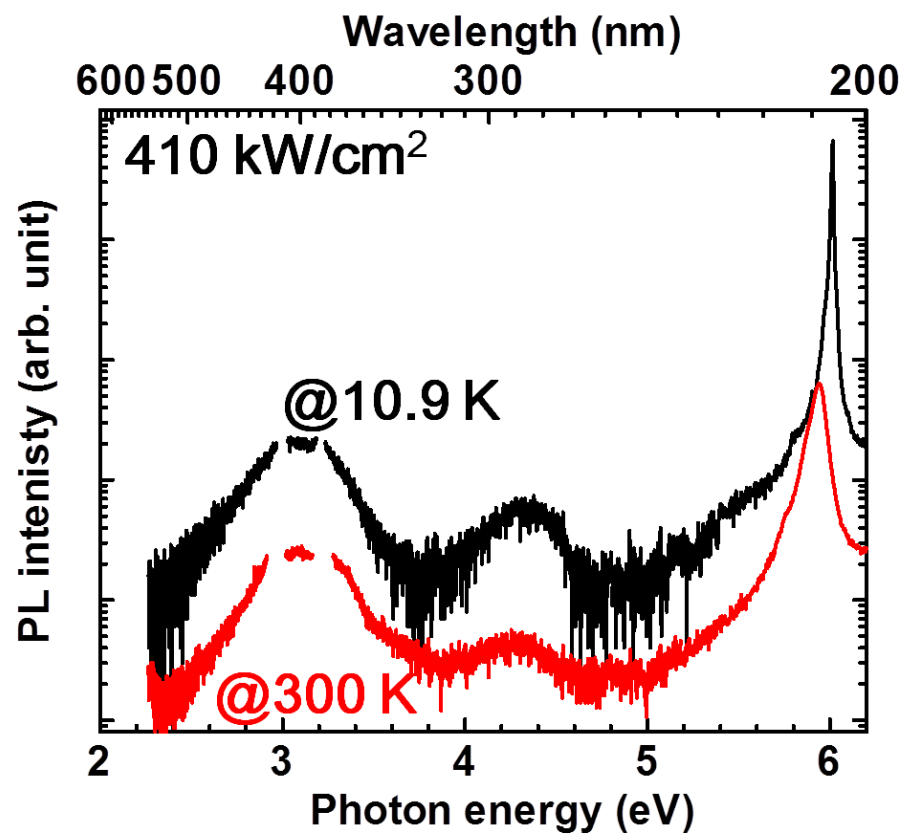


Figure 3.10: PL spectra of the *r*-plane AlN film at 10.9 and 300 K.

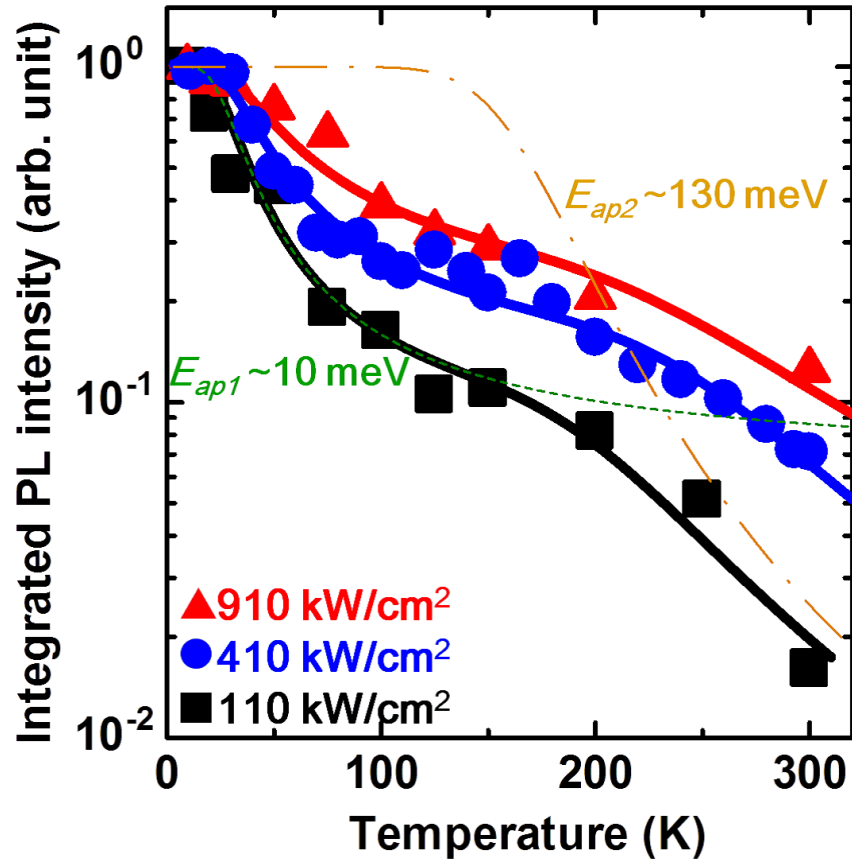


Figure 3.11: Integrated PL intensities of NBE emission of the *r*-plane AlN film under various excitation powers. The intensities are normalized by maximum intensity of each excitation condition. The solid lines are fitting lines by Eq. (3.25) assuming two different PDs, P1 and P2.

3.4.2 Deep level emissions

Subsequently, the variation of the deep level emission spectra of the r -plane AlN film due to temperature is discussed using Fig. 3.12. Although the deep level emissions peaking at 3.0 and 4.3 eV are mainly observed at low temperatures, they get weaker at elevated temperatures. The emission around 3.0 eV cannot be well separated, but it seems to involve various components as suggested by the shoulders at ~ 3.3 and ~ 3.8 eV. On the other hand, the origin of the emission at 4.3 eV has often been ascribed to defects related to carbon impurities [29]. However, it is uncertain whether or not this is the case in our samples because we confirmed that the carbon impurities in our samples are below the detection limit ($< 2 \times 10^{16} \text{ cm}^{-3}$) of secondary ion mass spectrometry (SIMS). Unlike the aforementioned deep level emissions at 3.0 and 4.3 eV, the emissions at ~ 3.2 and 3.5–3.7 eV are pronounced above 200 K. The emission enhancement means that the carrier transfer to the deep-level states are promoted with an increase of temperature.

To further investigate the thermal quenching and a carrier transfer, we perform numerical analyses based on a rate equation. The rate equation for deep level emissions can be expressed as

$$\frac{d\Delta p_D}{dt} = g_D - \frac{\Delta p_D}{\tau_{\text{Drad}}} - \frac{\Delta p_D}{\tau_{\text{Dnonrad}}} + \frac{\Delta p}{\tau_{\text{trans}}}, \quad (3.26)$$

where Δp_D and g_D are the excess carrier (exciton) density in the deep-level state and the generation rate of carriers directly excited from the ground state to the deep-level state, respectively. τ_{Drad} and τ_{Dnonrad} is the carrier recombination lifetimes for Δp_D with and without the deep level emissions, respectively. Note that Δp is the excess carrier density in the excited state (not in the deep-level state), and τ_{trans} is the carrier transfer lifetime from the excited state to the deep-level state. Therefore, the last term of Eq. (3.26) means the carrier transfer rate from the excited state. $d\Delta p_D/dt$ equals to zero in equilibrium, and we obtain

$$\frac{\Delta p_D}{\tau_{\text{Drad}}} = \frac{\tau_{\text{Drad}}^{-1}}{\tau_{\text{Drad}}^{-1} + \tau_{\text{Dnonrad}}^{-1}} \left(g_D + \frac{\Delta p}{\tau_{\text{trans}}} \right). \quad (3.27)$$

From Eqs. (3.18) and (3.19), Δp can be expressed as

$$\Delta p = \frac{I_{\text{NBE}}(T)}{I_{\text{max}}S} \cdot g \cdot \tau_{\text{rad}}. \quad (3.28)$$

Substituting Eq. (3.28) into Eq. (3.27), we have

$$\frac{\Delta p_D}{\tau_{\text{Drad}}} = \frac{1}{1 + \tau_{\text{Drad}}\tau_{\text{Dnonrad}}^{-1}} \cdot \left(1 + \frac{gI_{\text{NBE}}(T)}{gDI_{\text{max}}S} \cdot \tau_{\text{rad}}\tau_{\text{trans}}^{-1} \right) \cdot g_D. \quad (3.29)$$

$\Delta p_D/\tau_{\text{Drad}}$ is proportional to the deep level emission intensity (I_{Deep}). τ_{trans} is one of the nonradiative recombination lifetimes for the carriers in the excited state. Therefore, τ_{Drad}

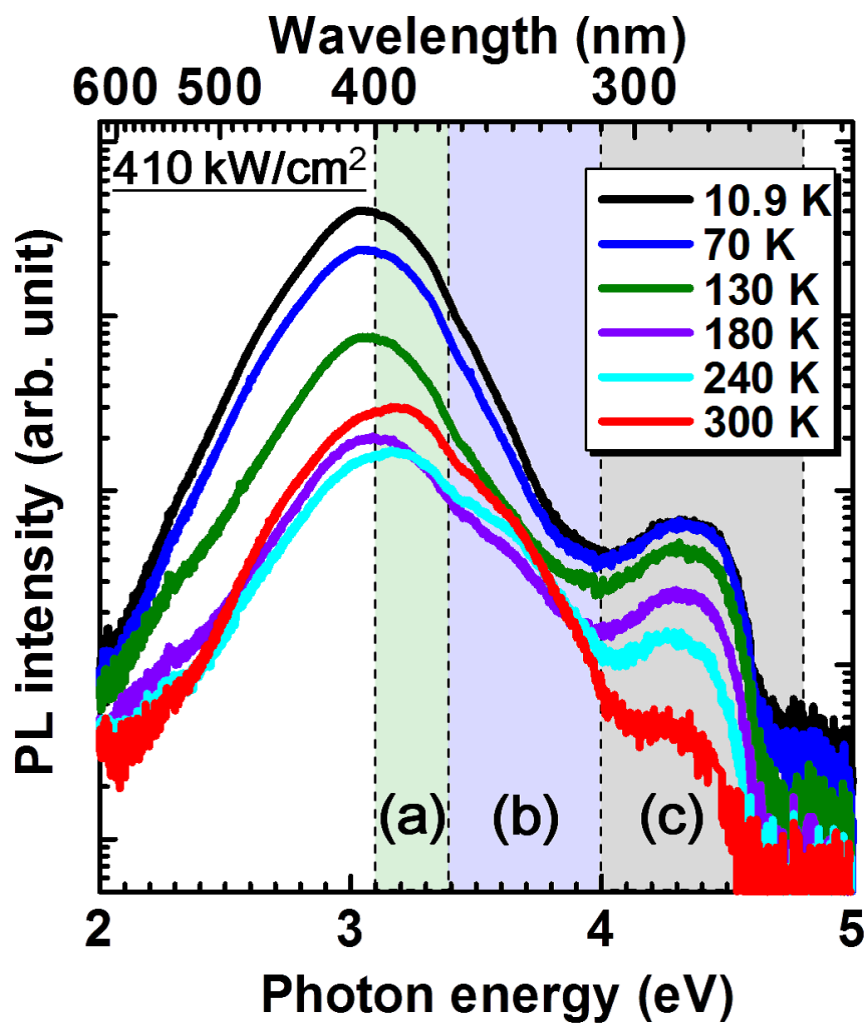


Figure 3.12: Deep level emission spectra of the *r*-plane AlN film at various temperatures. The spectral ranges (a), (b), and (c), which span 3.1–3.4, 3.4–4.0, and 4.0–4.8 eV, respectively, show distinctive PL behavior. The emission intensity enhancement is clearly observed for the emissions at ~ 3.2 and 3.5–3.7 eV above 200 K.

and τ_{trans} can be expressed in the same form as Eq. (3.21). Then, applying the same approximation as in Eq. (3.25) yields

$$I_{\text{Deep}}(T) \approx \frac{1 + dI_{\text{NBE}}(T) \exp\left(-\frac{E_{a2}}{k_{\text{B}}T}\right)}{1 + c \exp\left(-\frac{E_{a1}}{k_{\text{B}}T}\right)} \cdot I_{\text{Deep}}(0), \quad (3.30)$$

where $I_{\text{Deep}}(0)$ is deep level emission intensity at $T = 0$, and c and d are constants related to the thermal quenching and the carrier transfer to the deep level, respectively. E_{a1} and E_{a2} are the activation energies for the thermal quenching and the carrier transfer, respectively. For simplicity, we assume a single recombination path for the thermal quenching of the deep level emission. To exactly consider the temperature dependence of Δp , the same excitation powers should be used for $I_{\text{NBE}}(T)$ and for $I_{\text{Deep}}(T)$ in Eq. (3.30) because $I_{\text{NBE}}(T)$ strongly depends on the excitation power as shown in Fig. 3.11.

Although Eq. (3.30) assumes only one deep-level state, the broad PL spectra shown in Fig. 3.12 apparently consist of multiple components, which are difficult to unambiguously separate by multicomponent spectral fitting. Therefore, the PL intensities are integrated in three different spectral ranges [(a)–(c) shown in Fig. 3.12] which indicate the distinctive behaviors, and we use them for the discussion with Eq. (3.30). The spectral ranges (a), (b), and (c) span 3.1–3.4, 3.4–4.0, and 4.0–4.8 eV, respectively.

The temperature dependences of the integrated deep level emission intensities in ranges (a)–(c) of the r -plane AlN film are plotted in Fig. 3.13. The thermal behavior of the deep level emission intensity integrated in the full spectral range (2.0–5.0 eV) is almost the same as that in range (a). In ranges (a) and (b), the emission intensities are thermally quenched below 200 K but are enhanced above 200 K due to the emissions peaking at ~ 3.2 and 3.5–3.7 eV, respectively. In range (c), the integrated PL intensity is dominated by the emission at 4.3 eV, and thermally quenches monotonically, different from in ranges (a) and (b).

The solid lines in Fig. 3.13 are the fitting lines with Eq. (3.30), and they well agree with the experimental results. $I_{\text{NBE}}(T)$ under the same excitation condition (410 kW/cm²) as in Fig. 3.13 is used for the fittings. The estimated activation energy of the thermal quenching (E_{a1}) is ~ 50 meV for all the spectral ranges, and that of the carrier transfer (E_{a2}) is ~ 130 meV for ranges (a) and (b). It is noteworthy that d in range (c) is negligibly small and the emission intensity is not enhanced. This is probably because the trap density or the capture cross section of the deep-level state related to the 4.3-eV emission is too small to capture the excess carriers in the excited state. As a result, the majority of the carriers transfer to other deep-level states at elevated temperatures, and only the thermal quenching is observed in range (c).

The estimated E_{a1} is different from the activation energies of the aforementioned PDs (E_{ap1} and E_{ap2}) because the thermal quenching of the deep level emissions and that of the NBE emission are completely different phenomena: The configuration coordinate diagrams among the ground state (U_{ground}), the excited state (U_{excited}), and the deep-level state are

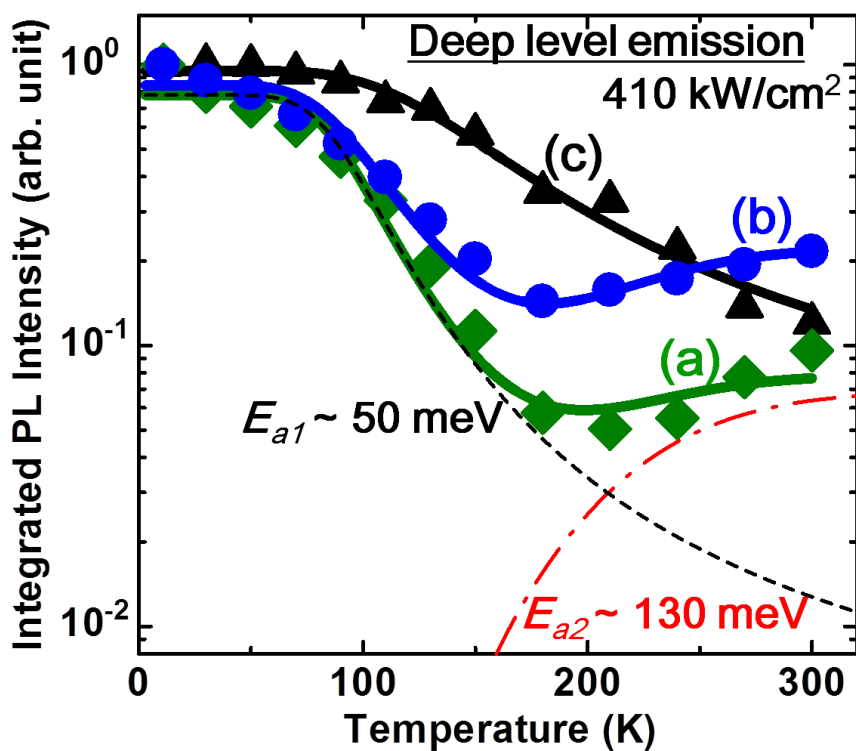


Figure 3.13: Integrated PL intensities of deep level emissions of the *r*-plane AlN film as functions of temperature. The emission intensities are integrated in ranges (a)–(c), defined in Fig. 3.12. The solid lines are the fitting lines with Eq. (3.30) assuming the activation energies E_{a1} and E_{a2} for the thermal quenching and the carrier transfer to the deep levels, respectively.

shown in Fig. 3.14. As an example, the deep level state due to P2 (U_{p2}) is drawn in the figure. E_{ap2} is related to thermal quenching of the NBE emission, whereas, E'_{ap2} is related to that of the deep level emission. Therefore, E_{ap2} and E'_{ap2} are the different in most cases. In addition, carrier transfer from U_{p2} to other deep-level states causes thermal quenching of the U_{p2} -related emission. Therefore, the estimated E_{a1} can be different from E_{ap1} and E_{ap2} .

The estimated E_{a1} (~ 50 meV) is almost the same value in all the spectral ranges (a)–(c) in spite that they should be related to different deep-level states. Considering E_{a1} is very close to the exciton binding energy of AlN (53.7 meV) [28], the thermal quenching of the deep level emissions in ranges (a)–(c) is ascribed to the exciton ionization, and E'_{ap2} in Fig. 3.14 is limited by exciton binding energy.

Because the thermal quenching of NBE emission above 200 K is dominated by P2 as we mentioned before, the deep level emission enhancements above 200 K in ranges (a) and (b) (Fig. 3.13) may be related to the P2 activation. When P2 is activated with elevating temperatures, holes in $U_{excited}$ is trapped by P2 and transferred to U_{ground} through path (i) or path (ii) in Fig. 3.14. In the case of path (i), deep level emission with the energy corresponding to the transition from the U_{p2} bottom to U_{ground} occurs. As a result, the deep level emission is enhanced. In fact, the activation energy of P2 ($E_{ap2} \sim 130$ meV) is almost the same as the transfer activation energy E_{a2} (~ 130 meV), which suggests that the P2 activation enhances the deep level emission. However, in spite of the enhanced carrier transfer to the P2 state at elevated temperatures, the total deep level emission intensity is weaker than that at low temperatures. This is because the recombination path (ii) is completely nonradiative process without any deep level emissions and the carriers captured by P2 recombine through either to path (i) or (ii). It is noteworthy that the deep level emission enhancement related to the P1 activation ($E_{ap1} \sim 10$ meV) is not observed, which suggests that the P1 activation is not accompanied by deep level emissions.

Because the enhanced emissions at 3.2 and 3.5–3.7 eV are caused by the carrier transfer to P2, these emissions may provide crucial information on the origin of P2. Although various PDs in AlN lead to the deep level emissions [29–32], impurities, which are a sort of PD, may be excluded from a possible origin of P2, because the un-doped AlN homoepitaxial films have very low densities of impurities such as silicon, carbon, and oxygen (in some cases, below the detection limit of SIMS [33]) as described in Chap. 2. Moreover, the formation energies of various PDs in AlN have been calculated [34–36], and those of Al vacancies (V_{Al}) and their complex defects in AlN with n-type conductivity are remarkably lower than those of simple substitutional impurity defects. Therefore, V_{Al} -related defects seem to be easily formed during the growth of un-doped AlN or un-doped Al-rich $Al_xGa_{1-x}N$ in theory. The V_{Al} -related defects act as acceptor-like defects and are the most stable in fully, negatively charged states when the Fermi level is in the upper part of the bandgap. Especially, a $V_{Al}-O_N$ complex defect is easily formed in n-type AlN (O_N is substitutional oxygen impurity defect), and the formation energies of $(V_{Al}-O_N)^{2-}$ and $(V_{Al}-2(O_N))^-$ are lower than that

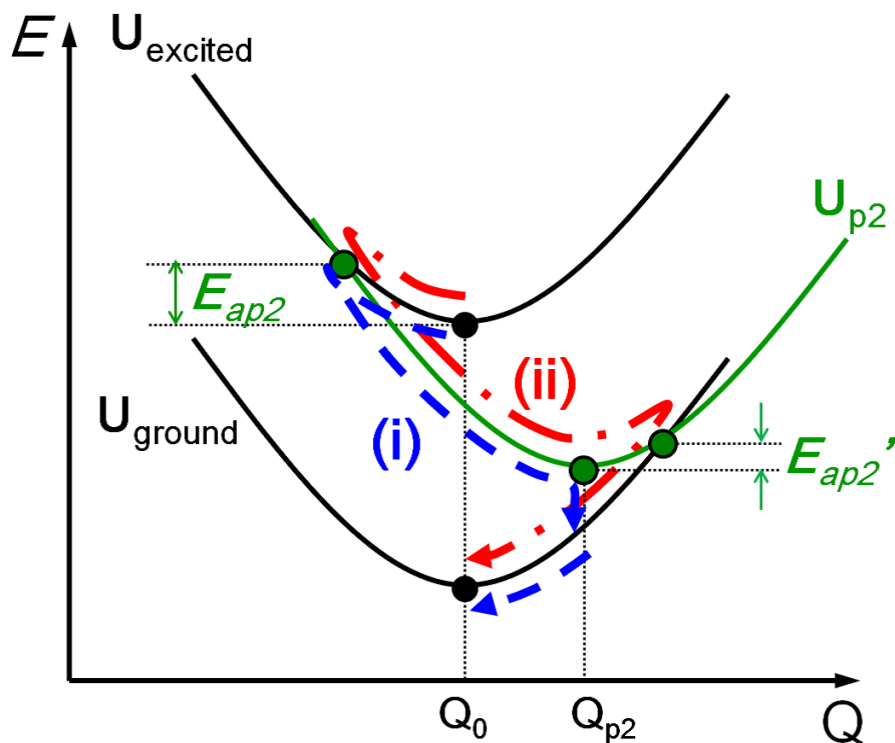


Figure 3.14: Carrier transfer or recombination paths mediated by P2 in configuration coordinate diagrams. Path (i) causes the radiative deep level emissions and path (ii) is completely nonradiative process.

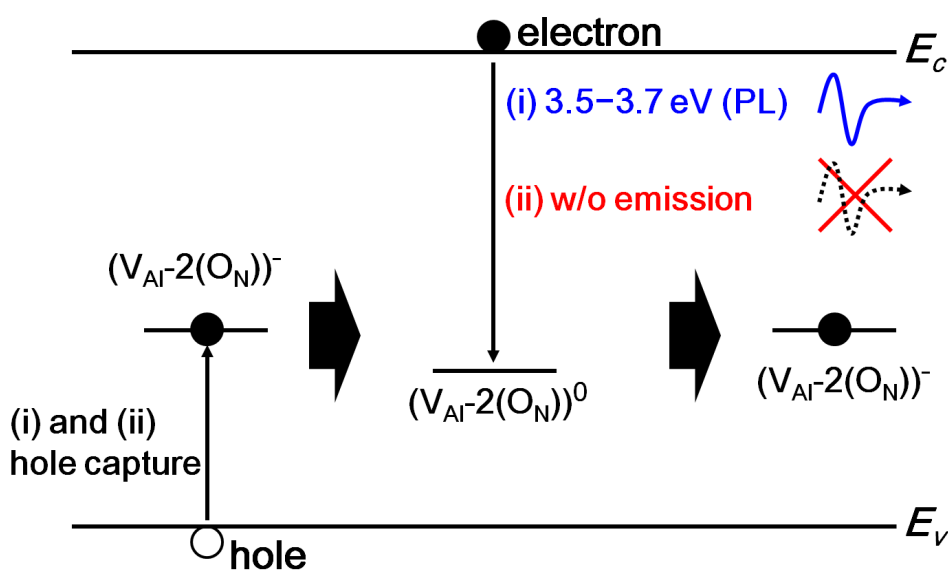


Figure 3.15: Schematic image of hole capture mediated by $(V_{Al-2}(O_N))^-$ state and the following deep level emission. (i) and (ii) are carrier paths illustrated in Fig. 3.14

of V_{Al}^{3-} for most Fermi level positions [36]. Such fully, negatively charged states of $V_{\text{Al}}\text{-O}_{\text{N}}$ complexes are unable to capture any additional electrons. However, once such defects capture holes to become $(V_{\text{Al}}\text{-O}_{\text{N}})^{-}$ and $(V_{\text{Al}}\text{-2(O}_{\text{N}}))^{0}$ states, they can capture electrons with emissions at 3.2 and 3.5 eV, respectively [36]. After the electron capture accompanied by the deep level emissions, these states return to the fully, negatively charged states again as shown in Fig. 3.15. As we mentioned above, because the deep level emissions at 3.2 and 3.5–3.7 eV are enhanced by hole transfer to P2, the dominant nonradiative recombination center P2 may be fully, negatively charged $V_{\text{Al}}\text{-O}_{\text{N}}$ complex defect. Although we cannot completely identify the origin of P2 as either $(V_{\text{Al}}\text{-O}_{\text{N}})^{2-}$ or $(V_{\text{Al}}\text{-2(O}_{\text{N}}))^{-}$, we consider that P2 is likely to be a $(V_{\text{Al}}\text{-2(O}_{\text{N}}))^{-}$ defect because the deep level emission at 3.5–3.7 eV is more significantly enhanced than that at 3.2 eV as shown in Fig. 3.13.

3.5 Combined analyses of CL and PL

3.5.1 Microscopic impacts of nonradiative recombination centers in the vicinity of TDs

In Sec. 3.5, we explain the temperature dependence of dark spot contrasts in the CL mapping (in Sec. 3.3) in detail using the activation energies obtained from the PL measurements in Sec. 3.4. Furthermore, the difference between AlN and GaN is discussed.

Although the impact of TDs is macroscopically negligible as discussed in Sec. 3.4, its influence near TDs has to be considered to explain the dark spot contrast. The nonradiative recombination lifetime due to a TD in the vicinity of the TD is defined as τ_{d} , which can be written as Eq. (3.21) (where $i = d$). Here, it should be noted that N_{td} is not TDD but the volume density of traps due to a TD in the vicinity of the TD. In other words, N_{td} is the volume trap density near the dislocation core and equals to zero far from TDs. Therefore, the microscopic emission intensity in the vicinity of a TD [$r = 0$ in Eq. (3.1)] is determined by the lifetimes τ_{d} , τ_{p} , and τ_{rad} . Then, we obtain

$$\begin{aligned}
 I_0(T) - I_{\text{D}}(T) &= \frac{\tau_{\text{rad}}^{-1}}{\tau_{\text{rad}}^{-1} + \tau_{\text{d}}^{-1} + \tau_{\text{p}}^{-1}} \cdot I_{\text{max}} \\
 &= \frac{I_{\text{max}}}{1 + \alpha T^{\gamma} \sqrt{\frac{3k_{\text{B}}T}{m^{*}}} \left[N_{td}\sigma_{0d} \exp\left(-\frac{E_{ad}}{k_{\text{B}}T}\right) + N_{tp1}\sigma_{0p1} \exp\left(-\frac{E_{ap1}}{k_{\text{B}}T}\right) + N_{tp2}\sigma_{0p2} \exp\left(-\frac{E_{ap2}}{k_{\text{B}}T}\right) \right]}.
 \end{aligned} \tag{3.31}$$

The CL contrast C_{max} can be written using Eqs. (3.2), (3.23) (where $n = 2$), and (3.31) as

$$\begin{aligned}
C_{\max}(T) &= \frac{I_D(T)}{I_0(T)} \\
&= \frac{\alpha T^\gamma \sqrt{\frac{3k_B T}{m^*}} N_{td} \sigma_{0d} \exp\left(-\frac{E_{ad}}{k_B T}\right)}{1 + \alpha T^\gamma \sqrt{\frac{3k_B T}{m^*}} \left[N_{td} \sigma_{0d} \exp\left(-\frac{E_{ad}}{k_B T}\right) + N_{tp1} \sigma_{0p1} \exp\left(-\frac{E_{ap1}}{k_B T}\right) + N_{tp2} \sigma_{0p2} \exp\left(-\frac{E_{ap2}}{k_B T}\right) \right]}.
\end{aligned} \tag{3.32}$$

We fitted the temperature dependence of CL contrasts in the *c*-plane and *r*-plane AlN films (Fig. 3.5) using Eq. (3.32), and Figs. 3.16 (a) and (b) show the respective fitted results as solid lines. When the experimental results are fitted with Eq. (3.32), we use E_{ad} and F_i ($i = d, p1$, and $p2$) as fitting parameters, where F_i is defined as

$$F_i = \alpha \sqrt{\frac{3k_B}{m^*}} N_{ti} \sigma_{0i}. \tag{3.33}$$

Note that E_{ap1} (~ 10 meV) and E_{ap2} (~ 130 meV) are estimated by the PL measurements in Sec. 3.4, and are fixed under the fittings. Furthermore, E_{ad} and F_d are common under the fittings for the *c*-plane and *r*-plane AlN films because τ_d (as well as E_{ap1} and E_{ap2}) should be intrinsically determined by the material considering the definition. Assuming $\gamma = 3/2$ for the AlN films, the fitting curves are uniquely determined. The activation energy of TDs (E_{ad}) is estimated to be ~ 2.5 meV from these fittings, and all activation energies of dominant nonradiative recombination centers near TDs are obtained as shown in Tab. 3.1.

Figures 3.16(d) and (e) show the correlations of radiative and nonradiative recombination lifetimes in the *c*-plane and *r*-plane AlN films that provide the best fits shown in Figs. 3.16(a) and (b), respectively. Here, the total recombination lifetime in the vicinity of a TD is expressed as

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_d} + \frac{1}{\tau_{p1}} + \frac{1}{\tau_{p2}}, \tag{3.34}$$

where τ_{p1} and τ_{p2} are nonradiative recombination lifetimes due to P1 and P2, respectively. Equation (3.34) tells us that the shortest lifetime dominates τ_{total} . In other words, a recombination process with the shortest lifetime is the dominant recombination path. Therefore, from Figs. 3.16(d) and (e), its temperature variation can be determined, as summarized in Tab. 3.2. The dominant nonradiative recombination paths in the vicinity of TDs are changed from TDs (or P1) to P2 by elevating temperature.

On the other hand, for $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{AlN}$ QWs, dark spots are not observed at any temperatures as shown in Fig. 3.5. Assuming that the nonradiative recombination lifetimes in QWs are the same as those in AlN films, we attribute the observation to the radiative recombination lifetime different from those in the films. Generally, the radiative recombination

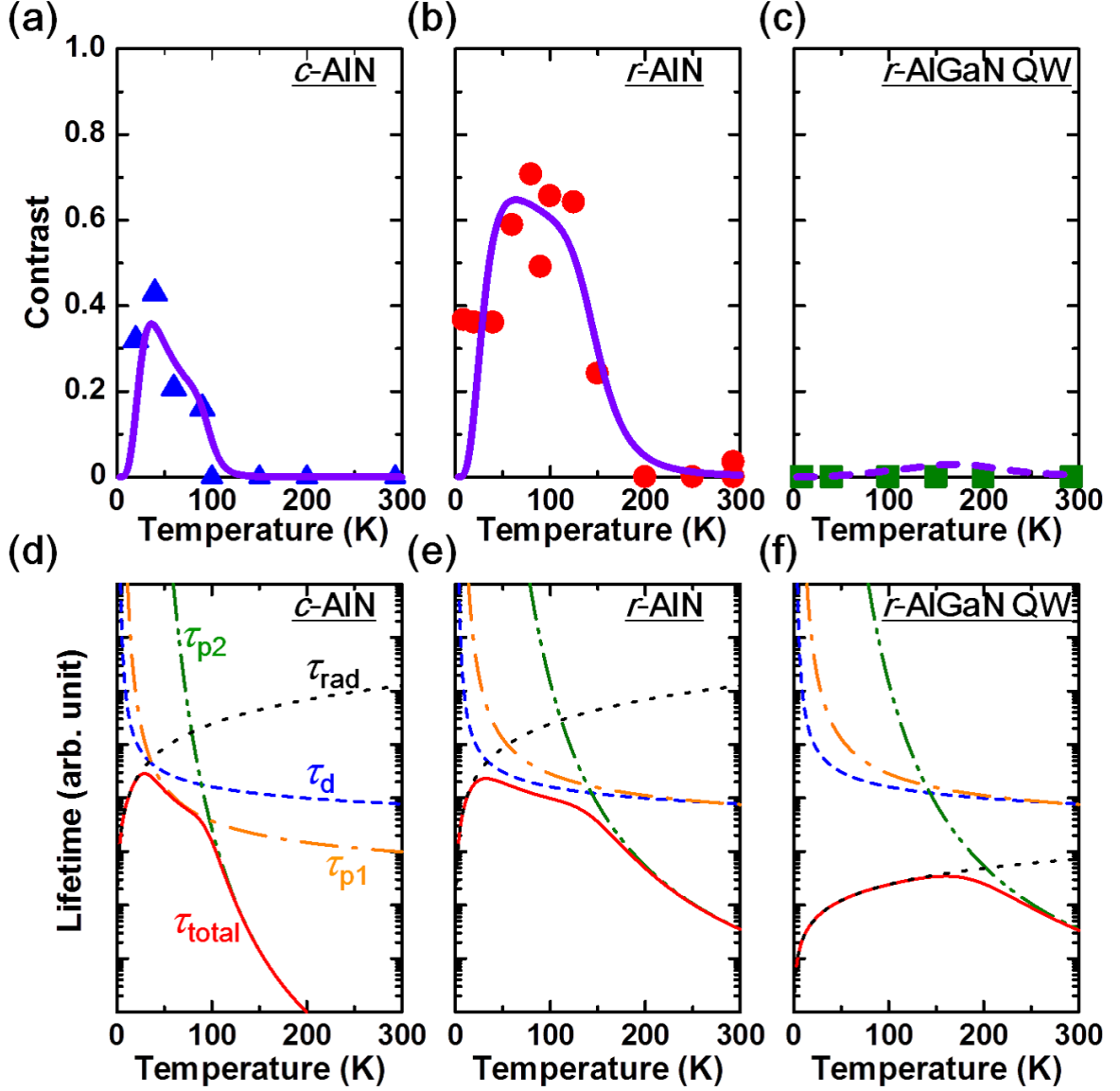


Figure 3.16: Temperature dependences of the dark spot contrasts in (a) the c -plane AlN films, (b) the r -plane AlN films, and (c) the r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs. In (a) and (b), the contrasts are fitted with Eq. (3.32), and the fitted results are shown as solid lines. In (c), the broken line is the calculated result based on the appropriate estimation of τ_{rad} . The temperature dependences of the recombination lifetimes in the c -plane AlN films, the r -plane AlN films, and the r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs are calculated as shown in (d), (e), and (f), respectively, which reproduce the solid and broken lines in (a), (b), and (c). In (d), (e), and (f), dotted, broken, dash-dotted, dash-double-dotted, and solid lines represent τ_{rad} , τ_d , τ_{p1} , τ_{p2} , and τ_{total} , respectively.

lifetimes in QWs are much shorter than those in films, and their temperature dependences are different [$\gamma = 3/2$ for bulk and 1 for QW in Eq. (3.22)]. With these conditions, the temperature variations of the contrasts and the recombination lifetimes are calculated and displayed in Figs. 3.16(c) and (f), respectively. Figures 3.16(f) shows that the dominant recombination paths are changed from radiative to P2-mediated nonradiative recombinations without going through the TD-dominant region as shown in Tab. 3.2, which is why dark spots are not observed at any temperatures. The emission intensities of QWs are less affected by TDs than those of AlN films.

For both AlN films and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ QWs, dark spot contrasts are considerably weakened at room temperature because P2 becomes the dominant recombination center. It is noteworthy that these contrast behaviors are completely different from those in GaN and Ga-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ [37–40]. For GaN, the dark spots due to TDs are clearly observed even at room temperature unlike AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$, which means that τ_d is shorter than τ_p even at room temperature. This may be because the density of Ga vacancies (V_{Ga}) in GaN is much lower than that of V_{Al} in AlN. This assertion is supported by the theoretical consideration showing that the formation energy of V_{Ga} is larger than that of V_{Al} [35]. Therefore, we have to pay more attentions to PDs and their activities in AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ compared with GaN and Ga-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$. In fact, the impacts of TDs in AlN (in Fig. 3.6) are much smaller than those of GaN [41].

To compare the impacts of nonradiative recombination centers on the emission intensity near TDs for c - and r -plane AlN films, we define the nonradiative recombination parameter M_i as $N_{ti}\sigma_{0i}$. Because σ_{0i} is the capture cross section at $T \rightarrow \infty$ [see Eq. (3.20)], M_i means carrier density which is captured by the defects (corresponding to i) at $T \rightarrow \infty$. Therefore, the nonradiative recombination rate due to the defect is proportional to M_i at any temperatures, and M_i is an effective index to characterize the impact of the defect. Note that σ_{0i} is basically determined by the material and the defect type.

When the dark spot contrasts are fitted with Eq. (3.32) as shown in Figs. 3.16(a) and (b), we obtain F_i [expressed as Eq. (3.33)] as the fitting parameters. Although α related to radiative recombination lifetime [see Eq. (3.22)] is not determined by the fittings, we can exclude the influence by calculating the ratio of F_i to F_d like

$$\begin{aligned} \frac{F_i}{F_d} &= \frac{N_{ti}\sigma_{0i}}{N_{td}\sigma_{0d}} \\ &= \frac{M_i}{M_d}. \end{aligned} \quad (3.35)$$

As we mentioned above, F_d (M_d) should be the same value in the c -plane and r -plane AlN films. Therefore, M_i/M_d can be a relative index which evaluates the impact of the PD with respect to TDs. M_i/M_d in the c -plane and r -plane AlN calculated by Eq. (3.35) are shown in Tab. 3.3. P1 and P2 predominantly act as nonradiative recombination centers,

Table 3.1: Activation energies of TDs and PDs in AlN. E_{ad} is estimated from the fittings of the CL contrast with Eq. (3.32), as shown in Figs. 3.16(a) and (b). E_{ap1} , and E_{ap2} are estimated from the fittings of the PL intensity with Eq. (3.25), shown in Fig. 3.11.

E_{ad} (meV)	E_{ap1} (meV)	E_{ap2} (meV)
2.5	10	130

Table 3.2: Dominant recombination paths in the vicinity of TDs in the whole temperature regions. Rad means radiative recombination.

Sample	0–30 K	30–100 K	100–140 K	140–200 K	200 K –
<i>c</i> -AlN	Rad	(TD →) P1	P2		
<i>r</i> -AlN	Rad	TD		P2	
QW	Rad				P2

Table 3.3: Nonradiative recombination parameters M_i ($= N_{ti}\sigma_{0i}$) normalized by M_d . Here, M_d is fixed in both the *c*-AlN and the *r*-AlN because N_{td} and σ_{0d} is basically determined by the material.

Sample	M_d/M_d	M_{p1}/M_d	M_{p2}/M_d
<i>c</i> -AlN	1.0	10	1.6×10^7
<i>r</i> -AlN		1.4	3.0×10^4

compared with TDs at sufficiently high temperatures even in the vicinity of TDs. In spite of the large activation energy, P2 can be a dominant nonradiative recombination center at room temperature in AlN films because M_{p2} is remarkably larger than M_d and M_{p1} . Considering that σ_{0i} should be the same for the same type of defects in AlN films, the relative trap density of the same type defects between the c -plane and r -plane AlN films can be calculated as

$$\begin{aligned} \frac{M_i^{(c)}/M_d}{M_i^{(r)}/M_d} &= \frac{M_i^{(c)}}{M_i^{(r)}} \\ &= \frac{N_{ti}^{(c)}}{N_{ti}^{(r)}}, \end{aligned} \quad (3.36)$$

where the superscript characters (c) and (r) mean the c -plane and r -plane, respectively. The P1 and P2 densities (N_{tp1} and N_{tp2}) in the c -plane AlN estimated by Eq. (3.36) are 7.6 times and 540 times as large as those in the r -plane AlN, respectively. This result well explains the shorter L_{eff} and the weaker C_{max} in the c -plane AlN at room temperature, as discussed in Sec. 3.3.

3.5.2 Prediction of the defect density dependence of macroscopic efficiency degradation

Thus far, we have demonstrated that the macroscopic emission efficiency of AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ with relatively low TDDs is determined by competition between the radiative recombination and nonradiative recombination due to PDs at any temperatures (see Fig. 3.7). On the other hand, local efficiency in the vicinity of TDs is affected by TDs or PDs, depending on temperature (see Fig. 3.16). Here, we predict the dominant nonradiative recombination center and the consequent macroscopic efficiency of AlN as functions of TDD and PD densities.

When the point defect densities are varied from N_{tp1} (N_{tp2}) to N'_{tp1} (N'_{tp2}), relative point defect density is defined as

$$R_i = \frac{N'_{ti}}{N_{ti}}, \quad (3.37)$$

where $i = p1$ or $p2$. The dark spot contrast (C_{max}) and effective diffusion length (L_{eff}) accordingly vary, and they are rewritten using Eqs. (3.3), (3.4), (3.32), (3.33), and (3.37) as

$$\begin{aligned}
C'_{\max}(T) &= \frac{1 + T^{\gamma+1/2} \left[F_d \exp\left(-\frac{E_{ad}}{k_B T}\right) + F_{p1} \exp\left(-\frac{E_{ap1}}{k_B T}\right) + F_{p2} \exp\left(-\frac{E_{ap2}}{k_B T}\right) \right]}{1 + T^{\gamma+1/2} \left[F_d \exp\left(-\frac{E_{ad}}{k_B T}\right) + F_{p1} R_{p1} \exp\left(-\frac{E_{ap1}}{k_B T}\right) + F_{p2} R_{p2} \exp\left(-\frac{E_{ap2}}{k_B T}\right) \right]} \cdot C_{\max}(T), \\
\end{aligned} \tag{3.38}$$

and

$$\begin{aligned}
L'^2_{\text{eff}}(T) &= \frac{D_{\text{diff}} \tau'_{\text{eff}}}{D_{\text{diff}} \tau_{\text{eff}}} \cdot L^2_{\text{eff}}(T) \\
&= \frac{1 + T^{\gamma+1/2} \left[F_{p1} \exp\left(-\frac{E_{ap1}}{k_B T}\right) + F_{p2} \exp\left(-\frac{E_{ap2}}{k_B T}\right) \right]}{1 + T^{\gamma+1/2} \left[F_{p1} R_{p1} \exp\left(-\frac{E_{ap1}}{k_B T}\right) + F_{p2} R_{p2} \exp\left(-\frac{E_{ap2}}{k_B T}\right) \right]} \cdot L^2_{\text{eff}}(T), \tag{3.39}
\end{aligned}$$

respectively, where τ'_{eff} is the effective carrier recombination lifetime reflecting the changes of the defect densities. $C_{\max}(T)$ and $L_{\text{eff}}(T)$ at certain temperatures are experimentally obtained, and the remaining parameters except for R_i have already been estimated by the aforementioned fittings.

η_{TD} in Eq. (3.16), which is an index of the impact of TDs on efficiency degradation, can be described as a function of R_i using $C'_{\max}(T)$ and $L'_{\text{eff}}(T)$ expressed in Eqs. (3.38) and (3.39), respectively, instead of $C_{\max}$ and L_{eff} , respectively. When the TDD is fixed to be $1 \times 10^8 \text{ cm}^{-2}$, η_{TD} at 293 K is calculated as shown in Fig. 3.17(a), where N_{tp1} and N_{tp2} are relatively varied with respect to the trap densities in the r -plane AlN [use $N_{ti}^{(r)}$ as a denominator of R_i in Eq. (3.37)]. In Fig. 3.17(a), $\eta_{\text{TD}} = 100\%$ means that dominant nonradiative recombination centers are PDs, and both the c -plane and r -plane AlN films investigated in this study are located in the P2-dominant region. For example, to achieve $\eta_{\text{TD}} < 50\%$ in the r -plane AlN film, Fig. 3.17(a) indicates that P2 should be decreased by $< 1/65$. For the c -plane AlN film, on the other hand, additional P1 reduction followed by substantial decrease in P2 ($< 1/10^4$) is required. This is due to the large M_{p1} as shown in Tab. 3.3.

The NBE emission intensity $I_{\text{NBE}}(T)$ defined as Eq. (3.19) can also be evaluated. The relative NBE emission intensity is expressed using Eqs. (3.3), (3.10), and (3.15) as

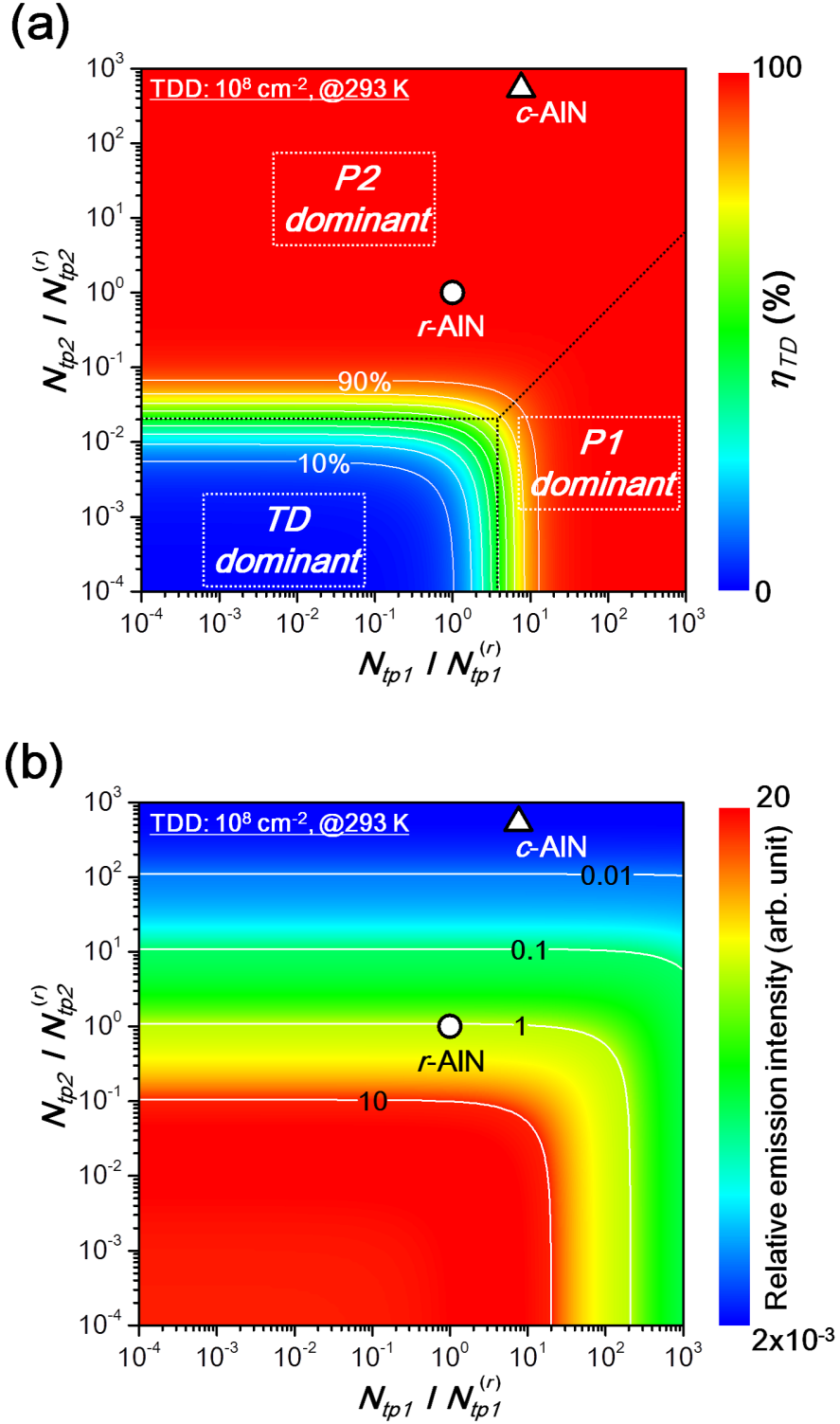


Figure 3.17: (a) Calculated η_{TD} at 293 K when TDD is fixed to be $1 \times 10^8 \text{ cm}^{-2}$, while N_{tp1} and N_{tp2} are varied. N_{tp1} and N_{tp2} relatively varied with respect to the trap densities in the *r*-plane AlN. (b) The relative emission intensity is calculated under the same conditions as (a).

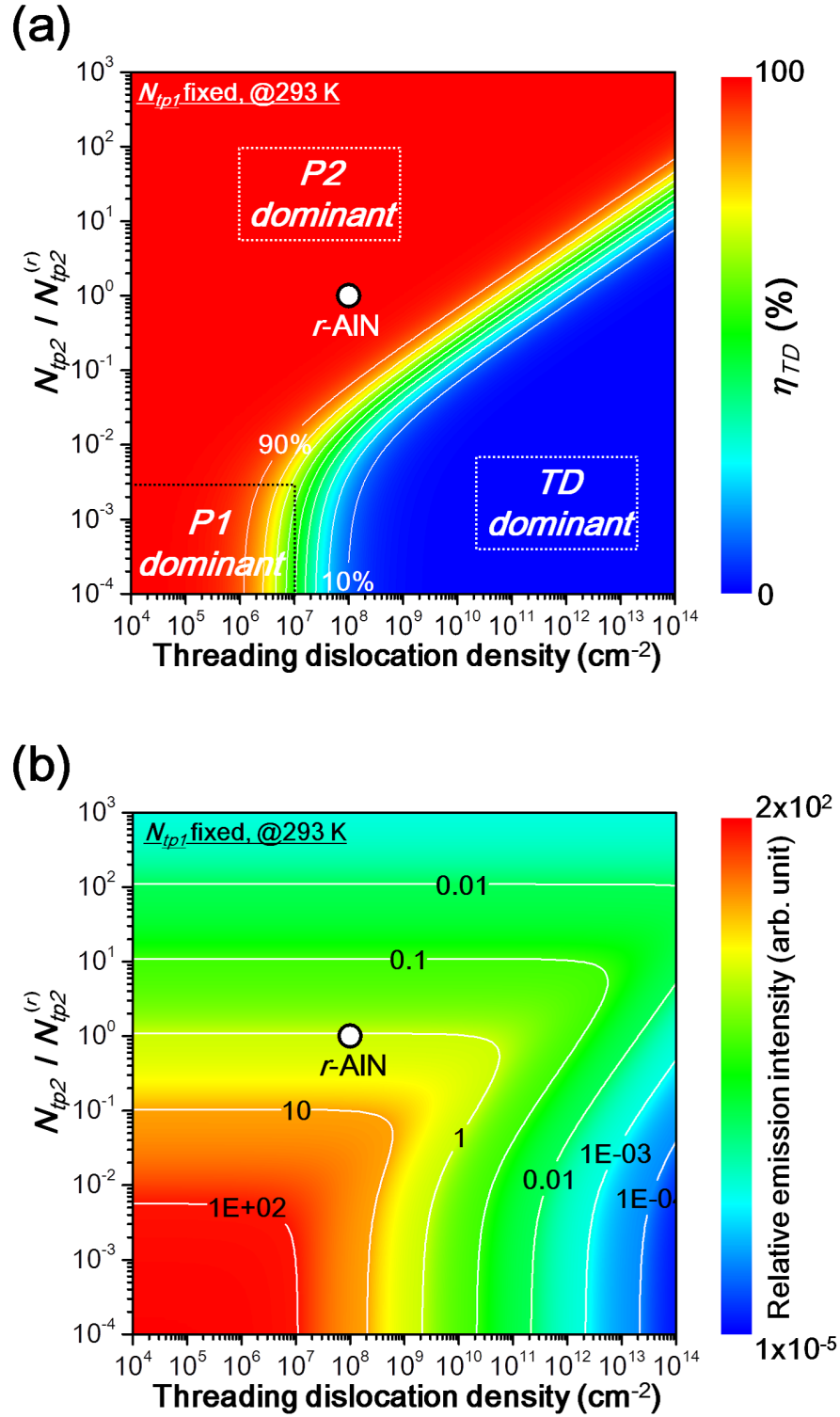


Figure 3.18: (a) Calculated η_{TD} at 293 K when N_{tp1} is fixed, while TDD and N_{tp2} are varied. N_{tp2} relatively varied with respect to the trap density in the r -plane AlN. (b) The relative emission intensity is calculated under the same conditions as (a).

$$\begin{aligned}
\frac{I'_{\text{NBE}}(T)}{I_{\text{NBE}}(T)} &= \frac{\eta'_{\text{TD}} \tau'_{\text{eff}}}{\eta_{\text{TD}} \tau_{\text{eff}}} \\
&= \frac{\eta'_{\text{TD}} L_{\text{eff}}'^2(T)}{\eta_{\text{TD}} L_{\text{eff}}^2(T)},
\end{aligned} \tag{3.40}$$

where η'_{TD} means η_{TD} reflecting the variations of the defect densities and has already been calculated in Fig. 3.17(a).

Then, the relative NBE emission intensity at 293 K normalized by that of the *r*-plane AlN under the same conditions as Fig. 3.17(a) is calculated using Eq. (3.40). Figure 3.17(b) shows the calculation result. The emission intensity of the *r*-plane AlN is not improved by the reduction of P1, whereas it can be 20 times as intense as the current emission intensity by P2 reduction ($< 1/65$). A similar tendency also occurs for the *c*-plane AlN, and the intensity improvement rate by the P2 reduction ($< 1/10^4$) is expected to be three orders of magnitude higher than the *r*-plane AlN. This is due to the large M_{p2} in the *c*-plane AlN as shown in Tab. 3.3.

In the same way as Fig. 3.17(a), η_{TD} at 293 K is calculated with fixed N_{tp1} ($= N_{tp1}^{(r)}$), while TDD and N_{tp2} are varied. Figure 3.18(a) shows the calculated result, where N_{tp2} is relatively varied with respect to the trap density in the *r*-plane AlN. Furthermore, Fig. 3.18(b) shows the emission intensity at 293 K normalized by that of the *r*-plane AlN under the same conditions as in Fig. 3.18(a). Figures 3.18(a) and (b) clearly indicate that the emission intensity of the *r*-plane AlN is not improved by the reduction of TDs similarly in the case of P1 reduction [Fig. 3.17(b)], whereas P2 reduction can remarkably strengthen the emission intensity¹ as we mentioned above. After the P2 reduction, TDs become the dominant nonradiative recombination centers, and the decrease of TDD to 10^6 cm^{-2} can achieve about 200 times larger emissions than the current intensity. At this stage, we are approaching the P1-dominant region [Fig. 3.18(a)], and therefore, P1 reduction is necessary for further improvement.

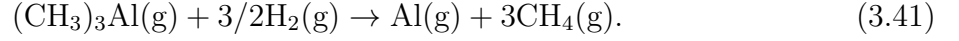
3.6 Growth pressure effects on PD density

As we mentioned above, the density of PDs (both P1 and P2) in the *r*-plane AlN epilayer is much lower than that in the *c*-plane AlN (see Tab. 3.3). In addition to the difference of growth directions, the growth conditions for those AlN films are quite different. To achieve smooth surfaces, a high reactor pressure (500 Torr) is used for the semipolar-plane growth, whereas 76 Torr is used for the *c*-plane growth to suppress the parasitic reactions. Herein,

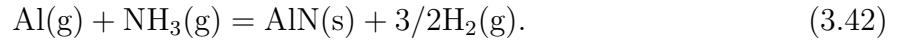
¹When the TDD is too high (for example, $> 10^{13} \text{ cm}^{-2}$), P2 reduction may decrease the emission intensity. This is because the excited carriers more easily to be captured by TDs due to the elongated diffusion length.

we discuss the effects of growth pressures on PD density based on thermodynamic analyses for the AlN growth.

Equilibrium partial pressures of the gases introduced in a MOVPE reactor can be calculated by the thermodynamic analysis [42]. The supplied TMA into a reactor is irreversibly decomposed near the substrate surface according to the following reaction,



The decomposed Al vapor chemically reacts with NH_3 on the heated substrate, producing an AlN film. The chemical reaction is written as



From Eqs. (3.41) and (3.42), we have

$$P_{\text{Al}}^0 - P_{\text{Al}} = P_{\text{NH}_3}^0 - P_{\text{NH}_3}, \quad (3.43)$$

$$P_{\text{CH}_4} = 3P_{\text{Al}}^0, \quad (3.44)$$

where P_{Al}^0 and $P_{\text{NH}_3}^0$ are the input partial pressures of TMA and NH_3 , and P_i are the equilibrium partial pressures. The total reactor pressure is given by

$$P_{\text{total}} = P_{\text{Al}} + P_{\text{NH}_3} + P_{\text{H}_2} + P_{\text{CH}_4}. \quad (3.45)$$

The equilibrium constant (K_{AlN}) for the reaction in Eq. (3.42) is reported as [42]

$$\log_{10} K_{\text{AlN}} = -14.2 + \frac{3.17 \times 10^4}{T_{\text{g}}} + 2.33 \log_{10} T_{\text{g}}. \quad (3.46)$$

where T_{g} (K) is growth temperature. Using Eqs. (3.42)–(3.46), we calculated the equilibrium partial pressures in a MOVPE reactor. Here, we used gas fluxes of H_2 , TMA, and NH_3 as 89.3 mmol/min, 4.11 $\mu\text{mol}/\text{min}$, and 893 $\mu\text{mol}/\text{min}$, respectively. In this study, we exclude the thermal decomposition of NH_3 for the simplicity.

Considering the actual growth temperature 1200°C, the reactor pressure dependence of the equilibrium partial pressures are calculated as shown in Fig. 3.19(a). The driving force for the epitaxy ($\Delta P_{\text{Al}} = P_{\text{Al}}^0 - P_{\text{Al}}$) is sufficiently large to grow AlN, and it gets larger with an increase of total pressure. In general, ΔP_{Al} is proportional to the growth rate for MOVPE growth because there are a lot of N atoms on the substrate surface due to the much higher partial pressure of NH_3 than that of Al vapor. In the experimental results, however, higher reactor pressures lead to lower growth rates due to the parasitic reactions between TMA and NH_3 [43, 44] as described in Chap. 2. Thus, in order to make the discussion more realistic, we should take the effect of parasitic reactions into account for the calculations.

From the experimental results and a previous work [43], it was clarified that the growth

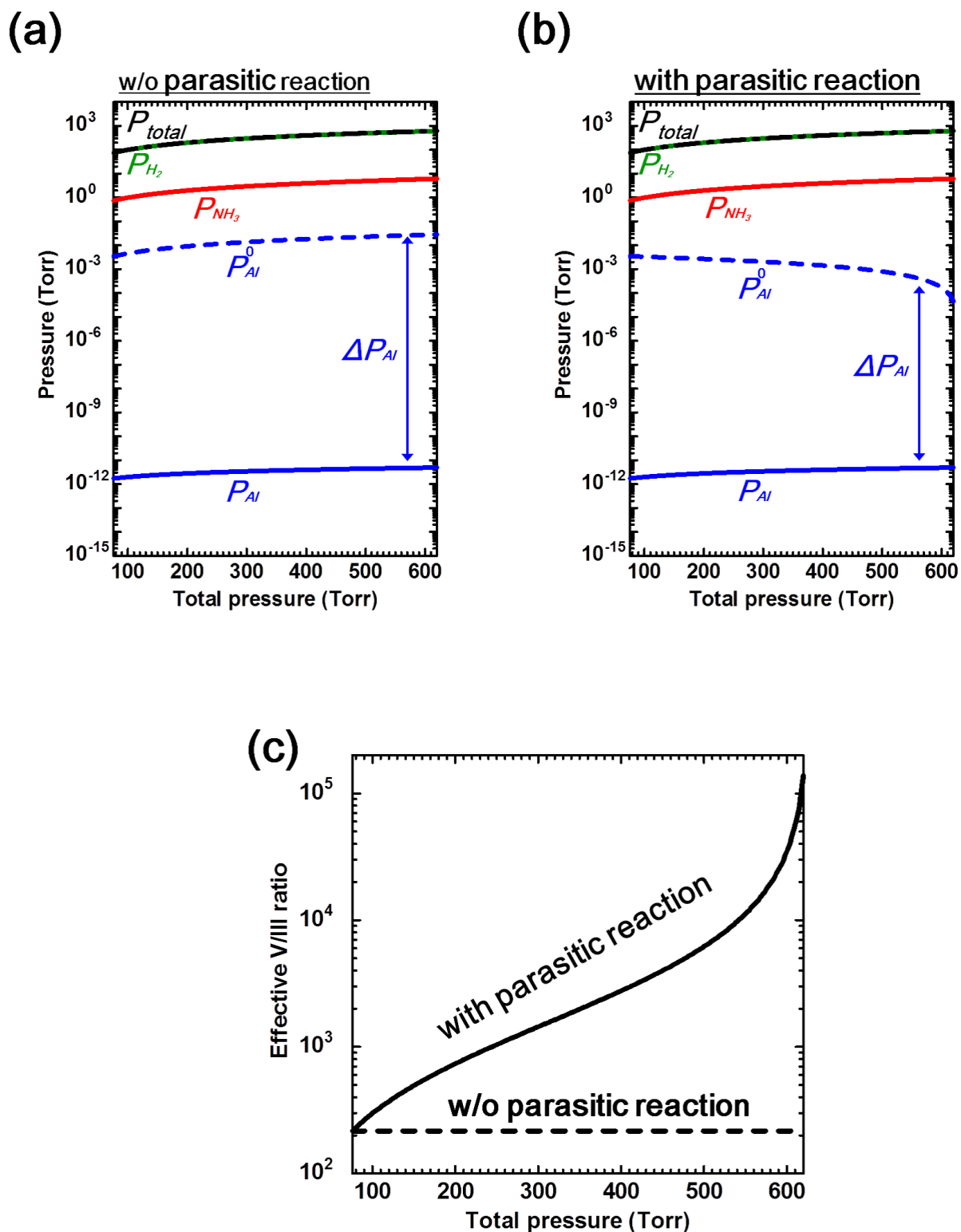


Figure 3.19: Total reactor pressure dependences of the calculated equilibrium partial pressures (a) with and (b) without considering the parasitic reactions. (c) Total pressure dependences of effective V/III ratio which are calculated using the effective input partial pressures.

rates of AlN films are linearly reduced with respect to the total reactor pressures due to the pre-reactions. Then, we revised the effective input partial pressures of TMA and NH_3 considering the wasted precursors in the pre-reactions, which are estimated by the growth rate variations. Here, we assume that the parasitic reactions can be neglected at the normal growth condition (76 Torr), and the approximation $R_g \propto \Delta P_{\text{Al}} \sim P_{\text{Al}}^0$ is satisfied, where R_g is the growth rate of AlN. Total reactor pressure dependences of the calculated equilibrium partial pressures with considering the parasitic reactions are shown in Fig. 3.19(b). In contrast to Fig. 3.19(a), ΔP_{Al} gets smaller for higher reactor pressures due to the parasitic reaction. At the same time, the effective input partial pressures are varied with the total reactor pressures. Figure 3.19(c) shows the total reactor pressure dependences of effective V/III ratio which are calculated by the effective input partial pressures. In the calculated result considering the parasitic reaction, high reactor pressures lead to high V/III ratio in contrast to the calculation excluding the parasitic reaction. This is because the actual input NH_3 flux is much larger than the input TMA flux and the pre-reaction between TMA and NH_3 occurs with the ratio of 1 : 1.

Subsequently, we investigated the equilibrium partial pressures when V/III ratio is adjusted by various methods. In general, V/III ratio of AlN growth is adjusted by NH_3 and TMA fluxes. Thus, we calculated the equilibrium partial pressures as a function of V/III ratio when it was adjusted by reactor pressure, NH_3 flux, and TMA flux as shown in Figs. 3.20(a)–(c), respectively. In the calculations, the total reactor pressure was fixed to 76 Torr when NH_3 or TMA flux varied, and the gas fluxes were fixed when total reactor pressure varied. Parasitic reaction was not considered for the calculation varying NH_3 or TMA flux, and the growth conditions except for the variable factors were fixed to the normal conditions (T_g : 1200°C, P_{total} : 76 Torr, H_2 : 89.3 mmol/min, TMA: 4.11 $\mu\text{mol/min}$, and NH_3 : 893 $\mu\text{mol/min}$).

Figures 3.20(a)–(c) indicate that the driving forces ΔP_{Al} for all of the adjusting methods are large enough throughout the entire V/III ratio to neglect the desorption of Al atoms from growth surfaces. Because the calculated equilibrium partial pressures mean the respective vapor pressures on AlN surfaces, they should be reflecting the density of respective adatoms on the growth surfaces. Therefore, for the discussion of the impact of growth conditions on V_{Al} -related PD density, P_{Al} behaviors particularly deserve to be discussed. The P_{Al} means the partial pressure of Al vapor on the growth surface, and it should be proportional to the density of Al adatoms on the surface considering the ideal gas law. Hence, high P_{Al} may lead low V_{Al} -related PD density.

Then, V/III ratio dependences of the P_{Al} for the various adjusting methods are summarized in Fig. 3.21. We found that high reactor pressure leads to high P_{Al} . The calculated result well agrees with the fact that the P2 density in the *r*-plane AlN film grown at 500 Torr is much lower than that in the *c*-plane AlN film grown at 76 Torr. Furthermore, the high V/III ratio caused by high reactor pressures should suppress the migration of Al adatoms on the growth surfaces. It also corresponds to the experimental result that the high density

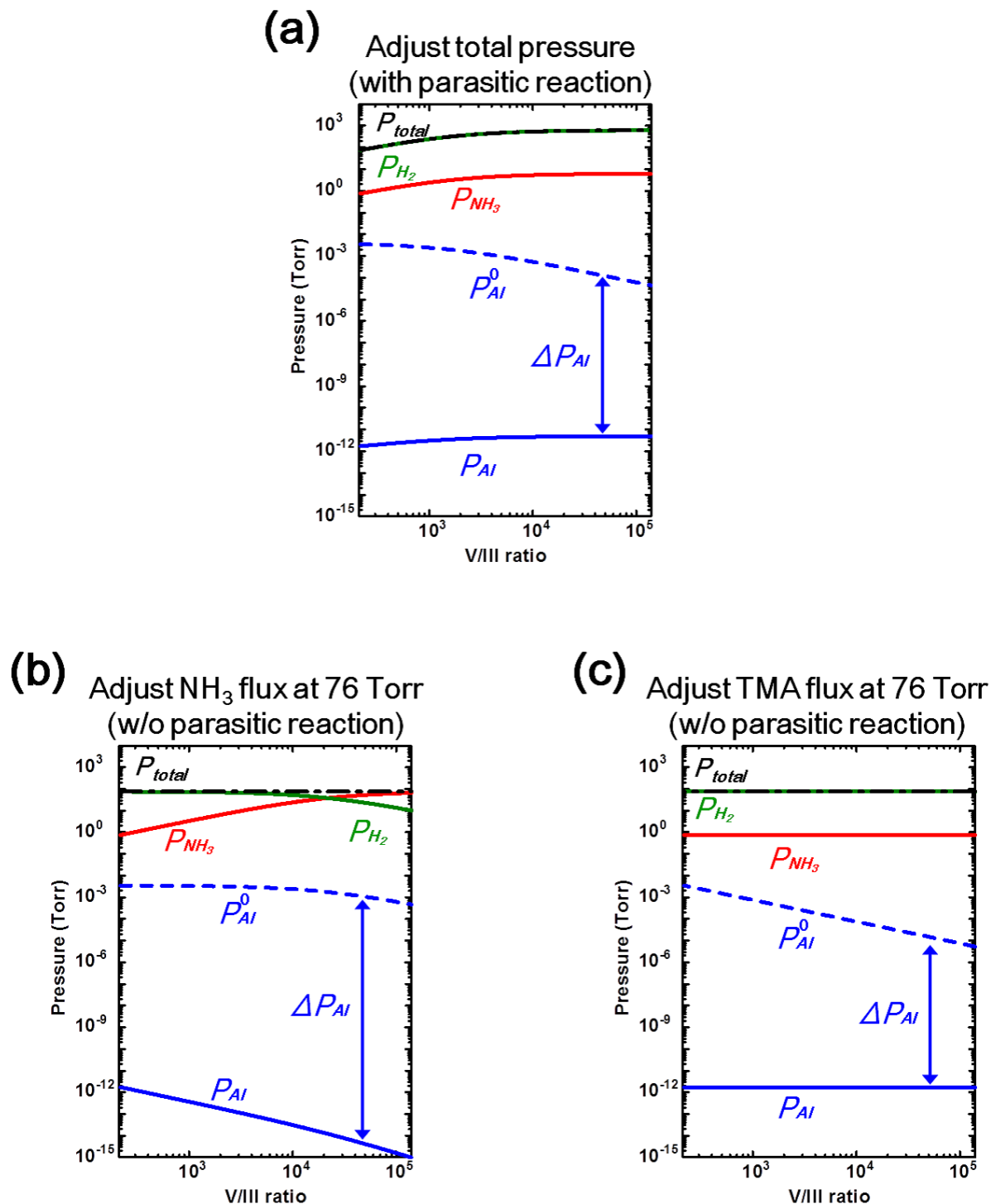


Figure 3.20: Equilibrium partial pressures as a function of V/III ratio when it was adjusted by (a) total reactor pressure, (b) NH_3 flux, and (c) TMA flux.

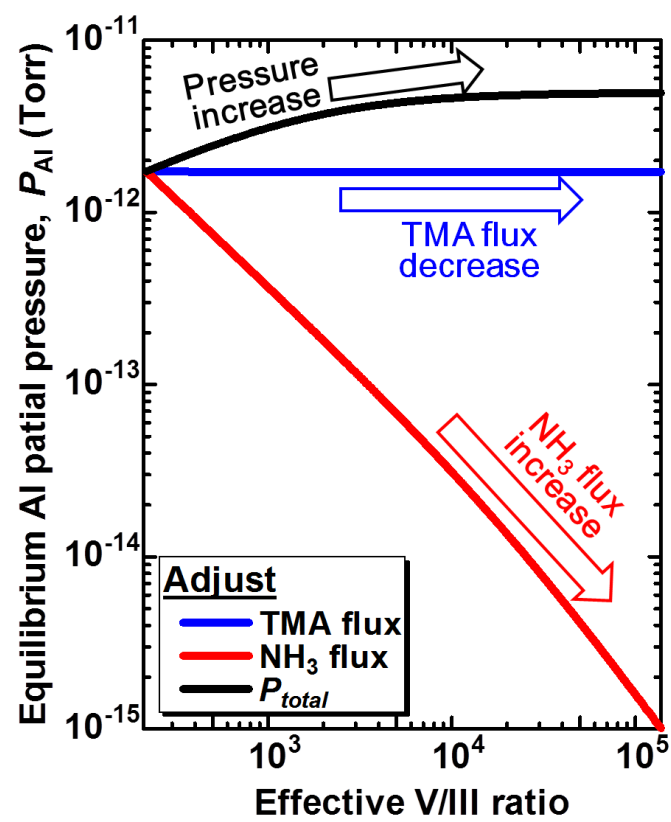


Figure 3.21: V/III ratio dependences of P_{Al} for the various adjusting methods.

of nucleation, which enables to achieve pit-free semipolar AlN surfaces (the details were described in Chap. 2), is promoted by high pressure growth, and supports the validity of the calculation results. Therefore, these findings indicate that high pressure growth is very effective method to reduce P2, which act as dominant nonradiative recombination centers in Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ related materials, because the high reactor pressure leads to high P_{Al} . In the case of the c -plane growth, however, the surface roughenings are induced by high pressure growth due to the excess suppressions of Al migrations as described in Chap. 2. On the other hand, Fig. 3.21 also indicates that the decrease of NH_3 flux leads to high P_{Al} and low V/III ratio, which can enhance the Al migration. Thus, we predict that the decrease of NH_3 flux may also reduce V_{Al} -related defects and realize high quality c -plane AlN films with atomically smooth surfaces. It is noteworthy that the increase of TMA flux also leads to low V/III ratio, but it scarcely varies P_{Al} . Therefore, the reduction of P2 cannot be expected by the adjustment of TMA flux.

Thus far, we discussed the importance of the growth conditions to reduce PDs based on the thermodynamic study without considering the crystal orientations. Strictly, the surface energy difference between c -plane and r -plane AlN should be considered for the calculations. Recently, A. Kusaba *et al.* proposed a new thermodynamic analysis method for the vapor phase epitaxy considering the impacts of the crystal orientation on the growth dynamics [45]. In the report, the surface energy of InN was incorporated by ab-initio calculations. Hence, further analyses considering the growth direction are needed as the future works.

3.7 Summary

We performed the CL and PL measurements to clarify the dominant nonradiative recombination paths in AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ structures. TDs and two types of PDs (P1 and P2) mainly act as nonradiative recombination centers, and their activation energies are estimated to be ~ 2.5 , 10, and 130 meV respectively. In spite of the large activation energy, P2 predominantly affects the emission intensity at room temperature due to its high trap density. Therefore, we firstly have to reduce P2 (not TDs) to improve the IQE of AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ structures. Since the deep level emissions at 3.2 and 3.5–3.7 eV were enhanced by hole transfers to P2 near room temperature regions, we pointed out that the P2 may be fully, negatively charged $V_{\text{Al}}\text{-O}_{\text{N}}$ complex defects. The formation energy of V_{Al} in AlN is smaller than that of V_{Ga} in GaN, and P2 can be easily generated in AlN and Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ structures. As a result, the impacts of TDs in AlN are much smaller than those of GaN. Because P2 density may be changed by the growth conditions, the optimization of growth conditions with particular focus on the PD reduction is very important. From the thermodynamic study on AlN epitaxy, we clarified that high reactor pressure and decrease of NH_3 flux lead to high equilibrium Al partial pressures, which may reduce V_{Al} -related defects such as P2. In terms of the realization of smooth surfaces, we particularly recommend

the former method for semipolar plane growth and the latter method for c -plane growth.

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Chapter 4

Critical thickness for AlGa_N/AlN heterostructures

4.1 Introduction

Heteroepitaxial growth, which is an alloy of AlN and GaN, is an important technique used for QW structures in DUV emitters and AlGa_N/GaN structures in high electron mobility transistors. Because the lattice parameters of AlN are quite different from those of GaN (*a*-axis lattice mismatch $\sim 2.4\%$), AlGa_N epitaxial layers grown on AlN or GaN bulk substrates (or templates) inevitably involve large elastic strains. When epitaxial films are grown beyond the critical thickness, misfit dislocations (MDs), which remarkably degrade device performances, are generated in the heterointerface between the epitaxial and underlying layers.

Theoretical calculations of critical thickness for isotropic materials such as diamond and zincblende structures have been well discussed for many years, and several models have been advocated to explain the experimental results. For example, Matthews–Blakeslee (M–B) model well reproduces the critical thickness of InGaAs/GaAs and GaAsP/GaAs systems [1, 2], whereas People–Bean model [3] is used for SiGe/Si structures. In M–B model, a force balance for the dislocation bending is calculated, and MDs are generated by glides of pre-existing threading dislocations (TDs) in the crystals. Because there are an adequate quantity of TDs in GaAs substrates ($50\text{--}10^3\text{ cm}^{-2}$) for the dislocation glides [4, 5], M–B model is applied to InGaAs/GaAs and GaAsP/GaAs systems. Fischer *et al.* [6] developed M–B model taking into account effects of the free-surface and elastic interaction between dislocations. On the other hand, for SiGe/Si structures, MDs are newly induced in the heterointerfaces by the energetic equilibrium (People–Bean model) because there are almost no TDs in Si substrates.

Recently, critical-thickness calculations for anisotropic wurtzite semiconductors such as InGa_N/GaN and AlGa_N/GaN systems have been performed by extending the aforementioned models to wurtzite structures [7, 8]. Typical TD densities (TDDs) in current GaN

bulk (AlN bulk) substrates and GaN templates (AlN templates) grown on sapphire substrates are $\sim 10^5$ (10^2 – 10^4) [9] and $> 10^8$ ($> 10^9$) cm^{-2} , respectively. The TDDs are higher than GaAs substrates, and the extended M–B model (or Fischer model) seems to be applicable for AlGa_N heterostructures. However, it has been reported that AlGa_N films with thicknesses exceeding the critical thickness based on the M–B model by more than an order of magnitude are pseudomorphically grown on (0001) (*c*-plane) AlN substrates [10], and the mechanism of such phenomena has yet to be clear. Although the lattice relaxations are generally determined by X-ray diffraction (XRD) measurements, synchrotron-based X-ray topography measurement has clarified that the sensitivity of the XRD measurement for lattice relaxations is not necessarily good in the case of partial relaxations for ZnSe/GaAs structures [11].

In this chapter, we characterize the lattice relaxations of AlGa_N/AlN heterostructures investigating the surface morphologies and the optical properties in addition to the conventional XRD measurements. To explain the results, a novel slip system is advocated to reproduce the experimental results.

4.2 Experimental procedures

c-Plane AlGa_N heterostructures were grown on *c*-plane AlN bulk, *c*-plane sapphire, and *a*-plane sapphire substrates using the MOVPE method. The AlN substrates were prepared by physical vapor transport method, and the surfaces were chemically mechanically polished. Prior to epitaxy, the AlN substrates were wet etched in a 3:1 H₂SO₄:H₃PO₄ mixture for 10 min at 90 °C in order to remove an aluminum hydroxide layer formed on the surface. Wet-etched substrates were then rinsed in deionized water for 15 min, dried with flowing nitrogen, and transferred into a reactor for MOVPE. The temperature was increased under H₂ and ammonia (NH₃) atmosphere, and AlN substrates were annealed for 15 min at 1215°C just before growth.

For the sapphire substrates, *in-situ* nitridation treatments using NH₃ in the MOVPE reactor were performed instead of the annealing [12, 13]. We experimentally confirmed that *c*-plane AlN epitaxial films were grown on *a*-plane sapphire substrates by appropriately adjusting the *in-situ* nitridation conditions [13]. AlN epitaxial layers were grown at 1200°C after the substrate treatments, and AlGa_N/AlN or AlGa_N/AlGa_N heterostructures were subsequently fabricated on the AlN layers at lower temperatures for Ga incorporation. Note that we used cap layers with the same Al compositions as the barrier layers (or underlying layers of the heterostructures) for all of the samples to suppress the decomposition of Ga atoms from the epilayers below the cap layers. Trimethylaluminum (TMA), trimethylgallium (TMG), and NH₃ were used for AlGa_N/AlN growth as precursors for Al, Ga, and N, respectively. In the growth, TMA, TMG, and NH₃ was supplied with 4.11, 8.18, and 893 $\mu\text{mol}/\text{min}$, respectively. TMG and triethylgallium (TEG) were used as Ga precursors

for well layers and barrier layers in AlGa_N/AlGa_N structures, respectively. (The precursor difference has no scientific reasons but for the restriction of the growth machine.) All the growth processes and surface treatments in an MOVPE reactor were performed at 76 Torr.

XRD measurements were performed to determine the Al compositions and thicknesses of AlGa_N heterostructures, and to assess lattice relaxation. The surface morphologies were assessed by laser scanning microscopy (LSM).

The optical properties were characterized by photoluminescence (PL) and time-resolved PL (TRPL) spectroscopy. The excitation light source for TRPL was a Ti:Al₂O₃ fourth harmonic generation laser with a pulse repetition rate and width of 4 MHz (0.8 MHz) and 1.5 ps, respectively. In TRPL measurements, to selectively excite the AlGa_N layers, the excitation wavelength was adjusted to ~ 210 nm, and the estimated initial carrier density in AlGa_N/AlN QWs and AlGa_N/AlGa_N QWs were $0.95\text{--}5.0 \times 10^{14}$ and 1.0×10^{15} cm⁻³, respectively (sufficiently weak excitation condition). TRPL signals were detected by a streak camera.

Selectively-excited, time-integrated PL for AlGa_N layers was also performed using the above-mentioned Ti:Al₂O₃ fourth harmonic generation laser, but the pulse repetition rate was adjusted to 80 MHz. Additionally, above-bandgap-excited PL was performed using a pulsed ArF excimer laser (193 nm) with a repetition frequency of 25 Hz and a pulse duration of 4 ns. The PL signals were focused on the entrance of a 50-cm monochromator and the detection was ensured by a liquid-N₂-cooled CCD camera.

4.3 Definition of coordinates

Here, we define two orthogonal coordinate systems for the following discussions in this chapter. The (x', y', z') coordinate is defined for an arbitrary growth plane as shown in Fig. 4.1. The x' and y' axes are in the growth plane, while the z' axis is parallel to the growth direction. The y' axis is parallel to a line intersection between (0001) and the growth plane. The x' axis is orthogonal to the y' axis within the growth plane. On the other hand, the (x, y, z) coordinate is defined for wurtzite structures (see Fig. 4.1). The x and y axes are in (0001). The y axis is defined to agree with the y' axis, and the x axis is perpendicular to the y axis within (0001). The z axis is parallel to [0001]. Furthermore, we define θ as an angle between the z and z' axes, and ϕ as an angle between the y (y') axis and $\langle 11\bar{2}0 \rangle$ ($0^\circ \leq \theta \leq 90^\circ$, $0^\circ \leq \phi \leq 30^\circ$). Therefore, the angles ϕ and θ determine the off-direction and the off-angle of the growth plane, respectively. When (0001) is the growth plane without any off angles, the z' axis corresponds with the z axis. In such a case, x and y (x' and y') axes are two arbitrary perpendicular directions in (0001).

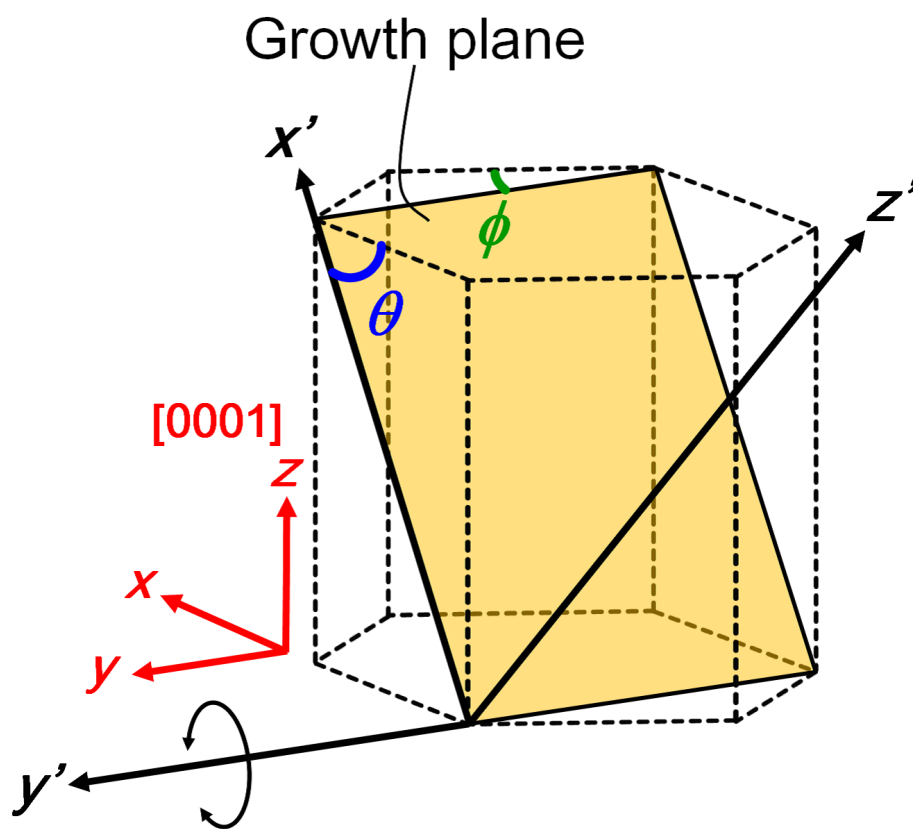


Figure 4.1: Definitions of the (x, y, z) and (x', y', z') coordinates. θ means an off-angle of a growth plane and ϕ determines the off-direction (x direction). ($0^\circ \leq \theta \leq 90^\circ$, $0^\circ \leq \phi \leq 30^\circ$)

4.4 Conventional slip systems for (0001) growth and sensitivity of XRD measurements

Herein, we review the conventional slip systems and critical thickness for (0001) heterostructures, and the calculated results are compared with the reported experimental results obtained by XRD measurements.

Critical thickness based on the M–B model and Fischer model can be calculated by considering the force balance on dislocation lines. When the force due to the misfit strain (F_a) is larger than the line tension of the dislocation (F_l), a MD is generated at the heterointerface by a dislocation glide. F_a is expressed as

$$F_a = \sigma b h \cos \lambda, \quad (4.1)$$

where σ , b , and h are the in-plane stress due to the lattice mismatch, the magnitude of the Burgers vector, and the epitaxial layer thickness which corresponds with the length of threading dislocations, respectively. λ is the angle between the Burgers vector and the direction in the growth plane, normal to the dislocation line [1]. In the case of the M–B model for (0001) growth without any off-angles ($\theta = 0^\circ$), σ induced by isotropic in-plane lattice mismatch is expressed as

$$\sigma = \frac{(C_{11} + C_{12}) C_{33} - 2C_{13}^2}{C_{33}} \epsilon, \quad (4.2)$$

where ϵ and C_{ij} are the in-plane misfit strain and the elastic stiffness coefficients, respectively. Using the a -axis lattice constants of the substrate (a_{sub}) and the epilayers (a_{epi}), ϵ is written as

$$\epsilon = \frac{a_{\text{sub}} - a_{\text{epi}}}{a_{\text{epi}}}. \quad (4.3)$$

In the Fischer model, σ is modified considering the effects of the free-surfaces as

$$\sigma' = \frac{(C_{11} + C_{12}) C_{33} - 2C_{13}^2}{C_{33}} \left(\epsilon - \frac{b \cos \lambda}{2h} \right). \quad (4.4)$$

When epitaxial films are grown on (0001), F_l , which is equivalent to dislocation elastic energy per unit length, is written as

$$F_l = \frac{1}{4\pi} (K_s b_s^2 + K_{e\perp} b_{e\perp}^2 + K_{e\parallel} b_{e\parallel}^2) \ln \left(\frac{h}{r_0} \right), \quad (4.5)$$

where r_0 is the dislocation core radius, which is b/e (e is base of natural logarithm) in the M–B model ($r_0 = b$ in the Fischer model). Here, b_s is a screw component of a Burgers vector, whereas $b_{e\perp}$ and $b_{e\parallel}$, which are edge components of the Burgers vector, are perpendicular and parallel to the c -axis direction, respectively. Therefore, the total edge component (b_e)

of the Burgers vector can be written as $\sqrt{b_{e\perp}^2 + b_{e\parallel}^2}$. K_s , $K_{e\perp}$, and $K_{e\parallel}$ are the respective dislocation energy coefficients, which depend only on the elastic constants [8, 14]. They are defined as

$$K_s = \sqrt{\frac{C_{44}(C_{11} - C_{12})}{2}}, \quad (4.6)$$

$$K_{e\perp} = \left(\sqrt{C_{11}C_{33}} + C_{13}\right) \sqrt{\frac{C_{44}(\sqrt{C_{11}C_{33}} - C_{13})}{C_{33}(\sqrt{C_{11}C_{33}} + C_{13} + 2C_{44})}}, \quad (4.7)$$

$$K_{e\parallel} = \left(\sqrt{C_{11}C_{33}} + C_{13}\right) \sqrt{\frac{C_{44}(\sqrt{C_{11}C_{33}} - C_{13})}{C_{11}(\sqrt{C_{11}C_{33}} + C_{13} + 2C_{44})}}. \quad (4.8)$$

In the force balance model, $F_a = F_l$ is satisfied at the critical thickness ($h = h_c$) for each slip system. Some typical slip systems of wurtzite III-nitride semiconductors are shown in Fig. 4.2, where slip planes and Burgers vectors not only for polar plane but also semi/non polar planes are illustrated. Semipolar $\{11\bar{2}2\}$ and $\{1\bar{1}01\}$ slips [Fig. 4.2(b)] have been conventionally considered for (0001) heterostructures [7, 8, 15, 16], whereas (0001) slip [Fig. 4.2(a)] has been advocated for semipolar plane growth. In the case of nonpolar plane heteroepitaxial growth, nonpolar plane slips [Fig. 4.2(c)] are generally used for the explanations of lattice relaxations [17].

Particularly for the semipolar plane $\{11\bar{2}2\}$ and $\{1\bar{1}01\}$ slips in (0001) growth, MDs with Burgers vectors $1/3\langle 11\bar{2}3 \rangle$ are generally considered as lattice relaxation sources. Therefore, the b equals to $\sqrt{a^2 + c^2}$, where a and c are the a -axis and c -axis lattice constants. In the case of the $\{11\bar{2}2\}\langle 11\bar{2}3 \rangle$ slip system, the b_s , $b_{e\perp}$, and $b_{e\parallel}$ are obtained as

$$b_s = 0, \quad (4.9)$$

$$b_{e\perp} = a, \quad (4.10)$$

$$b_{e\parallel} = c. \quad (4.11)$$

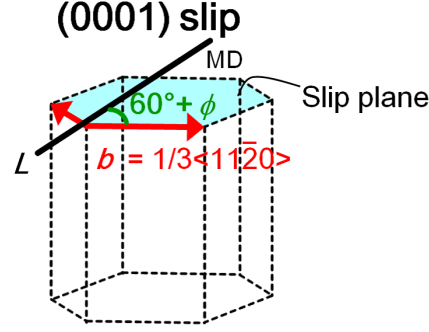
Similarly, for the $\{1\bar{1}01\}\langle 11\bar{2}3 \rangle$ slip system, the each component of the Burgers vector is expressed as

$$b_s = a/2, \quad (4.12)$$

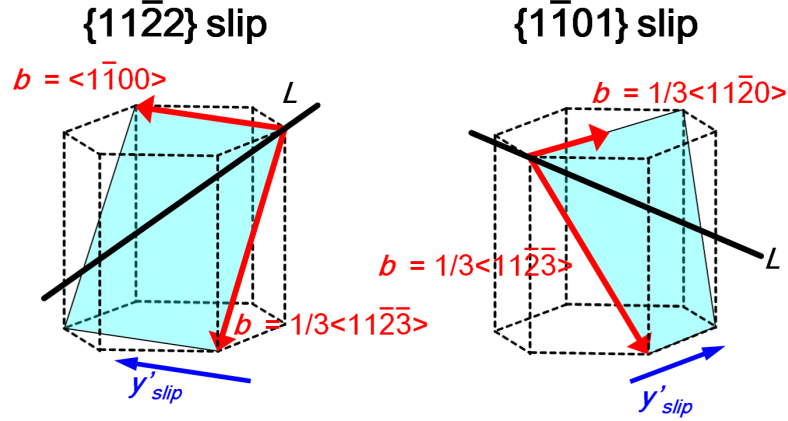
$$b_{e\perp} = \sqrt{3}a/2, \quad (4.13)$$

$$b_{e\parallel} = c. \quad (4.14)$$

(a) Polar plane slip



(b) Semipolar plane slips



(c) Nonpolar plane slips

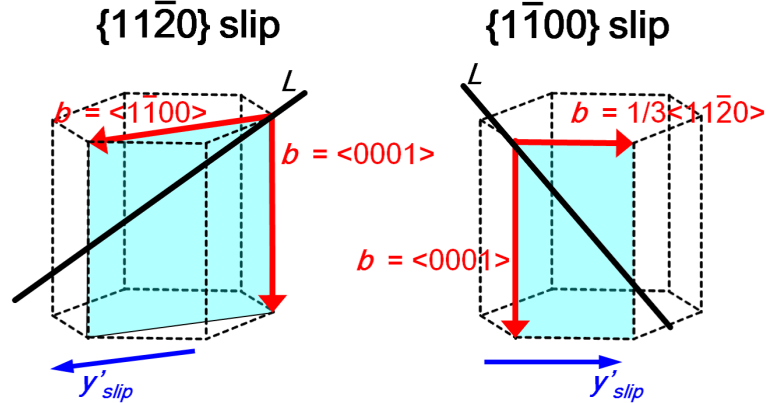


Figure 4.2: Typical slip systems of wurtzite III-nitride semiconductors. (a) Polar plane slip (0001) $\langle 11\bar{2}0 \rangle$ system. (b) Semipolar plane slips $\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$, $\{11\bar{2}2\} \langle 1\bar{1}00 \rangle$, $\{1\bar{1}01\} \langle 11\bar{2}3 \rangle$, and $\{1\bar{1}01\} \langle 11\bar{2}0 \rangle$ systems. (c) Nonpolar plane slips $\{11\bar{2}0\} \langle 0001 \rangle$, $\{11\bar{2}0\} \langle 1\bar{1}00 \rangle$, $\{1\bar{1}00\} \langle 0001 \rangle$, and $\{1\bar{1}00\} \langle 11\bar{2}0 \rangle$ systems. L and y'_{slip} are discussed later with Fig. 4.11 and the related text.

For both of the slip systems, the angle λ is obtained by

$$\cos \lambda = \frac{b_e}{b} \cos \alpha, \quad (4.15)$$

where α is the angle between the slip plane and growth plane.

The calculated critical thickness of the $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ system for (0001) AlGa_N/AlN heterostructures is depicted as lines in Fig. 4.3. (For simplicity, the critical thickness of the $\{1\bar{1}01\} \langle 11\bar{2}\bar{3} \rangle$ system is omitted here.) A solid line and a broken line in Fig. 4.3 are the critical thicknesses based on the M–B model and Fischer model, respectively. Some reports on lattice relaxations for (0001) AlGa_N/AlN heterostructures determined by XRD measurements [10, 18–26] are also plotted in Fig. 4.3. We found that the experimentally obtained boundaries of the pseudomorphically grown and relaxed samples are scarcely depend on the substrates, AlN or sapphire. Because there is an adequate quantity of TDs in AlN templates to relax the lattice mismatch by dislocation glides, the critical-thickness calculations based on the force balance model should be appropriate method for the current AlGa_N/AlN heterostructures even on the AlN substrates (TDD: 10^2 – 10^4 cm^{−2}).

However, the critical thickness estimated by XRD measurements exceeds the calculated results by more than one order of magnitude. Furthermore, to reproduce the experimental results using the M–B model with the $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ system, the induced in-plane misfit strains must be only 5% of the actual values (see a dash-dotted line in Fig. 4.3). This is a quite unusual condition, and we think that the sensitivity of XRD measurements for lattice relaxations of AlGa_N/AlN heterostructures may not be good, similar to ZnSe/GaAs structures [11]. Thus, we investigated the lattice relaxations (0001) AlGa_N/AlN heterostructures using other characterization methods as follows.

4.5 Extraordinary growth surface

Subsequently, we fabricated Al_{0.7}Ga_{0.3}N films with various thicknesses (3–490 nm) on AlN homoepitaxial layers, and they were capped with 310-nm-thick AlN layers. The surface morphologies of the AlN cap layers were assessed by LSM. When the AlGa_N layers are relatively thin, the surface morphologies of the cap layers are very smooth without any structural defects. On the other hand, when the thickness of AlGa_N layers is more than 15 nm, we found that stripe-shaped defects appear on the AlN surfaces as shown in Fig. 4.4. The stripe-shaped defects are not cracks because the stripe areas are higher (~ 10 μ m) than the other smooth areas. It was clarified that the density of the stripe defects become higher with increasing the AlGa_N layer thickness. In addition, there are some large pits, which are deeper than 100 μ m, on the AlN surface fabricated on 490-nm-thick AlGa_N layers.

However, we experimentally confirmed that such structural defects cannot be observed on thick AlGa_N surfaces without AlN cap layers. Therefore, it was clarified that the AlN cap layers are extraordinarily grown on the thick AlGa_N films. It is noteworthy that we

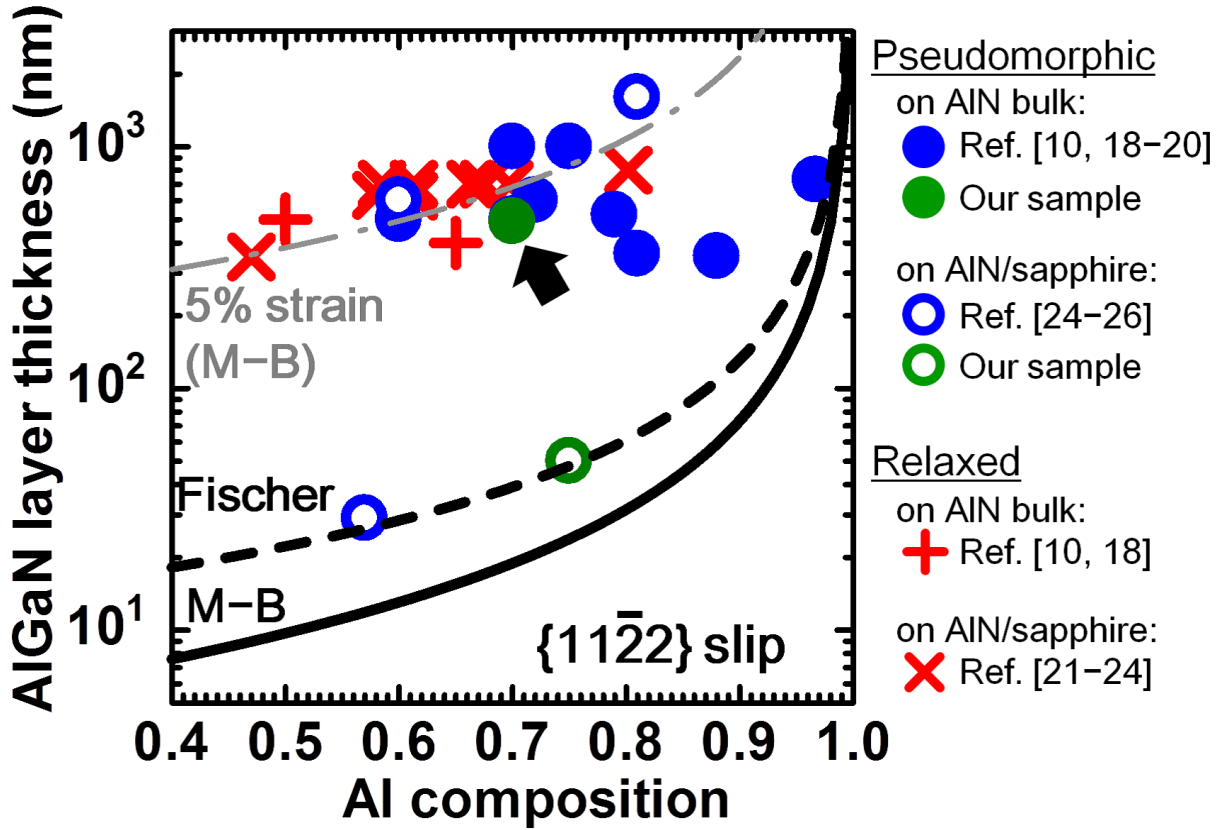


Figure 4.3: Lattice relaxations of (0001) AlGaIn/AlN heterostructures experimentally determined by XRD measurements [10, 18–26]. Calculated critical thicknesses based on the M–B and Fischer models considering a conventional slip system for (0001) growth ($\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$ system) are shown as a solid and a broken lines, respectively. A dash-dotted line is a calculated result using the M–B model assuming 5% of in-plane misfit strains.

can observe the extraordinary growth surfaces only when the underlying AlGa_N layers are thicker than a certain thickness. This result indicates that the extraordinary growth surfaces are caused by the lattice mismatch between the AlN cap layers and relaxed underlying AlGa_N layers. Because the thick AlGa_N films on AlN templates should be partially relaxed, thicker AlGa_N layers cause the higher density of surface defects due to the higher relaxation degrees.

Furthermore, we performed reciprocal space mapping (RSM) measurements for the 490-nm-thick Al_{0.7}Ga_{0.3}N layer, which is marked by the arrow in Fig. 4.3. The RSMs of the sample around (10 $\bar{1}$ 5) and (11 $\bar{2}$ 4) are shown in Figs. 4.5(a) and (b), respectively. Although RSM measurements are generally used for the characterization of a lattice relaxation, we cannot confirm any lattice relaxations of the thick AlGa_N layers in the both RSMs. Thus, we found that the 490-nm-thick Al_{0.7}Ga_{0.3}N layers seem to be pseudomorphically grown on AlN along any in-plane directions in terms of XRD measurements, in spite of the extraordinary growth surface as shown in Fig. 4.4. These results indicate that the sensitivity of the XRD measurements for lattice relaxations of (0001) AlGa_N heterostructures is not necessarily good in the case of partial relaxations.

4.6 Optically determined critical thickness

4.6.1 TRPL decay curves

To further elucidate the poor sensitivity of the XRD measurements for lattice relaxations, we investigated the evidence of lattice relaxations through some optical characterizations in addition to the above mentioned extraordinary growth surface.

At first, we performed TRPL measurements at 6.5 K for *c*-plane AlGa_N/AlN QWs fabricated on AlN substrates. Figure 4.6 shows the TRPL decay curves at the peak emission energies of *c*-plane Al_{0.8}Ga_{0.2}N/AlN 3QWs with various well widths. The TRPL decay curves were single exponentially fitted using

$$I_{\text{TRPL}} = A \exp\left(-\frac{t}{\tau}\right), \quad (4.16)$$

where τ is the carrier recombination lifetime and A is a coefficient. When the well widths are varied from 1.4 to 4.7 nm, the estimated carrier lifetimes are increased from 63.4 to 277 ns. This is because wider wells are more strongly affected by the internal electric field and have lower radiative recombination probabilities. Therefore, the estimated carrier lifetimes of the QWs with 1.4 and 4.7 nm well layers are mainly determined by radiative recombination processes. On the other hand, when the well widths are further widened from 4.7 to 6.8 nm, the carrier lifetimes are drastically decreased from 277 to 6.0 ns. In addition to the lifetime shortening, the time-integrated emission intensity also becomes weaker for the 6.8-nm-thick QW ($< 1/5$). These experimental results indicate that nonradiative recombination processes

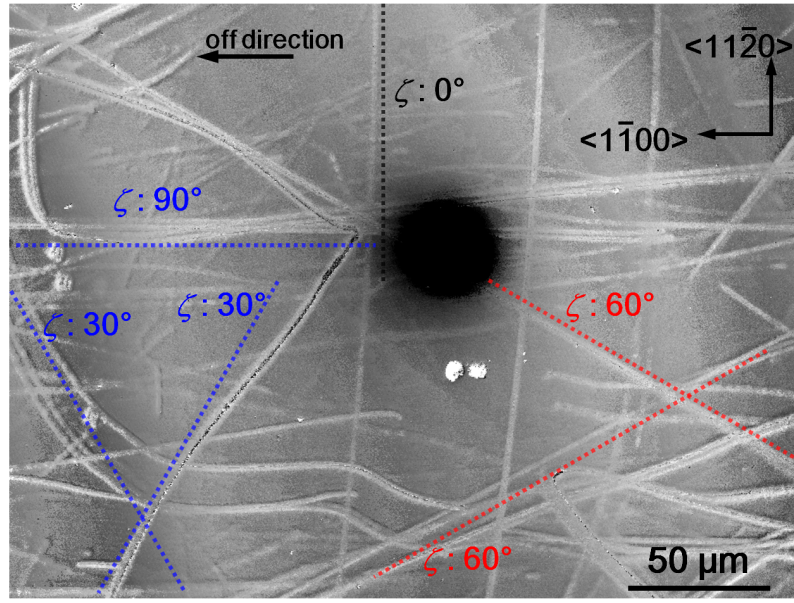


Figure 4.4: Surface morphology of a 310-nm-thick AlN cap layer fabricated on the 490-nm-thick $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$ film on the AlN homoepitaxial layer assessed by LSM. In the image, bright areas mean higher regions compared with the other smooth areas, whereas dark areas mean the recessed regions. The stripe-shaped defects, which are higher ($\sim 10 \mu\text{m}$) than smooth areas, appear on the surfaces. In addition, some large pits, which are deeper than $100 \mu\text{m}$, are observed. ζ is defined in Fig. 4.11, and each dotted line indicates the possible MD line direction due to the lattice relaxation by each slip system with the respective ζ .

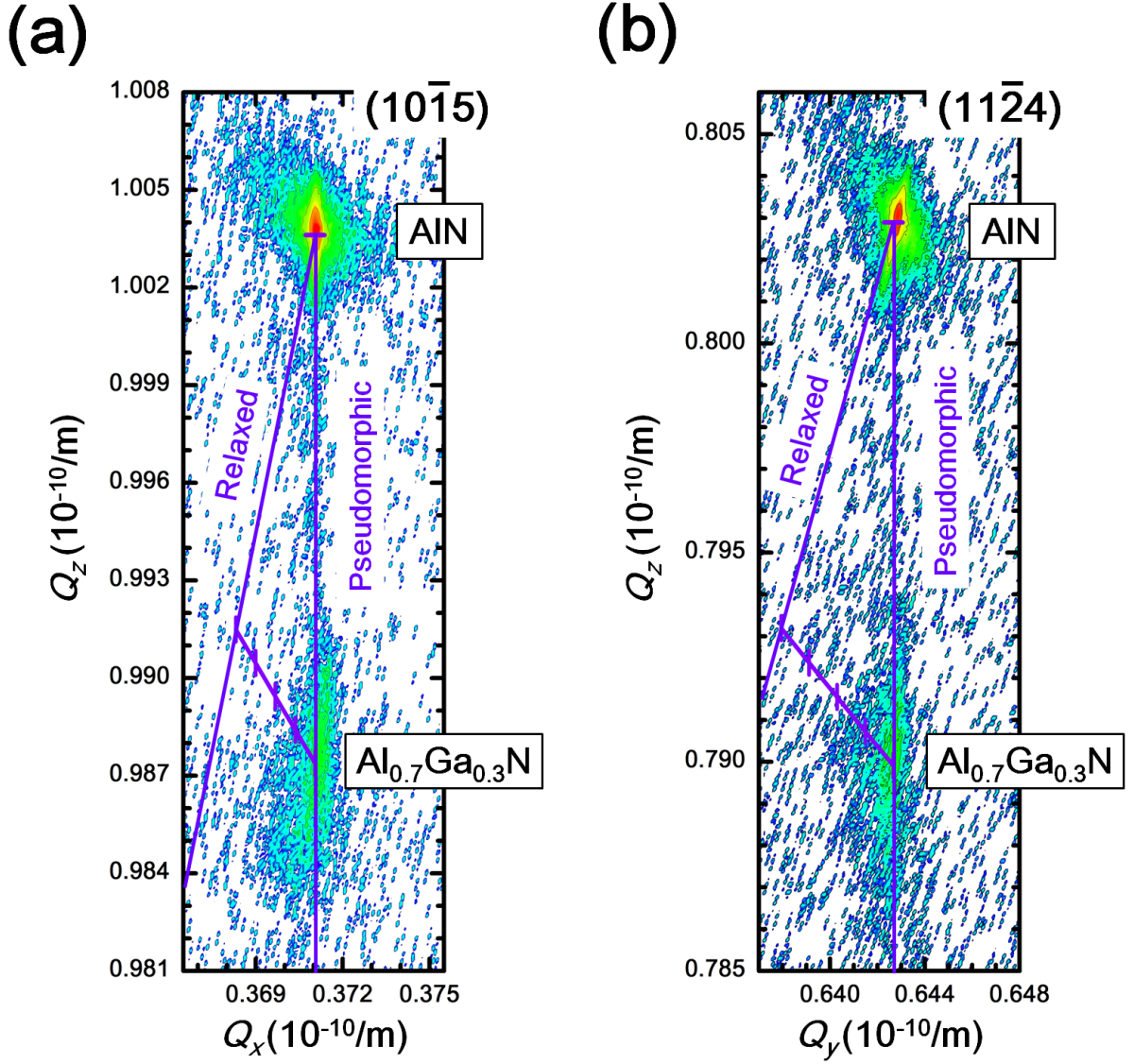


Figure 4.5: RSMs of a 490-nm-thick $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$ layer on AlN, which is marked by the arrow in Fig. 4.3, around (a) $(10\bar{1}5)$ and (b) $(11\bar{2}4)$.

are enhanced in the 6.8-nm-thick QW due to the MD generations. Thus, the obtained carrier lifetime of the 6.8-nm-thick QW is dominated by the nonradiative recombination processes due to the lattice relaxations. Therefore, we found that the TRPL measurement is much more sensitive for lattice relaxations of AlGa_N/AlN heterostructures compared with the observation of surface morphologies and the conventional XRD measurements.

4.6.2 Photon energy dependence of recombination lifetime

Within a spectrum, the carrier lifetimes estimated by TRPL measurements often depend on the emission wavelengths. As an example of the phenomenon, there is a weakly localized model [27], which is well known for compound semiconductor materials including InGa_N/Ga_N QWs. In the model, compositional and well-width fluctuations in QWs cause potential fluctuations and create carrier localization centers. In such a case, the estimated carrier lifetimes at the higher emission energies are shorter than those at the lower emission energies because the carriers excited at the higher energy states are rapidly transferred to the potential minima. On the other hand, the estimated lifetimes at lower energy states are well approximate radiative recombination lifetimes.

Figures 4.7(a)–(c) shows the photon energy dependence of the carrier lifetimes estimated by TRPL measurements for Al_{0.8}Ga_{0.2}N/AlN 3QWs with various well widths (1.4–6.8 nm). In the case of 1.4- and 4.7-nm-thick QWs, the estimated lifetimes are shorter for higher energy states as predicted by the weakly localized model, and the results also support that the estimated carrier lifetimes of these QWs in Fig. 4.6 are mainly determined by radiative recombination processes. Note that the short lifetimes at the energies lower than 4.6 eV in Fig. 4.7 (b) may be due to the effect of LO phonon replicas.

In contrast, for the 6.8-nm-thick QW which has MDs because of the lattice relaxations (see Fig. 4.6), the estimated lifetimes are longer for higher energy states. This result indicates that the nonradiative recombination processes due to the MDs are enhanced at lower energy states. For AlGa_N QW structures, the emission energies at the Ga-rich and wider-well regions are theoretically lower than those at the other regions. Therefore, the MDs in the 6.8-nm-thick QW are preferably generated at the Ga-rich or wider-well regions, where the forces due to the misfit strains (F_a) expressed in Eq. (4.1) are particularly large. These are quite reasonable results, which also well agree with the cathodoluminescence mapping result reported in Ref. [28].

4.6.3 Emission line width and PL peak energy

In addition to the carrier lifetimes, we also investigated other optical properties in the relaxed samples. Figure 4.8(a) shows the full width at half maximums (FWHMs) of PL spectra of *c*-plane Al_{0.80}Ga_{0.20}N/AlN QWs on AlN substrates and *c*-plane Al_{0.79}Ga_{0.21}N/AlN QWs fabricated on sapphire substrates. The QWs on sapphire substrates are grown by a

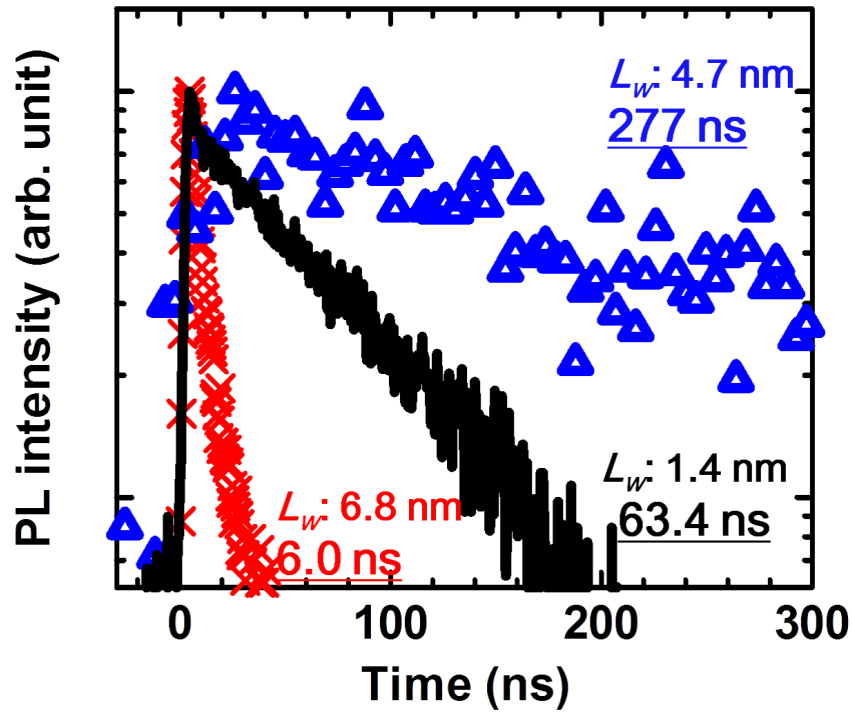


Figure 4.6: TRPL decay curves at the peak emission energies of c -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ 3QWs with various well widths (1.4–6.8 nm). The measurements were performed at 6.5 K. The drastic lifetime shortening is observed in 6.8-nm-thick QW, which indicates the enhanced nonradiative recombination processes due to the MD generations.

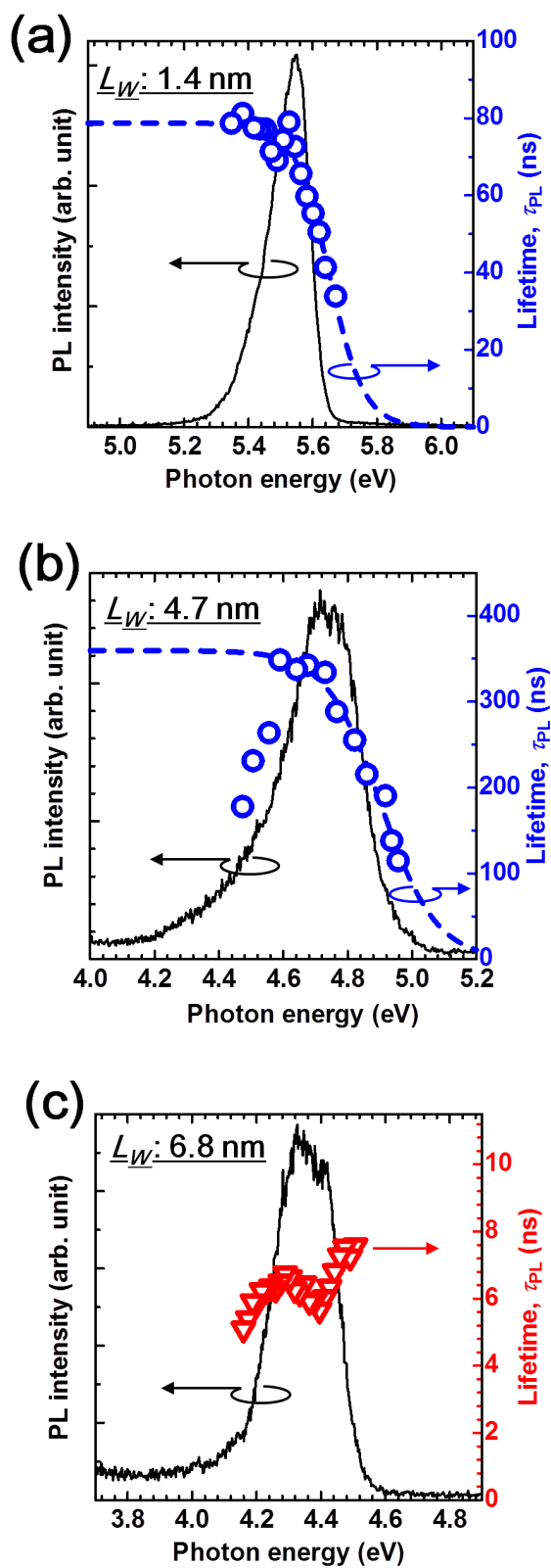


Figure 4.7: Photon energy dependences of the carrier lifetimes at 6.5 K estimated by TRPL measurements for Al_{0.8}Ga_{0.2}N/AlN 3QWs with (a) 1.4-, (b) 4.7-, and (c) 6.8-nm-thick well layers.

modified-MEE (migration enhanced epitaxy) method with a unique precursor supply [29] without *in-situ* nitridation treatments.

The emission line widths theoretically become broader for wider QWs because the effects of Al compositional fluctuations get stronger with increasing well widths due to the internal electric fields in the QWs as described in Chap. 2. However, the FWHMs of the PL spectra of the wide QWs, for which the experimental results of the other optical characterizations suggest lattice relaxation, are narrower than those of pseudomorphically grown samples as shown in Fig. 4.8(a). Considering the lattice relaxations in the wider QWs, the narrow line widths may be related to the MDs. As we mentioned above, the MDs are preferably generated at the Ga-rich or wider-well regions in the QW structures. Therefore, the emission intensities at the lower energy states should be drastically weakened due to the MDs, and only the emissions at the higher energy states may be dominantly observed as the PL spectra. As a consequence, the emission line widths may become narrower compared with the pseudomorphically grown samples.

Thus, we calculated the energy fluctuations for Al_{0.8}Ga_{0.2}N/AlN QWs considering the well-width and Al composition fluctuations as shown in Fig. 4.8(b). Here, we assumed ± 1 ML well-width fluctuations and $\pm 1\%$ Al compositional fluctuations for the pseudomorphically grown samples. For the relaxed samples, we calculated the potential fluctuations assuming -1 ML well-width and $+1\%$ compositional fluctuations because the emissions from the lower energy states cannot be observed due to the MDs generated at the Ga-rich and wider-well regions. Note that we do not consider the decrease of the internal electric fields due to the strain relaxations for the relaxed samples because the lattice relaxations should partially occur and are insufficient to obviously decrease the internal electric fields. In Fig. 4.8(b), broken lines, dash-dotted lines, and solid lines are the calculated energy fluctuations due to the well-width, Al compositional, and their total fluctuations, respectively.

Comparing Figs. 4.8(a) and (b), the experimental results well agree with the calculated results particularly for the pseudomorphic samples and the relaxed 10-nm-thick Al_{0.79}Ga_{0.21}N/AlN QW. Therefore, the results also support the assumption that the spectral narrowings are caused by the lattice relaxations. For the relaxed 6.8-nm-thick Al_{0.80}Ga_{0.20}N/AlN QW, the experimental result is located between the calculated results for the pseudomorphic and relaxed samples. It means that the annihilation of the emissions at lower energy states due to MDs is weaker than the assumption in the calculation. This is because the lattice relaxation in the 6.8-nm-thick Al_{0.80}Ga_{0.20}N/AlN QW may be weak.

The emission annihilation at lower energy states should also affect the well-width dependence of the PL peak energies. Figure 4.9 shows the well width dependence of the PL peak energies of Al_{0.80}Ga_{0.20}N/AlN and Al_{0.65}Ga_{0.35}N/AlN QWs fabricated on *c*-plane AlN substrates. The calculated results of the transition energies of the QWs assuming the respective internal electric fields of 2.3 and 4.2 MV/cm are depicted as solid lines. Although the calculated results well reproduce the experimental results for the pseudomorphically grown QWs, the experimental PL peak energies of the relaxed samples are hardly varied

with increasing the well widths. This is partially because the MDs generated at the potential minima interfere the red shifts for wider QWs due to the emission annihilation at lower energy states. Another reason for the interference of the red shifts may be the decrease of the internal electric fields due to the strain relaxations (but as discussed above, this effect seems minor).

4.6.4 Comparison between optically determined critical thickness and calculation results

Even when lattice relaxations are not detected by XRD measurements, latently relaxed samples give off some unique optical signals as we described above. In particular, the carrier lifetime shortening observed by the TRPL measurement is the most sensitive for the MD generations, and we can optically determine the critical thickness using TRPL measurements instead of the conventional XRD measurements. Figure 4.10 shows the optically determined lattice relaxations for various (0001) AlGa_N/AlN QWs on the different AlN templates. The calculated critical thicknesses based on the M–B model considering the conventional $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ system and a novel (0001) $\langle 11\bar{2}0 \rangle$ system are depicted as a broken line and a solid line, respectively. (In the calculations, we assumed the unintentional off-angle ($\theta = 0.15^\circ$, $\phi = 15^\circ$) using the equations which will be discussed in the following Sec. 4.7.) The horizontal axis of Fig. 4.10 is an effective Al composition, which is the averaged Al composition of the entire MQW except for the cap layer. In the case of MQW structures, calculated critical thickness considering the effective composition has well reproduced the experimental results for semipolar InGa_N/Ga_N MQWs [8].

Regardless of the kind of the AlN templates, optically determined critical thickness is more than two orders of magnitude thinner than the critical thickness estimated by the conventional XRD measurements as shown in Fig. 4.3. Furthermore, it was clarified that the experimental results well agree with the calculated critical thickness based on the (0001) $\langle 11\bar{2}0 \rangle$ slip system instead of the conventional $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ system. However, (0001) slip is generally excluded for (0001) heterostructures because the slip plane corresponding with the heterointerface does not experience a shear component of the lattice mismatch stress [15]. On the other hand, practical growth planes must have unintentional off-angles, and lattice relaxations due to the (0001) $\langle 11\bar{2}0 \rangle$ slips seems possible even for (0001) heterostructures with small off-angles in theory. In Sec. 4.7, we discuss the possibility of (0001) slip for the practical (0001) heterostructures by extending the conventional calculation models.

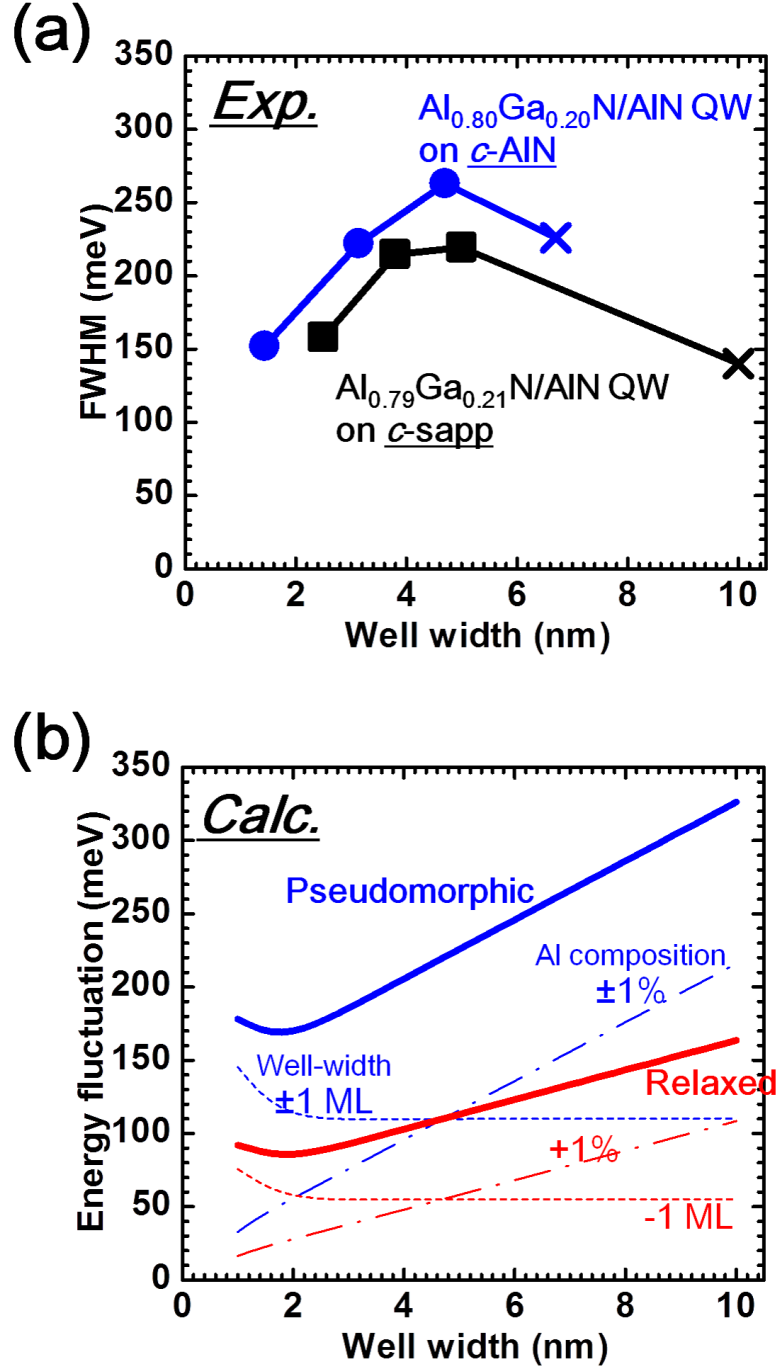


Figure 4.8: (a) FWHMs of the PL spectra of $\text{Al}_{0.80}\text{Ga}_{0.20}\text{N/AlN}$ QWs on AlN substrates and $\text{Al}_{0.79}\text{Ga}_{0.21}\text{N/AlN}$ QWs fabricated on sapphire substrates. (b) Calculated energy fluctuations for the pseudomorphically grown samples assuming the ± 1 ML well-width and $\pm 1\%$ Al compositional fluctuations. For the relaxed samples, we assumed -1 ML well width and $+1\%$ compositional fluctuations. Note that we do not consider the decrease of the internal electric fields due to the strain relaxations for the relaxed samples because the lattice relaxations should partially occur and are insufficient to obviously decrease the internal electric fields.

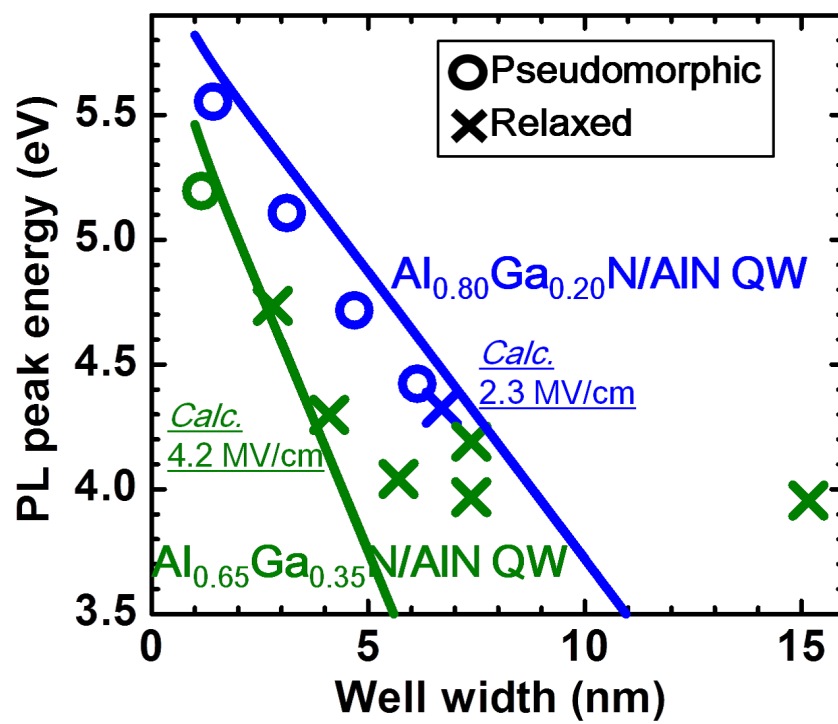


Figure 4.9: Well-width dependences of PL peak energies of $\text{Al}_{0.80}\text{Ga}_{0.20}\text{N}/\text{AlN}$ and $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}/\text{AlN}$ QWs fabricated on AlN substrates. Calculated results of the transition energies of the QWs assuming the respective internal electric fields of 2.3 and 4.2 MV/cm are depicted as solid lines.

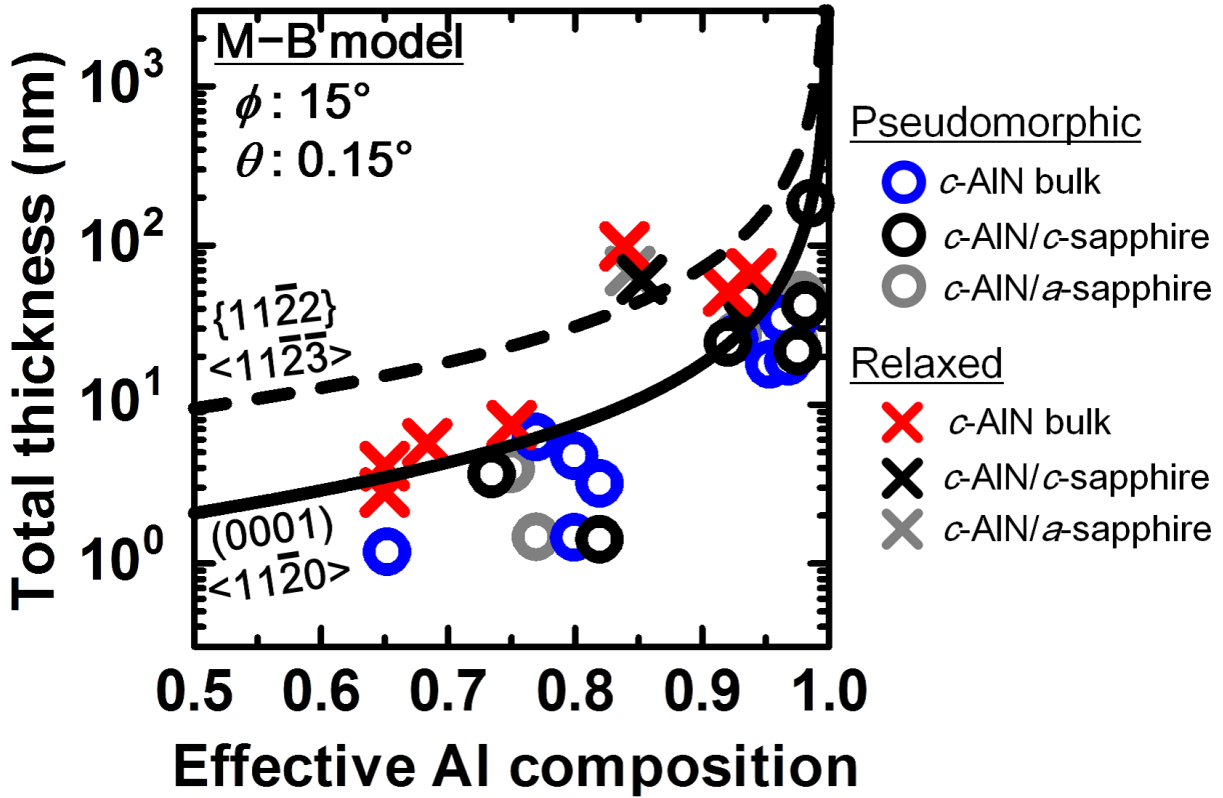


Figure 4.10: Symbols indicate optically determined lattice relaxations for various (0001) AlGaN/AlN QWs on the different AlN templates. Calculated critical thicknesses based on the M-B model considering the conventional $\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$ system and a novel (0001) $\langle 11\bar{2}0 \rangle$ system are depicted as a broken line and a solid line, respectively. In the calculations, we assumed the unintentional off-angle ($\theta = 0.15^\circ$, $\phi = 15^\circ$) using the equations which will be discussed in Sec. 4.7. Here, we set “+” in Eqs. (4.29) and (4.30) for (0001) $\langle 11\bar{2}0 \rangle$ system in Sec. 4.7.

4.7 Possibility of (0001) slip in (0001) growth

4.7.1 Extension of critical-thickness calculation based on the force balance model

Prior to the discussion about the possibility of (0001) slips for (0001) heterostructures, critical-thickness calculations considering the off-angles are demonstrated. Thus, we extend the conventional force balance models with arbitrary slip systems for arbitrary growth planes (arbitrary θ and ϕ) in this section.

As depicted in Fig. 4.2, the semipolar and nonpolar slip planes are inclined toward $\langle 11\bar{2}0 \rangle$ or $\langle 1\bar{1}00 \rangle$, which is defined as $\{11\bar{2}n\}$ or $\{1\bar{1}0m\}$ slip, respectively (n and m are arbitrary integers). Here, we define a y'_{slip} axis as the direction parallel to the line intersection between (0001) and the slip plane.

Figure 4.11 shows a schematic image of the correlation between a slip plane and a growth plane. MD lines ($\mathbf{L}$) are along the line intersection between the slip plane and growth plane, and the angle between $\mathbf{L}$ and (0001) is defined as γ ($0^\circ \leq \gamma \leq 90^\circ$). Additionally, we define the angles β ($0^\circ \leq \beta \leq 90^\circ$), ζ ($0^\circ \leq \zeta \leq 90^\circ$), and ρ as an angle between the slip plane and (0001), an angle between y' (y) and y'_{slip} , and an angle between $\mathbf{L}$ and y'_{slip} , respectively.

4.7.1.1 Strain tensor elements

The force due to the misfit strain (F_a) expressed in Eq. (4.1) is drastically changed by the in-plane strain condition. When the growth planes are inclined from (0001), the in-plane strains become anisotropic states reflecting the wurtzite structure. Herein, we discuss the expression of the anisotropic strains to extend the calculation model.

The expressions of the strain tensor elements, which we used in this study, are basically the same as those in Ref. [30]. ϵ_{ij} , which represents strain tensor elements, in the (x, y, z) coordinate can be written as

$$\epsilon_{xx} = \epsilon_{xx0} + R \frac{\sin \theta}{\cos \theta} \epsilon_{xz}, \quad (4.17)$$

$$\epsilon_{yy} = \epsilon_{yy0}, \quad (4.18)$$

$$\epsilon_{zz} = \epsilon_{zz0} + R^{-1} \frac{\cos \theta}{\sin \theta} \epsilon_{xz}, \quad (4.19)$$

$$\epsilon_{xy} = \epsilon_{yz} = 0, \quad (4.20)$$

where

$$\epsilon_{xx0} = (1 - r_{x0}) \frac{a_{\text{sub}} - a_{\text{epi}}}{a_{\text{epi}}}, \quad (4.21)$$

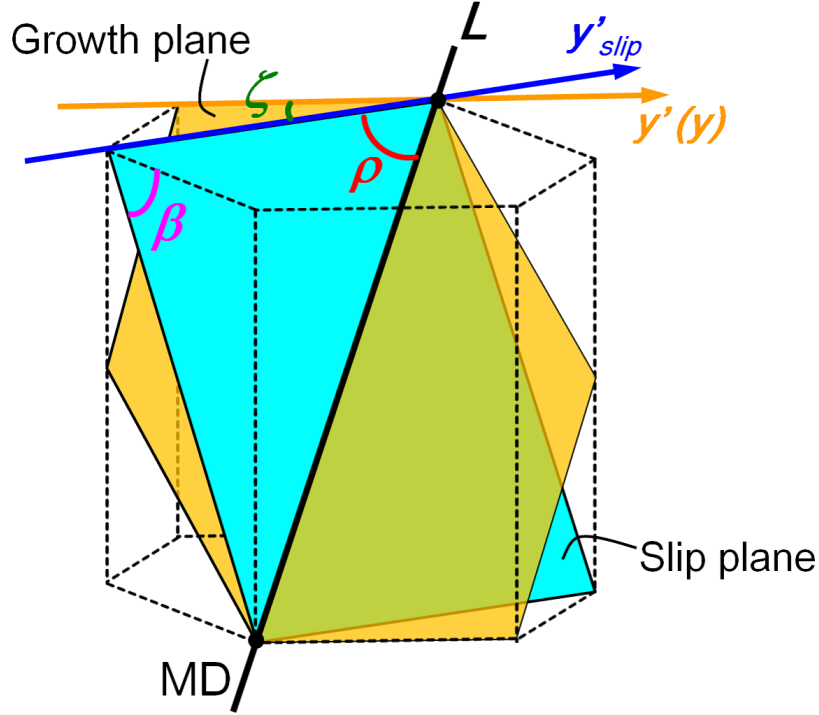


Figure 4.11: Schematic image of the correlation between a slip plane and a growth plane. MD lines (L) are along the line intersection between slip and growth planes. We define the angles β ($0^\circ \leq \beta \leq 90^\circ$), ζ ($0^\circ \leq \zeta \leq 90^\circ$), and ρ as an angle between the slip plane and (0001), an angle between y' (y) and y'_{slip} , and an angle between L and y'_{slip} , respectively.

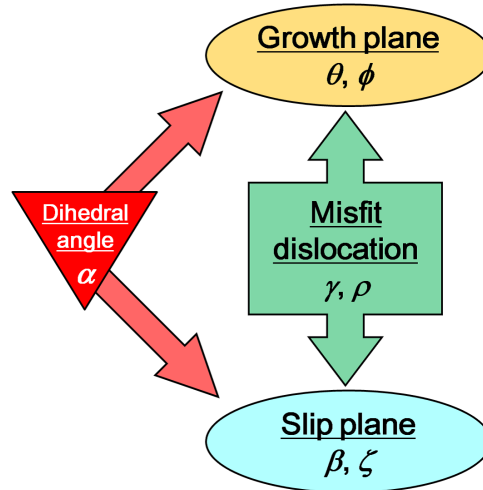


Figure 4.12: Correlations of the angles used in this study are summarized. The angles θ and ϕ determine the growth planes, and the slip planes can be expressed by β and ζ . ζ is a function of ϕ as described in Eqs. (4.36) and (4.37). Thus, the dihedral angle (α) of the slip plane and growth plane is obtained by functions of θ , β , and ζ (ϕ). The directions of MDs are determined by the angles γ and ρ , which are also expressed by θ , β , and ζ (ϕ) as written in Eqs. (4.39) and (4.40).

$$\epsilon_{yy0} = (1 - r_{y0}) \frac{a_{\text{sub}} - a_{\text{epi}}}{a_{\text{epi}}}, \quad (4.22)$$

$$\epsilon_{zz0} = (1 - r_{z0}) \frac{c_{\text{sub}} - c_{\text{epi}}}{c_{\text{epi}}}, \quad (4.23)$$

$$R = \frac{1 + \epsilon_{xx0}}{1 + \epsilon_{zz0}}, \quad (4.24)$$

$$\begin{aligned} \epsilon_{xz} = & \\ & - \frac{[(C_{11}\epsilon_{xx0} + C_{12}\epsilon_{yy0} + C_{13}\epsilon_{zz0}) \sin^2 \theta + (C_{13}\epsilon_{xx0} + C_{13}\epsilon_{yy0} + C_{33}\epsilon_{zz0}) \cos^2 \theta] \sin \theta \cos \theta}{C_{11}R \sin^4 \theta + [(R + R^{-1}) C_{13} + 4C_{44}] \sin^2 \theta \cos^2 \theta + C_{33}R^{-1} \cos^4 \theta}. \end{aligned} \quad (4.25)$$

Here, r_{i0} ($0 \leq r_{i0} \leq 1$) is related to the relaxation degree of epilayers along the i axis, and we use $r_{i0} = 0$ for fully strained epilayers. [r_{i0} can be calculated by the following Eqs. (4.103)–(4.105) after MDs are generated.] ϵ_{ij} in the (x', y', z') coordinate can be written as

$$\epsilon_{x'x'} = \epsilon_{xx} \cos^2 \theta + \epsilon_{zz} \sin^2 \theta - \epsilon_{xz} \sin 2\theta, \quad (4.26)$$

$$\epsilon_{y'y'} = \epsilon_{yy} = \epsilon_{yy0}, \quad (4.27)$$

$$\epsilon_{z'z'} = \epsilon_{xx} \sin^2 \theta + \epsilon_{zz} \cos^2 \theta + \epsilon_{xz} \cos 2\theta. \quad (4.28)$$

Assuming $\theta = 0^\circ$ and $r_{i0} = 0$, $\epsilon_{x'x'} = \epsilon_{xx} = \epsilon_{y'y'} = \epsilon_{yy} = \epsilon$ is satisfied, and we can confirm the isotropic in-plane strains for (0001) growth without any off-angles. In addition, a famous equation, $\epsilon_{z'z'} = \epsilon_{zz} = -2C_{13}/C_{33}\epsilon$ is also obtained.

4.7.1.2 Expression of F_a and F_l

The forces F_a and F_l depend on the $\mathbf{L}$ and Burgers vector, and are determined by the correlation between the growth plane and slip system. As shown in Fig. 4.11, MDs are generated along the line intersection of the slip plane and growth plane. In this study, we consider the MDs with the Burgers vectors along y' direction or the line intersections between the m -plane and slip plane (see Fig. 4.2). Note that only the Burgers vectors along $\langle 11\bar{2}0 \rangle$ are considered for (0001) slips.

(a) Burgers vector components in $(0001)\langle 11\bar{2}0 \rangle$ system

At first, we discuss MDs caused by $(0001)\langle 11\bar{2}0 \rangle$ slips. Dislocations with the Burgers vectors $1/3\langle 11\bar{2}0 \rangle$ are generally known as “*a*-type” dislocations in hexagonal materials because the magnitudes correspond with the *a*-axis lattice constants.

For the $(0001)\langle 11\bar{2}0 \rangle$ slip system, generated MDs should lay on (0001) and the directions are perpendicular to the growth off-directions. Therefore, the angles between $\mathbf{b}$ and $\mathbf{L}$ are expressed as $(60^\circ \pm \phi)$, and the screw and edge components of the Burgers vectors are

$$b_s = b \sin(60^\circ \pm \phi), \quad (4.29)$$

$$b_e = b \cos(60^\circ \pm \phi), \quad (4.30)$$

where

$$b = a. \quad (4.31)$$

The “ $\pm$ ” in Eqs. (4.29) and (4.30) are derived from the two equivalent Burgers vectors as depicted in Fig. 4.2(a). Note that b_s and b_e are uniquely determined for $\langle 1\bar{1}00 \rangle$ off samples ($\phi = 0^\circ$). The b_e for (0001) slips can be further resolved into three orthogonal components as

$$b_{ex} = b_e, \quad (4.32)$$

$$b_{ey} = 0, \quad (4.33)$$

$$b_{ez} = 0, \quad (4.34)$$

where b_{ei} are the *i* direction components of b_e . Considering the correspondence of the *y* and *y'* axes, Eqs. (4.32)–(4.34) indicate that MDs caused by the (0001) slips cannot relax the in-plane misfit strains along *y'* direction. Therefore, the lattice relaxations due to the $(0001)\langle 11\bar{2}0 \rangle$ system cause the anisotropic in-plane relaxation processes.

To obtain the strain force (F_a), the angle α is also an important factor as written in Eqs. (4.1) and (4.15). For the (0001) slip, α is given by

$$\alpha = \theta. \quad (4.35)$$

(b) Burgers vector components in semipolar- and nonpolar-plane slip systems

Subsequently, we discuss MDs caused by semipolar and nonpolar plane slips. In these slip systems, the angles β , ζ , and ρ shown in Fig. 4.11 should be additionally considered, different from the (0001) slips. Furthermore, we consider two types of the Burgers vectors

for all the non- c -plane slip systems in this study (Fig. 4.2). One is parallel to y'_{slip} direction, the other is along the line intersections between the m -plane and slip plane. The former type of Burgers vectors does not have “ c -type” component, whereas the latter type of Burgers vectors has “ c -type” component.

The angle ζ is determined by the correlation between the off-directions of the growth plane and slip plane. For $\{1\bar{1}0m\}$ slips, ζ is written as

$$\zeta = \phi, \quad 60^\circ + \phi, \quad 60^\circ - \phi \quad (4.36)$$

whereas ζ for $\{11\bar{2}n\}$ slips is expressed as

$$\zeta = 90^\circ - \phi, \quad 30^\circ - \phi, \quad 30^\circ + \phi. \quad (4.37)$$

Hence, there are basically two calculation results for each slip system in the following discussions due to the different ζ , which are derived from the equivalent slip planes. Using the angle ζ , α is obtained by

$$\cos \alpha = \cos \theta \cos \beta + \sin \theta \sin \beta \cos \zeta. \quad (4.38)$$

Assuming $\beta = 0^\circ$ in Eq. (4.38), we can confirm the relation $\alpha = \theta$, which is obtained for the (0001) slips as described in Eq. (4.35). In addition, the angles ρ and γ are given by

$$\tan \rho = \frac{\sin \theta \sin \zeta}{\sin \beta \cos \theta + \cos \beta \sin \theta \cos \zeta}, \quad (4.39)$$

$$\sin \gamma = \sin \rho \sin \beta, \quad (4.40)$$

respectively, where γ is the angle between (0001) and $\mathbf{L}$.

The correlations of the angles used in this study are summarized in Fig. 4.12. The angles θ and ϕ determine the growth plane, and the slip plane can be expressed by β and ζ . The ζ is a function of ϕ as described in Eqs. (4.36) and (4.37). Thus, the dihedral angle (α) of the slip plane and growth plane is obtained as functions of θ , β , and ζ (ϕ). The direction of MDs ($\mathbf{L}$) is determined by the angles γ and ρ , which are expressed by θ , β , and ζ (ϕ) as written in Eqs. (4.39) and (4.40).

(b-i) MDs with “ c -type” components

Herein, we discuss MDs with Burgers vectors which have “ c -type” components. Using the angles that we mentioned above, b_s and b_e for $\{1\bar{1}0m\}$ slips are expressed as

$$b_s = \frac{b}{\sqrt{3 + \cos^2 \beta}} \left| \sqrt{3} \sin \rho \mp \cos \rho \cos \beta \right|, \quad (4.41)$$

$$b_e = \frac{b}{\sqrt{3 + \cos^2 \beta}} \left| \sqrt{3} \cos \rho \pm \sin \rho \cos \beta \right|, \quad (4.42)$$

respectively. The “ $\mp$ ” and “ $\pm$ ” in Eqs. (4.41) and (4.42) are derived from the two equivalent Burgers vectors, which are similar to “ $\pm$ ” in Eqs. (4.29) and (4.30) for (0001) slips.

On the other hand, the b_s and b_e for $\{11\bar{2}n\}$ slips are written as

$$b_s = b \sin \rho, \quad (4.43)$$

$$b_e = b \cos \rho. \quad (4.44)$$

The b_s and b_e are uniquely determined for $\{11\bar{2}n\}$ slips in contrast to $\{1\bar{1}0m\}$ slips as described in Eqs. (4.43) and (4.44) because the Burgers vectors are always perpendicular to the y'_{slip} axes on these slip planes.

The edge components of the Burgers vectors for $\{1\bar{1}0m\}$ and $\{11\bar{2}n\}$ slips as expressed by Eqs. (4.42) and (4.44) are further resolved into

$$b_{ex} = b_e |\cos \rho \cos \zeta \cos \beta - \sin \rho \sin \zeta|, \quad (4.45)$$

$$b_{ey} = b_e (\cos \rho \sin \zeta \cos \beta + \sin \rho \cos \zeta), \quad (4.46)$$

$$b_{ez} = b_e \cos \rho \sin \beta. \quad (4.47)$$

It is noteworthy that the edge components exist along any directions unlike in (0001) slips. It means that the lattice relaxations caused by semipolar plane slips may occur along any directions. Assuming $\beta = \zeta = 0^\circ$ in Eqs. (4.45)–(4.47), we can obtain Eqs. (4.29)–(4.34) for (0001) slips.

The magnitude of the Burgers vector in $\{1\bar{1}01\}$ $\langle 11\bar{2}\bar{3} \rangle$ and $\{11\bar{2}2\}$ $\langle 11\bar{2}\bar{3} \rangle$ slips is expressed as

$$b = \sqrt{a^2 + c^2}. \quad (4.48)$$

Dislocations with such Burgers vectors are generally called as “***a+c*** type” dislocations in hexagonal materials. For nonpolar plane slips, the magnitude of the Burgers vector is

$$b = c. \quad (4.49)$$

Such dislocations are called as “***c***-type” dislocations.

(b-ii) MDs without “***c***-type” components

Furthermore, we discuss MDs with Burgers vectors which do not have “***c***-type” components. For any semipolar and nonpolar plane slips, the b_s and b_e are uniquely determined as follows,

$$b_s = b \cos \rho, \quad (4.50)$$

$$b_e = b \sin \rho, \quad (4.51)$$

respectively, because the Burgers vectors without “*c*-type” components are always parallel to the y'_{slip} axes. The edge components of the Burgers vectors are further resolved into

$$b_{ex} = b_e \sin \zeta, \quad (4.52)$$

$$b_{ey} = b_e \cos \zeta, \quad (4.53)$$

$$b_{ez} = 0. \quad (4.54)$$

Because the Burgers vector without “*c*-type” component is on (0001), the b_{ez} always equals to zero. However, the edge components of the Burgers vectors may exist along any in-plane directions as shown in Eqs. (4.52)–(4.53) in contrast to (0001) slips.

The magnitude of the Burgers vector for $\{1\bar{1}0m\} \langle 11\bar{2}0 \rangle$ slips is given by

$$b = a, \quad (4.55)$$

which corresponds to $1/3 \langle 11\bar{2}0 \rangle$. On the other hand, $\mathbf{b}$ equals to $\langle 1\bar{1}00 \rangle$ for $\{11\bar{2}n\} \langle 1\bar{1}00 \rangle$ slips. Thus, we have

$$b = \sqrt{3}a. \quad (4.56)$$

(c) $\mathbf{F}_a$ and stress expressions for arbitrary slip systems

Here, we obtain the expression of the force (F_a) due to the in-plane misfit strain using the aforementioned Burgers vector components. The stress along x' direction is expressed as

$$\sigma_{x'x'} = \frac{S'_{22}\epsilon_{x'x'} - S'_{12}\epsilon_{y'y'}}{S'_{11}S'_{22} - S'^2_{12}}, \quad (4.57)$$

where

$$S'_{11} = S_{11} \cos^4 \theta + S_{33} \sin^4 \theta + \frac{2S_{13} + S_{44}}{4} \sin^2 2\theta, \quad (4.58)$$

$$S'_{12} = S_{12} \cos^2 \theta + S_{13} \sin^2 \theta, \quad (4.59)$$

$$S'_{22} = S_{11}. \quad (4.60)$$

Here, S_{ij} are the elastic compliances, and the correlation between S_{ij} and C_{ij} are written as

$$S_{11} = \frac{C_{11}C_{33} - C_{13}^2}{\Delta}, \quad (4.61)$$

$$S_{12} = \frac{C_{13}^2 - C_{12}C_{33}}{\Delta}, \quad (4.62)$$

$$S_{13} = \frac{(C_{12} - C_{11})C_{13}}{\Delta}, \quad (4.63)$$

$$S_{33} = \frac{C_{11}^2 - C_{12}^2}{\Delta}, \quad (4.64)$$

$$S_{44} = \frac{1}{C_{44}}, \quad (4.65)$$

$$S_{66} = \frac{2}{C_{11} - C_{12}}, \quad (4.66)$$

where

$$\Delta = (C_{11} - C_{12}) [(C_{11} + C_{12}) C_{33} - 2C_{13}^2]. \quad (4.67)$$

Similarly, the stress along y' direction is expressed as

$$\sigma_{y'y'} = \frac{S'_{11}\epsilon_{y'y'} - S'_{12}\epsilon_{x'x'}}{S'_{11}S'_{22} - S'^2_{12}}. \quad (4.68)$$

In the calculation of F_a , the in-plane stress perpendicular to $\mathbf{L}$ should be considered. The stress is determined by the edge components of the Burgers vectors of MDs. Thus, using the b_{ex} , b_{ey} , and b_{ez} in each slip system, we obtain the in-plane stress (σ) along the lattice relaxation direction as

$$\sigma = \frac{(b_{ex} \cos \theta + b_{ez} \sin \theta)^2}{(b_{ex} \cos \theta + b_{ez} \sin \theta)^2 + b_{ey}^2} \sigma_{x'x'} + \frac{b_{ey}^2}{(b_{ex} \cos \theta + b_{ez} \sin \theta)^2 + b_{ey}^2} \sigma_{y'y'}. \quad (4.69)$$

Here, the term related to $\sigma_{x'y'}$ is omitted because $\sigma_{x'y'}$ equals to zero in the definition of the basis. The coefficient of $\sigma_{x'x'}$ ($\sigma_{y'y'}$) on the right hand side of Eq. (4.69) means the cosine (sine) squared of the angle between the x' axis and lattice relaxation direction. In the case of $b_{ey} = 0$, for example, the σ equals to $\sigma_{x'x'}$ because the lattice relaxations occur only along x' direction, which corresponds with the (0001) slips [see Eq. (4.33)]. In addition, when

$\epsilon_{x'x'}$ equals to $\epsilon_{y'y'}$ ($\theta = 0^\circ$), the σ always corresponds to $\sigma_{x'x'}$ ($= \sigma_{y'y'}$). This is the same condition as the (0001) heterostructures without any off-angles described in Eq. (4.2).

For the Fischer model, the $\sigma_{x'x'}$ and $\sigma_{y'y'}$ in Eq. (4.69) should be modified as

$$\sigma'_{x'x'} = \left(\sigma_{x'x'} - \frac{S'_{22}b \cos \lambda / 2h}{S'_{11}S'_{22} - S'^2_{12}} \right), \quad (4.70)$$

$$\sigma'_{y'y'} = \left(\sigma_{y'y'} - \frac{S'_{11}b \cos \lambda / 2h}{S'_{11}S'_{22} - S'^2_{12}} \right), \quad (4.71)$$

respectively.

Moreover, $\cos \lambda$ can be obtained by Eq. (4.15), and the force F_a due to the in-plane misfit strain can be calculated by Eqs. (4.1), (4.15), and (4.69) using b , b_e , and α of the slip system.

(d) F_l expression for all arbitrary slip systems

The line tension (F_l) of a TD against a glide strongly depends on the $\mathbf{L}$ direction due to the anisotropy of the hexagonal structure. In a conventional slip model for (0001) heterostructures, $\mathbf{L}$ is always perpendicular to c -axis ($\gamma = 0^\circ$), whereas in our calculation model, γ is determined by Eq. (4.40) and is not necessarily zero. For arbitrary $\mathbf{L}$ directions, the expression of F_l should be modified as

$$F_l = \frac{1}{4\pi} (K'_s b_s^2 + K'_e b_e^2 + 2K'_{es} b_e b_s) \ln \left(\frac{h}{r_0} \right), \quad (4.72)$$

where K'_s , K'_e , and K'_{es} are the dislocation energy coefficients, which depend on the elastic constants and the $\mathbf{L}$ direction. It is noteworthy that the dislocation energy factor involves the cross term (K'_{es}) between the edge and screw components of the dislocation unless the dislocation is perpendicular or parallel to the c -axis ($\gamma = 0^\circ, 90^\circ$) [31]. Considering the edge components of the Burgers vector out of and in (0001), K'_e is expressed as

$$K'_e = K_{e1} \cos^2 \chi + K_{e2} \sin^2 \chi, \quad (4.73)$$

where K_{e1} and K_{e2} are energy coefficients for the edge components out of and in (0001), respectively. Here, $b_e \cos \chi$ and $b_e \sin \chi$ mean the magnitudes of the respective edge components of the Burgers vector, and the angle χ is given by

$$\tan \chi = \frac{1}{\tan \beta \cos \rho}. \quad (4.74)$$

Similarly, the cross term K'_{es} in Eq. (4.72) is expressed as

$$K'_{es} = K_{es} \cos \chi. \quad (4.75)$$

Therefore, the $K'_{es}b_eb_s(=K_{es}b_e\cos\chi b_s)$ in Eq. (4.72) is considered for the edge component, which is out of (0001), and the screw component of the Burgers vector. Here, K'_s , K_{e1} , K_{e2} , and K_{es} are written as [31]

$$K'_s = \frac{C_{44}}{\delta_3} + \frac{1}{2C_{44}} \left[\frac{g(C_{11} - C_{12})^2 + \delta_{13}(2C_{44} - C_{11} + C_{12})^2}{8C_{11}C_{44}\sqrt{\delta_2 + 2\delta_1}} \sin^2 2\gamma \right. \\ \left. + (C_{11} - C_{12})(2C_{44} - C_{11} + C_{12}) \left(\sqrt{\delta_2 + 2\delta_1} - 2\delta_3 \right) \sin^2 \gamma \right], \quad (4.76)$$

$$K_{e1} = \frac{(C_{11} - C_{12})^2}{4C_{44}} \left[\frac{g \sin^4 \gamma + \delta_{13}\delta_3^4}{C_{11}C_{44}\sqrt{\delta_2 + 2\delta_1}} - 2\delta_3^2 \left(\sqrt{\delta_2 + 2\delta_1} - 2\delta_3 \right) \tan^2 \gamma \right], \quad (4.77)$$

$$K_{e2} = \frac{(C_{11} - C_{12})^2}{4C_{44}\delta_1} \left[\frac{g \sin^4 \gamma + \delta_{13}\delta_3^4}{C_{11}C_{44}\sqrt{\delta_2 + 2\delta_1}} + 2\delta_3 \left(\delta_3 \sqrt{\delta_2 + 2\delta_1} - 2\delta_1 \right) \tan^2 \gamma \right], \quad (4.78)$$

$$K_{es} = \frac{C_{11} - C_{12}}{4C_{44}} \left\{ \frac{\delta_{13}\delta_3^2(2C_{44} - C_{11} + C_{12}) - g(C_{11} - C_{12})\sin^2 \gamma}{2C_{11}C_{44}\sqrt{\delta_2 + 2\delta_1}} \sin 2\gamma \right. \\ \left. + [C_{11} - C_{12} + (2C_{44} - C_{11} + C_{12})\cos 2\gamma] \left(\sqrt{\delta_2 + 2\delta_1} - 2\delta_3 \right) \tan \gamma \right\}, \quad (4.79)$$

where δ_1 , δ_2 , δ_3 , δ_{13} , and g is defined as

$$\delta_1 = \sqrt{1 - \frac{C_{11} - C_{33}}{C_{11}} \cos^4 \gamma + \frac{C_{11}(C_{33} - 2C_{44}) - C_{13}(C_{13} + 2C_{44})}{4C_{11}C_{44}} \sin^2 2\gamma}, \quad (4.80)$$

$$\delta_2 = 2 + \frac{C_{11}(C_{33} - 2C_{44}) - C_{13}(C_{13} + 2C_{44})}{C_{11}C_{44}} \cos^2 \gamma, \quad (4.81)$$

$$\delta_3 = \sqrt{\sin^2 \gamma + \frac{2C_{44}}{C_{11} - C_{12}} \cos^2 \gamma}, \quad (4.82)$$

$$\delta_{13} = C_{11}C_{33} - C_{13}^2, \quad (4.83)$$

$$g = C_{11}C_{33} - (C_{13} + 2C_{44})^2. \quad (4.84)$$

In the case of $\theta = 0^\circ$, we can confirm that the K'_s , K_{e1} and K_{e2} correspond with the K_s , $K_{e||}$ and $K_{e\perp}$ in Eqs. (4.6)–(4.8), respectively. Additionally, $b_e \cos \chi$ and $b_e \sin \chi$ equal to

$b_{e\parallel}$ and $b_{e\perp}$ expressed in Eqs. (4.9)–(4.14), respectively. Therefore, calculated F_l at $\theta = 0^\circ$ is the same value as the conventional calculation model, which means that the extended calculation model considering the off-angle also involves the conventional slip system.

In the case of (0001) slip ($\beta = \zeta = 0^\circ$), $\rho = \gamma = 0^\circ$ and $\chi = 90^\circ$ are obtained by Eqs. (4.39), (4.40), and (4.74). Thus, we can write the energy coefficients of dislocations as

$$K'_s = \sqrt{\frac{C_{44}(C_{11} - C_{12})}{2}}, \quad (4.85)$$

$$K'_e = K_{e2} = \left(\sqrt{C_{11}C_{33}} + C_{13} \right) \sqrt{\frac{C_{44}(\sqrt{C_{11}C_{33}} - C_{13})}{C_{33}(\sqrt{C_{11}C_{33}} + C_{13} + 2C_{44})}}, \quad (4.86)$$

$$K'_{es} = 0. \quad (4.87)$$

When MDs are parallel to the c -axis direction ($\gamma = 90^\circ$), we have $\rho = \beta = 90^\circ$ and $\zeta \neq 0^\circ$.¹ At the same time, $\chi = 0^\circ$ is obtained, and the energy factors of dislocations are expressed as

$$K'_s = C_{44}, \quad (4.88)$$

$$K'_e = K_{e1} = \frac{C_{11}^2 - C_{12}^2}{2C_{11}}, \quad (4.89)$$

$$K'_{es} = 0. \quad (4.90)$$

Equation (4.39), $\rho = \beta = 90^\circ$, and $\zeta \neq 0^\circ$ give $\theta = 90^\circ$. The relations $\beta = 90^\circ$ and $\theta = 90^\circ$ mean the nonpolar plane slips for nonpolar plane growth, and the expressions described in Eqs. (4.88)–(4.90) correspond with those in Ref. [8]. Therefore, the expression of F_l can be extended for arbitrary slip systems and growth planes by Eq. (4.72) in addition to F_a .

4.7.2 Calculation results based on the extended force balance model

Here, we discuss the calculation results using our extended force balance model. All of the following calculation results are based on the extended M–B model. Solid lines in Fig. 4.13 show the off-angle and off-direction dependences of the calculated critical thicknesses due to the (0001) $\langle 11\bar{2}0 \rangle$ slip in $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ structures. The plus or minus signs in the figure correspond with the signs in Eqs. (4.29) and (4.30). It was clarified that the calculated critical thicknesses assuming “+” in Eqs. (4.29) and (4.30) are thinner than those assuming

¹In the case of $\zeta = 0^\circ$, $\mathbf{L}$ should be in (0001) as predicted from Eqs. (4.39) and (4.40) (see Fig. 4.11). Therefore, $\zeta \neq 0^\circ$ must be satisfied for $\gamma = 90^\circ$.

“−” for any growth planes. This is because the edge component of the Burgers vector assuming “+” is always larger than those assuming “−”, which causes larger F_a .

Similarly, Fig. 4.14 shows the off-angle and off-direction dependences of calculated critical thickness due to the $\{1\bar{1}01\}\langle 11\bar{2}3\rangle$ slip in Al_{0.7}Ga_{0.3}N/AlN structures. The angles in the figure mean ζ expressed in Eq. (4.36), and the plus or minus signs in the figure correspond with the sign “ $\pm$ ” in Eq. (4.42). [Meanwhile, the opposite sign is chosen for Eq. (4.41) due to the correlation between the Burgers vector and $\mathbf{L}$.] Fig. 4.14 indicates that the critical thicknesses assuming “+” in Eq. (4.42) are thinner than those assuming “−” for each ζ , similar to the $(0001)\langle 11\bar{2}0\rangle$ slip. Then, we use “+” in Eqs. (4.29) and (4.42) for the following critical-thickness calculations because MDs are more easily generated in such cases due to the thinner critical thicknesses.

Solid lines in Fig. 4.15 show the off-angle and off-direction dependences of the calculated critical thicknesses due to $\{1\bar{1}01\}$ and $\{11\bar{2}2\}$ slips in Al_{0.7}Ga_{0.3}N/AlN structures. The angles in the figure mean ζ expressed in Eqs. (4.36) and (4.37). When the off-direction is $\langle 11\bar{2}0\rangle$, $\{11\bar{2}2\}\langle 11\bar{2}3\rangle$ slip ($\zeta = 0^\circ$) is the most dominant slip system in semipolar plane slips for any off-angles. On the other hand, when the off-direction is $\langle 1\bar{1}00\rangle$, $\{11\bar{2}2\}\langle 11\bar{2}3\rangle$ slip ($\zeta = 30^\circ$) and $\{1\bar{1}01\}\langle 11\bar{2}3\rangle$ slip ($\zeta = 0^\circ$) are dominant slip systems for $0^\circ \leq \theta \leq 23^\circ$ and $23^\circ \leq \theta \leq 90^\circ$, respectively.

Solid lines in Fig. 4.16 show the off-angle and off-direction dependences of the calculated critical thicknesses due to the nonpolar $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ slips in Al_{0.7}Ga_{0.3}N/AlN structures. The angles in the figure mean ζ expressed in Eqs. (4.36) and (4.37). The $\{11\bar{2}0\}\langle 0001\rangle$ slip ($\zeta = 0^\circ$) and $\{1\bar{1}00\}\langle 0001\rangle$ slip ($\zeta = 0^\circ$) are the most dominant slip systems in the nonpolar plane slips when the off-directions are $\langle 11\bar{2}0\rangle$ and $\langle 1\bar{1}00\rangle$, respectively.

As we described above, critical thicknesses determined by various slip systems were calculated, and the dominant slip systems were indicated for all the off-angles as shown in Figs. 4.13–4.16. However, the calculated results have a crucial issue that the critical thicknesses can be calculated even when the slip planes are the same as the growth planes. Because the slip plane corresponding to the heterointerface does not experience a shear component of the lattice mismatch stress [15], the results are seemingly strange. Thus, we will discuss the limitation of slip systems in the next section to take the crucial issue the calculation model.

4.7.3 Limitation of slip system

Here, we discuss the limitation of slip systems from the perspectives of the line intersection density and the friction force due to the Peierls stress.

4.7.3.1 Line intersection density

As we mentioned above, MDs are generated on the line intersections between the slip planes and growth plane (see Fig. 4.11). Therefore, the line intersection density [LID (cm^{−1})] at

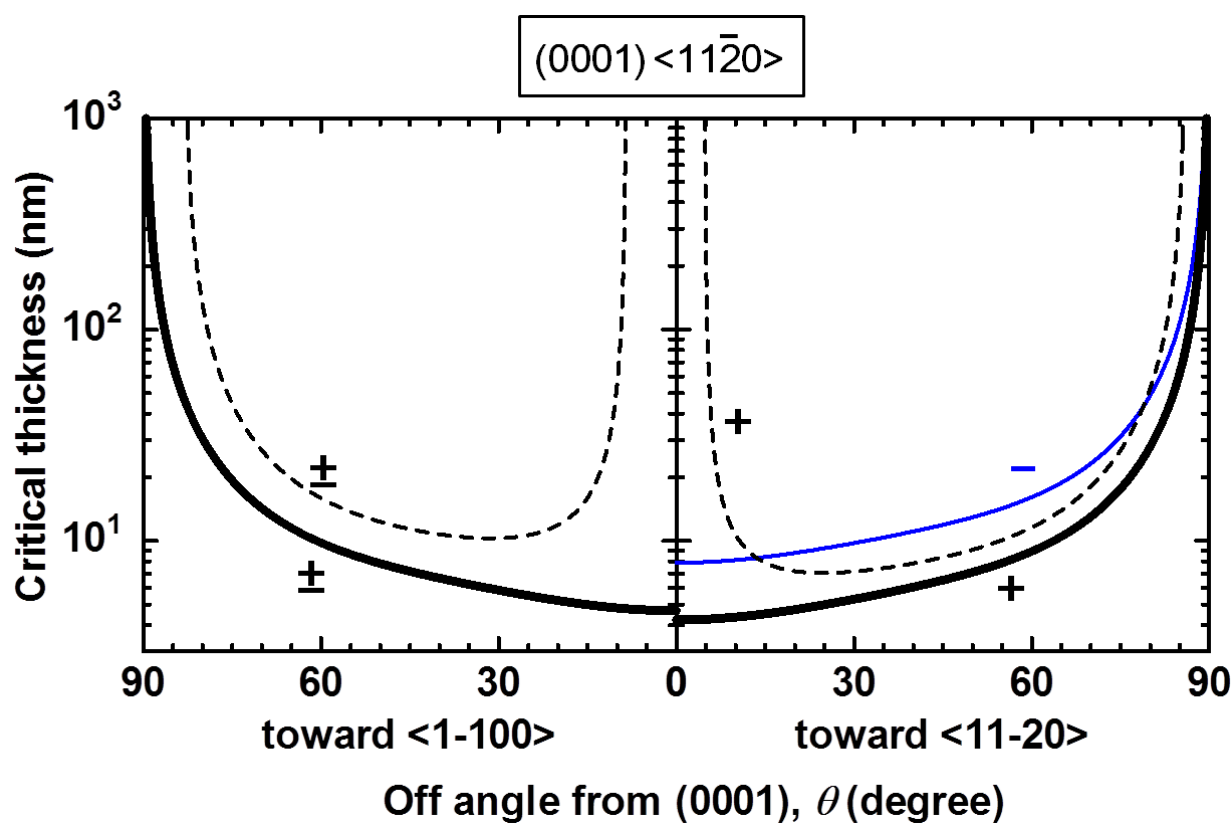


Figure 4.13: Off-angle and off-direction dependences of the calculated critical thicknesses due to the (0001) slip in $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ structures. The plus or minus signs correspond to the signs in Eqs. (4.29) and (4.30). The calculation results are based on the extended M–B model, and the solid lines are obtained by the relation $F_a = F_l$. Broken lines indicate the calculated critical thicknesses given by Eq. (4.96), which considers the effect of friction force due to the Peierls stress (Thermal assist is not considered here).

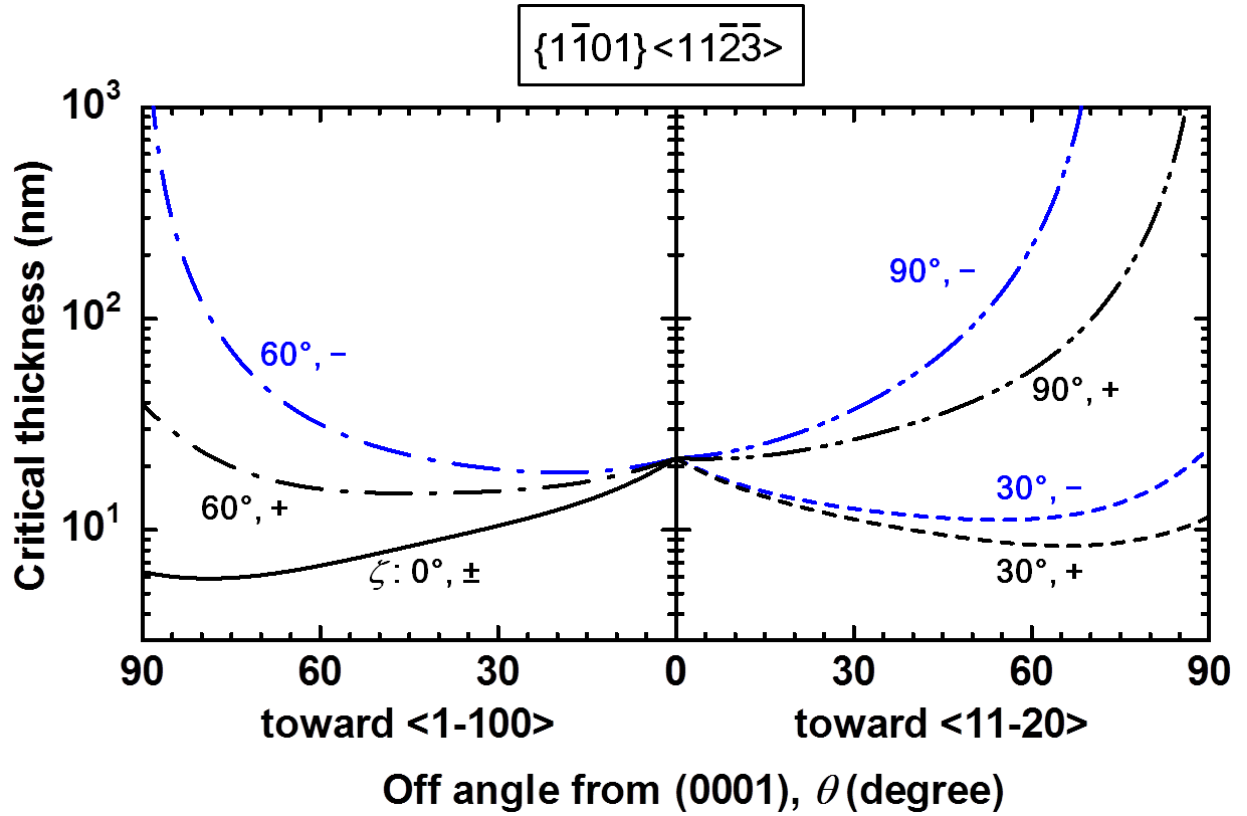


Figure 4.14: Off-angle and off-direction dependences of the calculated critical thicknesses due to the semipolar $\{1\bar{1}01\}\langle 11\bar{2}3\rangle$ slip in $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ structures. The angles in the figure mean ζ expressed in Eq. (4.36), and the plus or minus signs correspond to the sign “ $\pm$ ” in Eq. (4.42). [Meanwhile, the opposite sign is chosen for Eq. (4.41).] The calculation results are based on the extended M–B model and are obtained by the relation $F_a = F_l$.

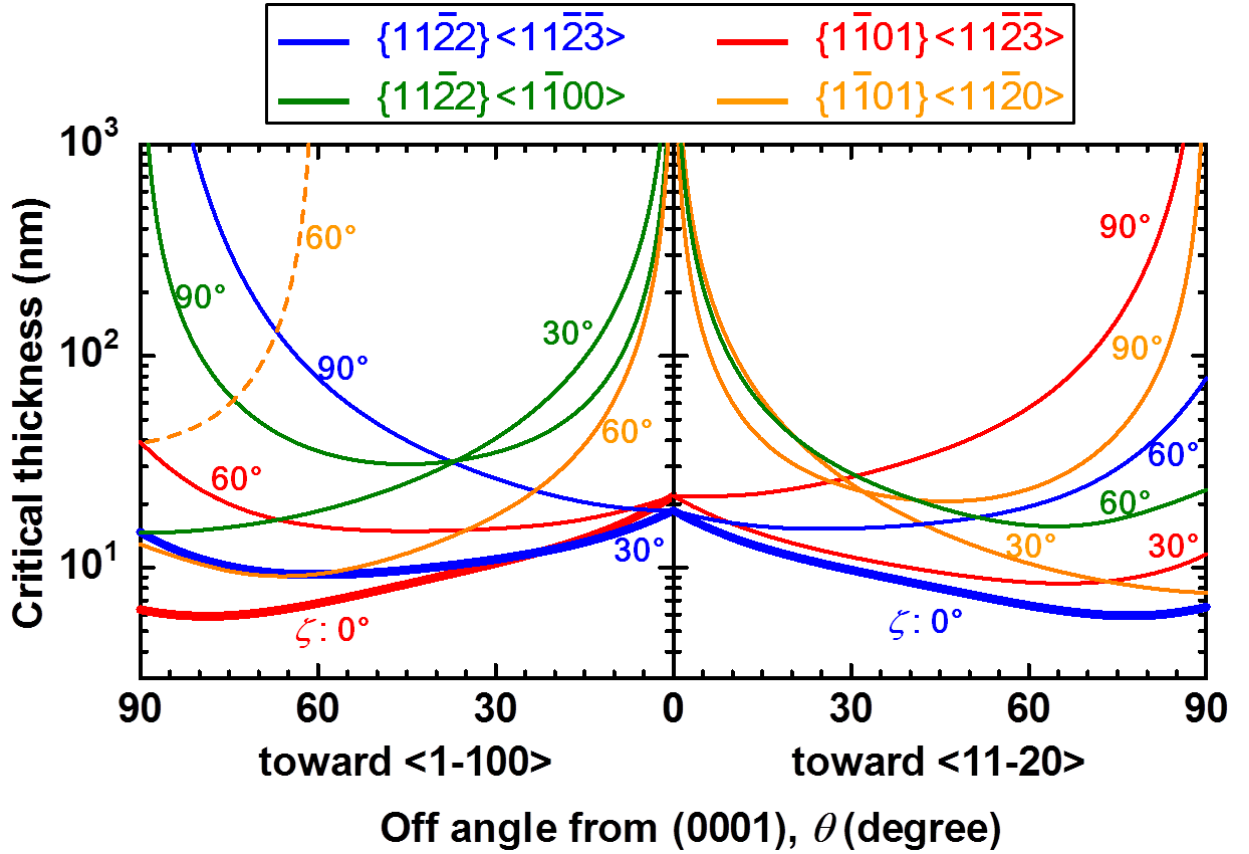


Figure 4.15: Off-angle and off-direction dependences of the calculated critical thicknesses due to the semipolar $\{1\bar{1}01\}$ and $\{11\bar{2}2\}$ slips in $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ structure. The angles in the figure mean ζ expressed in Eqs. (4.36) and (4.37). The calculation results are based on the extended M–B model, and the solid lines are obtained by the relation $F_a = F_l$. A broken line indicates the calculated critical thickness given by Eq. (4.96), which considers the effect of friction force due to the Peierls stress (Thermal assist is not considered here).

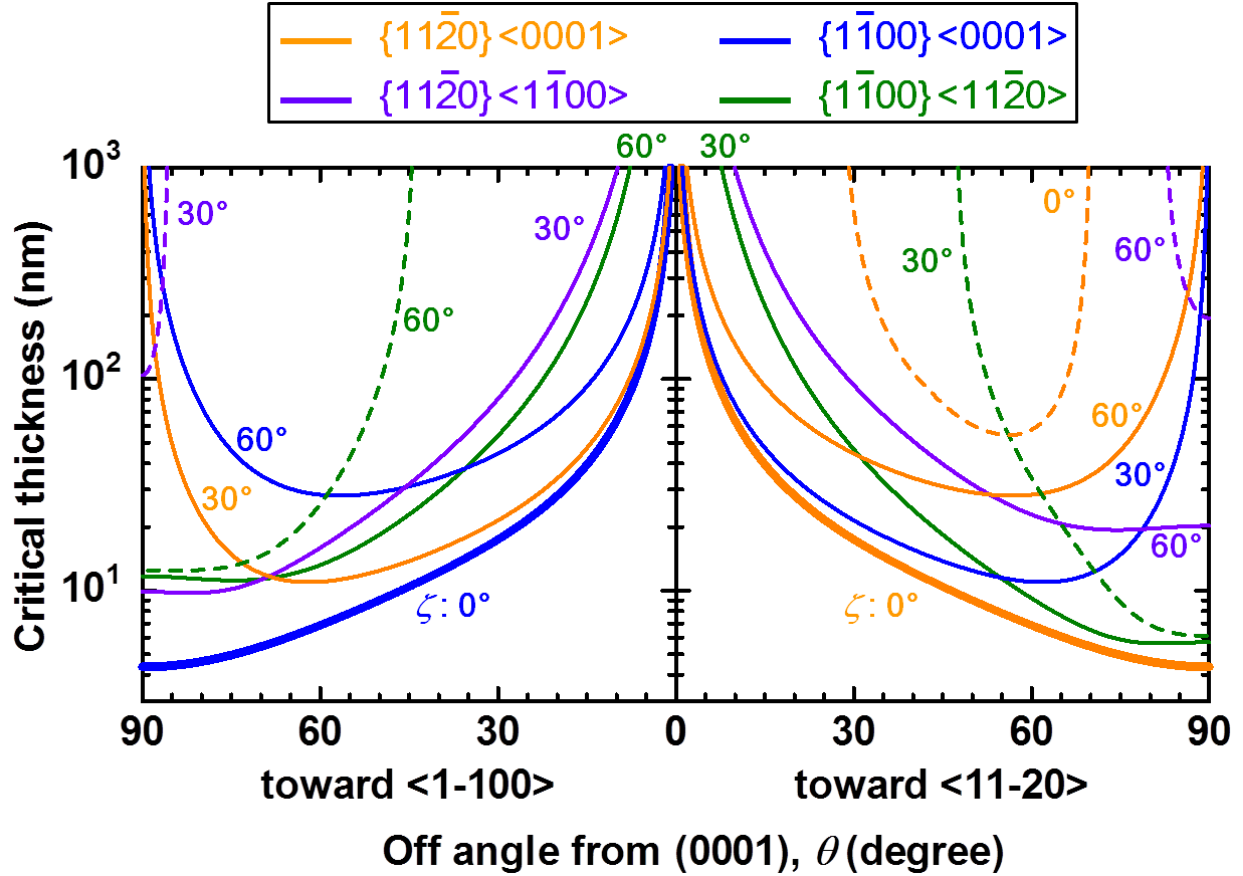


Figure 4.16: Off-angle and off-direction dependences of the calculated critical thicknesses due to the nonpolar $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ slips in Al_{0.7}Ga_{0.3}N/AlN structures. The angles in the figure mean ζ expressed in Eqs. (4.36) and (4.37). The calculation results are based on the extended M–B model, and the solid lines are obtained by the relation $F_a = F_l$. Broken lines indicate the calculated critical thicknesses given by Eq. (4.96), which considers the effect of friction force due to the Peierls stress (Thermal assist is not considered here).

the heterointerface is the maximum MD density [MDD (cm^{-1})] caused by the slip system. The LID can be written as

$$LID = \frac{\sin \alpha}{d_{\text{slip}}}, \quad (4.91)$$

where d_{slip} is the spacing of the slip planes. Thus, MDs can be newly generated at the heterointerface when $MDD^{(i)} < LID^{(i)}$, where i means each slip plane.

Figure 4.17(a) shows the schematic image of (0001) AlGa_N/AlN heterointerface with an off-angle, and the red dotted-lines are the line intersections between (0001) and the heterointerface. For the (0001) slip, $\alpha = \theta$ is satisfied as described in Eq. (4.35), and d_{slip} equals to $c/2$. Thus, $LID = 2 \sin \theta / c$ is obtained by Eq. (4.91). Figure 4.17(b) shows the off-angle dependence of the LID for the (0001) slip, and clarified that the LID becomes higher with an increase of θ and equals to zero for $\theta = 0^\circ$. However, if the growth plane has a small unintentional off-angle ($\theta > 0.015^\circ$), the LID is higher than 10^4 cm^{-1} . It means that an adequate quantity of MDs can be generated by (0001) slips due to the unintentional off-angle.

From Eq. (4.91), $LID = 0$ is also satisfied when α equals to 0° for other slip planes, which indicates that the slip plane completely same as the heterointerface cannot cause the generation of MDs. However, if the growth plane has a slight mis-orientation from the slip plane ($\alpha > 0^\circ$), MDs can be generated within the limitation of the LID .

4.7.3.2 Friction force due to the Peierls stress

In addition to the aforementioned limitation of LID , we also discuss the friction force due to the Peierls stress in this section. When dislocations move in a crystal, they have to exceed potential barriers formed by the periodic crystal lattice. The potential barrier is called as the Peierls barrier, and the stress, which is required to exceed the potential, is called as the Peierls stress [32, 33]. Therefore, the Peierls stress may play an important role as a friction force in impeding the dislocation glides. If the dislocation motion is dominated by a diffusive glide, a friction force depends on the dislocation velocity [34]. In such a manner of dislocation glide, the friction force equals to zero when the dislocation velocity is zero. However, if the dislocation motion is caused by a mechanical glide under the stress over the Peierls barrier, the Peierls–Nabarro approach [32, 33] is valid and the Peierls stress is independent of the dislocation velocity.

In the Peierls–Nabarro approach, an entire epi-threading dislocation slowly moves when the stress exceeds the Peierls barrier by quasi-static mechanical means. The force balance calculations such as the M–B model and Fischer model are based on mechanical glides, and can involve the effect of the friction force due to the Peierls stress.

Using the shear modulus G and Poisson's ratio ν , the Peierls stress (τ_P) for cubic materials is expressed as [35]

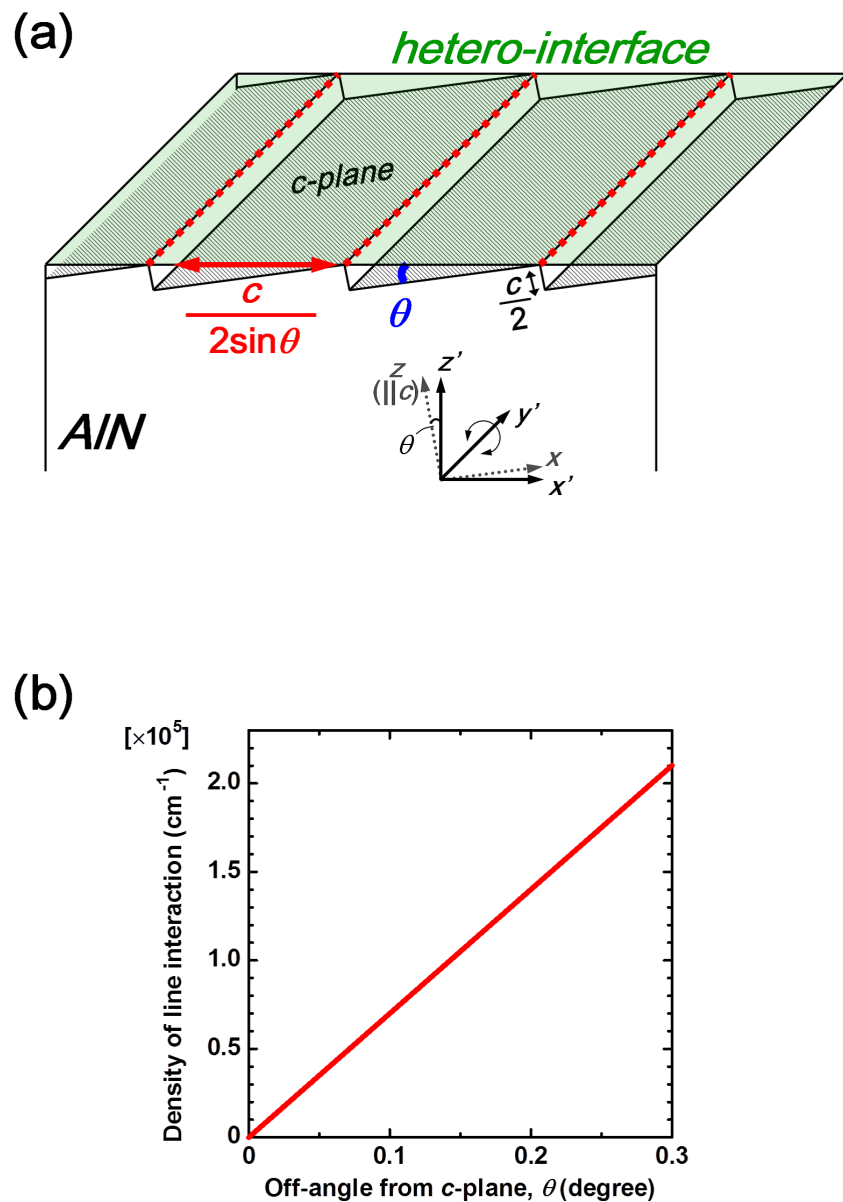


Figure 4.17: (a) Schematic image of (0001) AlGa_N/AlN heterointerface with an off-angle. The red dotted-lines are the line intersections between (0001) and the heterointerface. (b) Off-angle dependence of LID for the (0001) slip. The $LID(= 2 \sin \theta / c)$ is obtained by Eq. (4.91) for AlN.

$$\tau_P = 2G \left(\frac{1 - \nu b_s^2/b^2}{1 - \nu} \right) \omega \exp \left(-\frac{2\pi d_{slip}}{b} \omega \cdot \frac{1 - \nu b_s^2/b^2}{1 - \nu} \right), \quad (4.92)$$

where ω is a material constant given by [36, 37]

$$\omega = \exp \left(\frac{4\pi^2 s k_B T}{5GV} \right). \quad (4.93)$$

Here, s is the number of atoms per unit cell, V is the volume of the unit cell, k_B is Boltzmann constant, and T is the highest processing temperature [15, 35]. Considering the growth temperature for AlGa_N-related structures using the MOVPE method (generally $T < 2000^\circ\text{C}$), $\omega \sim 1$ is satisfied. Thus, we omit ω in the following discussions for simplicity.

For hexagonal materials, we revise the Peierls stress as

$$\tau_P = 2 \left(K'_s \frac{b_s^2}{b^2} + K'_e \frac{b_e^2}{b^2} + 2K'_{es} \frac{b_e b_s}{b^2} \right) \exp \left[-\frac{2\pi d_{slip}}{bK'_s} \left(K'_s \frac{b_s^2}{b^2} + K'_e \frac{b_e^2}{b^2} + 2K'_{es} \frac{b_e b_s}{b^2} \right) \right]. \quad (4.94)$$

Eqs. (4.92) and (4.94) indicate that slip systems which have large Burgers vectors cause larger Peierls stresses. (b_s and b_e is proportional to b .) This means that the lowest Peierls barrier is formed along the $\langle 11\bar{2}0 \rangle$ direction for hexagonal materials because $1/3\langle 11\bar{2}0 \rangle$ is the minimum Burgers vector.

Friction force (F_p) on an epi-threading dislocation due to the Peierls stress can be written as [15, 35]

$$F_p = \tau_P b h \frac{1}{\sin \alpha}. \quad (4.95)$$

$h/\sin \alpha$ indicates the distance between the heterointerface and growth surface measured on the slip plane. Thus, the friction force is proportional to epilayer thickness and becomes infinite value in the case of $\alpha = 0^\circ$.

Figures 4.18–4.20 show the off-angle and off-direction dependences of the friction forces due to the Peierls stress for (0001), semipolar, and nonpolar plane slips in Al_{0.7}Ga_{0.3}N/AlN structures, respectively. The friction forces were calculated at the epilayer thicknesses where $F_a = F_l$ are satisfied in M–B model. Because thick epitaxial layers are required to generate MDs for the relation $F_a \geq F_l$, the F_p depicted in Figs. 4.18–4.20 mean the minimum friction forces, which should be exceeded to generate MDs.

As shown in Fig. 4.18, the friction forces of the (0001) $\langle 11\bar{2}0 \rangle$ system are very small and are only several nano newtons at various off-angles except near 0° and 90° . For the semipolar plane slips, the F_p of $\{1\bar{1}01\}$ slips are basically smaller than those of $\{11\bar{2}2\}$ slips, and the $\{1\bar{1}01\}\langle 11\bar{2}0 \rangle$ system has particularly small F_p (see Fig. 4.19). This is because small τ_P is achieved for the slip system with the smallest Burgers vector, $1/3\langle 11\bar{2}0 \rangle$, as we mentioned above, and the F_p additionally becomes smaller due to the relatively thin critical thickness

(see Fig. 4.15). On the other hand, the F_p of the other semipolar plane slips are about two orders of magnitude greater than those of the (0001) slips at various off-angles. Similarly, for the nonpolar plane slips shown in Fig. 4.20, the $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ system has small friction forces because of the small Burgers vector, and those of the other slip systems are about an order of magnitude larger than those of the (0001) slips. It is noteworthy that the F_p of all the slip systems are quite large for $\theta \simeq 0^\circ$.

The force balance equation considering the friction force is expressed as

$$F_a = F_l + F_p. \quad (4.96)$$

Using Eq. (4.96), critical thickness was recalculated for each slip system, and the results are shown as broken lines in Figs. 4.13, 4.15, and 4.16.

In Fig. 4.13, the calculated critical thicknesses considering F_p are thicker than those obtained by the relation $F_a = F_l$ at any off-angles, and they approach infinity near $\theta = 0^\circ$ and 90° . In particular, the behaviours near $\theta = 0^\circ$ are quite different from the previous calculation results depicted as solid lines. This is because the F_p drastically become large when $\alpha (= \theta)$ approaches 0° in Eq. (4.95).

For the semipolar and nonpolar plane slips, on the other hand, a lot of slip systems do not have the solutions in Eq. (4.96) as shown in Figs. 4.15 and 4.16. This is because the relation $F_a < F_l + F_p$ is always satisfied in such slip systems due to large F_p . Particularly for the MDs with “c-type” component Burgers vectors, the F_p magnitudes are relatively large compared with those with the Burgers vectors $1/3\langle 11\bar{2}0\rangle$ and $\langle 1\bar{1}00\rangle$. The large Burgers vectors give large τ_P in Eq. (4.94), and most of the slip systems with “c-type” component Burgers vectors cannot calculate the critical thicknesses by solving Eq. (4.96).

Moreover, the detailed reason for the relation $F_a < F_l + F_p$ is subsequently discussed. In general, the relation $F_a > F_l$ is easily obtained for thick epilayers in various slip systems. The partial derivative of $(F_a - F_l)$ with respect to h is expressed as

$$\frac{\partial}{\partial h} (F_a - F_l) = \sigma b \cos \lambda - \frac{1}{4\pi h} (K'_s b_s^2 + K'_e b_e^2 + 2K'_{es} b_e b_s). \quad (4.97)$$

When h approaches infinity, Eq. (4.97) is rewritten as

$$\begin{aligned} \left. \frac{\partial}{\partial h} (F_a - F_l) \right|_{\infty} &= \sigma b \cos \lambda \\ &= \sigma b_e \cos \alpha. \end{aligned} \quad (4.98)$$

Here, we use Eq. (4.15) for the transformation. If we have $b_e \neq 0$ and $\alpha \neq 90^\circ$, $\left. \frac{\partial}{\partial h} (F_a - F_l) \right|_{\infty} > 0$ is obtained, thereby indicates that $F_a > F_l$ is necessarily satisfied for thick epilayers.

On the other hand, the partial derivative of $(F_a - F_l - F_p)$ at $h \rightarrow \infty$ is expressed as

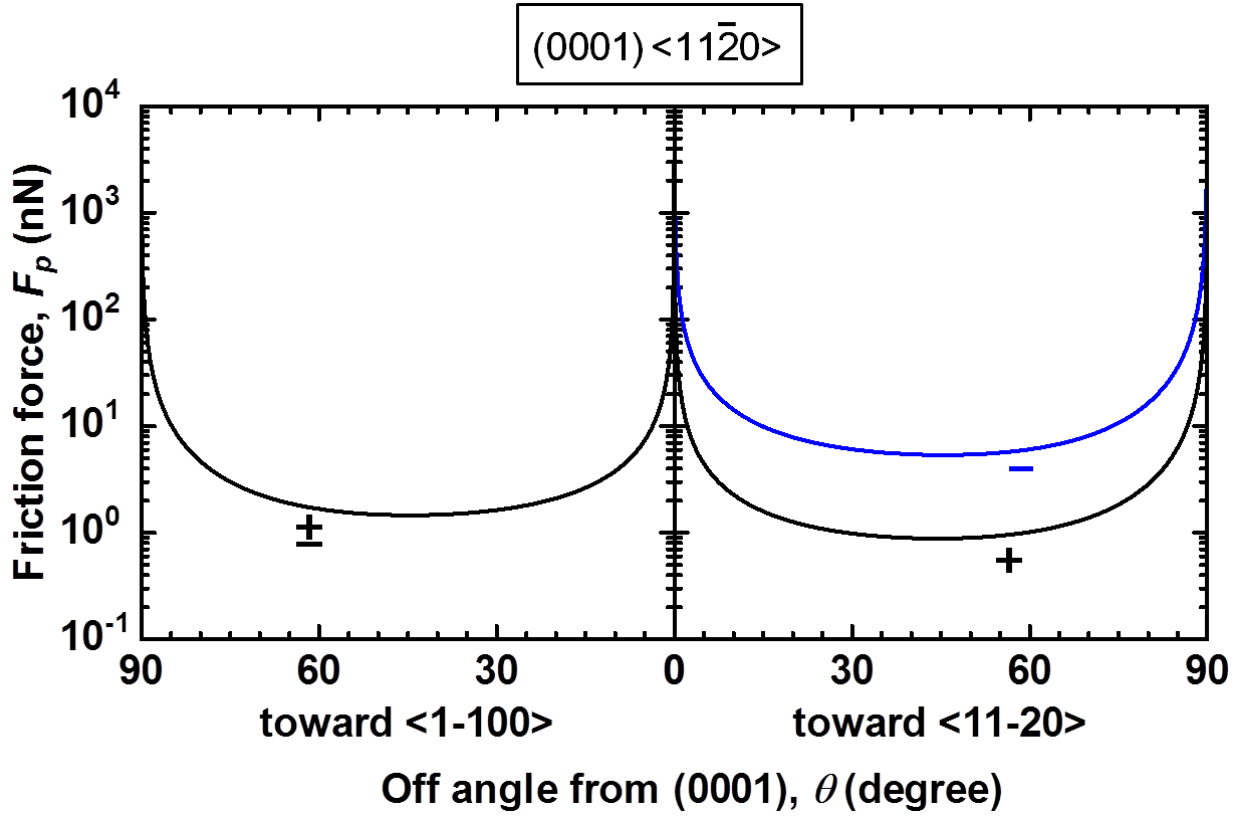


Figure 4.18: Off-angle and off-direction dependences of the friction forces due to the Peierls stress for (0001) slip in $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ structures at the epilayer thickness where $F_a = F_l$ is satisfied in the M-B model. The plus or minus signs in the figure correspond to the signs in Eqs. (4.29) and (4.30).

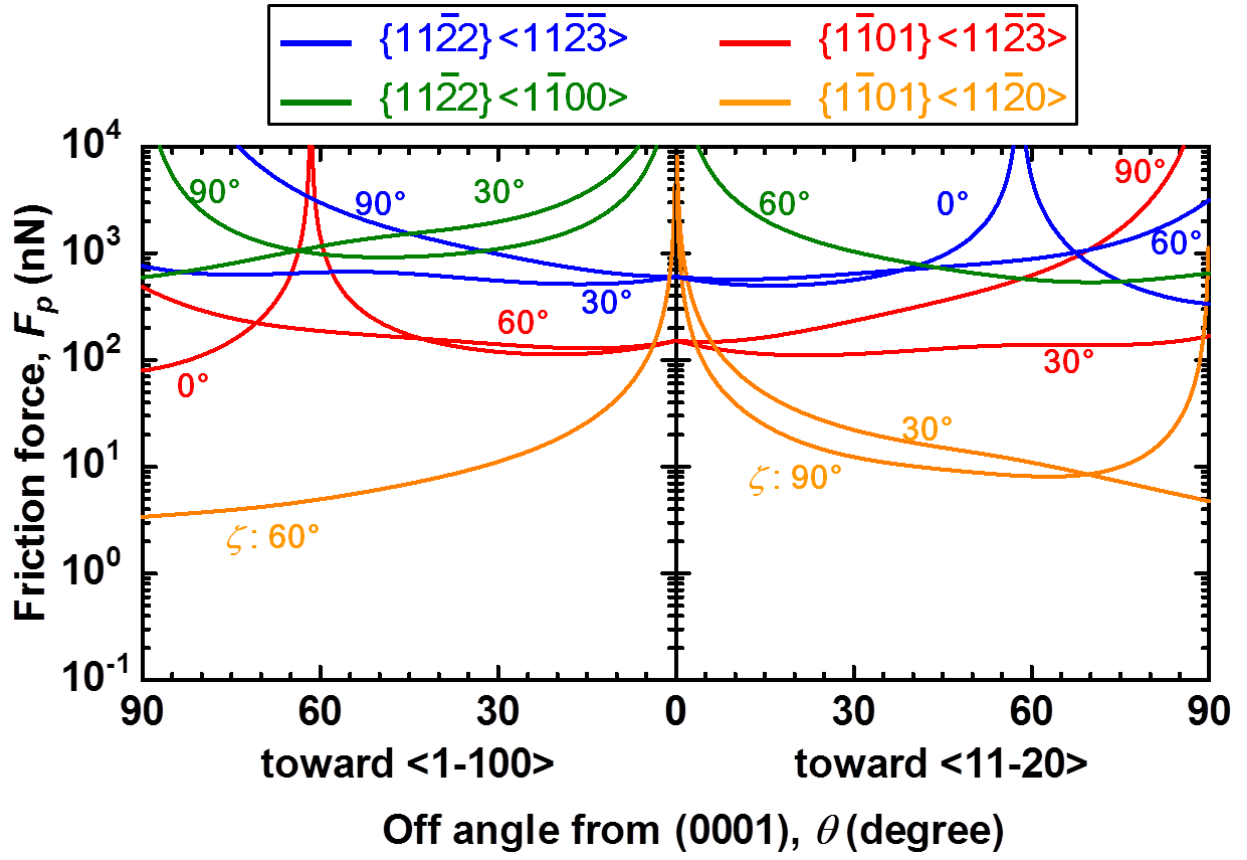


Figure 4.19: Off-angle and off-direction dependences of the friction forces due to the Peierls stress for semipolar plane slips in Al_{0.7}Ga_{0.3}N/AlN structures at the epilayer thickness where $F_a = F_l$ is satisfied in the M–B model.

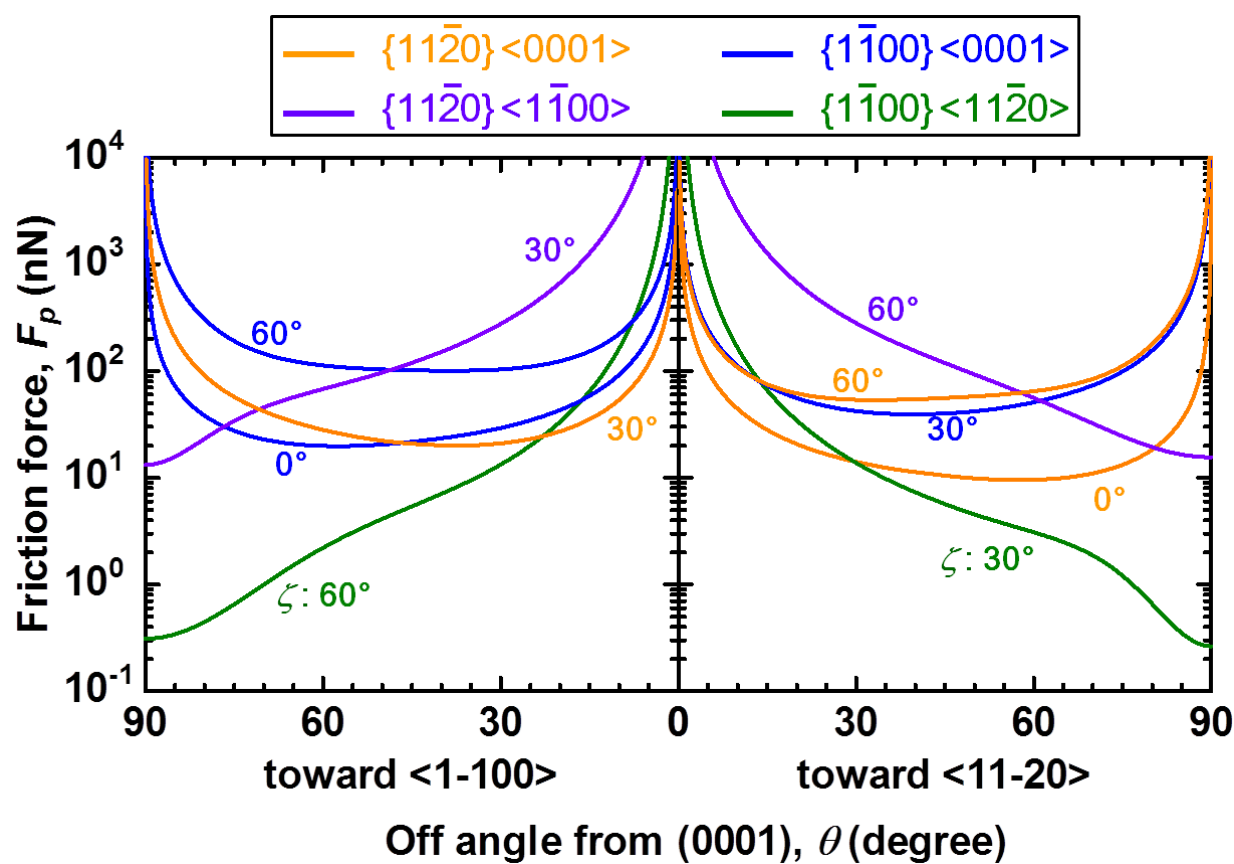


Figure 4.20: Off-angle and off-direction dependences of the friction forces due to the Peierls stress for nonpolar plane slips in $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ structures at the epilayer thickness where $F_a = F_l$ is satisfied in the M-B model.

$$\left. \frac{\partial}{\partial h} (F_a - F_l - F_p) \right|_{\infty} = \sigma b_e \cos \alpha - \frac{\tau_P b}{\sin \alpha}, \quad (4.99)$$

Equation (4.99) indicates that $\left. \frac{\partial}{\partial h} (F_a - F_l - F_p) \right|_{\infty}$ is not necessarily positive in contrast to $\left. \frac{\partial}{\partial h} (F_a - F_l) \right|_{\infty}$. In order to solve Eq. (4.96), the following relation is required,

$$\sigma > \frac{\tau_P b}{b_e \sin \alpha \cos \alpha}. \quad (4.100)$$

In such a case, dislocations can move even considering the effect of F_p for thick epitaxial layers. Hence, relatively small τ_P is required with respect to the stress caused by lattice mismatch for the solution of Eq. (4.96). This is the reason why many semipolar and nonpolar plane slips with “c-type” component Burgers vectors do not have the solutions of Eq. (4.96). In addition, the right hand side of Eq. (4.100) near $\alpha = 0^\circ$ and 90° becomes drastically large, and the relation $F_a < F_l + F_p$ is always satisfied for any slip systems, which corresponds to the calculation results for the (0001) slips as shown in Fig. 4.13.

It is noteworthy that all of the slip systems examined cannot satisfy Eq. (4.100) near $\theta = 0^\circ$. This means that no critical thicknesses exist for the (0001) Al_{0.7}Ga_{0.3}N/AlN heterostructures. In practice, however, there are many experimental results which indicate the semipolar plane slips for the (0001) heteroepitaxial growth, and our calculated results considering F_p do not agree with them. Thus, we further improve the calculation model using the friction force due to the Peierls stress.

Strictly, the Peierls stress means the stress which is required to move dislocations at 0 K, and it is often neglected because the thermal energy during the high temperature process such as MOVPE growth is high enough to exceed the Peierls barriers with small τ_P . Although τ_P in some slip systems are relatively large for AlGa_{0.7}N/AlN heterostructures as we mentioned above, the thermal assist for dislocation glides should be considered in the calculation.

At a high processing temperature, dislocations slightly vibrate due to lattice vibrations. When there are no external forces on dislocations, the probability that dislocations thermally move while feeling the Peierls barrier can be written as $\exp(-F_p \Delta l / k_B T)$, where Δl is the moved distance. In a process of MD generation, the force (F_a) due to the lattice mismatch exists as an external force, and the line tension (F_l) prevents generating a MD. Thus, the probability is modified as $\exp[-(F_p + F_l - F_a) \Delta l / k_B T]$, and Δl corresponds with the minimum length of a MD. As a consequence, the frequency (f) for dislocation glides (MD generations) can be written as

$$f = v \exp \left[-\frac{(F_p + F_l - F_a) \Delta l}{k_B T} \right], \quad (4.101)$$

where v is frequency of dislocation vibration related to the lattice vibration. Note that MDs repeat the generation and annihilation in the case of $F_a < F_l$ because the state without MDs

is more energetically stable in such a case. Therefore, Eq. (4.101) indicates the frequency of MD generations only when the relation $F_a \geq F_l$ is satisfied. Here, we assume that MDs can be generated when f is larger than a certain threshold frequency f_{th} . Substituting f_{th} into f , Eq. (4.101) is rewritten as

$$\begin{aligned} F_a &= F_l + F_p - \frac{k_B T}{\Delta l} \ln \left(\frac{v}{f_{th}} \right) \\ &= F_l + (F_p - F_q), \end{aligned} \quad (4.102)$$

where $F_q [= \frac{k_B T}{\Delta l} \ln (v/f_{th})]$ can be considered as a thermally assisted force. Because $f \geq \nu$ are ensured by Eq. (4.101), F_q is larger than or equals to zero, and $(F_p - F_q)$ means the effective friction force. However, we have to take care of the case $F_q > F_p$ because this condition requires $F_a < F_l$ to satisfy Eq. (4.102). As we mentioned above, MDs are not generated in the case of $F_a < F_l$ because MDs are unstable. Therefore, if F_q is larger than F_p , we should consider that the thermal energy is high enough to neglect the Peierls barrier and the effective friction force is equals to zero. In other words, to calculate the critical thickness, Eq. (4.102) should be used for $F_q \leq F_p$, and the ordinary relation $F_a = F_l$ should be used for $F_q > F_p$. Although the factors Δl , f_{th} , and ν should be determined to precisely obtain F_q , the determination by experiments is very difficult. Thus, we roughly predict F_q by combining our calculation results and the reported results.

For (0001) Al_{0.17}Ga_{0.83}N/GaN heterostructures (540-nm-thick epilayer), MDs due to the conventional slip system $\{11\bar{2}2\}\langle 11\bar{2}\bar{3}\rangle$ are experimentally confirmed by TEM measurements [38]. In the $\{11\bar{2}2\}\langle 11\bar{2}\bar{3}\rangle$ system for $\theta = 0^\circ$, the calculated F_p at the epilayer thickness that satisfies $F_a = F_l$, is 1.28 μN . The calculated F_p is the minimum friction force to be exceeded for MD generations, and is calculated like Figs. 4.18–4.20. Therefore, thermally assisted force F_q should be larger than the F_p (1.28 μN) at least to glide dislocations and to generate MDs. Then, although there are small differences of the MOVPE growth temperatures and of Al compositions between their samples and our samples, we use 1.28 μN as a rough estimation of F_q for the following discussions in this study.

Using Eq. (4.102), the critical thicknesses are recalculated. Figure 4.21 shows the off-angle and off-direction dependences of the critical thicknesses for various slip systems of Al_{0.7}Ga_{0.3}N/AlN heterostructures considering the effect of the friction force and thermally assisted force. Here, we select certain slip systems which lead to relatively thin critical thicknesses. A lot of slip systems have solutions of Eq. (4.102) due to the thermally assisted force, in contrast to Eq. (4.96), and the critical thicknesses can be calculated even near $\theta = 0^\circ$ unlike the broken lines in Figs. 4.13, 4.15, and 4.16. When a small off-direction error ($\phi \rightarrow \phi \pm \Delta\phi$) due to an unintentional miscut exists, the critical thickness by the $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ ($\zeta = \Delta\phi = 0.3^\circ$) system is calculated as shown by a broken line in Fig. 4.21. Note that the critical thicknesses in the other slip systems are almost the same as in the

case of $\Delta\phi = 0^\circ$.

The primary and secondary slip systems in Al_{0.7}Ga_{0.3}N/AlN heterostructures are summarized in Tabs. 4.1 and 4.2 for arbitrary off-angles. The calculated results indicate that the unintentional off-angle from (0001), which is larger than 0.03° , can cause the (0001) slips as the primary slip system even in the case of (0001) heteroepitaxial growth. The typical off-angle accuracy of currently available (0001) substrates is about 0.1° due to the limitation of the polishing technique. Therefore, the primary slip plane is (0001) in the practically used (0001) heterostructures, and the result well agrees with the optically determined critical thicknesses as shown in Fig. 4.10.

For nonpolar plane growth, on the other hand, the $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ is the primary slip system even when the mis-orientation is about 0.1° . In fact, the $\{1\bar{1}00\}$ slips are experimentally confirmed in the case of *m*-plane heteroepitaxial growth [17]. These findings support the validity of our calculation model of the critical thickness based on Eq. (4.102) that considers the friction forces and thermally assisted forces.

4.7.4 Lattice relaxation process

To elucidate the reason why the (0001) slips for the *c*-plane heterostructures was not reported so far, we discuss the lattice relaxation process due to the generation of MDs in this section.

When crystal growth is continued after the epilayer thickness exceeds the critical thickness, the lattice relaxation is promoted accompanied with the increase of the MD density. The behavior of lattice relaxation process strongly depends on the slip system because the relaxation direction and magnitude of Burgers vector are quite different.

Along the *x* direction, for example, the total difference in the lattice constants between the epilayer and substrate at the heterointerface is expressed as $N|a_{\text{epi}} - a_{\text{sub}}|$, where *N* is the number of lattices at the heterointerface. Meanwhile, because the distance of the substrate surface along *x* direction can be written as $N(a_{\text{sub}} \cos \theta + c_{\text{sub}} \sin \theta)$, $N(a_{\text{sub}} \cos \theta + c_{\text{sub}} \sin \theta) \times MDD$ means the number of MDs generated at the heterointerface. If a MD is generated, the misfit strain along *x* direction tends to relax with a degree corresponding to b_{ex} . Therefore, the generated MDs relax the epilayer lattices with totally $N(a_{\text{sub}} \cos \theta + c_{\text{sub}} \sin \theta) b_{ex} \cdot MDD$. Thus, the relaxation degree with respect to the strains ϵ_{xx0} , ϵ_{yy0} , and ϵ_{zz0} expressed in Eqs. (4.21)–(4.23) can be written as

$$r_{x0} = \sum_i \frac{b_{ex}^{(i)} \cdot MDD^{(i)}}{|a_{\text{epi}} - a_{\text{sub}}| / (a_{\text{sub}} \cos \theta + c_{\text{sub}} \sin \theta)}, \quad (4.103)$$

$$r_{y0} = \sum_i \frac{b_{ey}^{(i)} \cdot MDD^{(i)}}{|a_{\text{epi}} - a_{\text{sub}}| / (a_{\text{sub}} \cos \theta + c_{\text{sub}} \sin \theta)}, \quad (4.104)$$

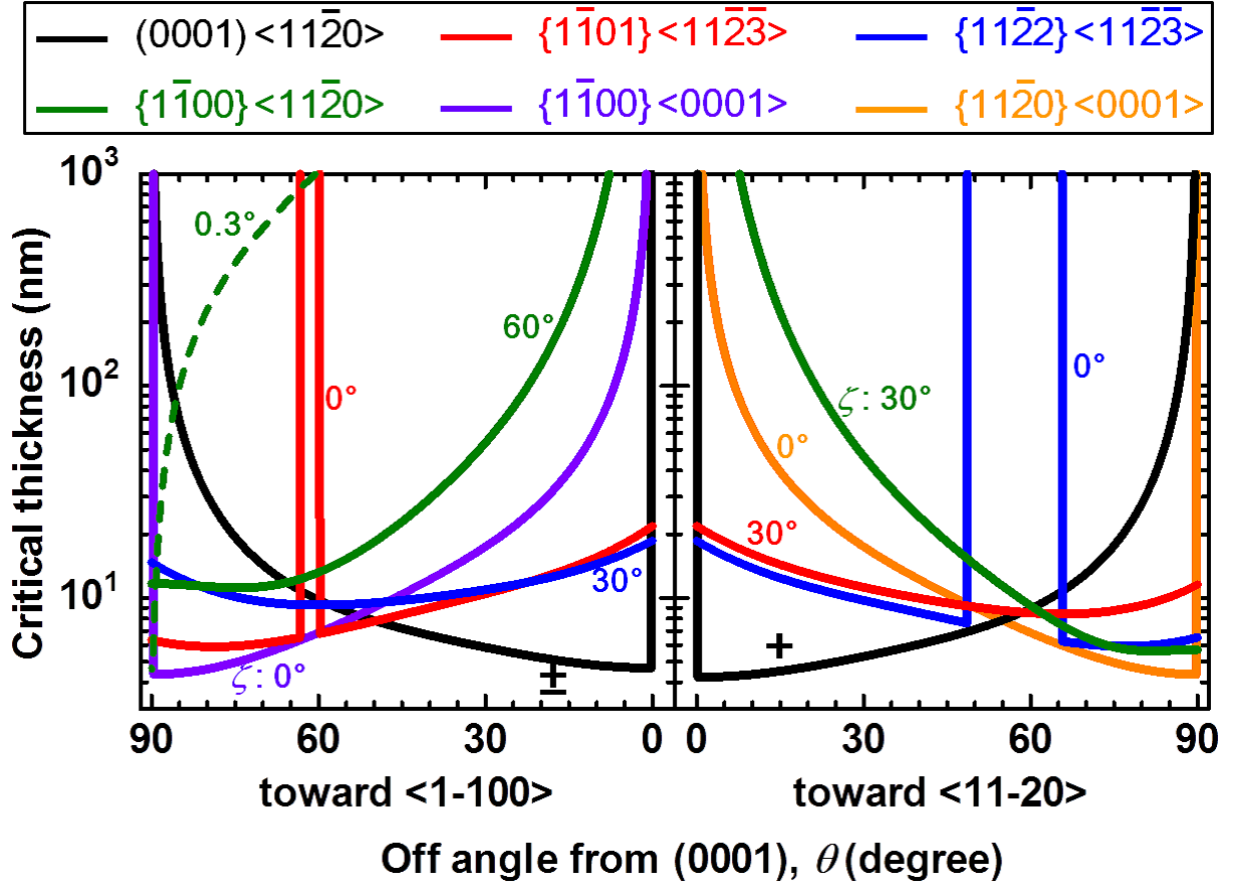


Figure 4.21: Off-angle and off-direction dependences of the critical thicknesses for various slip systems of $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ heterostructures. Slip systems which lead to relatively thin critical thicknesses are selected, and we use $1.28 \mu\text{N}$ as a thermally assisted force. The plus or minus signs in the figure correspond to the signs in Eqs. (4.29) and (4.30). A broken line is the critical thickness considering a small off-direction error of $\Delta\phi = 0.3^\circ$.

Table 4.1: Off-angle dependence of the primary and secondary slip systems of Al_{0.7}Ga_{0.3}N/AlN heterostructures. The off-direction is toward $\langle 1\bar{1}00 \rangle$.

Off-angle, θ	Primary slip system	Secondary slip system
0° $\downarrow$ 0.029°	$\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$ $(\zeta = 30^\circ)$	$\{1\bar{1}01\} \langle 11\bar{2}3 \rangle$ $(\zeta = 0^\circ)$
0.029° $^*\downarrow$ $\sim 20^\circ$	$(0001) \langle 11\bar{2}0 \rangle$	$\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$ $(\zeta = 30^\circ)$
$\sim 20^\circ$ $\downarrow$ $\sim 50^\circ$		$\{1\bar{1}01\} \langle 11\bar{2}3 \rangle$ $(\zeta = 0^\circ)$
$\sim 50^\circ$ $\downarrow$ $\sim 60^\circ$	$\{1\bar{1}01\} \langle 11\bar{2}3 \rangle$ $(\zeta = 0^\circ)$	$\{1\bar{1}00\} \langle 0001 \rangle^\ddagger$ $(\zeta = 0^\circ)$
$\sim 60^\circ$ $\downarrow$ 89.71°	$\{1\bar{1}00\} \langle 0001 \rangle$ $(\zeta = 0^\circ)$	$\{1\bar{1}01\} \langle 11\bar{2}3 \rangle^\ddagger$ $(\zeta = 0^\circ)$
89.71° $^\dagger\downarrow$ 90°	$\{1\bar{1}00\} \langle 11\bar{2}0 \rangle^\S$ $(\zeta = \Delta\phi)$	$\{1\bar{1}01\} \langle 11\bar{2}3 \rangle$ $(\zeta = 0^\circ)$

*practical c -plane growth

† practical m -plane growth

‡ Although a major secondary slip system is described, there are actually several slip systems.

§ This is the case that the actual off-direction is slightly different from $\langle 1\bar{1}00 \rangle$ [$\phi = \Delta\phi (\neq 0)$].

Table 4.2: Off-angle dependence of the primary and secondary slip systems of $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ heterostructures. The off-direction is toward $\langle 11\bar{2}0 \rangle$.

Off-angle, θ	Primary slip system	Secondary slip system
0° $\downarrow$ 0.017°	$\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$ $(\zeta = 0^\circ)$	$\{1\bar{1}01\} \langle 11\bar{2}3 \rangle$ $(\zeta = 30^\circ)$
0.017° $^*\downarrow$ $\sim 50^\circ$	$(0001) \langle 11\bar{2}0 \rangle$	$\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$ $(\zeta = 0^\circ)$
$\sim 50^\circ$ $\downarrow$ $\sim 55^\circ$		$\{11\bar{2}0\} \langle 0001 \rangle$ $(\zeta = 0^\circ)$
$\sim 55^\circ$ $\downarrow$ $\sim 75^\circ$	$\{11\bar{2}0\} \langle 0001 \rangle$ $(\zeta = 0^\circ)$	Several slip systems
$\sim 75^\circ$ $\downarrow$ 89.86°		$\{1\bar{1}00\} \langle 11\bar{2}0 \rangle$ $(\zeta = 30^\circ)$
89.86° $^\dagger\downarrow$ 90°	$\{1\bar{1}00\} \langle 11\bar{2}0 \rangle$ $(\zeta = 30^\circ)$	$\{1\bar{1}01\} \langle 11\bar{2}3 \rangle$ $(\zeta = 30^\circ)$

*practical c -plane growth † practical a -plane growth

$$r_{z0} = \sum_i \frac{b_{ez}^{(i)} \cdot MDD^{(i)}}{|c_{\text{epi}} - c_{\text{sub}}| / (a_{\text{sub}} \cos \theta + c_{\text{sub}} \sin \theta)}, \quad (4.105)$$

respectively. Here, i indicates the each slip system. The calculated r_{j0} values can be more than 1 as a consequence of the increase in MDD , which means that the strain sign is reversed due to excessive lattice relaxations. This is not practical, and in the following calculations, r_{j0} is kept 1 after reaching unity.

The in-plane strain is also expressed as a function of (r_{x0}, r_{y0}, r_{z0}) , and the in-plane relaxation degree $r_{x'}$ ($r_{y'}$) along the x' (y') direction can be calculated by

$$r_{x'} = \frac{\epsilon_{x'x'}(0, 0, 0) - \epsilon_{x'x'}(r_{x0}, r_{y0}, r_{z0})}{\epsilon_{x'x'}(0, 0, 0)}, \quad (4.106)$$

$$r_{y'} = \frac{\epsilon_{y'y'}(0, 0, 0) - \epsilon_{y'y'}(r_{x0}, r_{y0}, r_{z0})}{\epsilon_{y'y'}(0, 0, 0)}, \quad (4.107)$$

respectively. Here, we define the averaged in-plane relaxation degree as

$$r_{x'y'} = \frac{r_{x'} + r_{y'}}{2}. \quad (4.108)$$

Figure 4.22 shows the lattice relaxation process without considering F_p for a (0001) Al_{0.7}Ga_{0.3}N/AlN heterostructure assuming $\phi = 0^\circ$ and $\theta = 0.15^\circ$, which corresponds with the off-angles for the AlN bulk substrates used in this study. From the figure, it was clarified that the (0001) $\langle 11\bar{2}0 \rangle$ slip occurs as the first step of the relaxation, and the $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ slip subsequently occurs as the second step after the end of the (0001) slip. Figure 4.23 shows the relaxation process focusing on the $r_{x'}$ and $r_{y'}$ for the (0001) Al_{0.7}Ga_{0.3}N/AlN heterostructures with various off-angles. We found that the lattice relaxation along the x' direction occurs in advance of the y' direction relaxation when the off-angles are not zero. Therefore, Figs. 4.22 and 4.23 indicate that the (0001) slip can relax the strain only along x' direction, whereas the $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ slip can isotropically relax the in-plane strain. This is because the (0001) slip does not have any other equivalent slip planes and have no b_{ey} component of the Burgers vector as written in Eq. (4.33). On the other hand, $\{11\bar{2}2\}$ is the six-fold symmetrical plane and can generate both b_{ex} and b_{ey} by changing ζ as shown in Fig. 4.22. Moreover, the (0001) slip cannot fully relax the strain even along the x' direction for small off-angle samples ($\theta < 0.40^\circ$) as shown in Fig. 4.23. This is because the limitation of LID appears in the relaxation processes for small α [see Eq. (4.91)].

Subsequently, we discuss the relaxation process considering the effect of F_p based on Eq. (4.102) and compare the results. Figures 4.24 and 4.25 show the lattice relaxation processes considering the effect of F_p , and corresponds to Figs 4.22 and 4.23, respectively. Similarly, the (0001) $\langle 11\bar{2}0 \rangle$ slip also occurs at the first step of the relaxation, and the slip is finished due to the limitation of LID . After the end of the (0001) slip, the $\{11\bar{2}2\} \langle 11\bar{2}\bar{3} \rangle$ slip subsequently occurs as the second step of the relaxation, and the in-plane strain is

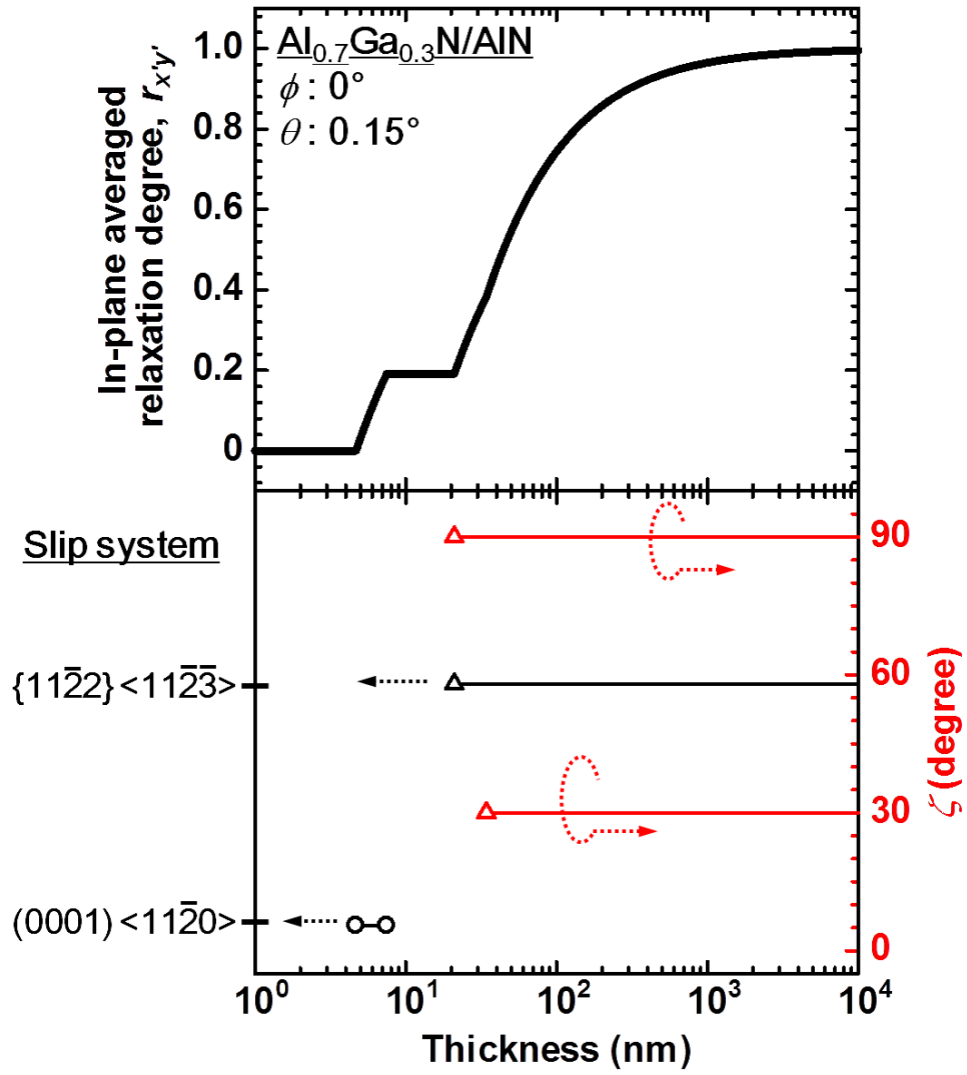


Figure 4.22: Lattice relaxation process without considering F_p for a (0001) $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ heterostructure assuming $\phi = 0^\circ$ and $\theta = 0.15^\circ$, which corresponds to the off-angle of an AlN bulk substrate used in this thesis. The symbols for ζ correspond to those of the slip systems.

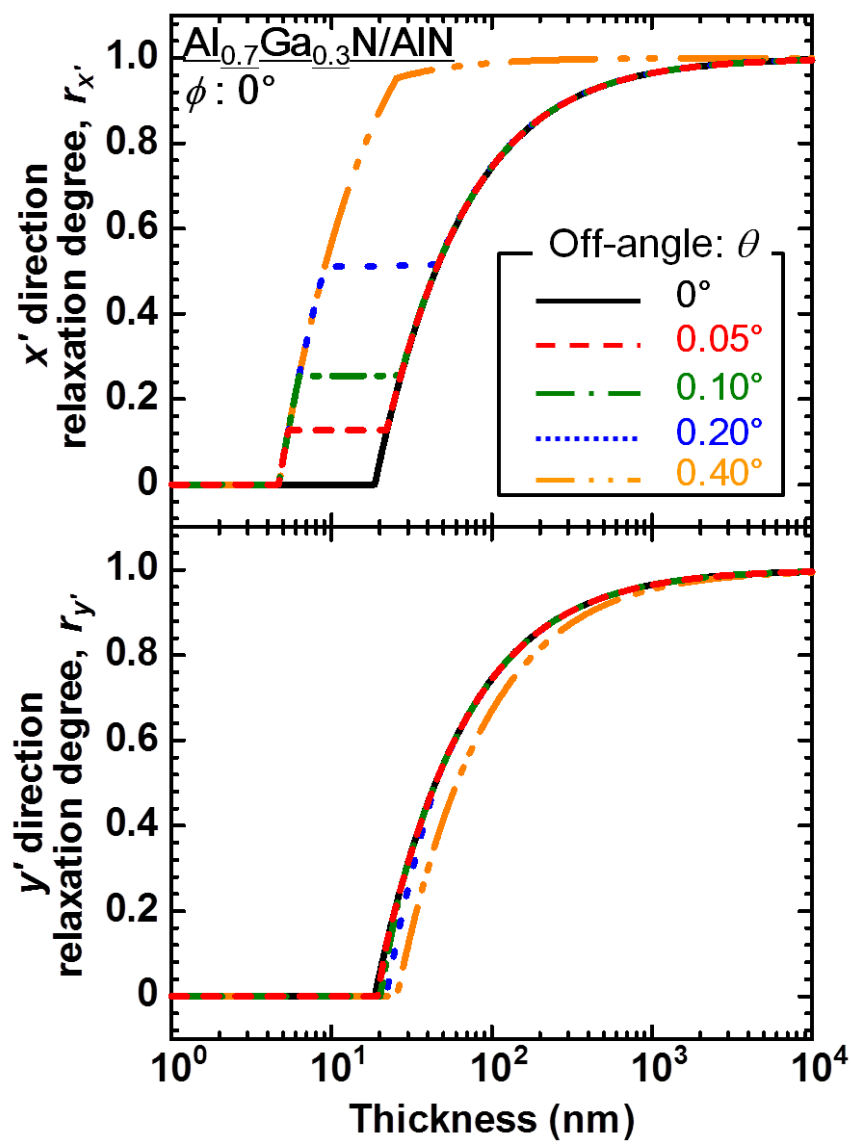


Figure 4.23: Lattice relaxation process focusing on $r_{x'}$ and $r_{y'}$ for a (0001) Al_{0.7}Ga_{0.3}N/AlN heterostructure. In these calculations, the effect of F_p is not considered.

isotropically relaxed by different ζ . However, the second slip system is also finished in the middle of the relaxation, and the $\{1\bar{1}01\}\langle 11\bar{2}3\rangle$ slip newly occurs as the third step in contrast to the previous results in Fig 4.22. The end of the second slip system is caused by large F_p for thick epilayers and small F_a due to the relaxation. The third slip system is also finished before fully relaxing the in-plane strains due to the same reason. Because there are no slip systems which can get over the effect of F_p , subsequent slips do not occur (by typical slip systems used in this study).

Then, we can predict that the three slip systems generate MDs with the different line directions determined by ζ with respect to the off-direction. When the 490-nm-thick $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$ film was grown on an AlN substrate whose off-direction is toward $\langle 1\bar{1}00\rangle$ ($\phi \sim 0^\circ$), the surface morphology of the capped AlN layer was extraordinarily roughened by the generation of MDs as shown in Fig. 4.4. The predicted MD lines ($\mathbf{L}$) for the sample caused by the three slip systems are drawn into Fig. 4.4 as dotted lines. Figure 4.4 clarified that the observed stripe-shaped defects are along the predicted MD lines. Thus, we found that the results also support the validity of the calculation model considering F_p .

The lattice relaxation in the thick $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$ sample was not confirmed by XRD measurement as shown in Fig. 4.5. The fact that the lattice relaxations are prevented by the effect of F_p may be one of the reasons for the bad sensitivity of the XRD measurement for the (0001) heterostructures. However, according to the calculated result in Fig. 4.24, the in-plane lattice relaxation beyond 80% is expected for the sample. It means that the actual lattice relaxation rate with respect to the epilayer thickness must be slower than expected in the calculation. In our calculation model, many factors that can impede the diffusion of MDs such as impurity atoms, grain boundaries, and interaction between MDs are not considered other than the Peierls barrier. Furthermore, the diffusive glides, which are affected by the dislocation velocity as we mentioned above, are not considered. Therefore, we consider that our calculation model gives the ideal relaxation process, which is not hampered by a lot of factors, and the actual relaxation rate is slower than the calculated results. As a consequence, we could not confirm the lattice relaxation by the XRD measurement.

In addition, because a large part of the lattice relaxations for the (0001) heterostructures is caused by the semipolar plane slips which is conventionally considered as the primary slip systems for the (0001) heterostructures (see Fig. 4.24), the initial (0001) slip may be difficult to observe by the TEM and XRD measurements.

4.8 Relaxation position control

Through the critical-thickness calculations, we discuss the structural optimization of (0001) AlGa_xN QWs (particularly for Ga-rich QWs).

At first, we fabricated a *c*-plane $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ SQW with 1.5- and 15-nm-thick well (L_w) and barrier layers (L_b), respectively, after the growth of a $\sim 3\text{-}\mu\text{m}$ -thick AlN film on

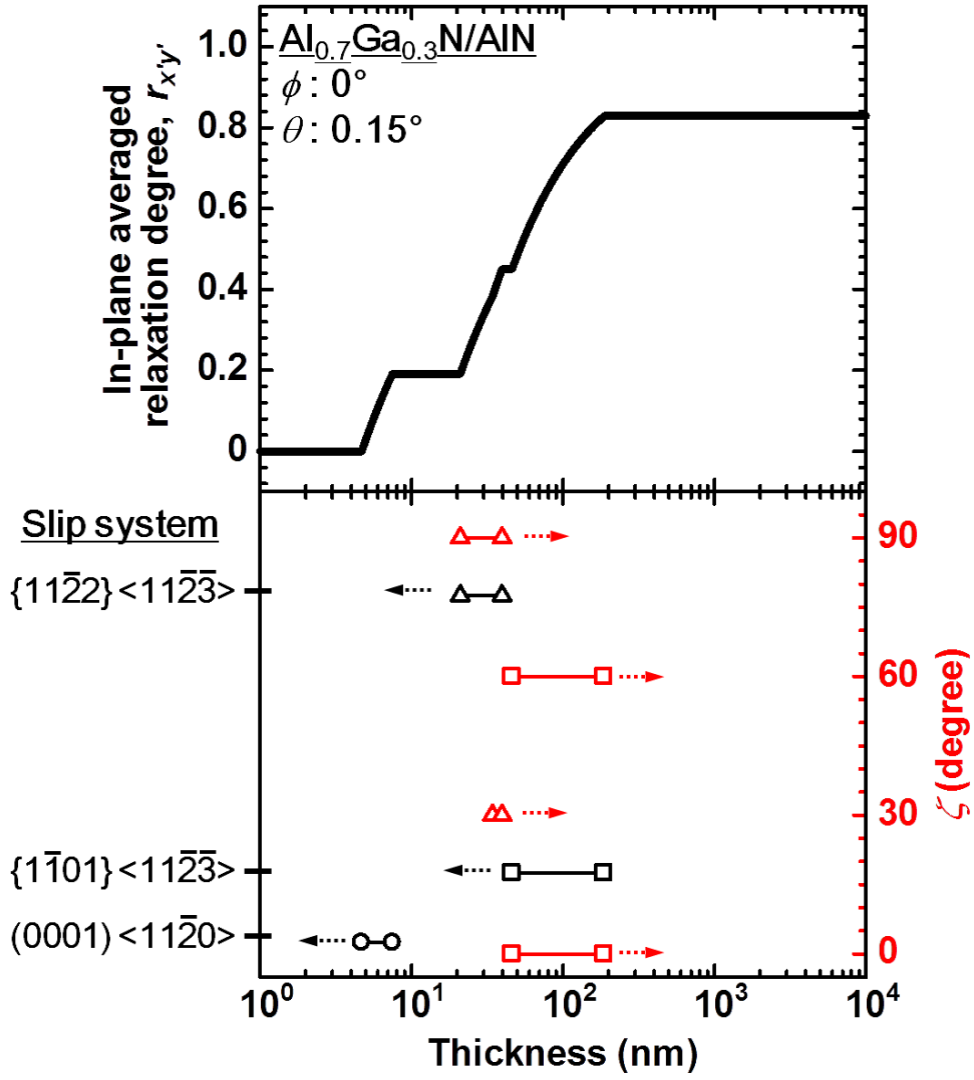


Figure 4.24: Lattice relaxation process considering the effect of F_p for a (0001) $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ heterostructure assuming $\phi = 0^\circ$ and $\theta = 0.15^\circ$, which corresponds with the off-angle of an AlN bulk substrate used in this thesis. The symbols for ζ correspond to those of the slip systems.

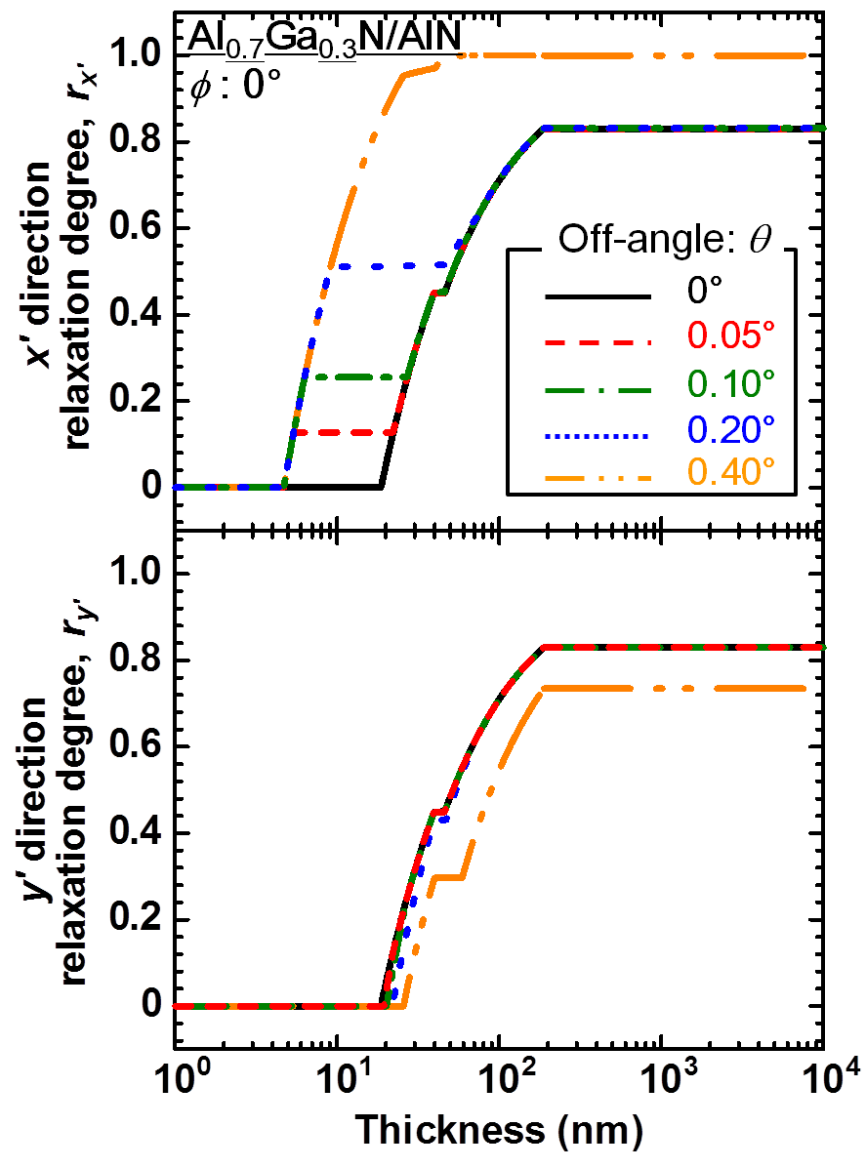


Figure 4.25: Lattice relaxation process focusing on $r_{x'}$ and $r_{y'}$ for a (0001) $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ heterostructure. In these calculations, the effect of F_p is considered.

a *c*-plane sapphire substrate. Then, PL measurements were performed at 6.7 K using a Ti:Al₂O₃ fourth harmonic generation laser as an excitation source for the selective excitation of the well layer. The PL spectrum of Al_{0.5}Ga_{0.5}N/AlN SQW is shown in Fig. 4.26, where the near band edge emission is not observed. The result implies that the MDs, which act as nonradiative recombination centers, are introduced in the well layer. From the well width and Al composition, we consider that the primary (0001) slips with the quite thin critical thickness were induced due to the unintentional off-angle ($\theta \sim 0.05^\circ$), and caused such a significant degradation.

On the other hand, when we increased the QW period to three without modifying other QW parameters such as L_w and L_b , the strong near band edge emission appeared at ~ 250 nm, as shown in Fig. 4.26. Because the induced strain energy of the 3QW due to the lattice mismatch must be much larger than that of the SQW, we conclude that 3QW should involve MDs similar to the SQW. For both of the QWs, the greatest strain energies should be induced at the heterointerfaces between the underlying AlN and bottom AlGa_{0.5}N well layers. Thus, we presume that MDs in the 3QW are mainly generated at the bottom heterointerface, and are suppressed in the top and second well layers as shown in Fig. 4.27(a). In such a case, excited carriers in the bottom well layer are captured by MDs, whereas those in the top and second well layers can contribute to the radiative recombinations, which result in the strong near band edge emission.

Then, we suggest novel AlGa_{0.5}N QW structures, which are optimized for strong emissions, by making use of the aforementioned unique lattice relaxation processes (as discussed in Fig. 4.26). Because the bottom heterointerface has the greatest strain energy which causes MDs, we expect that the generation of MDs in well layers can be avoided by inserting a new AlGa_{0.5}N layer below the bottom QW as shown in Fig. 4.27(b). The inserted AlGa_{0.5}N layer is referred to as a “relax layer” for the following discussions. In the heterostructure, the strain energy at the interface between the AlN and relax layer is the greatest, and we expect that the lattice relaxations and MD generations should mainly occur at the interface, which is far from the active layers. Herein, we specifically suggest Al_{*x*}Ga_{1-*x*}N/Al_{*y*}Ga_{1-*y*}N MQW structures on Al_{*z*}Ga_{1-*z*}N relax layers for the suppression of nonradiative recombinations due to MDs. In this study, Al compositions (thicknesses) of the well layers and barrier layers were designed to be $x \sim 0.55$ ($L_w \sim 1.5$ nm) and $y \sim 0.75$ ($L_b \sim 15$ nm), respectively for the emissions at 250 nm. Furthermore, based on our critical-thickness calculation, we optimize the relax layer thickness (L_R) and the Al composition to effectively introduce MDs under the relax layer and to avoid MD generations in the well layers.

Critical thickness for a MQW structure can be calculated by using the total-MQW thickness (without the cap layer) and the averaged composition of the entire MQW (without the cap layer) [8]. Therefore, in the case of the Al_{0.55}Ga_{0.45}N/Al_{0.75}Ga_{0.25}N MQW on Al_{*z*}Ga_{1-*z*}N relax layer, the effective Al composition and epilayer thickness, which are considered from the relax layer to the top well layer, should be used to calculate the critical thickness for the relaxation at the interface between the AlN and relax layer. For the cal-

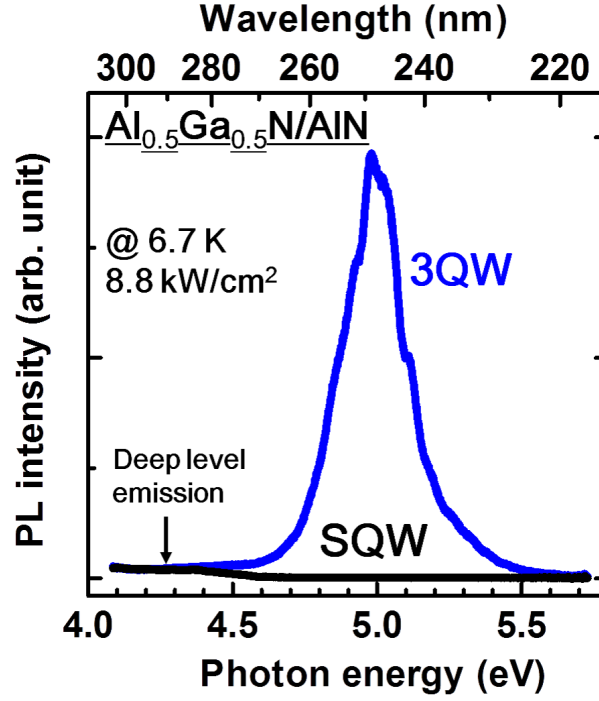


Figure 4.26: PL spectra of *c*-plane $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ SQW and 3QW ($L_w \sim 1.5$ nm, $L_b \sim 15$ nm) on *c*-plane sapphire substrates.

(a)



(b)

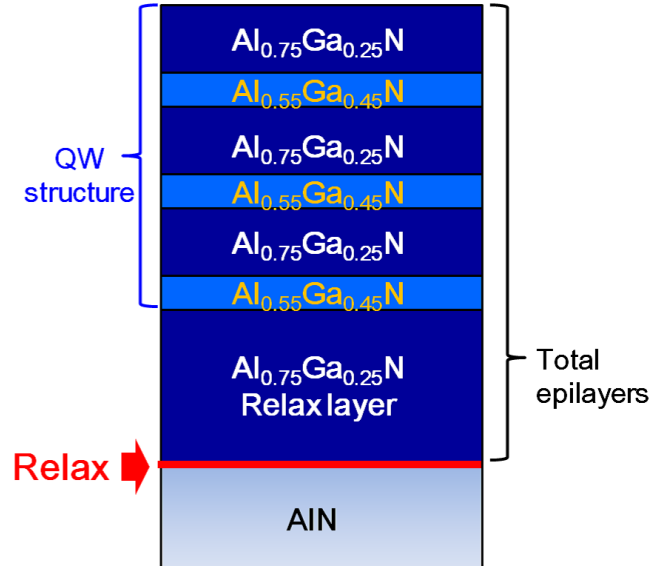


Figure 4.27: Schematic images of (a) $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QW and (b) $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ 3QW, which has a 50-nm-thick $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layer to suppress nonradiative recombinations in the well layers due to MDs. For both of the QWs, the well and barrier layer thicknesses are about 1.5 and 15 nm, respectively.

ulation of relaxation at the interface between the relax layer and bottom well layer, on the other hand, the averaged Al composition and epilayer thickness should be considered from the bottom well layer to the top well layer. Figure 4.28 shows the correlation between averaged Al compositions and total epilayer thickness in the case of $z = 0.75$ and $L_R = 50$ nm, where total epilayer thickness means the thickness from the relax layer to the surface. The averaged Al composition for the total epilayers is expressed as a solid line and that for the QW structure is depicted as a broken line.

The critical thicknesses for the relax layer and well layer were calculated as a function of total epilayer thicknesses, and we refer the former critical thickness to h_c^R and the latter critical thickness to h_c^{QW} in the following discussions. In order to generate MDs under the relax layer and to suppress the nonradiative recombinations in the well layers, h_c^R must be thinner than h_c^{QW} . Then, we calculated h_c^R and h_c^{QW} , and their magnitude correlation are depicted in Fig. 4.29 as functions of the L_R and in-plane relaxation degree [$r_{x'y'}$ in Eq. (4.108)] of the relax layer with respect to AlN. Here, we consider the in-plane anisotropic relaxation process for the relax layer as shown in Fig. 4.30.

Figures 4.29(a) and (b) show the calculated results assuming $\theta = 0.05^\circ$, $\phi = 15^\circ$, and $z = 0.75$ without and with considering the effects of F_p , respectively. The θ and ϕ are the typical off-angle and off-direction for the AlN films on sapphire substrates in this study. The relation $h_c^{QW} > h_c^R$ ($h_c^{QW} < h_c^R$) is satisfied in red (blue) regions, and h_c^{QW} equals to h_c^R on the solid lines. Therefore, to effectively suppress MDs in the well layers, we should design the relax layer thickness to locate in the red region in Fig. 4.29. Note that the in-plane relaxation degree of the relax layer increases with increasing the number of the MQW period. In this sense, the available margin of the relaxation degree should be as large as possible, and therefore, thicker L_R is seemingly more effective to suppress MDs in the well layers. However, too thick L_R may cause some bad effects on the efficiency such as generations of cracks and half-loop dislocations due to the large strain. Hence, we should choose moderate L_R .

Figure 4.29(a) indicates that L_R exceeding 20 nm is effective to relax the misfit strains under the relax layer. In Fig. 4.29(b), the magnitude correlations between h_c^R and h_c^{QW} are quite different from Fig. 4.29(a) due to the effect of F_p . A black dotted line is the calculation result of the relaxation process in Al_{0.75}Ga_{0.25}N/AlN, which means the relaxation degree of the relax layer without fabricating MQWs on it when the relaxation ideally proceeds. (the actual relaxation rate is slower than the calculated result as we described in the previous section.) Region (i) is located above a black dotted line and the blue region. It means that the samples located in region (i) must go through the blue region in the progress of the relaxation. In other words, to reach region (i), the QW is relaxed, so that it has the same meaning as a blue region. Region (ii) is over the upper limit of the relaxation degree by dislocation glides due to the F_p effect. If the relaxation degree of the relax layer exceeds the upper limit due to some other effects such as generation of cracks, the region (ii) becomes a blue region because the relation $h_c^{QW} < h_c^R$ is satisfied. Consequently, Fig. 4.29(b) indicates

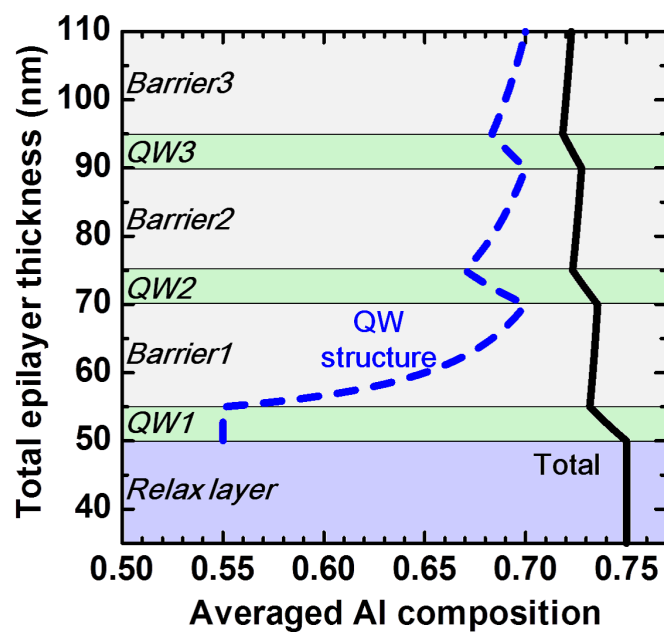


Figure 4.28: Correlation between averaged Al compositions and total epilayer thickness in the case of $x = 0.55$, $y = 0.75$, $z = 0.75$, $L_w = 1.5$ nm, $L_b = 15$ nm, and $L_R = 50$ nm, where total epilayer thickness means the thickness from the relax layer to the surface. The averaged Al composition for the total epilayers is expressed as a solid line and that for the QW structure is depicted as a broken line.

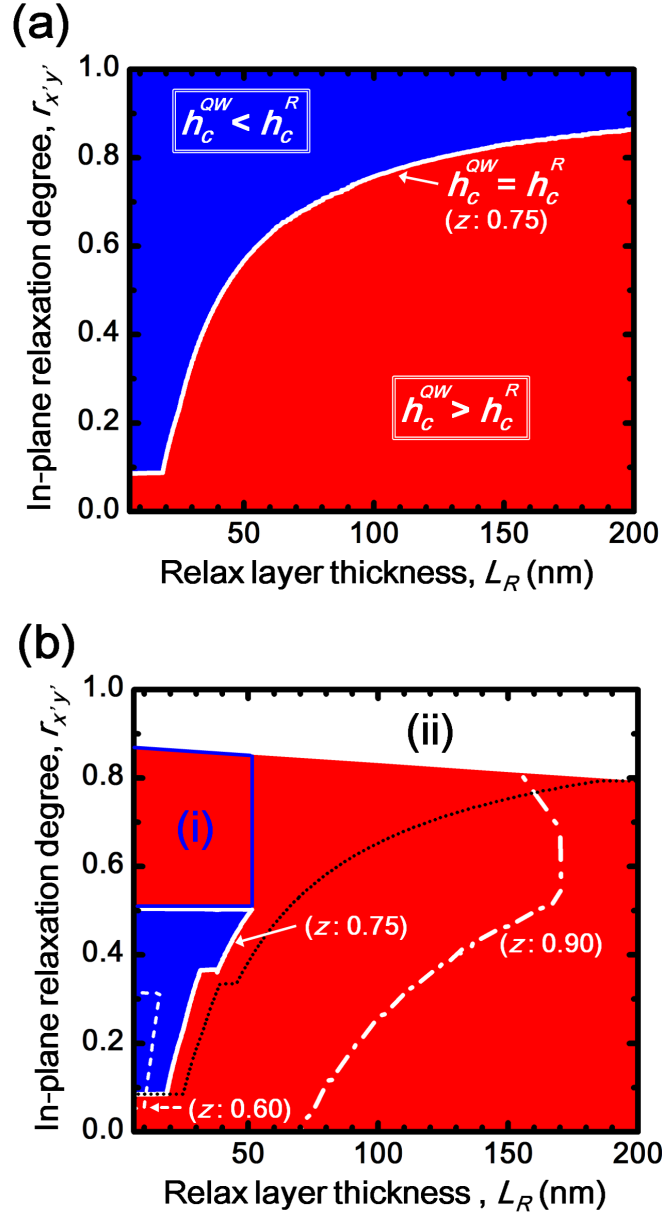


Figure 4.29: Magnitude correlations between h_c^R and h_c^{QW} are depicted as functions of L_R and in-plane relaxation degree of the relax layer with respect to AlN. The calculations with c -plane $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ MQWs on $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layers assume $\theta = 0.05^\circ$ and $\phi = 15^\circ$. The effects of F_p is considered in (a), but is not in (b). The relation $h_c^{QW} > h_c^R$ ($h_c^{QW} < h_c^R$) is satisfied in red (blue) regions, and h_c^{QW} equals to h_c^R on the solid lines. In (b), a broken line and a dash-dotted line are $h_c^{QW} = h_c^R$ lines in the case of $z = 0.60$ and $z = 0.90$, respectively. A black dotted line is the calculated relaxation process in $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}/\text{AlN}$, which means the relaxation degree of the $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layer without fabricating MQWs on it when the relaxation ideally proceeds. Although region (i) is a red region by the calculation result, it has the same meaning as a blue region. Region (ii) is over the upper limit of the relaxation degree by dislocation glides due to the F_p effect.

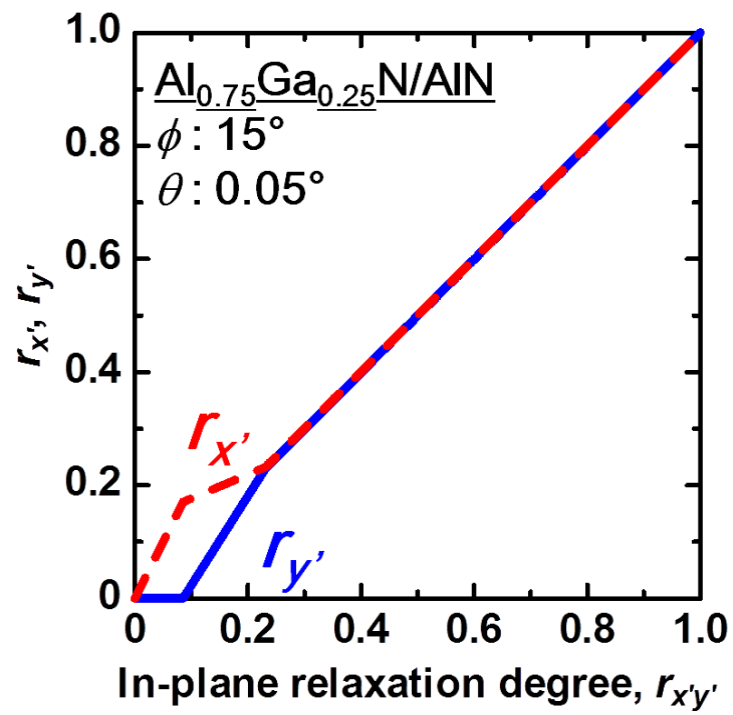


Figure 4.30: In-plane anisotropic relaxation process for the relax layer with respect to AlN.

that L_R exceeding 50 nm is effective to suppress MDs in the well layers.

Similarly, we calculated the cases of $z = 0.60$ and $z = 0.90$, and $h_c^{QW} = h_c^R$ lines are depicted as a dotted line and a dash-dotted line in Fig. 4.29(b), respectively. The results clarified that Ga-richer relax layers have a lot of flexibility in designing QWs in terms of the relaxation position control. However, the Ga-richer AlGa_{0.55}N layer with respect to the barrier layers may cause absorption of the QW emissions (considering the quantum confinement effect). From these findings, we propose an Al_{0.55}Ga_{0.45}N/Al_{0.75}Ga_{0.25}N QW ($L_w \sim 1.5$ nm, $L_b \sim 15$ nm) on a 50-nm-thick Al_{0.75}Ga_{0.25}N relax layer as an optimized structure for a 250 nm emission.

Figure 4.31 shows the PL spectra of the Al_{0.45}Ga_{0.55}N/Al_{0.75}Ga_{0.25}N SQW ($L_w : 2.0$ nm, $L_b : 12$ nm) and Al_{0.55}Ga_{0.45}N/Al_{0.75}Ga_{0.25}N 3QW ($L_w : 1.3$ nm, $L_b : 12$ nm) fabricated on 50-nm-thick Al_{0.75}Ga_{0.25}N relax layers. The difference of the Al compositions and epilayer thicknesses from the designed structures have no structural reasons but caused by the growth machine conditions. The PL measurements were performed at 6.5 K, and a Ti:Al₂O₃ fourth harmonic generation laser was used for excitation. The selective excitation conditions could not be realized because the excitation laser could not reach the barrier layer energy of 5.35 eV (~ 232 nm). It is noteworthy that the strong near band edge emissions are observed from both of the QWs in contrast to the conventional Al_{0.5}Ga_{0.5}N/AlN SQW, indicating that MDs are generated but are effectively confined at the interfaces between the AlN layers and relax layers, and nonradiative recombinations in the well layers are suppressed.

To compare the emission intensities of the Al_{0.55}Ga_{0.45}N/Al_{0.75}Ga_{0.25}N and Al_{0.5}Ga_{0.5}N/AlN 3QWs, PL measurements using an ArF excimer laser (193 nm) were performed at 11 K. We can compare the emission intensities because the barrier layers are equally excited in both of the QW structures using the ArF excimer laser. The obtained PL spectra of the QWs are shown in Fig. 4.32. The emission intensity of the newly designed Al_{0.55}Ga_{0.45}N/Al_{0.75}Ga_{0.25}N 3QW is 2.6 times as strong as that of the conventional Al_{0.5}Ga_{0.5}N/AlN 3QW. Therefore, we confirmed that the optimized structure based on our critical-thickness calculation contributes to highly efficient DUV emissions. Meanwhile, the large increase in the emission intensity also implies that the enhanced IQE is not only due to the suppression of MDs in the bottom well layer. Then, we subsequently performed TRPL measurements for the QWs.

Figure 4.33 shows the TRPL decay curves of the Al_{0.55}Ga_{0.45}N/Al_{0.75}Ga_{0.25}N and Al_{0.5}Ga_{0.5}N/AlN 3QWs near PL peak energies at 6.5 K. To avoid the many-body effects and screening effects of the internal electric fields, the weak excitation condition was used for the measurements. The estimated initial carrier density in the QWs was $1 \times 10^{15} \text{ cm}^{-3}$. The TRPL decay curves were fitted with a double exponential function expressed as

$$I_{\text{TRPL}} = A_{\text{fast}} \exp\left(-\frac{t}{\tau_{\text{fast}}}\right) + A_{\text{slow}} \exp\left(-\frac{t}{\tau_{\text{slow}}}\right), \quad (4.109)$$

where τ_{fast} and τ_{slow} represent the fast and slow components of lifetimes. A_{fast} and A_{slow}

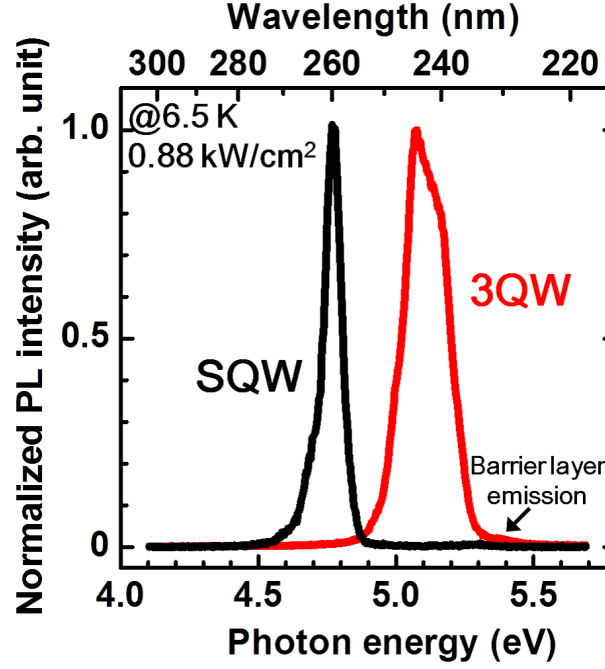


Figure 4.31: PL spectra of the $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ SQW (L_w : 2.0 nm, L_b : 12 nm) and $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ 3QW (L_w : 1.3 nm, L_b : 12 nm) fabricated on 50-nm-thick $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layers. The PL measurements were performed at 6.5 K, and a $\text{Ti}:\text{Al}_2\text{O}_3$ forth harmonic generation laser was used for the excitation.

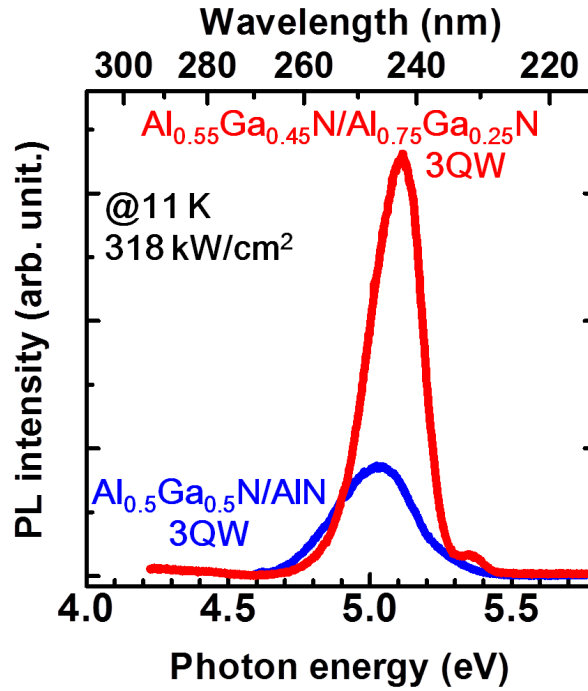


Figure 4.32: PL spectra of the $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QWs excited by an ArF excimer laser (193 nm) at 11 K. The emission intensity of the $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ 3QW is 2.6 times as strong as that of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QW.

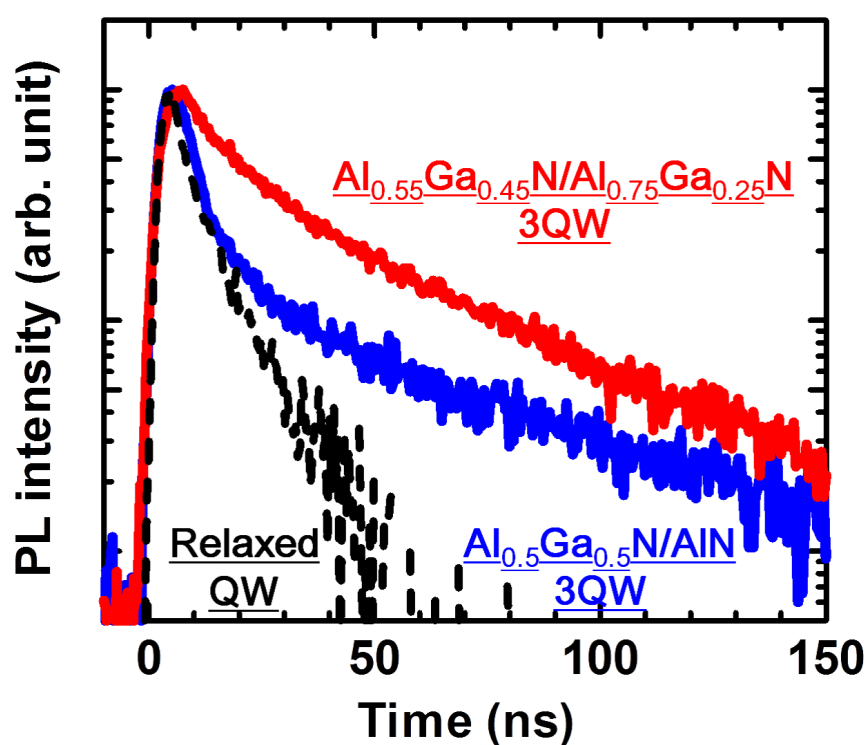


Figure 4.33: TRPL decay curves of the $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QWs near PL peak energies are expressed as solid lines. The initial carrier density in the QWs was estimated to be $1 \times 10^{15} \text{ cm}^{-3}$. A broken line is the decay curve of the relaxed $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW depicted in Fig. 4.6.

are the coefficients for the respective lifetimes. The τ_{fast} of the $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QWs are 13.1 and 5.5 ns, respectively, whereas the τ_{slow} of the respective QWs are 45.9 and 54.6 ns. Considering the radiative recombination lifetimes in the c -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs discussed in Fig. 4.6, the τ_{slow} for the QWs are the lifetimes dominantly affected by radiative recombination processes. $A_{\text{fast}}\tau_{\text{fast}}/A_{\text{slow}}\tau_{\text{slow}}$ of the $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QWs are 0.40 and 0.93, respectively, which are smaller than 1 and mean that the radiative recombination processes are dominant in both of the QWs. Here, we also depict a TRPL decay curve of the relaxed $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW (L_w : 6.8 nm in Fig. 4.6) as a broken line in Fig. 4.33. The decay curve is dominated by nonradiative recombinations due to MDs, and the estimated lifetime is 6.0 ns. The initial decay of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QW is quite similar to that of the relaxed sample, and the obtained τ_{fast} (5.5 ns) is also close to 6.0 ns. The result means that the τ_{fast} may be dominated by nonradiative recombinations due to MDs. However, the decay curve of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QW should be derived from the top and second well layers because the emission from the bottom well layer cannot be observed due to the MDs considering the results in Fig. 4.26. Therefore, the τ_{fast} of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QW may reflect a slight number of MDs in the top and second well layers, and they also cause the PL intensity difference shown in Fig. 4.32. Furthermore, the τ_{slow} related to radiative recombinations of the $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ 3QW is shortened compared with that of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 3QW. We consider that this is because the polarization field is divided into the well and barrier layers in the case of $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$ QW. Consequently, the effect may also lead to the strong PL intensity of the $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ 3QW. These results indicate that $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$ QWs optimized based on our critical-thickness calculation are very attractive for highly efficient DUV emissions.

4.9 Discussion on semipolar-plane heterostructures

Finally, we discuss semipolar AlGa_N/AlN heterostructures. The critical thickness for semipolar planes can be also calculated by our extended model described in Sec. 4.7. From the calculated results in Fig. 4.21, Tab. 4.1 and Tab. 4.2, we found that the critical thicknesses of many semipolar AlGa_N/AlN heterostructures are several times as thick as that of the c -plane AlGa_N/AlN with unintentional off-angles. In particular, the critical thickness of a semipolar plane with $\theta = 50^\circ\text{--}55^\circ$ off is the thickest among various growth planes. r -Plane and $(11\bar{2}2)$, on which AlGa_N/AlN QWs are realized in Chap. 2, have off-angles of 43° and 58° , respectively, and they are attractive growth planes in terms of the suppression of MDs, in addition to the small internal electric fields.

Let us discuss the lattice relaxation process and control of the relaxation position in semipolar-plane QWs in a similar way to c -plane QWs. Herein, we particularly focus on the r -plane QWs for simplicity. Figure 4.34 shows the lattice relaxation process consid-

ering the effect of F_p for the r -plane $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ heterostructure. We found that the $(0001)\langle 11\bar{2}0 \rangle$ slip initially occurs, and many semipolar and nonpolar plane slips subsequently occur one after another. As a result, the number of slip systems contributing to the lattice relaxation in the r -plane heterostructure is larger than that in the c -plane heterostructure (see Fig. 4.24), and almost all of the misfit strains are relaxed in contrast to the c -plane heterostructure. This is because the F_p of the r -plane $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ is very small in various slip systems as shown in Figs. 4.18–4.20, whereas that of the c -plane heterostructure diverges to infinity in most of the slip systems. The lattice relaxation process focusing on r_x and r_y for the r -plane $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}/\text{AlN}$ heterostructure is shown in Fig. 4.35. Because a lot of slip systems can contribute to the lattice relaxations for the r -plane sample due to the small F_p , the relaxation process is almost unchanged compared with the calculation result without considering the F_p in contrast to the c -plane growth (see Figs. 4.23 and 4.25).

Furthermore, the relaxation-position control of the r -plane AlGaN QWs is discussed similar to the c -plane QWs described in the previous section. r -Plane $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ MQW on an $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layer is used for the following discussion as proposed in Fig. 4.29. The critical thicknesses for the relax layer and well layer were calculated as a function of total epilayer thickness, and the correlation between the former critical thickness (h_c^R) and the latter critical thickness (h_c^{QW}) were investigated. In order to generate MDs under the relax layer, the relation $h_c^{QW} > h_c^R$ should be satisfied. Then, we calculate the h_c^R and h_c^{QW} , and their magnitude correlation are depicted in Fig. 4.36 as functions of the L_R and in-plane relaxation degree of the relax layer with respect to AlN. Figures 4.36(a) and (b) are the calculated results without and with considering the effects of F_p , respectively. The black dotted line in Fig. 4.36(b) is the calculated relaxation process in the r -plane $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}/\text{AlN}$, which means the relaxation degree of the $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layer without fabricating a MQW on it when the relaxation ideally proceeds. The relation $h_c^{QW} > h_c^R$ ($h_c^{QW} < h_c^R$) is satisfied in red (blue) regions, and h_c^{QW} equals to h_c^R on the solid lines. Therefore, to suppress MDs in the well layers, we should appropriately design the relax layer thickness, which locates in a red region in Fig. 4.36.

Comparing Figs. 4.36(a) and (b), there is no significant difference, regardless of the effect of F_p . This is because the F_p of the r -plane sample is quite small with respect to the thermally assisted force. Moreover, we found that even quite thin relax layers (< 10 nm) effectively suppress MDs in the well layers in contrast to the c -plane heterostructure. Thus, the calculation results indicate that the r -plane $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ structure has a lot of flexibility in designing QWs in terms of the relaxation-position control, compared with the c -plane structure (see Fig. 4.29). Because a lot of slip systems can relax the r -plane strain without large differences of the critical thickness (see Fig. 4.21), the relax layer with the greatest strain energy is more easily relaxed than the well layers for many slip systems. As a consequence, the r -plane $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ structure has such a high flexibility in designing QWs.

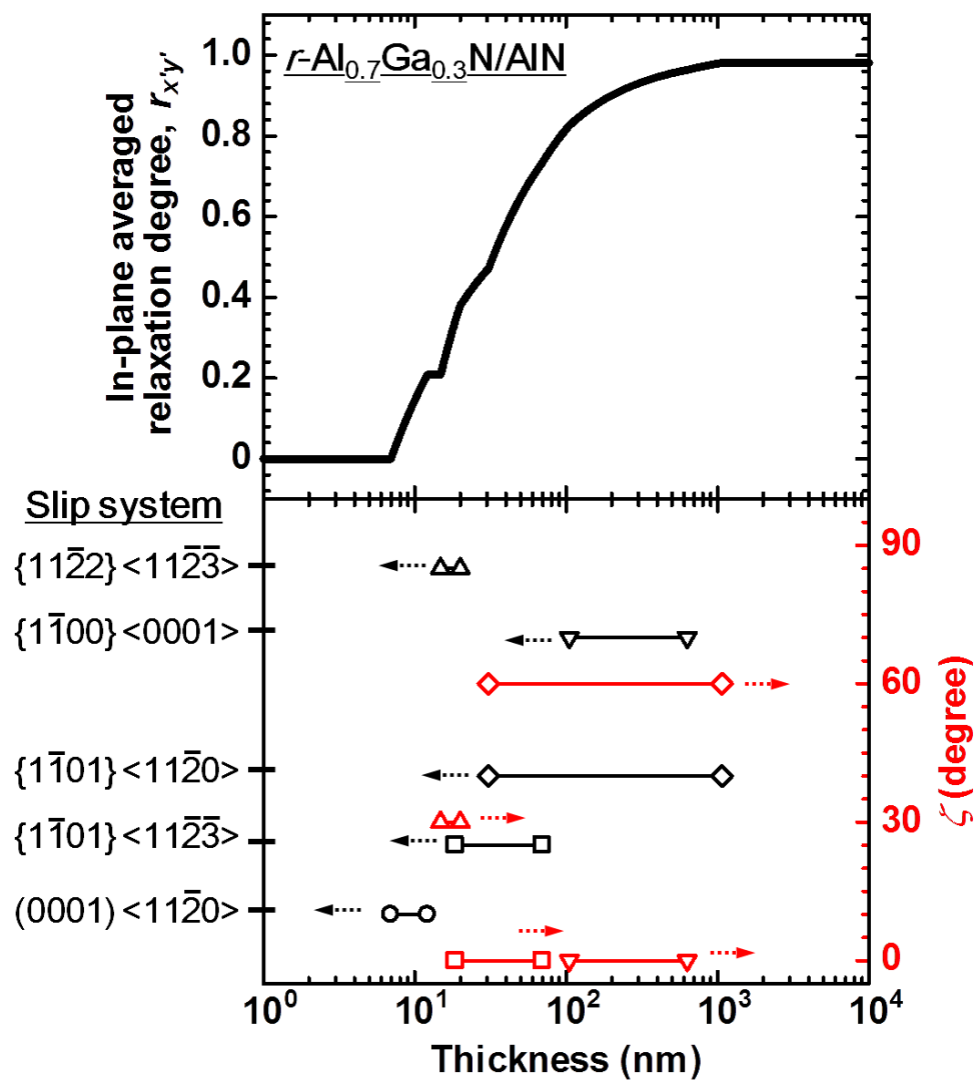


Figure 4.34: Lattice relaxation process considering the effect of F_p for the r -plane $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N/AlN}$ heterostructure. The symbols for ζ correspond to those of the slip systems.

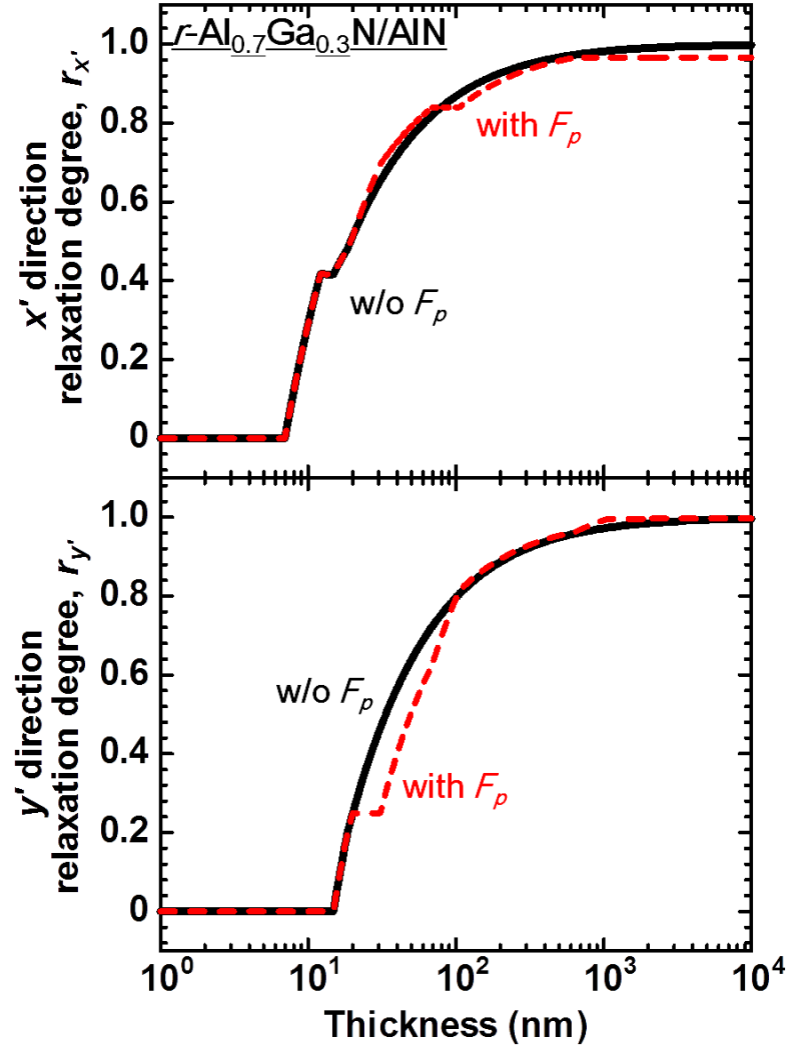


Figure 4.35: Lattice relaxation process focusing on $r_{x'}$ and $r_{y'}$ in the r -plane Al_{0.7}Ga_{0.3}N/AlN heterostructure. Broken lines and solid lines are the calculated results with and without considering the effects of F_p , respectively.

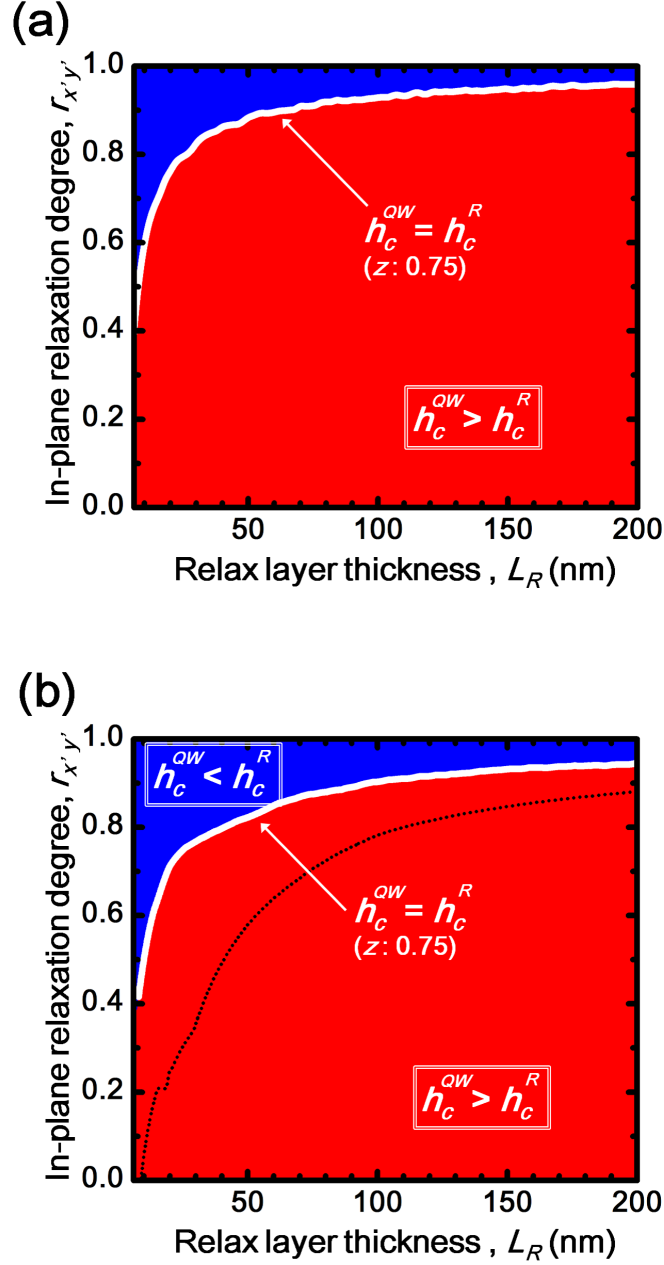


Figure 4.36: Magnitude correlations between h_c^R and h_c^{QW} are depicted as functions of L_R and in-plane relaxation degree of the relax layer with respect to AlN. (a) and (b) are the calculated results for r -plane $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}/\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ MQW on an $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layer without and with considering the effect of F_p , respectively. The relation $h_c^{QW} > h_c^R$ ($h_c^{QW} < h_c^R$) is satisfied in red (blue) regions, and h_c^{QW} equals to h_c^R on the solid lines. A black dotted line is the calculation result of the relaxation process in r -plane $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}/\text{AlN}$, which means the relaxation degree of the $\text{Al}_{0.75}\text{Ga}_{0.25}\text{N}$ relax layer without fabricating MQW on it when the relaxation ideally proceeds.

4.10 Summary

In this chapter, we investigated the calculation model of the critical thickness and lattice relaxation for AlGa_N/AlN heterostructures. Although the XRD measurement is generally used for the characterization of lattice relaxation, our experimental results show that the detection sensitivity is not necessarily good particularly for AlGa_N heterostructures. Even when lattice relaxations are not determined by the XRD, latently relaxed samples give off some unique optical signals, which suggest the lattice relaxations, such as unexpected shortenings of carrier recombination lifetimes, narrowing of line widths, and decrease of emission intensities. In particular, TRPL spectroscopy highlights the severity of the critical thickness of AlGa_N/AlN heterostructures, and it was clarified that the optically determined critical thickness cannot be well explained by conventional slip systems for wurtzite (0001) epitaxial layers.

Although the semipolar $\{11\bar{2}2\}$ and $\{1\bar{1}01\}$ slips have been conventionally considered for (0001) heterostructures, we proposed that the (0001) slip firstly occurs due to the unintentional off-angle, followed by such semipolar-plane slips. Our extended critical-thickness calculation model assuming the off-angles, friction forces, and thermally assisted forces well reproduced the experimental results of the (0001) AlGa_N/AlN heterostructures, and it scarcely depends on the threading dislocation density in the underlying layer. Subsequently, we clarified that the insertion of an AlGa_N relax layer under the active layers is effective method to avoid the efficiency degradation due to MDs.

From the calculations for semipolar AlGa_N/AlN heterostructures, we found that the critical thickness of semipolar planes with about 50°–55° off-angles, is the thickest among various growth planes. The results therefore indicate that *r*-plane and $(11\bar{2}2)$ QWs, which are realized in Chap. 2, are attractive growth planes in terms of the suppression of MDs in addition to the small internal electric fields.

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Chapter 5

Optical polarization control for DUV devices

5.1 Introduction

In the previous chapters, we discussed the improvement of IQE of AlGaIn QWs and clarified that semipolar-plane AlGaIn QWs grown at high reactor pressures are attractive for highly efficient emitters. This is because they can suppress the internal electric fields and can decrease the density of point defects, which act as dominant nonradiative recombination centers at room temperature. In addition, the calculated critical thickness for semipolar AlGaIn/AlN heterostructures with certain off-angles are thicker than the conventional *c*-plane heterostructures, which provides that semipolar AlGaIn QWs for a lot of flexibility in the structural designs.

In this chapter, in contrast to the previous chapters, we discuss the optical polarization control toward actual DUV devices. To obtain high EQE of DUV devices, high LEE is also required in addition to the improvement of IQE. Thus, the optical polarization, which determines the emission direction, should be controlled for higher LEE considering the respective device structures: For LEDs, the emissions from active layers are generally obtained from the surfaces, whereas the cleaved planes (edge faces of samples) are used as cavity mirrors for LDs. Therefore, the optical polarizations, which lead to strong surface emissions and strong light extractions from cleaved planes, are desired for LEDs and LDs, respectively.

In wurtzite semiconductors, the valence band maximums are splitted by the spin-orbit interactions and the non-cubic crystal fields near the Γ point in the Brillouin zones. As a consequence, AlN and GaN have three different states as valence bands, and they are called as heavy-hole (HH), light-hole (LH), and crystal-field split-off hole (CH) bands. These bands have irreducible representations of Γ_9 , Γ_7 , and Γ_7 , respectively. The order of the valence bands are determined by the splitting energies derived from the fundamental material properties. Figure 5.1 shows the schematic images of the band lineups of AlN and GaN. Because the crystal-field splitting energy (Δ_1) of AlN is negative (-221.5 meV [1]), whereas

that of GaN is positive (12.3 meV [2]), the order of the valence bands are quite different between AlN and GaN [1–8]. The topmost valence band in AlN is the CH band governed by the p_z -like state, whereas that in GaN is the HH band governed by p_x - and p_y -like states. Here, the z -axis corresponds to the c -axis in wurtzite structures and the x - and y -axes are in the c -plane. As a consequence of the nature of the top valence bands, the emission from AlN is dominantly polarized parallel to the c -axis ($\mathbf{E} \parallel c$), whereas that of GaN is polarized perpendicular to the c -axis ($\mathbf{E} \perp c$), where $\mathbf{E}$ is the electric field vector of emitted light.

According to the optical selection rule for AlN, although the strong light extraction can be expected from nonpolar planes, the emission from c -plane should be considerably weak unlike the case of GaN. This indicates that c -plane AlN-based LEDs are not desirable in terms of the LEE. On the other hand, the valence band lineups and the optical polarizations of AlGaIn alloys can be varied by the Al compositions because the topmost valence bands between AlN and GaN are different. In addition to the Al compositions, in the case of QW structures, the optical polarizations also strongly depend on the quantum confinement effects and the strains. Thus, we have to appropriately design the AlGaIn QWs considering the light extractions for the devices. However, the experimental and theoretical discussion for the optical polarization of semipolar AlGaIn QWs, which can significantly enhance the radiative recombination probabilities, are not sufficient in contrast to the c -plane and m -plane QWs [9, 10]. Then, we investigate the optical polarization control for semipolar r -plane AlGaIn/AlN QWs toward highly efficient DUV devices in this chapter.

5.2 Optical polarization calculation

We theoretically calculate the band structures of AlGaIn/AlN QWs using the $\mathbf{k} \cdot \mathbf{p}$ perturbation method, and compare the calculated results with the experimental results of the optical polarization degree.

Using the periodic part of the Bloch function $u_{n\mathbf{k}}(\mathbf{r})$ and the energy $E_n(\mathbf{k})$, the Schrödinger equation considering the spin-orbit effect near the band edge can be written as

$$\begin{aligned} \mathbf{H}_{\text{full}} u_{n\mathbf{k}}(\mathbf{r}) &\simeq \left(\mathbf{H}_0 + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} + \mathbf{H}_{\text{so}} \right) u_{n\mathbf{k}}(\mathbf{r}) \\ &= E_n(\mathbf{k}) u_{n\mathbf{k}}(\mathbf{r}), \end{aligned} \quad (5.1)$$

where the Hamiltonian $\mathbf{H}_0$ is given by

$$\mathbf{H}_0 = -\frac{\hbar^2}{2m_0} \nabla^2 + \frac{\hbar^2 \mathbf{k}^2}{2m_0} + V(\mathbf{r}). \quad (5.2)$$

Here, $V(\mathbf{r})$ is the periodic potential with the same periodicity as the crystal lattice and $\mathbf{H}_{\text{so}}$ accounts for the spin-orbit interaction. In addition, $\mathbf{k}$, m_0 , and n are wave number, mass

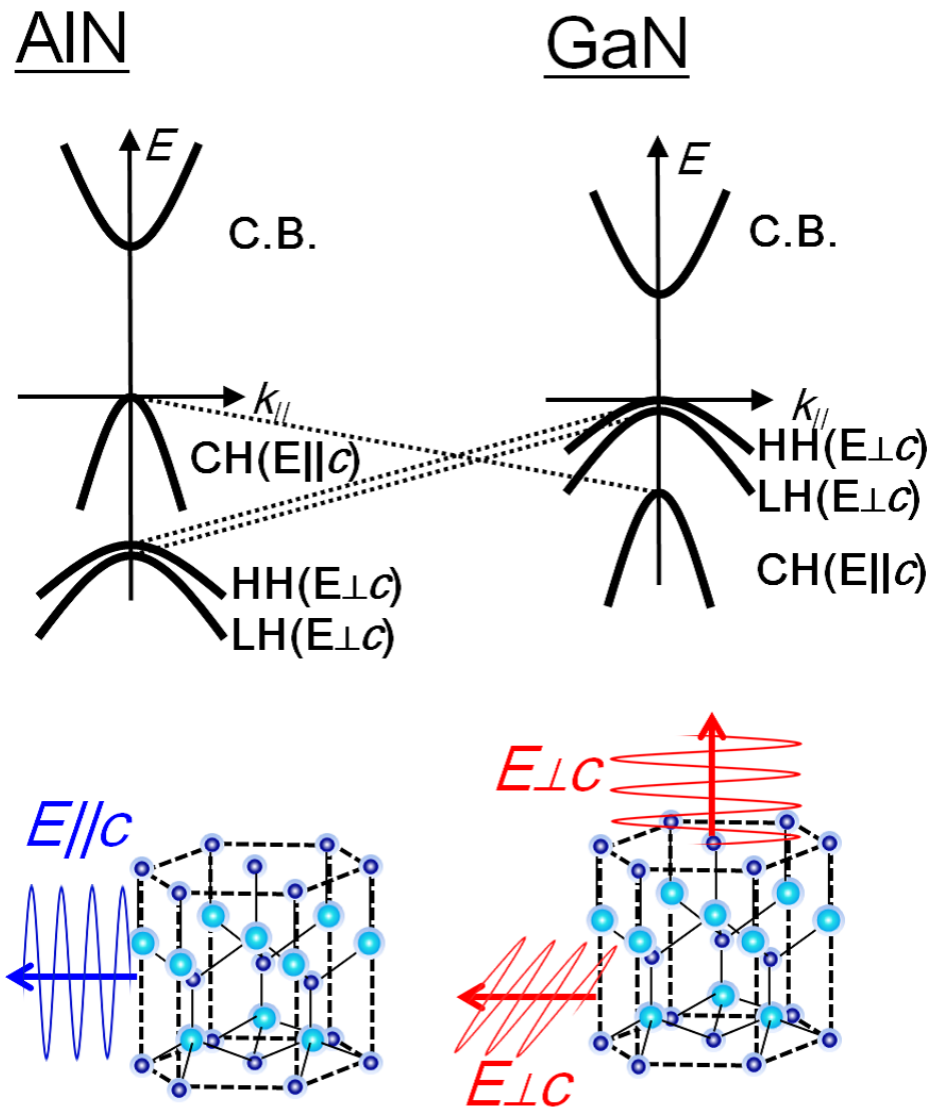


Figure 5.1: Schematic images of the band lineups of AlN and GaN. C. B. stands for the conduction band.

of an electron, and band index, respectively.

5.2.1 Hamiltonian and wavefunction for valence band

The Hamiltonian for the valence band structure has been derived by the $\mathbf{k} \cdot \mathbf{p}$ method as follows [11, 12],

$$\mathbf{H} = \begin{bmatrix} F & -K^* & -H^* & & & \\ -K & G & H & & & \Delta \\ -H & H^* & \Lambda & & \Delta & \\ & & & F & -K & H \\ & & \Delta & -K^* & G & -H^* \\ & \Delta & & H^* & -H & \Lambda \end{bmatrix}. \quad (5.3)$$

where

$$\left\{ \begin{array}{l} F = \Delta_1 + \Delta_2 + \Lambda + \Theta, \\ G = \Delta_1 - \Delta_2 + \Lambda + \Theta, \\ \Lambda = A_1 k_z^2 + A_2 (k_x^2 + k_y^2) + \Lambda_\epsilon, \\ \Lambda_\epsilon = D_1 \epsilon_{zz} + D_2 (\epsilon_{xx} + \epsilon_{yy}), \\ \Theta = A_3 k_z^2 + A_4 (k_x^2 + k_y^2) + \Theta_\epsilon, \\ \Theta_\epsilon = D_3 \epsilon_{zz} + D_4 (\epsilon_{xx} + \epsilon_{yy}), \\ K = A_5 (k_x + i k_y)^2 + D_5 (\epsilon_{xx} - \epsilon_{yy} + 2i \epsilon_{xy}), \\ H = A_6 k_z (k_x + i k_y) + D_6 (\epsilon_{xz} + i \epsilon_{yz}), \\ \Delta = \sqrt{2} \Delta_3. \end{array} \right. \quad (5.4)$$

Here, Δ_1 is the crystal-field splitting energy, and Δ_2 and Δ_3 are the energies related to the spin-orbit interaction; D_i and A_i ($i = 1, 2, \dots, 6$) are the deformation potentials and effective mass parameters for valence bands; and, k_i are the wave numbers along the respective direction. For the simplicity, we omit $(\hbar^2/2m_0)$ before the A_i . The expression of strain tensor ϵ_{ij} was described in Chap. 4. Here, we adopt the same orthogonal coordinate systems (x, y, z) and (x', y', z') as in Chap. 4. The (x, y, z) coordinate is defined for wurtzite structure. The x and y axes are in (0001), whereas the z axis corresponds to c -axis. On the other hand, the (x', y', z') coordinate is defined for an arbitrary growth plane. The z' axis is parallel to the growth direction inclined from the z axis with an angle θ . The x' and y' axes are on the growth plane, and the y' axis is defined to coincide with the y axis. Note that k_i and ϵ_{ij} should be obtained from $k_{i'}$ and $\epsilon_{i'j'}$ using the rotation matrix in the case of the semipolar plane samples.

Using the eigenfunction of Eq. (5.3) defined as

$$\mathbf{g} = \begin{bmatrix} g_1 & g_2 & g_3 & g_4 & g_5 & g_6 \end{bmatrix}^T, \quad (5.5)$$

the wavefunction for the valence band Ψ_v is written as

$$\Psi_v = \frac{1}{\sqrt{B}} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{i=1}^6 g_i |i\rangle, \quad (5.6)$$

where B is the volume of the entire space. Here, the eigenfunction $\mathbf{g}$ is normalized according to

$$\sum_{i=1}^6 |g_i|^2 = 1. \quad (5.7)$$

For QW structures, the wave number along the growth direction (z' direction) is discretized and $k_{z'}$ is substituted by $-i\partial/\partial z'$. Using the Hamiltonian for the valence band, the simultaneous Schrödinger equations for holes are expressed as

$$\begin{aligned} \sum_{j=1}^6 \left[H_{ij} \left(k_{x'}, k_{y'}, k_{z'} = -i\frac{\partial}{\partial z'} \right) + (E_v^{(0)} + e_0 E_{\text{int}}^{\text{well}} z') \delta_{ij} \right] g_j^m(k_{x'}, k_{y'}, z') \\ = E^m(k_{x'}, k_{y'}) g_i^m(k_{x'}, k_{y'}, z'), \end{aligned} \quad (5.8)$$

where $i = 1-6$ and m is valence-subband index. $E_v^{(0)}$, e_0 , and $E_{\text{int}}^{\text{well}}$ are the valence band potential, elementary charge, and the internal electric field in the well layer, respectively. The expression of $E_{\text{int}}^{\text{well}}$ was described in Chap. 2. $E_v^{(0)}$ for the well layer equals to zero and that for the barrier layer equals to the band offset for the valence band (it will be described in the following discussion). In this study, Eq. (5.8) is solved by the finite-difference method [13],¹ and $6N \times 6N$ Hamiltonian for the QW is given by

$$\mathbf{H}_{\text{QW}} = \begin{bmatrix} \mathbf{M}_{1,1} & \cdots & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & & \vdots \\ & & \mathbf{M}_{j-1,j-1} & \mathbf{M}_{j-1,j} & 0 \\ 0 & \cdots & \mathbf{M}_{j,j-1} & \mathbf{M}_{j,j} & \mathbf{M}_{j,j+1} & \cdots & 0 \\ & & 0 & \mathbf{M}_{j+1,j} & \mathbf{M}_{j+1,j+1} & & \\ \vdots & & & \vdots & & \ddots & \vdots \\ 0 & \cdots & & 0 & & \cdots & \mathbf{M}_{N,N} \end{bmatrix}. \quad (5.9)$$

Thus, valence band energies and the wavefunctions can be obtained by solving the following equation,

¹The detailed calculation method including the definition of $\mathbf{M}$ is described in Appendix B.

$$\mathbf{H}_{\text{QW}} \cdot \mathbf{g} = E \mathbf{g}, \quad (5.10)$$

where

$$\mathbf{g} = \begin{bmatrix} g_1^1 & g_2^1 & \cdots & g_6^1 & \cdots & g_1^j & g_2^j & \cdots & g_6^j & \cdots & g_1^N & g_2^N & \cdots & g_6^N \end{bmatrix}^T. \quad (5.11)$$

Here, the eigenfunction $\mathbf{g}$ is normalized according to

$$\sum_{i=1}^6 \int_{-\infty}^{\infty} |g_i(z', k'_x, k'_y)|^2 dz' = 1. \quad (5.12)$$

Solving Eq. (5.10) corresponds with the diagonalization of Eq. (5.9).

5.2.2 Hamiltonian and wavefunction for conduction band

The Hamiltonian for the conduction band can be written as [11, 12]

$$\mathbf{H}_c = \begin{pmatrix} E_c & 0 \\ 0 & E_c \end{pmatrix}, \quad (5.13)$$

where

$$E_c = E_v + E_{g0} + \frac{\hbar^2 k_z^2}{2m_e^{\parallel}} + \frac{\hbar^2 (k_x^2 + k_y^2)}{2m_e^{\perp}} + P_{c\epsilon}. \quad (5.14)$$

Here, $m_e^{\perp}$ and $m_e^{\parallel}$ are the electron effective masses perpendicular and parallel to the c -axis direction, respectively. E_{g0} is the bandgap under the unstrained condition, and the hydrostatic energy shift $P_{c\epsilon}$ is given by

$$P_{c\epsilon} = a_{cz}\epsilon_{zz} + a_{ct}(\epsilon_{xx} + \epsilon_{yy}), \quad (5.15)$$

where a_{cz} and a_{ct} are the deformation potentials in the conduction band and are used for the directions parallel and perpendicular to the c -axis, respectively. E_v is the energy of the valence band top under the unstrained condition at the Γ point and is obtained by

$$E_v = \begin{cases} E_1^0 = \Delta_1 + \Delta_2 & (E_1^0 > E_2^0) \\ E_2^0 = \frac{\Delta_1 - \Delta_2}{2} + \sqrt{\left(\frac{\Delta_1 - \Delta_2}{2}\right)^2 + 2\Delta_3^2} & (E_1^0 < E_2^0) \end{cases}. \quad (5.16)$$

Using the spherically symmetric wavefunction $|S\rangle$ and the electron spin ($\eta = \uparrow, \downarrow$), we can obtain the electron wavefunction as

$$\Psi_c^\eta = \frac{1}{\sqrt{B}} e^{i\mathbf{k} \cdot \mathbf{r}} |S\eta\rangle. \quad (5.17)$$

For QW structures, the wave number along the growth direction (z' direction) is discretized and $k_{z'}$ is substituted by $-i\partial/\partial z'$. As a consequence, the conduction band wavefunction Ψ_c is given by

$$\Psi_c^\eta(z') = \frac{1}{\sqrt{B}} e^{i\mathbf{k} \cdot \mathbf{r}} \phi(z') |S\eta\rangle, \quad (5.18)$$

where $\phi(z')$ is normalized according to

$$\sum_\eta \int_{-\infty}^{\infty} |\phi(z')|^2 dz' = 1. \quad (5.19)$$

5.2.3 Optical transition matrix elements

Optical transition matrix elements are obtained by the following equation,

$$|\hat{\mathbf{e}}' \cdot \mathbf{M}'^\eta|^2 = \left| \langle \Psi_c^\eta | \hat{\mathbf{e}}' \cdot \mathbf{p}' | \Psi_v \rangle \right|^2, \quad (5.20)$$

where $\hat{\mathbf{e}}'$ is polarization direction of the light. Substituting Eqs. (5.6) and (5.17) into Eq. (5.20), the transition matrix elements along the respective directions can be obtained as

$$|M_j|^2 = \frac{|M_j^\uparrow|^2 + |M_j^\downarrow|^2}{2} \quad (j = x', y', z'), \quad (5.21)$$

where

$$\left\{ \begin{array}{l} |M_{x'}^\uparrow|^2 = \left| \frac{1}{\sqrt{2}}(g_2 - g_1) \langle S | p_x | X \rangle \cos \theta - g_3 \langle S | p_z | Z \rangle \sin \theta \right|^2, \\ |M_{x'}^\downarrow|^2 = \left| \frac{1}{\sqrt{2}}(g_4 - g_5) \langle S | p_x | X \rangle \cos \theta - g_6 \langle S | p_z | Z \rangle \sin \theta \right|^2, \\ |M_{y'}^\uparrow|^2 = \left| -\frac{1}{\sqrt{2}}(g_1 + g_2) i \langle S | p_y | Y \rangle \right|^2, \\ |M_{y'}^\downarrow|^2 = \left| -\frac{1}{\sqrt{2}}(g_4 + g_5) i \langle S | p_y | Y \rangle \right|^2, \\ |M_{z'}^\uparrow|^2 = \left| \frac{1}{\sqrt{2}}(g_2 - g_1) \langle S | p_x | X \rangle \sin \theta + g_3 \langle S | p_z | Z \rangle \cos \theta \right|^2, \\ |M_{z'}^\downarrow|^2 = \left| \frac{1}{\sqrt{2}}(g_4 - g_5) \langle S | p_x | X \rangle \sin \theta + g_6 \langle S | p_z | Z \rangle \cos \theta \right|^2. \end{array} \right. \quad (5.22)$$

Note that the optical transition matrix elements for QWs are obtained by substituting $\langle \phi | g_i \rangle$ into g_i . Here, $\langle S | p_x | X \rangle$, $\langle S | p_y | Y \rangle$, and $\langle S | p_z | Z \rangle$ are expressed as

$$\begin{cases} \langle S | p_x | X \rangle = \langle S | p_y | Y \rangle = \frac{m_0}{\hbar} P_{\perp}, \\ \langle S | p_z | Z \rangle = \frac{m_0}{\hbar} P_{\parallel}, \end{cases} \quad (5.23)$$

where, $P_{\perp}$ and $P_{\parallel}$ are the Kane' parameters given by

$$\begin{cases} P_{\perp}^2 = \frac{\hbar^2}{2m_0} \left(\frac{m_0}{m_e^{\perp}} - 1 \right) \frac{(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - 2\Delta_3^2}{(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - \Delta_3^2}, \\ P_{\parallel}^2 = \frac{\hbar^2}{2m_0} \left(\frac{m_0}{m_e^{\parallel}} - 1 \right) \frac{E_g [(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - 2\Delta_3^2]}{E_g + 2\Delta_2}. \end{cases} \quad (5.24)$$

Here, we define the in-plane polarization degree (ρ_{in}) and out-of-plane polarization degree (ρ_{out}) as

$$\rho_{\text{in}} = \frac{|M_{y'}|^2 - |M_{x'}|^2}{|M_{y'}|^2 + |M_{x'}|^2}, \quad (5.25)$$

$$\rho_{\text{out}} = \frac{|M_{x'}|^2 + |M_{y'}|^2 - |M_{z'}|^2}{|M_{x'}|^2 + |M_{y'}|^2 + |M_{z'}|^2}. \quad (5.26)$$

5.2.4 Parameter sets and band offsets

As we described above, some material parameters such as deformation potentials (a_{cz} , a_{ct} , and D_i) and effective mass parameters (A_i) are needed for the calculation. However, the different parameters have been reported from several groups and the calculated optical polarizations strongly depend on the parameter sets. Table 5.1 lists the four parameter sets (Set1–Set4) of deformation potentials and the effective mass parameters for the valence bands used in this study. The Set1 and Set2 are taken from Refs. [8] and [14], respectively, and the respective deformation potentials are substituted by the parameters in Refs. [1, 2] for the Set3 and Set4. Here, C_i are the exciton deformation potentials.

For the calculation of the band structures of AlGaIn/AlN QWs, the band offsets at the boundaries between the well layers and barrier layers should be determined. In this study, we assume that the total bandgap difference (ΔE_g) is divided into conduction and valence band offsets with a ratio of 7:3. ($0.7\Delta E_g$ is the conduction band offset and $0.3\Delta E_g$ is the valence band offset.) Here, $\Delta E_g = E_g^{\text{AlN}} - E_g^{\text{QW}}$, where E_g^{AlN} is the bandgap of AlN and E_g^{QW} is the bandgap of well layers under the strained condition. Although the deformation potentials for the conduction band (a_{cz} and a_{ct}) have not been given in Ref. [1, 2, 14], this approximate expression of the band offset enables us to calculate the band structures only using the exciton deformation potentials (C_i).

Then, we calculate band structures using the C_i , A_i , and band offsets, and investigate

Table 5.1: Parameter sets of the deformation potential and the effective mass for the calculation in this study.

Parameters	Set1 [8]		Set2 [14]		Set3		Set4	
	AlN	GaN	AlN	GaN	AlN	GaN	AlN	GaN
$a_c z$ (eV)	-20.5	-8.6	—	—	Ref. [1]	—	Ref. [2]	—
$a_c t$ (eV)	-3.9	-6.8	—	—	—	—	—	—
C_1 (eV)	3.4	4.9	4.21	5.81	4.3	6.5	4.3	6.5
C_2 (eV)	11.8	11.3	12.07	8.92	11.5	11.2	11.5	11.2
C_3 (eV)	8.8	8.2	9.22	5.45	6.8	4.9	6.8	4.9
C_4 (eV)	-3.9	-4.1	-3.74	-2.97	-3.6	-5.0	-3.6	-5.0
C_5 (eV)	-3.4	-4.0	-3.30	-2.87	-2.8	-2.8	-2.8	-2.8
C_6 (eV)	-3.4	-5.5	-4.49	-3.95	-4.5	-3.1	-4.5	-3.1
A_1 ($\hbar^2/2m_0$)	-3.86	-7.21	-3.991	-5.947	Ref. [8]	-3.86 -7.21	Ref. [14]	-3.991 -5.947
A_2 ($\hbar^2/2m_0$)	-0.25	-0.44	-0.311	-0.528	-0.25	-0.44	-0.311	-0.528
A_3 ($\hbar^2/2m_0$)	3.58	6.68	3.671	5.414	3.58	6.68	3.671	5.414
A_4 ($\hbar^2/2m_0$)	-1.32	-3.46	-1.147	-2.512	-1.32	-3.46	-1.147	-2.512
A_5 ($\hbar^2/2m_0$)	-1.47	-3.40	-1.329	-2.510	-1.47	-3.40	-1.329	-2.510
A_6 ($\hbar^2/2m_0$)	-1.64	-4.90	-1.952	-3.202	-1.64	-4.90	-1.952	-3.202

which parameter sets listed in Tab. 5.1 are the most appropriate to predict the optical polarization of AlGa_N/AlN QW emissions comparing the calculations with experimental results.

5.3 Optical polarization of *r*-plane AlGa_N/AlN QWs

5.3.1 In-plane polarization calculation for AlGa_N/AlN QWs

From the discussion in Fig. 5.1, the emissions from AlGa_N/AlN QWs are polarized perpendicular or parallel to the *c*-axis direction. Therefore, the surface emissions observable from *c*-plane QWs are necessarily polarized along $\mathbf{E} \perp c$, and the in-plane polarization degree is theoretically zero. However, the surface emissions from semipolar QWs are strongly polarized in many cases due to the crystallographic isotropy, and the comprehensive understanding is required for practical devices. Thus, to elucidate which parameter set listed in Tab. 5.1 is the most appropriate, we compared the experimentally obtained in-plane polarization degrees with the calculations.

In order to use cleaved planes as reflecting mirrors for LDs based on semipolar-plane QWs, we have to control the in-plane polarization to be parallel to the cleaved plane. Figure 5.2 shows the schematic image of a semipolar-plane sample and the desirable polarization for the LD. Here, we define x' direction as c^* direction, where c^* is the direction parallel to the *c*-axis projection on the semipolar plane. For the semipolar plane samples, there are no cleavable planes perpendicular to the c^* direction because such planes are always semipolar planes, which cannot be obtained by cleavages. On the other hand, there are cleavable non-polar planes parallel to the c^* direction. In the case of *r*-plane QWs, for example, (11 $\bar{2}$ 0) (*a*-plane) mirrors are preferable in terms of the cleavages, and emissions strongly polarized along $\mathbf{E} \parallel c^*$ are desired. Thus, defining an in-plane polarization degree as

$$\rho_{\text{in}} = \frac{I_{\mathbf{E} \perp c^*} - I_{\mathbf{E} \parallel c^*}}{I_{\mathbf{E} \perp c^*} + I_{\mathbf{E} \parallel c^*}}, \quad (5.27)$$

$\rho_{\text{in}} < 0$ is needed for LDs, where I_i means the surface emission intensity polarized along the *i* direction [the definition corresponds to Eq. (5.25)].

Figures 5.3(a)–(d) show the calculated in-plane polarization degrees of *r*-plane AlGa_N/AlN QWs as functions of well width and Al composition using the parameter sets listed in Tab. 5.1 assuming the “finite” potential barriers. Although the in-plane polarization degrees depend on the parameter sets, the results using Set2–Set4 are similar.

Furthermore, we also calculated the in-plane polarization degrees for the same structures assuming “infinite” potential barriers as shown in Figs. 5.4(a)–(d). The “infinite” potential barrier calculations are effective to consider the quite narrow QWs because the “finite” potential barrier calculations were difficult for extremely thin well layers (< 0.5 nm). At the same time, however, the “infinite” potential barrier height causes the stronger

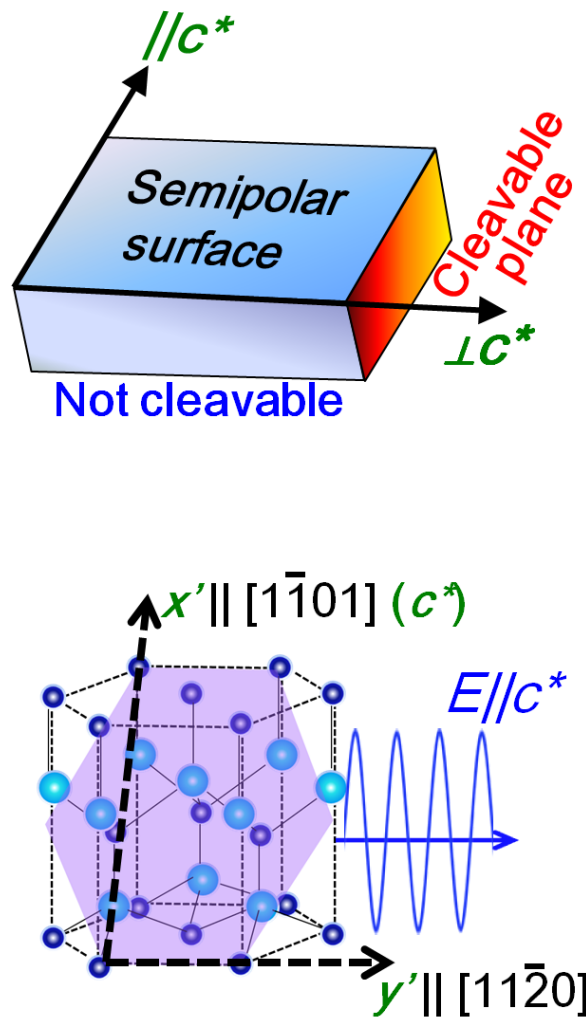


Figure 5.2: Schematic image of a semipolar-plane sample and the desirable polarization for LDs.

quantum confinement effect than the practical case. Therefore, we have to note that the discussions become qualitatively. (the well width in the “infinite” barrier calculation actually corresponds with the narrower well width in the “finite” potential calculation.) Comparing Figs. 5.3 and 5.4, we can confirm that the “infinite” potential calculations highlight the difference between the calculation results using Set2 (or Set4) and Set3 particularly for thin Ga-rich QWs.

5.3.2 Experimental procedures

AlGa_N/AlN QWs with various well widths and Al compositions were fabricated on semipolar 15° off,² *r*-plane, and (11 $\bar{2}$ 2) AlN substrates. All of the semipolar-plane samples were grown by MOVPE at 500 Torr, which is the optimized reactor pressure for the semipolar-plane growth as described in Chap. 2. The 400-nm-thick AlN epitaxial layers were initially grown on the substrates, and Al_{*x*}Ga_{1-*x*}N/AlN QWs were subsequently fabricated on them.

The fabricated QWs were characterized by polarization PL measurements at 9.5 K using an ArF excimer laser (193 nm) as an excitation source, and the typical excitation power density was about several MW/cm². The polarization PL setup is shown in Fig. 5.5. The samples were excited at an angle of 60° with the surface normal, and the PL signals were detected from the surface normal through a polarizer to investigate the in-plane polarization degrees.

Figures 5.6(a) and (b) show the obtained PL spectra at 9.5 K polarized along $\mathbf{E}||c^*$ or $\mathbf{E}\perp c^*$ of *r*-plane Al_{0.8}Ga_{0.2}N/AlN and *r*-plane GaN/AlN QWs. In both of the figures, we can observe the near band edge emissions from the QWs and found that the polarization degrees are varied by the well widths. In this study, the well widths of the AlGa_N/AlN QWs were estimated by XRD measurements, whereas those of the fabricated GaN/AlN QWs were estimated by the PL peak energies because the well widths are extremely narrow. Consequently, the well widths of the GaN/AlN QWs were roughly estimated to be 1–3 MLs.

5.3.3 Experimentally obtained in-plane polarization degrees

5.3.3.1 Al-rich AlGa_N/AlN QWs

Herein, we discuss the validity of the parameter sets listed in Tab. 5.1 comparing the results between the experiments and calculations mainly focusing on the *r*-plane QW emissions.

At first, we investigated the in-plane polarization degree of Al-rich *r*-plane AlGa_N/AlN QWs. Figures 5.7(a) and (b) show the well width dependences of the in-plane polarization degrees of the *r*-plane Al_{0.8}Ga_{0.2}N/AlN QWs obtained by the calculations and the experiments, respectively. The calculation results are based on the “finite” potential barrier calculations and are taken from the results in Fig. 5.3. All of the calculation results using various parameter sets indicate the negative ρ_{in} throughout the entire well width, and they

²(0001) with a tilt of 15° toward $\langle 11\bar{2}0 \rangle$.

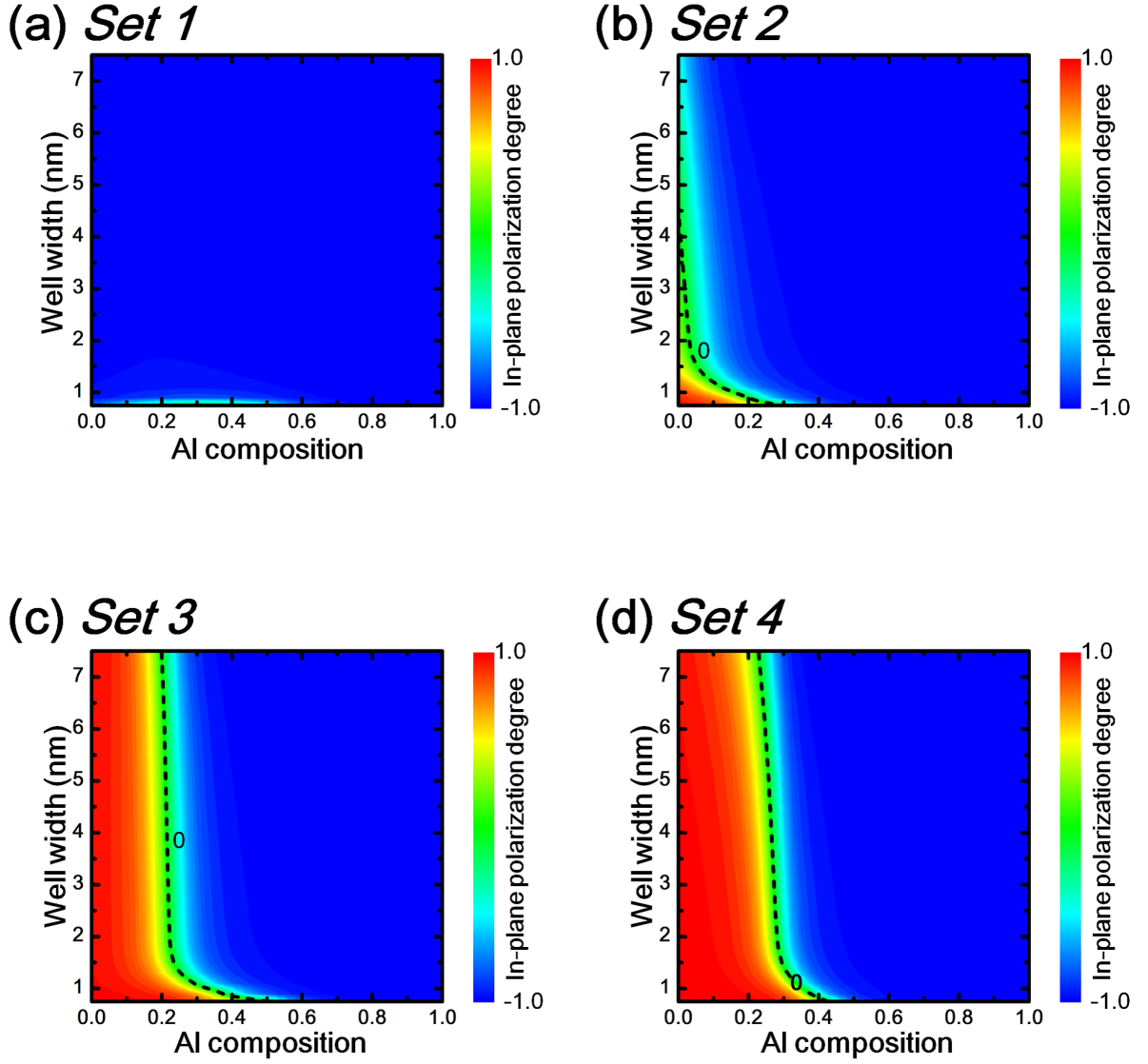


Figure 5.3: Calculated in-plane polarization degrees of r -plane AlGaIn/AlN QWs as functions of well width and Al composition using the parameter sets listed in Tab. 5.1. Here, we assume the “finite” potential barriers.

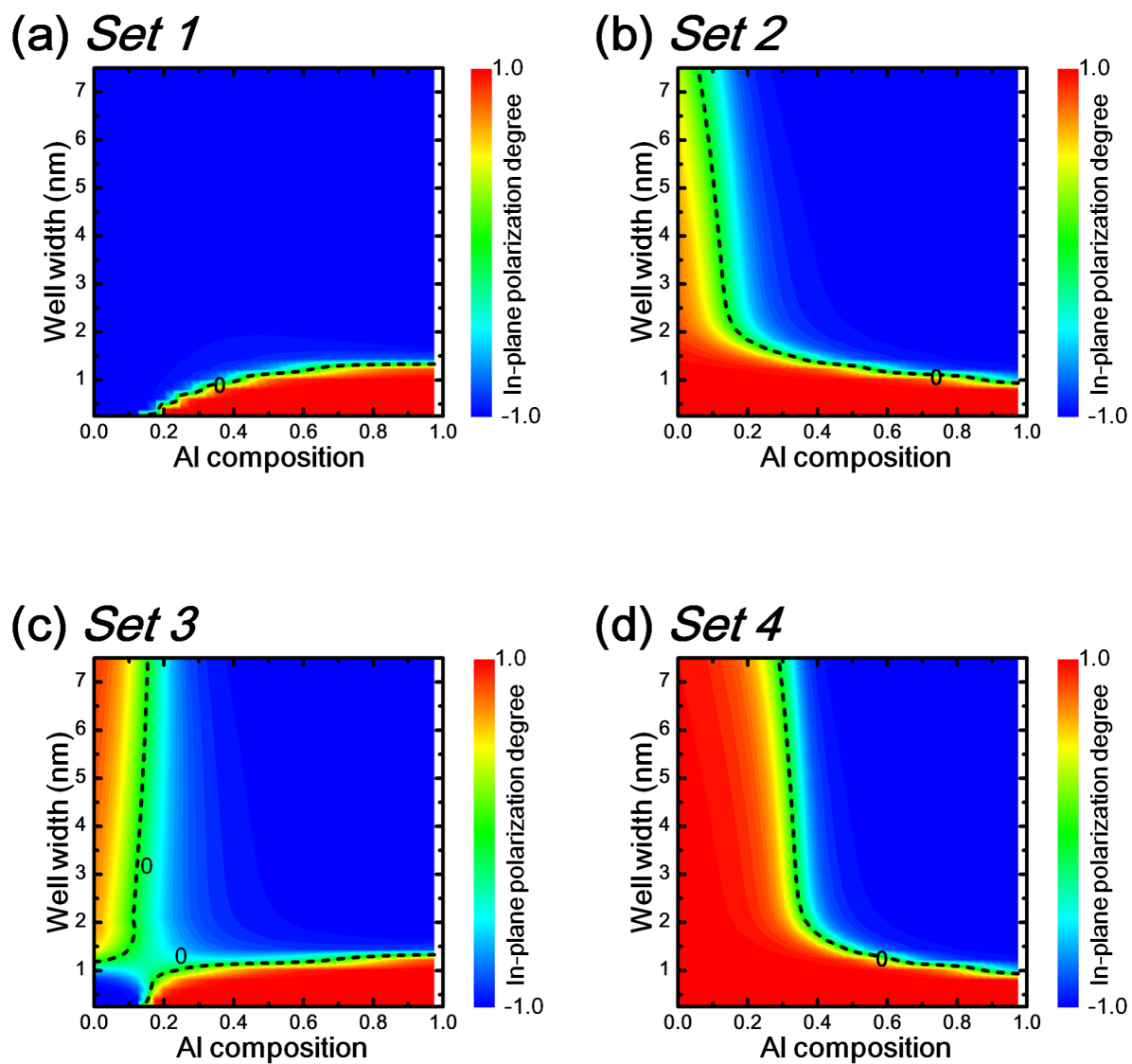


Figure 5.4: Calculated in-plane polarization degrees of r -plane AlGaIn/AlN QWs as functions of well width and Al composition using the parameter sets listed in Tab. 5.1. Here, we assume the “infinite” potential barriers.

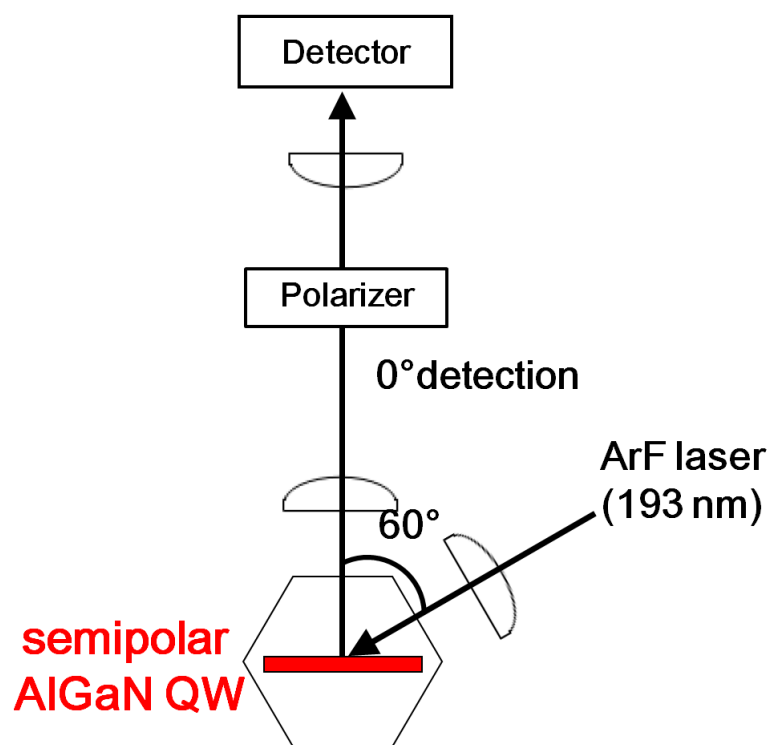
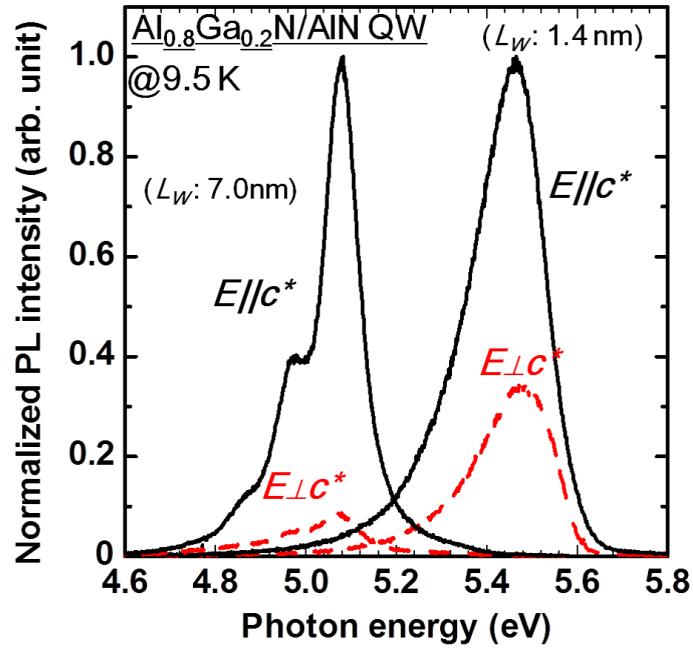


Figure 5.5: Polarization PL setup using an ArF excimer laser (193 nm) as an excitation source. Samples were excited at an angle of 60° with the surface normal, and the PL signals were detected from the surface normal through a polarizer to investigate the in-plane polarization degrees.

(a)



(b)

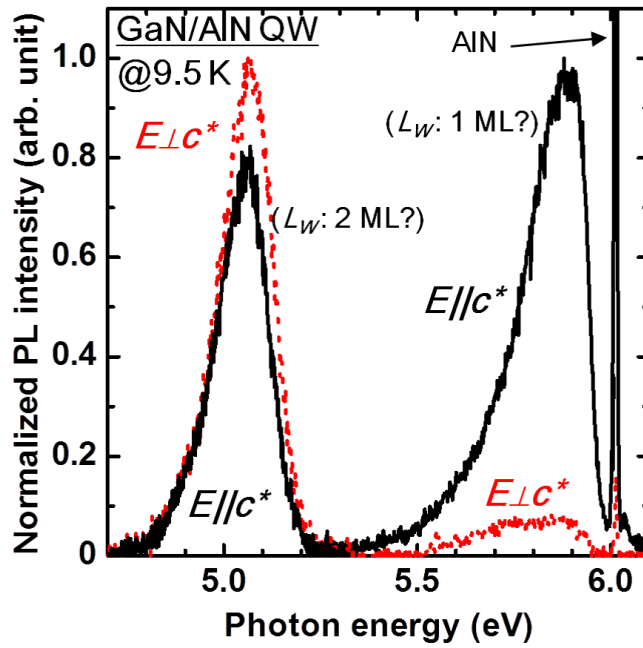


Figure 5.6: PL spectra at 9.5 K polarized along $E//c^*$ or $E\perp c^*$ of (a) r -plane Al_{0.8}Ga_{0.2}N/AlN and (b) r -plane GaN/AlN QWs.

well agree with the experimental results. As a consequence, we cannot determine the most appropriate parameter sets from the results of the *r*-plane Al-rich AlGaN/AlN QWs.

5.3.3.2 GaN/AlN QWs

Subsequently, we investigated the in-plane polarization degrees of the *r*-plane GaN/AlN QWs. Figures 5.8(a) and (b) show the well width dependences of the in-plane polarization degrees of the *r*-plane GaN/AlN QWs obtained by the calculations and the experiments, respectively. The calculation results are based on the “infinite” potential barrier calculations and are taken from Fig. 5.4 because the well widths are extremely narrow. From the Fig. 5.8(a), we found that the calculation results strongly depend on the parameter sets. The calculated ρ_{in} based on Set1 (Set2 and Set4) is negative (positive) throughout the entire well width, whereas that based on Set3 is changed from negative to positive with increasing the well width. The experimental results shown in Fig. 5.8(b) indicate that ρ_{in} is changed from negative to positive with an increase of well width, and they qualitatively agree with the calculation results based on Set3. Although the well widths where the polarization switching occur are different between the calculation based on Set3 and the experimental results, this may be caused by the too strong quantum confinement effect in the calculation due to the infinite potential barrier. Thus, the experimental results of the *r*-plane Al_{0.8}Ga_{0.2}N/AlN and GaN/AlN QWs suggest that parameter Set3 gives appropriate calculation results.

We discuss the reason why only Set3 can reproduce the experimental results. To elucidate the difference among the parameter sets, we calculated the effective masses in the valence bands along the growth direction in the *r*-plane AlGaN/AlN heterostructures (not QWs) as a function of Al composition, and the results are shown in Fig. 5.9. The effective masses were calculated for the HH (m_{HH}), LH (m_{LH}), and CH bands (m_{CH}). Though the calculated m_{HH} and m_{LH} are almost independent of the parameter sets, m_{CH} varies with the parameters particular for Ga-rich AlGaN/AlN. In the cases of Set1 and Set3, the m_{CH} become larger than m_{HH} for the GaN/AlN structures, and the relation leads to the negative ρ_{in} for the GaN/AlN QWs with narrow well widths because the holes in CH band ($\mathbf{E}||c^*$) should form the higher energy state than those in HH band ($\mathbf{E}\perp c^*$) due to the smaller quantum confinement effect. The relations of the effective mass are caused by the effective mass parameters (A_i) for GaN in Ref. [8]. Furthermore, the particularly large m_{CH} in Set3 is also affected by the deformation potential for GaN in Ref. [2]. On the other hand, the positive ρ_{in} for the thicker GaN/AlN QW observed in the calculation result of Set3 should be caused by the deformation potentials of GaN considering the weaker quantum confinement effects. We consider that the deformation potentials without the quasi-cubic approximation (in Ref. [2]) may cause the such differences of the calculated results. Thus, these findings indicate that the effective mass parameters in Ref. [8] cause the negative ρ_{in} for narrower GaN/AlN QWs, and the exciton deformation potentials in Ref. [2] cause the positive ρ_{in} for wider GaN/AlN QWs. As a consequence, the polarization switching in GaN/AlN QWs are

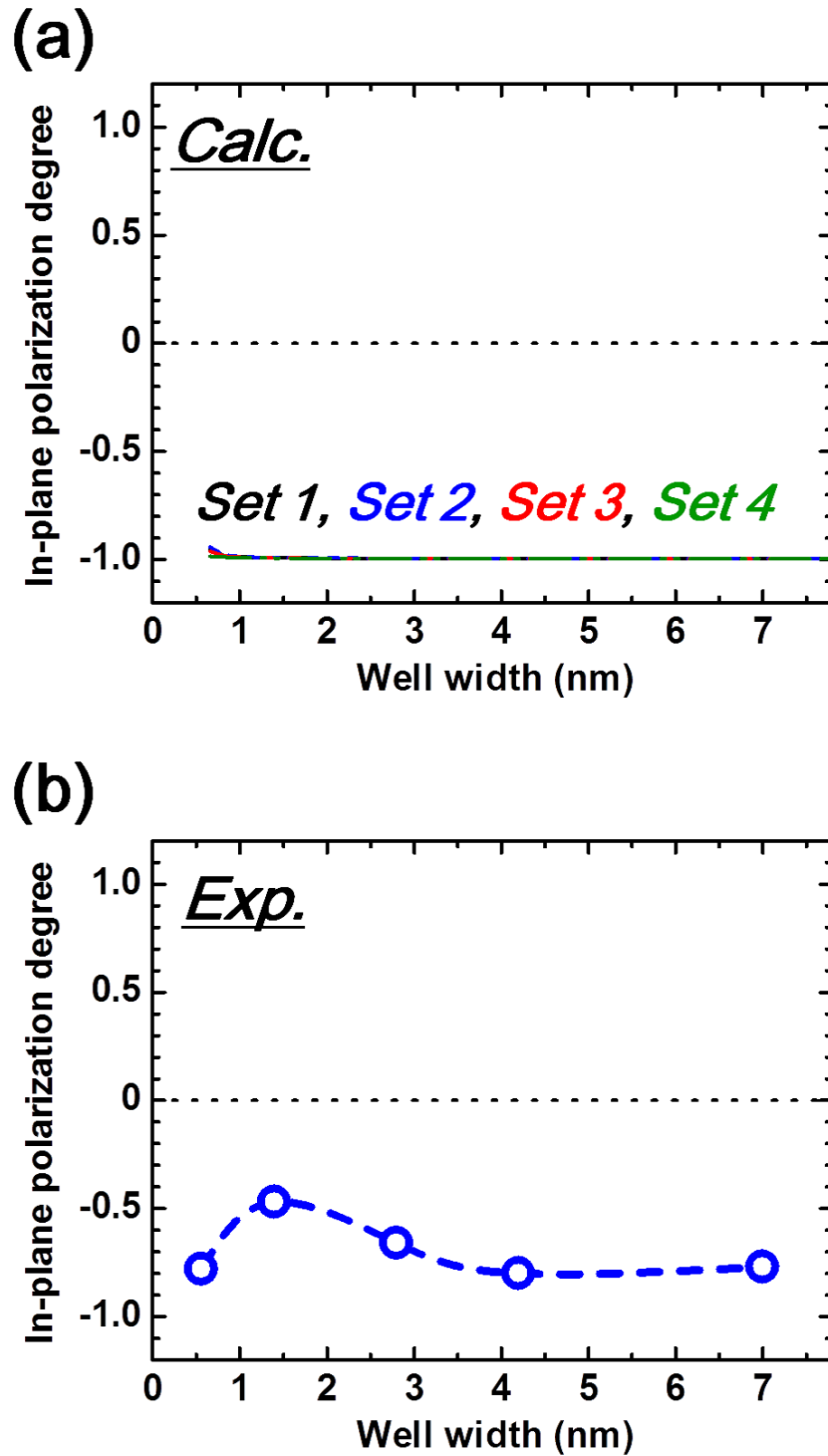


Figure 5.7: Well width dependences of the in-plane polarization degrees of the r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs obtained by (a) calculations and (b) experiments. The calculation results are based on the “finite” potential barrier calculations and are taken from the results in Fig. 5.3.

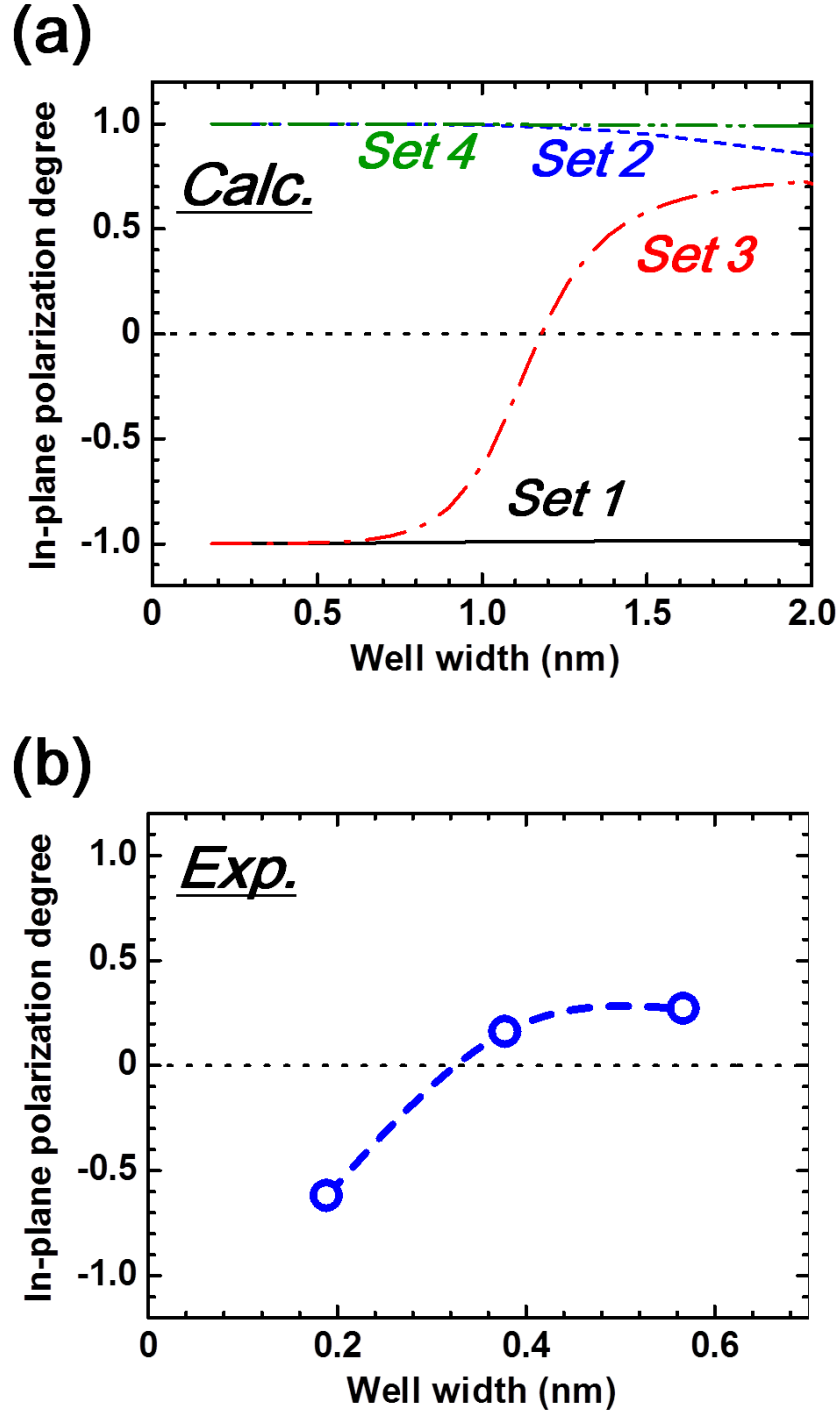


Figure 5.8: Well width dependences of the in-plane polarization degrees of the *r*-plane GaN/AlN QWs obtained by (a) calculations and (b) experiments. The calculation results are based on the “infinite” potential barrier calculations and are taken from the results in Fig. 5.4.

well expressed by the parameters listed in Set3.

To further clarify the validity of parameter Set3, we also investigated the in-plane polarization degree for the other semipolar GaN/AlN QWs in addition to the r -plane QWs. Figure 5.10 shows the off-angle dependences of the in-plane polarization degrees of 15° off, r -plane, and $(11\bar{2}2)$ GaN/AlN QWs.³ The plots are experimentally obtained ρ_{in} and the solid lines are to guide the eyes. It is noteworthy that the respective ρ_{in} get larger with increasing well widths.

Figures 5.11(a)–(d) show the calculated in-plane polarization degrees of GaN/AlN QWs with 0.2–2.0-nm-thick wells as functions of off-angle. The calculation results, which are depicted as solid lines, assume the “infinite” potential barriers because the experimental well widths in Fig. 5.10 are extremely narrow. The plots in Fig. 5.11 are the experimental results which correspond to the plots in Fig. 5.10. In Figs. 5.11(b) and (d), the in-plane polarization degree decreases with increasing the well width, and the tendency is inverse of that in the experimental results. In Fig. 5.11(a), though the tendency while increasing well widths agree with the experiments, the calculation results cannot reproduce the experimentally obtained in-plane polarization degree particular for the wider wells. On the other hand, the calculation results using the parameters in Set3 [see Fig. 5.11(c)] well reproduce the experimental results. These results also support that Set3 in Tab. 5.1 is the most appropriate parameter set to describe the optical polarization of AlGaIn/AlN QW emissions.

5.3.4 Out-of-plane polarization degree

As we described above, the parameters in Set3 are appropriate to calculate the optical polarization of AlGaIn/AlN QWs. Then, we discuss the out-of-plane polarization degree, which plays an important role in LEE of the LED structures, of AlGaIn/AlN QWs based on the calculation results using Set3. Here, we define the out-of-plane polarization degree as

$$\rho_{\text{out}} = \frac{I_{x'} + I_{y'} - I_{z'}}{I_{x'} + I_{y'} + I_{z'}}, \quad (5.28)$$

where I_i means the emission intensity polarized along the i direction, and $\rho_{\text{out}} > 0$ is needed for LEDs [the definition corresponds to Eq. (5.26)].

In the case of c -plane AlGaIn/AlN QWs, it was experimentally confirmed that the out-of-plane polarization switching occurs at $\sim 80\%$ of Al compositions, regardless of the well widths [10]. Figure 5.12(a) shows the calculated result of the out-of-plane polarization degree of c -plane AlGaIn/AlN QW as functions of well width and Al composition using the parameters in Set3 assuming the “finite” potential barriers. The calculation result indicates the polarization switching at $\sim 80\%$ of Al compositions almost independently of

³Although there are no experimental data for c -plane GaN/AlN QWs, ρ_{in} of c -plane QWs are theoretically zero.

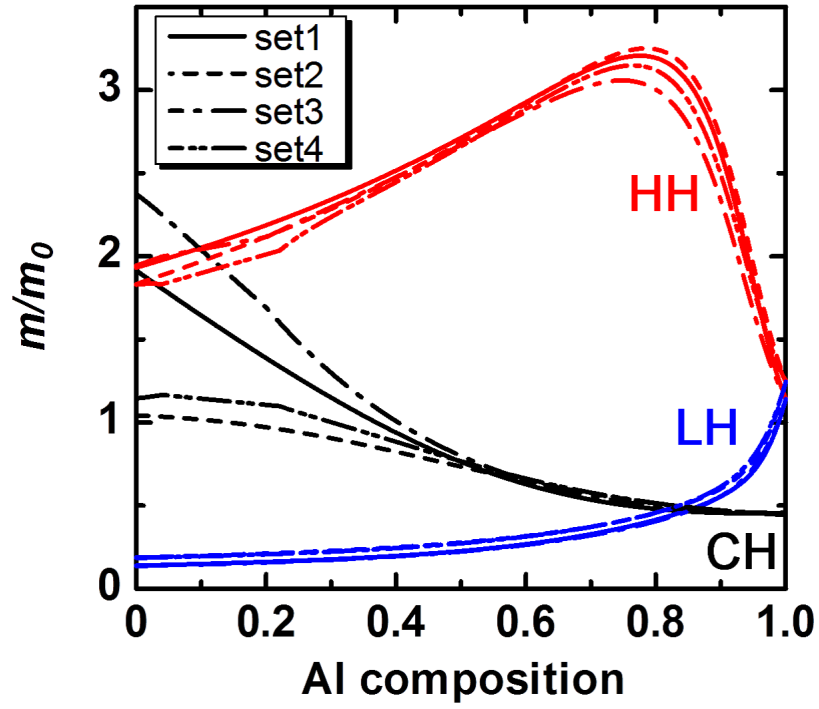


Figure 5.9: Calculated effective masses in the valence bands along the growth direction in the *r*-plane AlGa_N/AlN heterostructures as a function of Al composition.

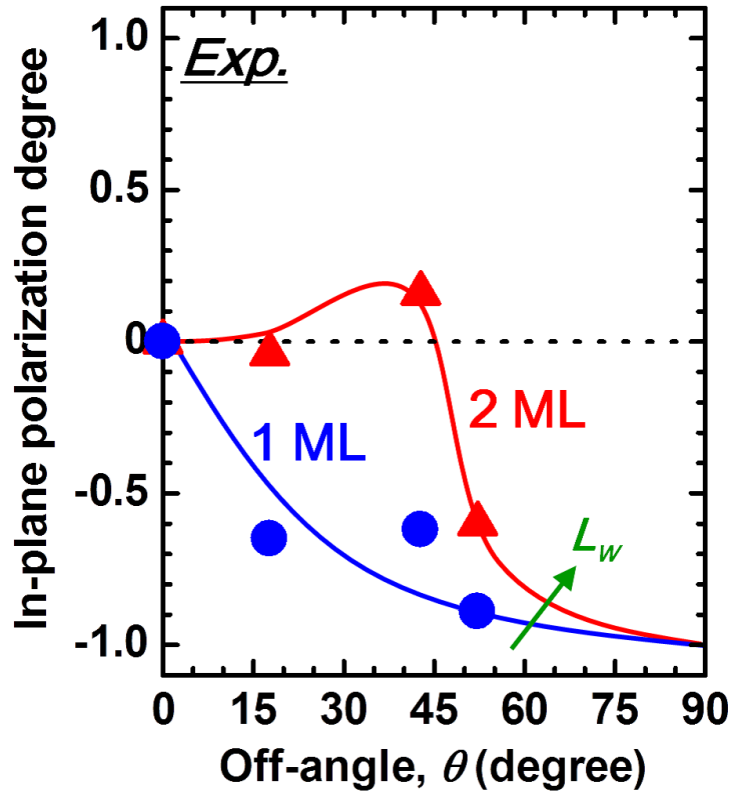


Figure 5.10: Off-angle dependences of the in-plane polarization degree of 15° off, *r*-plane, and (11 $\bar{2}$ 2) GaN/AlN QWs. Plots are experimentally obtained and the solid lines are to guide the eyes.

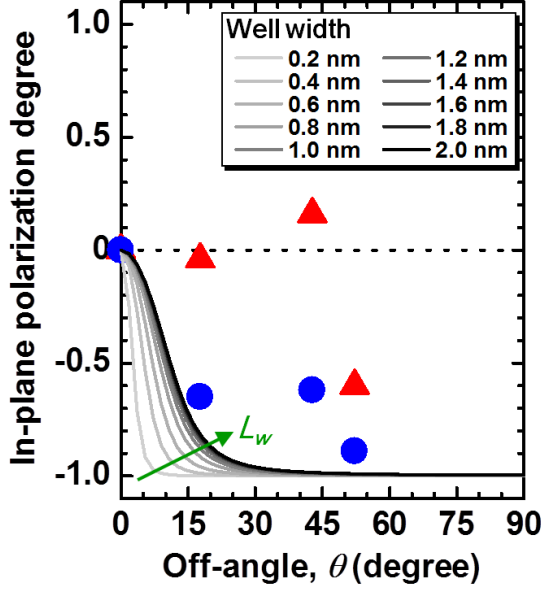
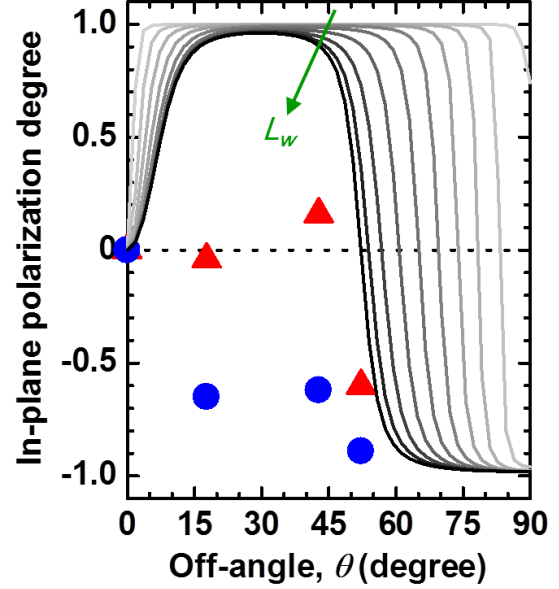
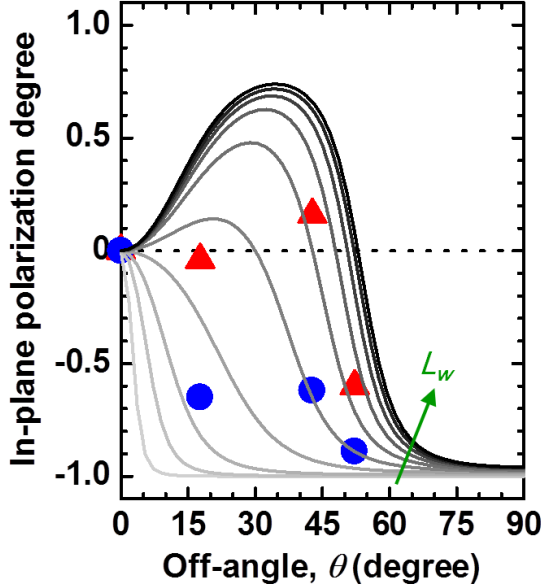
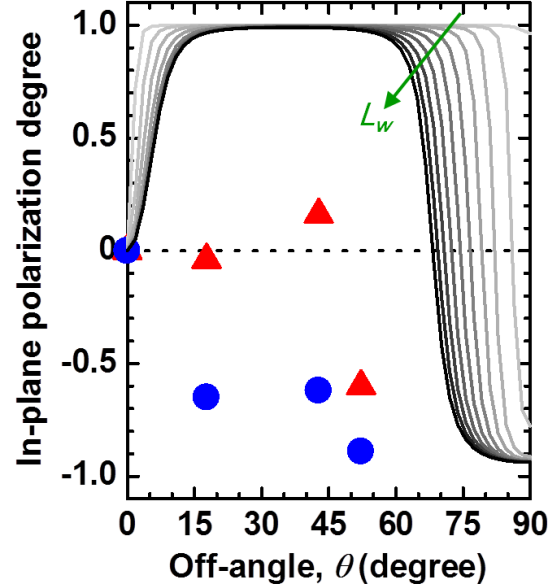
(a) *Set 1*(b) *Set 2*(c) *Set 3*(d) *Set 4*

Figure 5.11: Calculated in-plane polarization degrees of GaN/AlN QWs with 0.2–2.0-nm-thick wells as functions of off-angle are depicted as solid lines. The calculations assume the “infinite” potential barriers. Plots are the experimental results taken from Fig. 5.10. In the calculations, we used the parameters listed in (a) Set1, (b) Set2, (c) Set3, and (d) Set4.

the well widths, which well agrees with the experimental result reported in Ref. [10]. The result also means that *c*-plane AlGa_N/AlN QW based LEDs should be designed to have the Al compositions below 80% in terms of LEE, and this may be one of the reason for the low EQE of AlGa_N LEDs at short wavelengths.

On the other hand, Fig. 5.12(b) shows the calculated result of the out-of-plane polarization degree of *r*-plane AlGa_N/AlN QW as functions of well width and Al composition using the parameters in Set3 assuming the “finite” potential barriers. In contrast to the *c*-plane QW, *r*-plane QWs can keep positive ρ_{out} throughout the entire Al compositions. Particularly, narrow wells (< 5.5 nm) have large ρ_{out} , and the result indicates that the *r*-plane AlGa_N QWs are very attractive to fabricate DUV-LEDs emitting especially at short wavelengths from the perspective of LEE in addition to the high IQE.

5.4 Stimulated emissions from optically pumped *r*-plane AlGa_N QWs

In the previous sections, we discussed the importance of optical polarization control for the actual devices. Particularly in the case of LDs based on semipolar AlGa_N QWs, the in-plane polarization degree should be controlled to be negative value for the strong light extractions from the cleaved planes. For the practical devices, we have to design the QW structures considering the high IQE in addition to LEE. In this section, we investigate the LD structural design considering both IQE and LEE with a particular focus on the *r*-plane AlGa_N/AlN QW, and demonstrate the first stimulated emission from the semipolar AlGa_N QW by optical pumping measurements.

5.4.1 Structural design for high IQE

At first, we discuss the structural design for high IQE of *r*-plane AlGa_N/AlN QWs. For the practical devices, the emission wavelength should be chosen according to the applications. In general, there are two methods to vary the emission wavelength of AlGa_N QW structures. One is adjustment of Al compositions in the well layers, and the other is well width control. Although both high Al compositions and narrow well widths lead to short emission wavelengths, the impacts of the variations on the optical properties are completely different.

Figure 5.13(a) shows the well width dependences of the PL peak energy and the overlap integral between the electron and hole wave functions for Al_{0.8}Ga_{0.2}N/AlN QWs. The solid lines are the calculated results and the plots are the experimental results taken from Chap. 2. Here, the experimental results of the overlap integral squared are obtained by the constant multiplication of the reciprocals of the radiative recombination lifetimes⁴ assessed by the

⁴The lifetime of the QW with a 7-nm-thick well layer is longer than $1.25 \mu\text{s}$ because it cannot be detected under 0.8 MHz repetition frequency of the excitation laser. Therefore, $1.25 \mu\text{s}$ is the shortest limit.

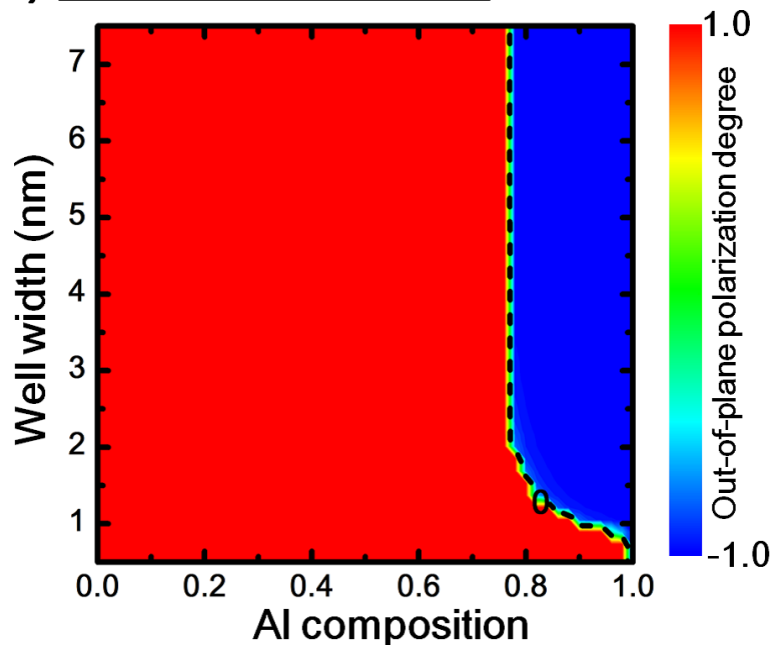
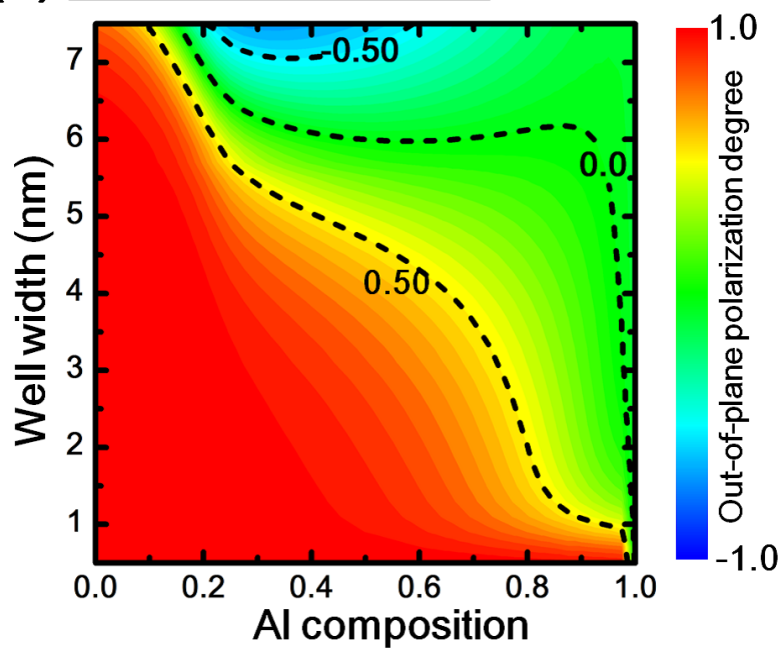
(a) c -AlGa N /Al N QW**(b) r -AlGa N /Al N QW**

Figure 5.12: Calculated results of out-of-plane polarization degree as functions of well width and Al composition using the parameters in Set3 assuming the “finite” potential barriers. The calculation results are for (a) c -plane and (b) r -plane AlGa N /Al N QWs.

TRPL measurements as we described in Chap. 2. We found that the wider QWs lead to longer emission wavelength, whereas the square of overlap integral drastically decreases with an increase of well width. The decrease of the overlap is caused by the internal electric fields. (Although the induced internal electric fields in *r*-plane QWs are much smaller than those in *c*-plane QWs, they are not zero unlike the case of nonpolar plane QWs.) Because the radiative recombination probability is proportional to the square of overlap integral, the wavelength control by widening well width is not good method for high IQE.

Then, we investigated the case that the wavelengths are controlled by Al compositions. Figure. 5.13(b) shows the calculated results of the wavelength dependence of the squared overlap integral for the *r*-plane AlGaIn/AlN QWs when the Al compositions or well widths are varied. When the Al compositions are varied, the well widths are fixed to be 1.5 nm, whereas Al compositions are fixed to be 80% while varying the well widths. It was clarified that the wavelength control by Al compositions scarcely degrades the radiative recombination probabilities in contrast to that by widening well widths throughout the entire DUV regions. Therefore, the emission wavelengths of semipolar AlGaIn/AlN QWs should be controlled by the Al compositions keeping the narrow well widths (~ 1.5 nm) for high IQE.

In addition to the calculations, we experimentally confirmed the impact of wavelength controls on emission intensities for *r*-plane AlGaIn/AlN QWs. We fabricated *r*-plane $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ QW with 1.7-nm-thick well layers, which was designed for a 250-nm emission, in addition to the $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs (discussed in Fig. 5.13). The fabricated QWs were characterized by weak excitation PL measurements, where a $\text{Ti}:\text{Al}_2\text{O}_3$ fourth-harmonic generation laser (~ 210 nm) was used as an excitation source and well layers are selectively excited. To avoid the many-body effects and the screening effects of the internal electric fields, weak excitation conditions were used. Figure 5.14(a) shows the PL spectra of the *r*-plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ (well width: 1.4 and 4.2 nm) and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ QWs at 6.5 K. We can confirm that the emission wavelengths of the QWs are changed from 224 to 250 nm by varying the Al compositions from 0.8 to 0.5 while the well widths are fixed to be ~ 1.5 nm. Moreover, the emission wavelengths of the QWs are also changed from 224 to 232 nm by widening the well widths from 1.4 to 4.2 nm. The temperature dependences of the integrated PL intensity of the QWs are shown in Fig. 5.14(b). The thermal quenching of the fabricated *r*-plane $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ QW is almost the same as that of the $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW with 1.4-nm-thick well layers, which has significantly higher IQE compared to the *c*-plane QW (described in Chap. 2), in spite of the large difference of the emission wavelengths. On the other hand, the thermal quenching of the $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW with 4.2-nm-thick well layers much stronger than that of the other QWs with narrower well layers in spite of the slight difference of the emission wavelengths from the $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QW with 1.4-nm-thick well layers. This is because the radiative recombination probability is scarcely degraded by the variations of Al compositions, whereas it is drastically degraded by widening the well widths as calculated in Fig. 5.13 (b). Thus, we experimentally confirmed that

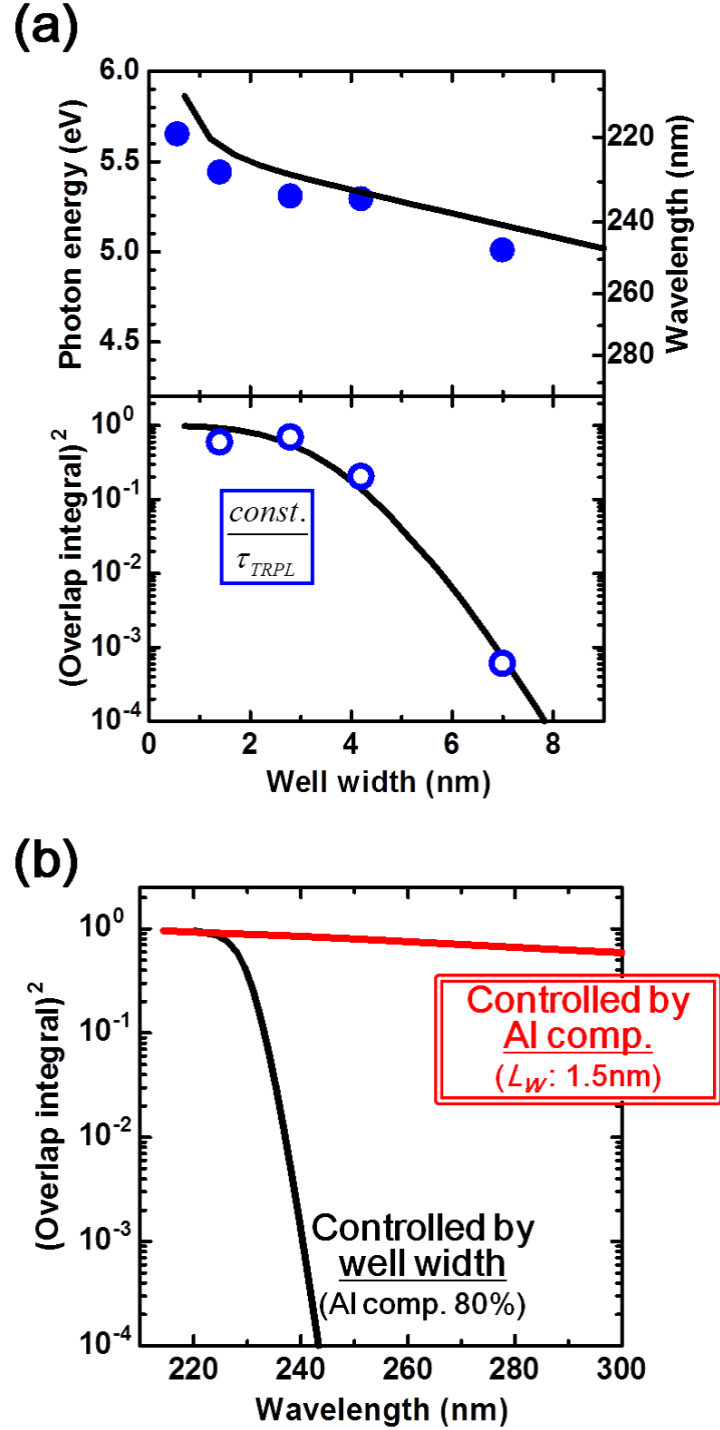


Figure 5.13: (a) Well width dependences of the PL peak energy and the overlap integral between the electron and hole wave functions for $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ QWs. Solid lines are the calculated results and the plots are the experimental results taken from Chap. 2. (b) Calculated results of the wavelength dependence of the squared overlap integral for the r -plane AlGaIn/AlN QWs when the Al compositions or well widths are varied. When the Al compositions are varied, the well widths are fixed to be 1.5 nm, whereas Al compositions are fixed to be 80% while varying the well widths.

the wavelength control by varying Al compositions while the well widths are fixed to be ~ 1.5 nm is effective way to keep high IQE of semipolar AlGa_{0.5}N/AlN QWs with various emission wavelengths.

5.4.2 Structural design for in-plane polarization control

Here, we discuss the structural design of *r*-plane AlGa_{0.5}N/AlN QWs toward LDs with high IQE considering the in-plane polarization degree. As we described above, the emission wavelengths of AlGa_{0.5}N/AlN QWs should be controlled by the Al compositions while the well widths are fixed to be narrow (~ 1.5 nm) to maintain the high IQE of the semipolar AlGa_{0.5}N QWs. At the same time, we have to realize a negative in-plane polarization degree for strong light extractions from cleaved mirrors. Then, we fabricated *r*-plane AlGa_{0.5}N/AlN QWs, which have about 1.5-nm-thick well layers, with various Al compositions, and the in-plane polarization degrees of them are experimentally investigated.

Figure 5.15(a) shows the Al composition dependence of the in-plane polarization degree for the *r*-plane AlGa_{0.5}N/AlN QWs. We experimentally confirmed that $\rho_{\text{in}} < 0$ is kept for the Al compositions more than 0.2. The experimental results well agree with the calculation results using the parameters listed in Set3 [see Fig. 5.3(c)]. This trend was re-plotted as a function of the emission wavelength as shown Fig. 5.15(b). From the figure, we found that the relation $\rho_{\text{in}} < 0$ is satisfied in the wide DUV spectral range (220–280 nm) by the *r*-plane AlGa_{0.5}N/AlN QWs. These results indicate that we can realize highly efficient LDs based on the *r*-plane AlGa_{0.5}N/AlN QWs emitting at 220–280 nm from the perspectives of both IQE and LEE by designing the QWs to have Al compositions more than 0.2 and to have narrow well widths (~ 1.5 nm).

5.4.3 Optical pumping measurements

We perform the optical pumping measurements for the appropriately designed *r*-plane AlGa_{0.5}N/AlN QW. We fabricated an *r*-plane Al_{0.5}Ga_{0.5}N/AlN 6QW with 1.7-nm-thick well layers, which was designed for a 250-nm emission. The in-plane polarization degree of the QW was characterized by polarization PL, and we confirmed that the surface emission is strongly polarized along $\mathbf{E}||c^*$ ($\rho_{\text{in}} = -0.63$) as shown in Fig. 5.16(a). Then, we performed the optical pumping measurement for the sample using the setup depicted in Fig. 5.16(b). The excitation source was an ArF excimer laser (193 nm) at a 25 Hz repetition rate with a pulse width of 4 ns. Fabry-Perot cavity with a length of 2 mm was formed by cleavage along the $[11\bar{2}0]$ direction. The fabricated sample was optically pumped from the surface by the ArF excimer laser at 11 K, and the emissions were detected from an *a*-plane facet. Note that no high-reflection coatings were applied on the cleaved *a*-planes.

Figure 5.17(a) shows the photoluminescence spectra of the *r*-plane Al_{0.5}Ga_{0.5}N/AlN 6QW with various excitation power densities. The peak wavelength is about 250 nm, and the

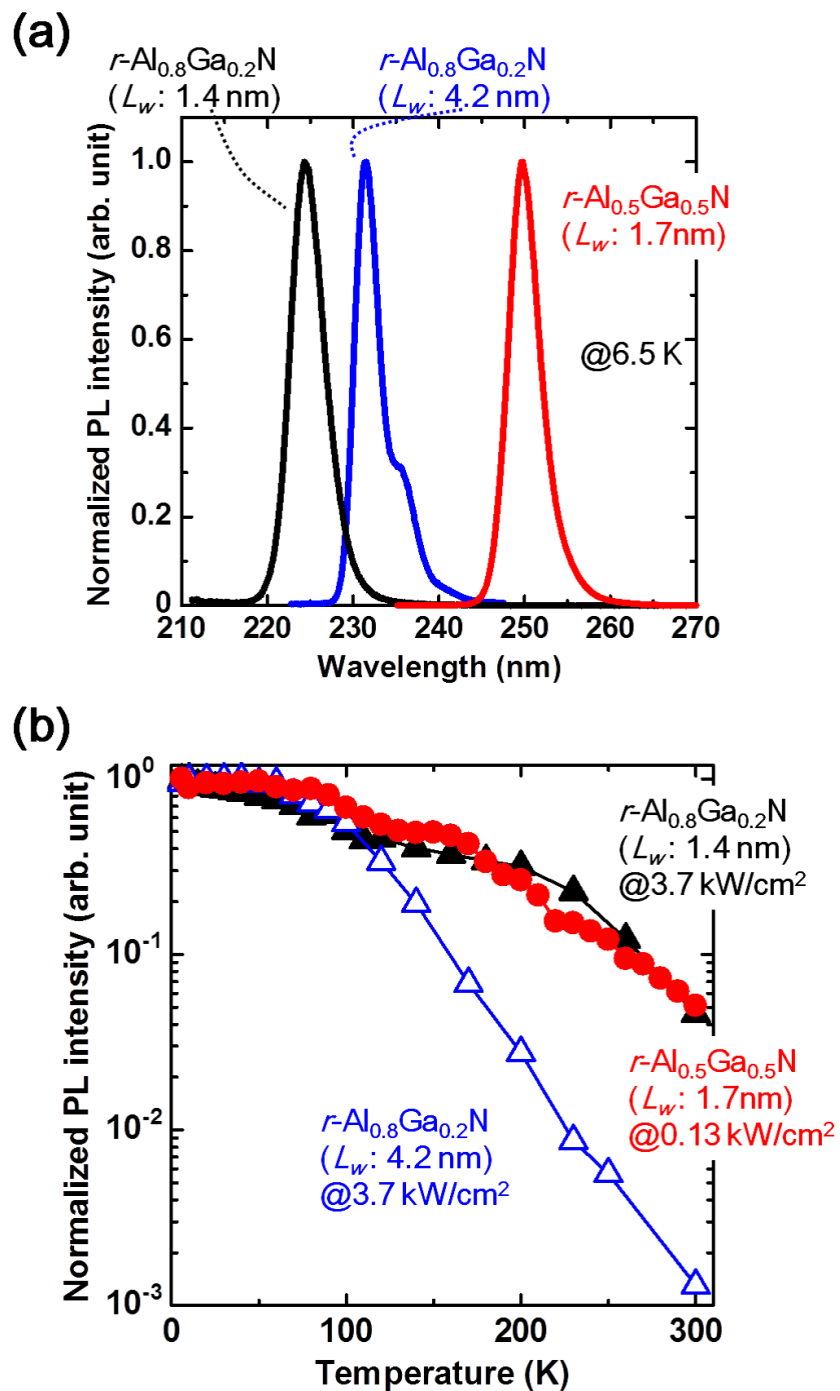


Figure 5.14: (a) PL spectra of the r -plane $\text{Al}_{0.8}\text{Ga}_{0.2}\text{N}/\text{AlN}$ (well width: 1.4 and 4.2 nm) and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ QWs (well width: 1.7 nm) at 6.5 K. (b) Temperature dependences of the integrated PL intensity of those QWs.

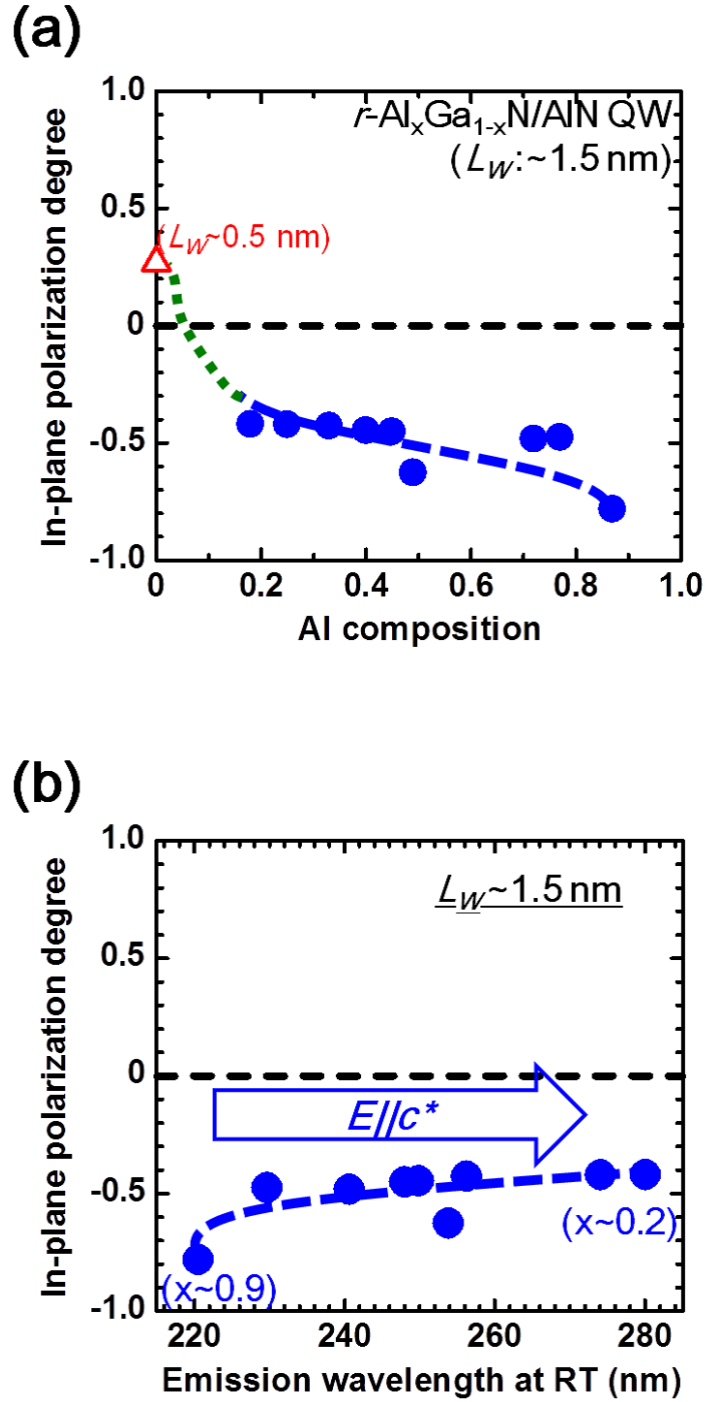


Figure 5.15: (a) Al composition dependence of the in-plane polarization degree for the *r*-plane AlGaIn/AlN QWs, which have about 1.5-nm-thick well layers. The well width of the GaN/AlN QW is ~ 0.5 nm. (b) Emission wavelength dependence of the in-plane polarization degree for the *r*-plane AlGaIn/AlN QWs.

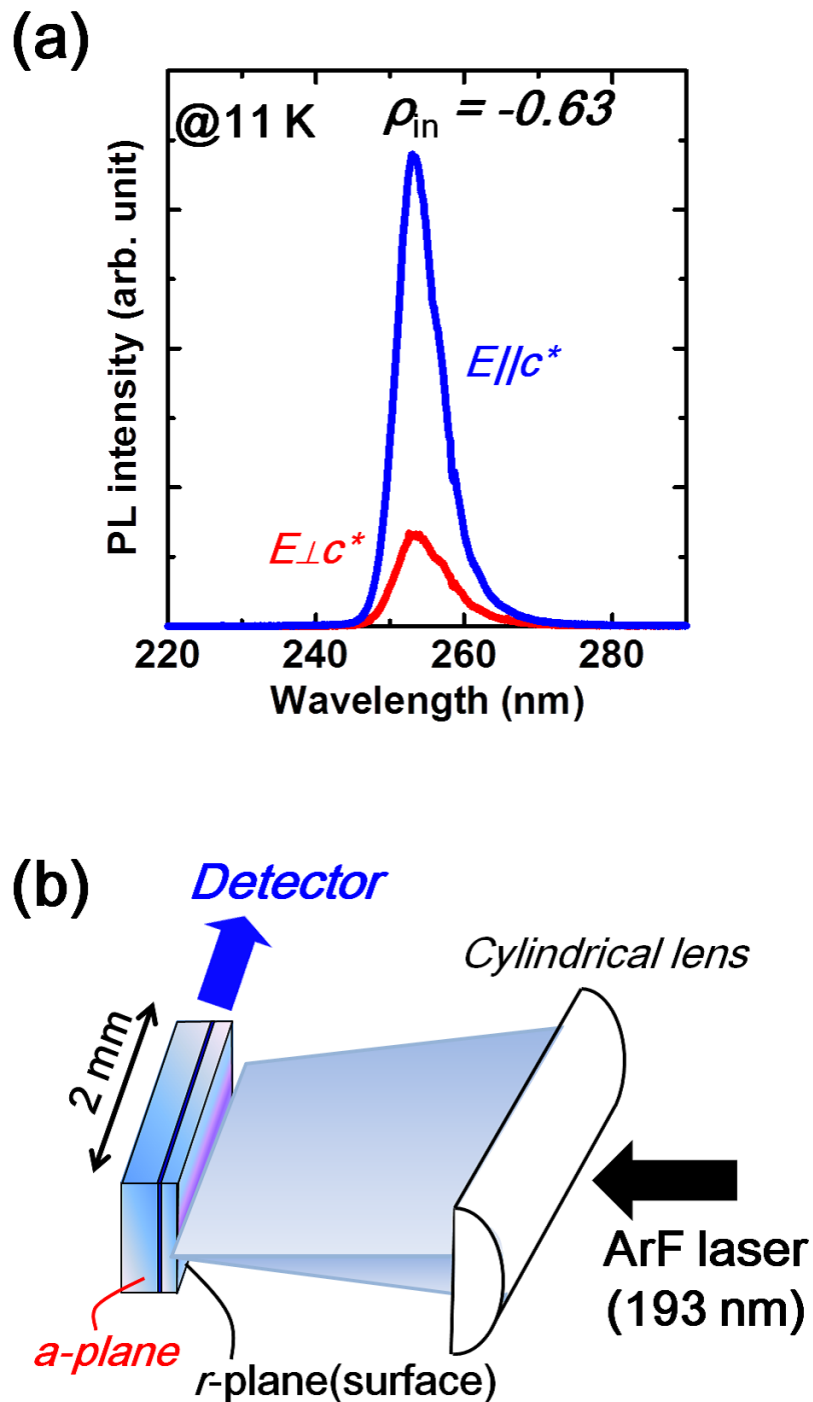


Figure 5.16: (a) Polarization PL spectra of the *r*-plane $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}$ 6QW with 1.7-nm-thick well layers. (b) Schematic image of optical pumping measurement setup using an ArF excimer laser (193 nm) as an excitation source.

stimulated emissions are clearly observed under strong excitation conditions. The excitation power dependences of the PL intensity and line width are plotted in Fig. 5.17(b). The spectral narrowing is clearly observed, and the lasing threshold power density is determined to be $\sim 500 \text{ kW/cm}^2$. This is the first demonstration of the stimulated emissions from the semipolar-plane AlGa_{0.5}N QW. We attribute the success to the appropriate structural design and high crystalline quality of the semipolar AlGa_{0.5}N QW.

The obtained threshold power density will be compared with the reported values. Recently, a lot of studies on optically pumped AlGa_{0.5}N MQWs emitting in the DUV regions have been reported. In 2004, a stimulated emission from an AlGa_{0.5}N MQW fabricated on SiC at a wavelength in sub 250-nm region was reported [15], but the threshold power density was as high as 1.2 MW/cm^2 . More recently, AlGa_{0.5}N-based optical pumped lasers fabricated on sapphire [16–22] and *c*-plane AlN [23–31] substrates were reported. The lasing wavelength dependence of the threshold power densities are summarized in Fig. 5.18. We found that the reported threshold power densities are scarcely varied by the substrates in spite of the high crystalline quality of *c*-plane AlN bulk substrates. This may be because the emission line widths and the density of the dominant nonradiative recombination centers (Al vacancy-related point defects at room temperature) are almost the same for *c*-plane AlGa_{0.5}N epilayers independently of the substrates, as we described in Chaps. 2 and 3.

The experimental result of the fabricated semipolar *r*-plane Al_{0.5}Ga_{0.5}N/AlN 6QW is also plotted in Fig. 5.18. Comparing the threshold power density with the reported values, our experimental result is neither better nor worse in spite of the superior optical properties such as high IQE and strongly polarized emissions. We consider that there are some reasons for this result. The first reason is that the *r*-plane Al_{0.5}Ga_{0.5}N/AlN QW structure does not have the carrier- and optical-confinement structures: Because the present *r*-plane QW does not have any waveguides and cladding layers, we should consider the appropriate structures for the strong optical confinement to further reduce the threshold power density. The second reason is the cleavability of the *a*-plane. In most cases of the previous reports, *m*-planes were used for the cavity mirrors. Although *a*-planes should be used for the cavity mirrors in semipolar-plane samples with the off-angles along $\langle 1\bar{1}00 \rangle$ directions such as *r*-plane QWs, the cleavability of the *a*-plane is generally worse than that of the *m*-plane. As a consequence, our *r*-plane QW may have a larger mirror loss compared with the reported samples. In order to compensate for the mirror loss, high-reflection coatings such as dielectric reflecting mirrors on the *a*-plane facets are effective. Meanwhile, because the *m*-plane can be used as cavity mirrors, semipolar QWs with the off-angles toward $\langle 11\bar{2}0 \rangle$ directions such as (11 $\bar{2}2$) QWs are also attractive to suppress the mirror loss. The detailed optical polarizations of (11 $\bar{2}2$) AlGa_{0.5}N QWs are discussed in Appendix C.

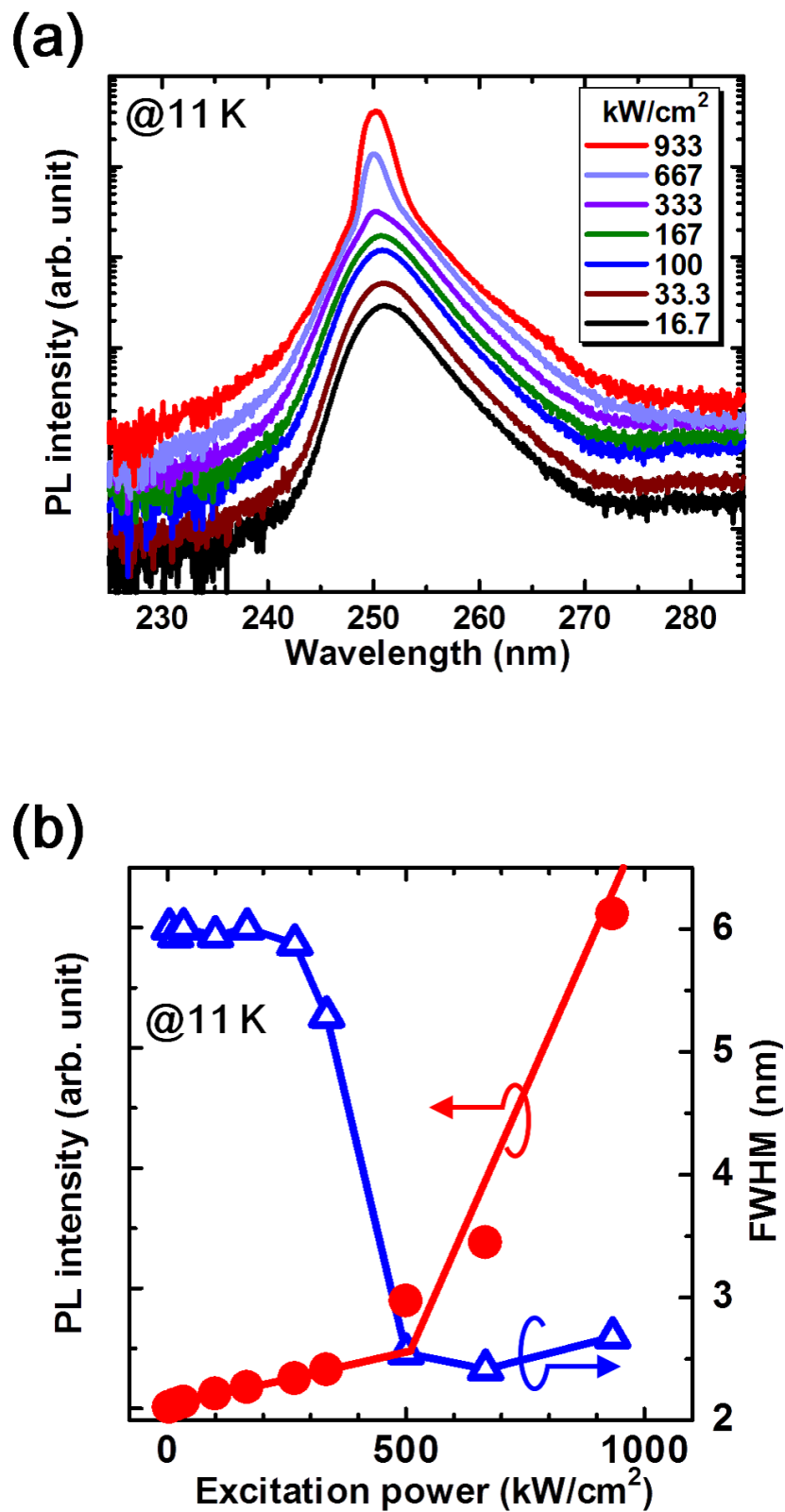


Figure 5.17: (a) Spontaneous and stimulated emission spectra of *r*-plane Al_{0.5}Ga_{0.5}N/AlN 6QW at 11 K. (b) Excitation power dependences of PL intensity and line width.

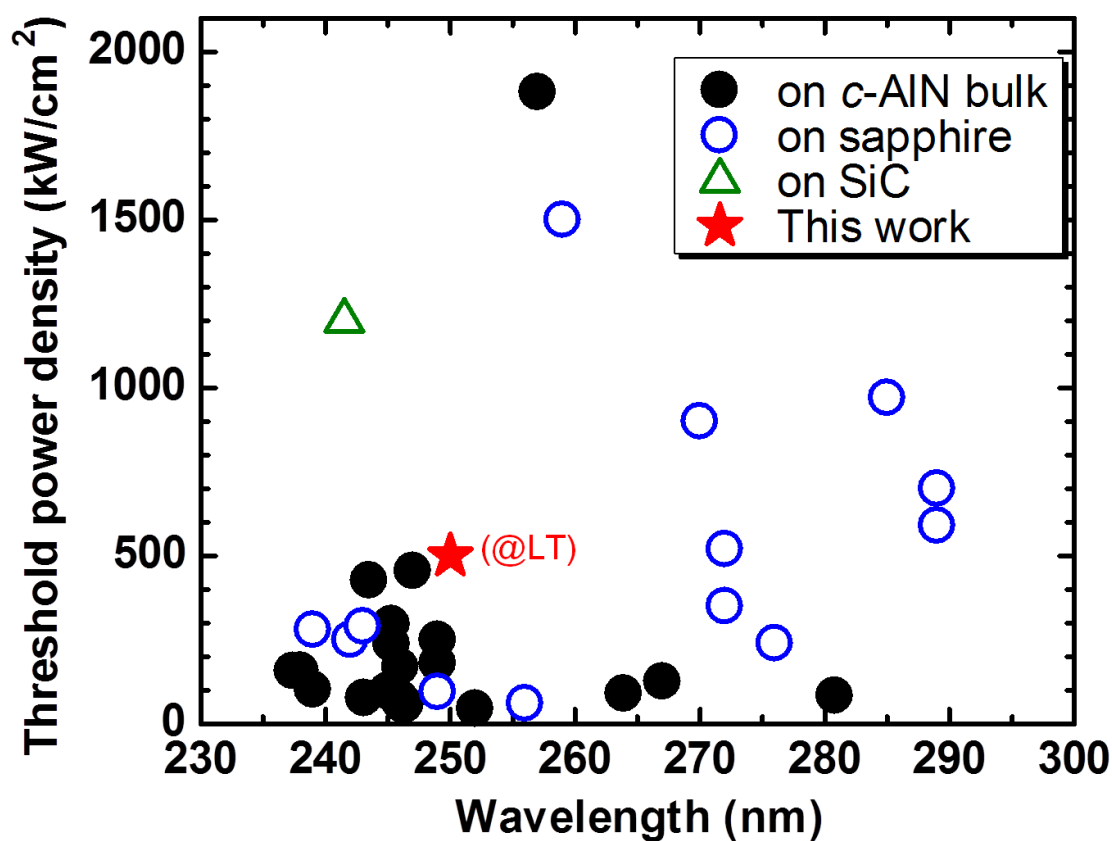


Figure 5.18: Lasing wavelength dependence of the reported threshold power densities for AlGa_{0.5}N MQWs fabricated on SiC [15], sapphire [16–22], and *c*-plane AlN [23–31] substrates. The experimental result of the fabricated semipolar *r*-plane Al_{0.5}Ga_{0.5}N/AlN 6QW is also plotted.

5.4.4 Reflectance calculation of dielectric reflecting mirrors

HfO₂/SiO₂ multilayers are frequently used as dielectric reflecting mirrors in the DUV region [32]. Due to the large refractive index contrast between HfO₂ and SiO₂, the distributed Bragg reflectors (DBRs) with high reflectivity and wide stop-band can be achieved. In fact, the HfO₂/SiO₂ DBR coated facets effectively reduced the threshold power density of AlGaIn-based optically pumped lasers [30, 31]. Thus, we calculated the reflectance of HfO₂/SiO₂ multilayers to improve the mirror loss of the *r*-plane Al_{0.5}Ga_{0.5}N/AlN QW for the future works.

DBR mirrors consist of two different optical materials, and the most frequently used design is an alternating sequence of the layers with the respective optical layer thickness corresponding to a quarter of the emission wavelength. Then, we design the thickness of HfO₂/SiO₂ as 29.5 and 39.1 nm, respectively, assuming the refractive indices (2.12 and 1.60, respectively) for a emission at 250 nm. Figure 5.19(a) shows the reflectance spectra of 3, 5, and 10 pairs of HfO₂/SiO₂ DBRs. The reflectances get higher with increasing the number of period and the 10 pairs of HfO₂/SiO₂ DBR shows the wide stop-band of ~ 50 nm. Figure 5.19(b) shows the correlation between the reflectance at 250 nm and the number of pairs. Although the reflectance is $\sim 15\%$ for the cleaved facets without coatings, 10 pairs of HfO₂/SiO₂ DBR realize the high reflectance beyond 99%. Therefore, we recommend the HfO₂/SiO₂ DBR coatings on the cleaved *a*-plane facets to reduce the mirror loss and to improve the threshold pumping power density of the fabricated *r*-plane Al_{0.5}Ga_{0.5}N/AlN MQW.

5.5 Summary

In this chapter, we investigated the appropriate parameter set for the calculation of the optical polarization degrees of AlGaIn/AlN QWs. Comparing the calculated results based on the $\mathbf{k} \cdot \mathbf{p}$ perturbation method with the experimentally characterized in-plane polarization degree of semipolar AlGaIn/AlN QWs, we suggest that the deformation potentials reported in Ref. [1, 2] and the effective mass parameters for valence bands reported in Ref. [8] give the reliable prediction of the optical polarization degree of AlGaIn/AlN QWs. In particular, the use of the deformation potentials without quasi-cubic approximations (in Ref. [1, 2]) may play an important role in calculating the band structures.

The calculated results for the out-of-plane polarization degrees of semipolar *r*-plane AlGaIn/AlN QWs indicate that the *r*-plane AlGaIn QWs are very attractive structures to fabricate DUV-LEDs emitting at short wavelengths in terms of the LEE in addition to the high IQE, because the *r*-plane QWs with narrow well widths (< 5.5 nm) can keep positive out-of-plane polarization degrees throughout the entire Al compositions in contrast to *c*-plane QWs.

Toward highly efficient LDs, we experimentally investigated the in-plane polarization de-

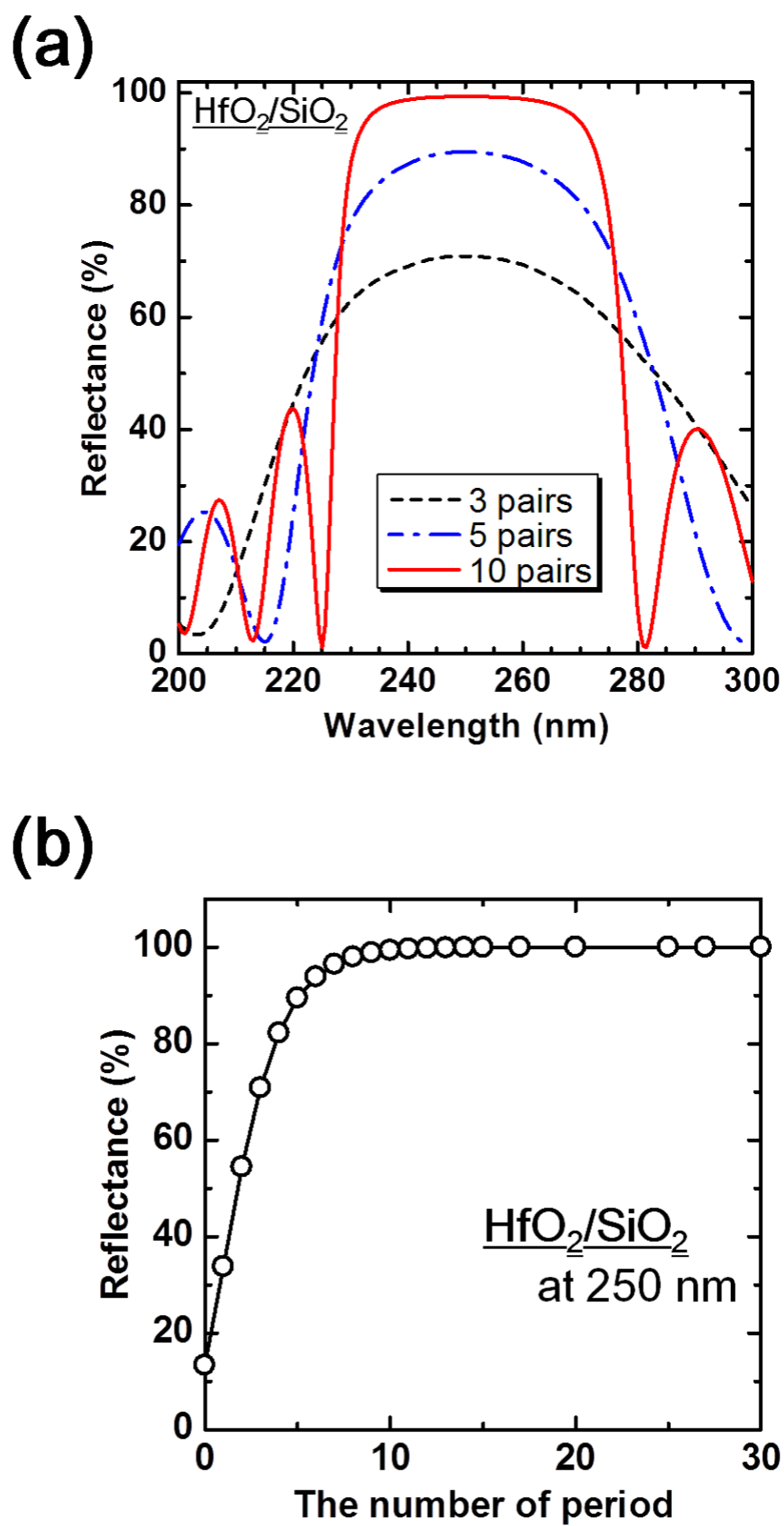


Figure 5.19: (a) Reflectance spectra of 3, 5, and 10 pairs of $\text{HfO}_2/\text{SiO}_2$ DBRs. (b) Correlation between the reflectance at 250 nm and the number of pairs.

gree and thermal quenching of the r -plane AlGa_{0.5}N/AlN QWs in addition to the calculations. It was clarified that we can realize highly efficient LDs based on the r -plane AlGa_{0.5}N/AlN QWs emitting at 220–280 nm from the perspectives of both IQE and LEE by designing the QWs to have Al compositions more than 0.2 and to have narrow well widths (~ 1.5 nm).

Finally, we performed the optical pumping measurement for the r -plane Al_{0.5}Ga_{0.5}N/AlN 6QW with 1.7-nm-thick well layers. The emission from the appropriately designed QW is strongly polarized along $\mathbf{E}||c^*$ ($\rho_{\text{in}} = -0.63$), which indicates strong light extractions from the a -planes. A Fabry-Perot cavity with a length of 2 mm was formed by cleavage along the $[11\bar{2}0]$ direction. The stimulated emissions at 250 nm were observed from the semipolar AlGa_{0.5}N QW under strong excitation conditions for the first time. The spectral narrowing was also clearly observed, and the lasing threshold power density was determined to be ~ 500 kW/cm² at 11 K. Comparing the threshold power density with the reported values, it is neither better nor worse in spite of the superior optical properties. Although there may be some reasons for the result, we considered the difficulty in the a -plane cleavages as one of the reasons. In order to compensate for the mirror loss caused by the a -plane cleavages, high-reflection coatings such as HfO₂/SiO₂ DBRs are effective. From the reflectance calculations, we suggested 10 pairs of HfO₂/SiO₂ DBR, which can realize the high reflectance beyond 99% at 250 nm, to reduce the threshold pumping power density of the fabricated r -plane Al_{0.5}Ga_{0.5}N/AlN MQW.

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Chapter 6

Conclusions

6.1 Conclusions

In this thesis, the carrier recombination paths and structural designs for AlGaIn QWs toward highly efficient DUV emitters were investigated. We particularly dedicated the great efforts to improve the IQE and LEE which are the components of EQE determining the device performances. Throughout the extensive experiments and the calculations for crystal growth, carrier recombinations, critical thickness, and optical polarizations, a lot of noteworthy conclusions were obtained as follows.

In Chapter 2, the crystal growth of semipolar AlGaIn QWs and the analyses of the optical properties were performed to enhance the radiative recombination probabilities for high IQE. Semipolar AlN homoepitaxial films and AlGaIn/AlN QWs were fabricated on 15° off,¹ r -plane, and $(11\bar{2}2)$ AlN substrates using the MOVPE method. For the conventional c -plane AlGaIn growth, low reactor pressures are generally preferred in order to enhance the migrations of Al adatoms and to decrease parasitic reactions between TMA and NH_3 . On the other hand, for the homoepitaxy on semipolar AlN substrates, it was clarified that the low pressure growth causes a lot of pits, which are derived from the defects generated at the initial growth stage, on the surfaces. However, we found that higher pressure growth could drastically decrease the pit density keeping the atomically smooth surfaces. To clarify the mechanism of the pit-elimination, semipolar AlN homoepitaxy was demonstrated at various reactor pressures in the range of 76 to 608 Torr. From the experiments, we elucidated that higher pressure growth led to higher nucleation density on the growth surface and the generated nuclei inside of pits buried the pits due to the three-dimensional growth. Particularly, we found that 500 Torr is the optimal reactor pressure for the pit-elimination in terms of the growth rate and the nucleation density. High quality semipolar AlN homoepitaxial films with atomically smooth surfaces were obtained. The strong near band edge emissions with narrow line widths ($\sim 1\text{--}2$ meV) and the suppressed deep level emissions were confirmed from the semipolar AlN films. Moreover, high quality semipolar AlGaIn/AlN QWs

¹(0001) with a tilt of 15° toward $\langle 11\bar{2}0 \rangle$.

with atomically smooth surfaces and abrupt interfaces were also obtained by the 500 Torr growth. The high quality semipolar AlGa_N/AlN QWs enabled us to investigate their fundamental optical properties. From the well-width dependence of the PL peak energy, the internal electric fields are estimated for the *c*-plane and semipolar-plane AlGa_N QWs. As a consequence, we experimentally confirmed that the internal electric fields in the semipolar AlGa_N QWs with large off-angles are remarkably suppressed and the estimated internal electric fields well agree with the calculation results. (The internal electric fields in the *r*-plane and (11 $\bar{2}$ 2) QWs were less than one-third of that in the *c*-plane QW.) Additionally, we investigated the impacts of the internal electric fields on carrier recombination lifetimes and emission intensities. We clarified that the small internal electric fields in semipolar-plane QWs significantly enhance the radiative recombination probabilities and realize much stronger emissions than the conventional *c*-plane QWs. Furthermore, the potential fluctuations in the semipolar AlGa_N QWs are also well suppressed by the small internal electric fields.

In Chapter 3, dominant recombination centers in AlGa_N-related materials were investigated. Although high quality semipolar AlGa_N/AlN QWs were realized in Chap. 2, the IQE remains only $\sim 5\%$ at most under weak excitation conditions. (The IQE of *c*-plane QWs is less than 1% .) Then, we tried to identify the dominant nonradiative recombination centers in AlGa_N-related structures through the CL and PL measurements. Based on the analyses using configuration coordinate diagrams, the experimental results of the CL mappings and temperature dependent PL for AlN films and AlGa_N QWs were characterized. We found that TDs and two types of PDs (P1 and P2) mainly act as nonradiative recombination centers, and their activation energies are estimated to be ~ 2.5 , 10 , and 130 meV, respectively. It was clarified that P2 predominantly affects the emission intensity at room temperature due to its high trap density in spite of the large activation energy. Therefore, we firstly have to reduce P2 (not TDs) to improve the IQE of the current AlN and Al-rich AlGa_N structures. Because the deep level emissions at 3.2 and $3.5\text{--}3.7$ eV were enhanced by hole transfers to P2 near room temperature regions, we pointed out that the P2 may be fully, negatively charged $V_{\text{Al}}\text{--}O_{\text{N}}$ complex defects. The theoretically calculated formation energy of V_{Al} in AlN is much smaller than that of V_{Ga} in GaN, and P2 can be easily generated in AlN and Al-rich AlGa_N structures. As a consequence, the impacts of TDs in AlN are much smaller than those of GaN. Because P2 density may be varied by the growth conditions, the optimization of growth condition with particular focus on the PD reduction is very important. From the thermodynamic study on AlN epitaxy, we clarified that high reactor pressure and suppressed NH_3 flux lead to high equilibrium Al partial pressures, which may reduce V_{Al} -related defects such as P2. In terms of the realization of smooth surfaces, we recommend the former method for semipolar plane growth and the latter method for *c*-plane growth.

In Chapter 4, we explored the calculation model of the critical thickness for wurtzite structures with arbitrary off-angles, and the respective primary slip systems were discussed.

Because misfit dislocations, which degrade the device performances, should be avoided to improve the IQE, appropriate structural designs of AlGaIn QWs considering the critical thickness are required. We characterized the lattice relaxations in AlGaIn/AlN heterostructures by careful observations of the surface morphologies and the optical properties in addition to the conventional XRD measurements. Although the XRD is widely used for the characterization of lattice relaxation, the experimental results clarified that the detection sensitivity is not necessarily good particularly for AlGaIn heterostructures. Even when lattice relaxations were not determined by XRD, latently relaxed samples gave off some unique optical signals suggesting lattice relaxations, such as the aberrant shortenings of carrier recombination lifetimes, narrowing of line widths, and decrease of emission intensities. In particular, TRPL spectroscopy highlights the severity of the critical thickness of AlGaIn/AlN heterostructures, and we found that the critical thickness cannot be well explained by the conventional slip system for wurtzite (0001) epitaxial layers. Although semipolar $\{11\bar{2}2\}$ and $\{1\bar{1}01\}$ slips have been conventionally considered for (0001) heterostructures, we proposed that the (0001) slip due to the unintentional off-angle firstly occurs before such semipolar-plane slips. Interestingly, the lattice relaxation scarcely depends on the threading dislocation density. Our extended calculation models assuming the off-angles, friction forces, and thermally assisted forces well reproduced the experimental results of (0001) AlGaIn/AlN heterostructures. Furthermore, we clarified that the insertion of AlGaIn relax layers under the active layers is an effective method to avoid the efficiency degradations due to MDs. From the calculations for semipolar AlGaIn/AlN QWs, we found that the critical thickness of semipolar QWs with about 50° – 55° off-angles, is the thickest among various growth planes including the c -plane. The results therefore indicate that r -plane and $(11\bar{2}2)$ QWs, which are realized in Chap. 2, are attractive growth planes in terms of the suppression of MDs in addition to the small internal electric fields.

In Chapter 5, we investigated the optical polarization control for semipolar AlGaIn/AlN QWs and demonstrated stimulated emissions from optically pumped r -plane AlGaIn/AlN QWs for the first time. To obtain highly efficient DUV devices, high LEE is also required in addition to the improvement of IQE which was discussed in the previous chapters. Thus, the optical polarization, which determines the emission direction, should be controlled considering the respective device structures. However, the different parameter sets were reported from several groups and the calculated optical polarizations strongly depended on the parameters. Therefore, we investigated the appropriate parameter set for the calculation of the optical polarization degree of AlGaIn/AlN QWs comparing the calculated results based on the $\mathbf{k} \cdot \mathbf{p}$ perturbation method with the experimentally obtained in-plane polarization degree. As a consequence, we clarified that the deformation potentials reported in Ref. [1, 2] and the effective mass parameters for valence bands reported in Ref. [3] give the reliable prediction of the optical polarization degree of AlGaIn/AlN QWs. In particular, the use of the deformation potentials without the quasi-cubic approximation (in Ref. [1, 2]) may play an important role in calculating the band structures. The calculated results for the out-of-plane

polarization degree of semipolar r -plane AlGaIn/AlN QWs indicate that the r -plane AlGaIn QWs are very attractive structures to fabricate DUV-LEDs emitting at short wavelengths in terms of the LEE in addition to the high IQE because the r -plane QWs with narrow well widths (< 5.5 nm) can keep positive out-of-plane polarization degrees throughout the entire Al compositions in contrast to c -plane QWs. Furthermore, the calculated and experimental in-plane polarization degree clarified that we can realize highly efficient LDs based on the r -plane AlGaIn/AlN QWs emitting at 220–280 nm from the perspectives of both IQE and LEE by designing the QWs to have Al compositions more than 0.2 and to have narrow well widths (~ 1.5 nm). Finally, we performed the optical pumping measurement for the r -plane Al_{0.5}Ga_{0.5}N/AlN 6QW with 1.7-nm-thick well layers. The emission from the appropriately designed QW is strongly polarized along $\mathbf{E}||c^*$, which indicates strong light extractions from the a -planes. A Fabry-Perot cavity with a length of 2 mm was formed by cleavage along the $[11\bar{2}0]$ direction. The stimulated emissions at 250 nm were firstly observed from the semipolar AlGaIn QW under strong excitation conditions. The spectral narrowing was also clearly observed, and the lasing threshold power density was estimated to be ~ 500 kW/cm² at 11 K. To further improve the threshold power density, we concluded that high-reflection coatings such as HfO₂/SiO₂ DBRs are effective. From the reflectance calculations, we suggested 10 pairs of HfO₂/SiO₂ DBR, which can realize the high reflectance beyond 99% at 250 nm.

6.2 Future works

In this thesis, high quality semipolar AlGaIn/AlN QWs and the much stronger emissions compared with the conventional c -plane QWs were achieved. However, the IQE of the semipolar QWs remains only $\sim 5\%$ under weak excitation conditions. To further improve the IQE, we have to reduce Al-vacancy-related PDs which acting dominant nonradiative recombination centers at room temperature. Some unique and crucial methods for the reduction of Al vacancies are needed for the future works in addition to the optimization of growth conditions as described in Chap. 3. Herein, we introduce some ideas, which includes some methods other than the PD reduction, to achieve highly efficient AlGaIn-based DUV emitters.

6.2.1 UV illumination growth

We can roughly classify the PD reduction methods into “*in-situ*” and “*ex-situ*” approaches. At first, we discuss the former “*in-situ*” approaches.

For the *in-situ* methods, PDs are reduced during the crystal growth by the variations of growth conditions such as adjustment of the precursor fluxes. Moreover, UV light illumination growth may be one of the effective *in situ* methods to reduce PDs. In theory, Fermi-level strongly affects the formation energy of PDs, and for example, the formation

energies of acceptor-like defects such as Al vacancies in n-type AlGaIn films get smaller for higher Fermi-levels [4–6]. Because AlGaIn films without any intentional dopings basically indicate n-type conductivities, the Fermi-levels should be in the upper half of the bandgaps. The UV illumination above bandgap can make the Fermi-level close to the midgap and may reduce acceptor-like defects due to the larger formation energies. In fact, the UV illumination method has been used for Si-doped n-type AlGaIn growth to reduce the compensating PDs, and it was confirmed that the carrier concentration and mobility are improved [7]. Therefore, we think that such UV illumination growth may be effective to reduce Al-vacancy-related PDs in un-doped QW structures.

6.2.2 Al ion implantation and Al dip

Here, we introduce “*ex-situ*” approaches. The “*ex-situ*” methods mean the treatments for the PD reduction after the crystal growth such as high temperature inert-gas annealing. We suggest two distinct approaches referring to other semiconductor materials as follows.

6.2.2.1 Al ion implantation

In 4H-SiC, $Z_{1/2}$ center, which is a deep level derived from a carbon vacancy, has a large capture cross section for both electrons and holes, and is the dominant lifetime-killing defect [8, 9]. The elimination of the $Z_{1/2}$ center has been achieved by either carbon ion implantation and subsequent high-temperature annealing [10, 11] or thermal oxidation [12–14]. In the both elimination methods, the fundamental mechanism is that the generated carbon interstitials are thermally diffused and recombine with carbon vacancies.

Then, we suggest the Al vacancy reduction method for AlGaIn materials using the Al ion implantation and subsequent high-temperature annealing. A 400-nm-thick AlN film was grown at 500 Torr on a semipolar *r*-plane AlN substrate using MOVPE method. The implanted Al ion distributions were calculated by the Monte Carlo simulation software SRIM² (the Stopping and Range of Ions in Matter) [15–17]. The calculated depth profiles of the Al concentrations implanted in AlN films are shown in Fig. 6.1. To effectively diffuse the Al interstitials in the epitaxial film, the Al ions were implanted at angle of 60° with the surface normal with rotating the sample (0.6 rps). Although high accelerating voltages can deeply implant Al ions, we adopted 150 kV considering the V_{Al} reduction in the epilayer and the suppression of implantation damage. The implantation dose was adjusted to $1 \times 10^{16} \text{ cm}^{-2}$, which generates excess Al atoms in the epilayer with the density of $\sim 8 \times 10^{20} \text{ cm}^{-3}$ (the distribution is depicted in Fig. 6.1). The Al implantation was performed at room temperature.

Figure 6.2 shows the schematic images of the experimental procedures. After the Al ion implantation, 240-nm-thick SiO₂ film was deposited on the surface by plasma enhanced

²SRIM is a group of programs which calculate the stopping and range of ions (up to 2 GeV/amu) into matter using a quantum mechanical treatment of ion-atom collisions.

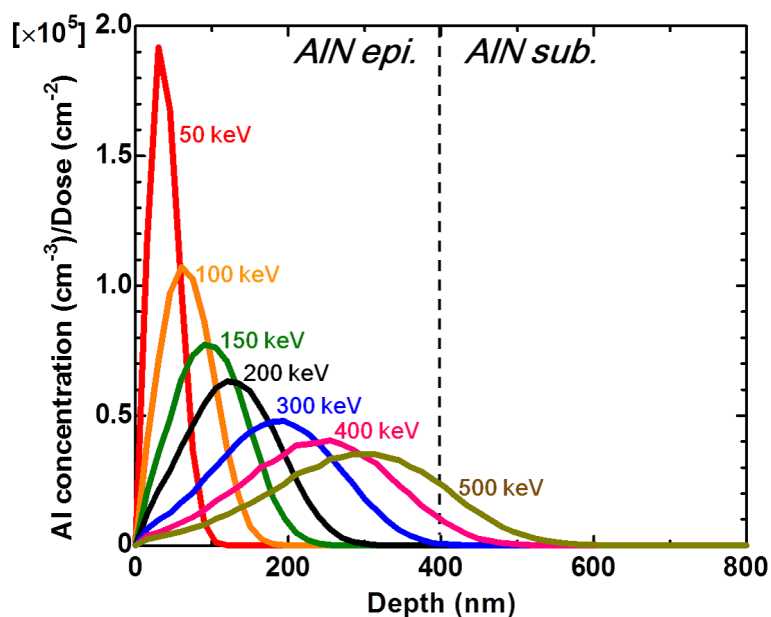


Figure 6.1: Depth profiles of Al concentrations implanted in AlN. The calculations were performed by the Monte Carlo simulations using SRIM. To effectively diffuse the Al interstitials in the epitaxial film, the Al ions were implanted at angle of 60° with the surface normal.

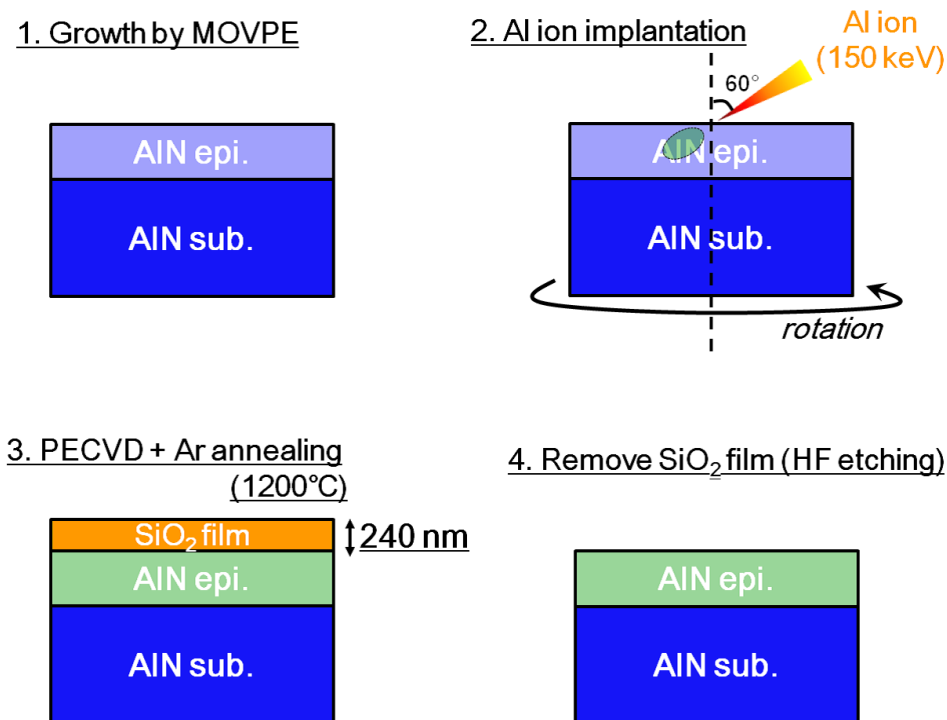


Figure 6.2: Schematic images of the experimental procedures.

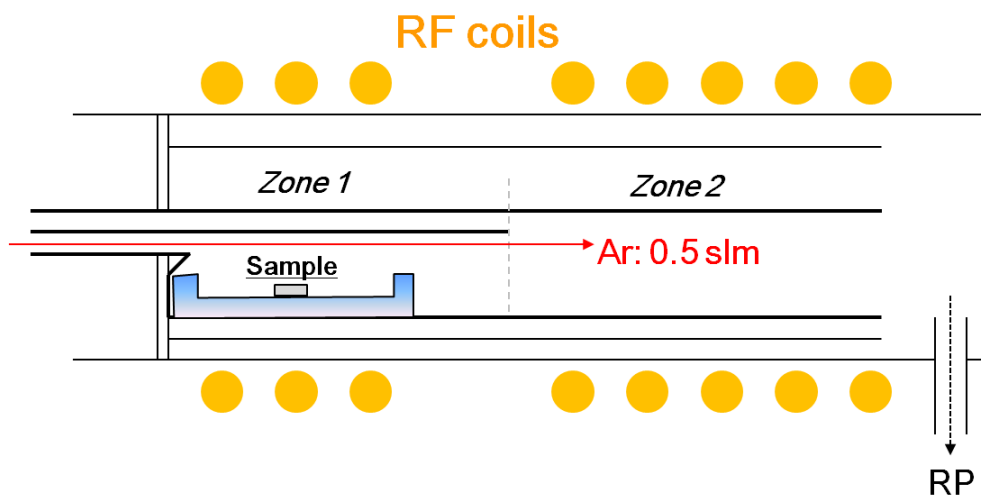


Figure 6.3: Schematic image of annealing furnace.

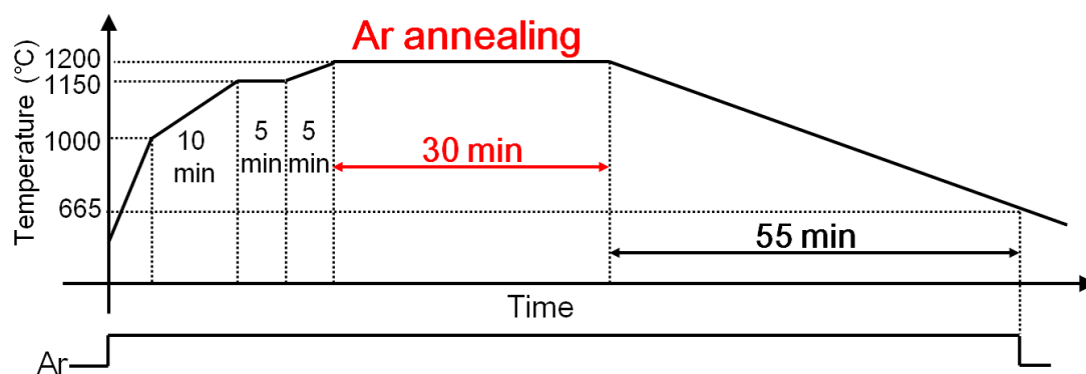


Figure 6.4: Annealing profile after the Al ion implantation.

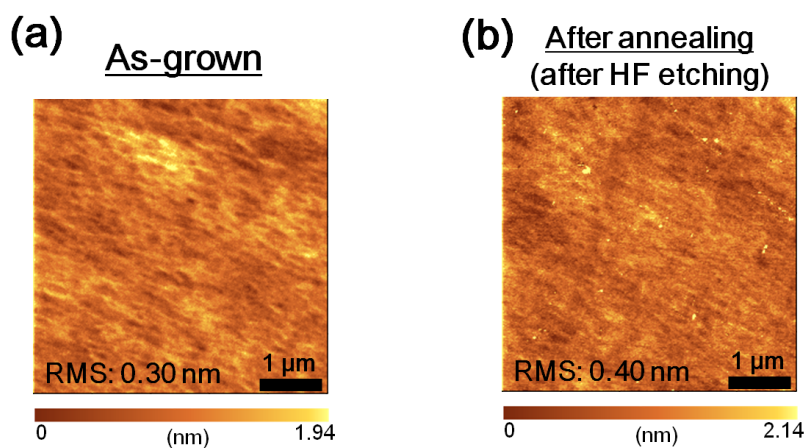


Figure 6.5: Surface morphologies of AlN films assessed by AFM before and after the Al implantation treatments. (a) As-grown surface and (b) AlN surface after annealing.

chemical vapor deposition (PECVD) for the suppression of N desorption from the AlN surface during the subsequent high-temperature annealing. Subsequently, we performed the high-temperature Ar annealing at 710 Torr to diffuse the implanted Al interstitials using the annealing furnace shown in Fig. 6.3. Although the annealing furnace has two radio-frequency induction heating systems for zone 1 and zone 2, we used the same temperatures for both heaters in this study. The annealing profile is depicted in Fig. 6.4. The sample was heated to 1200°C in Ar atmosphere and was annealed for 30 min to promote the diffusion of the implanted Al interstitials. We carefully cooled the sample after the annealing. The temperature dependence of vacancy density (D_V) is generally expressed as

$$D_V = s_0 \exp\left(-\frac{E_F}{k_B T}\right), \quad (6.1)$$

where s_0 is the atom site density and E_F is the formation energy of the vacancy. Here, k_B and T are Boltzmann constant and temperature. Therefore, higher density of vacancies are stable at higher temperatures due to the thermal equilibrium states, and the rapid coolings may freeze such high density of vacancies in samples even after the processes. Hence, after the high-temperature annealing, the sample was gradually cooled down to avoid freezing PDs as shown in Fig. 6.4. Finally, the SiO₂ film was removed by a HF rinse.

Figures 6.5(a) and (b) show the surface morphologies of AlN films assessed by AFM before and after the above mentioned treatments. From the AFM images, the surface morphologies were almost the same and no obvious surface damages through the Al ion implantation and annealing were confirmed. Subsequently, we performed PL measurements for the as-grown, as-implanted, and after-annealing samples using an ArF excimer laser (193 nm) as an excitation source. The samples were excited at an angle of 60° with the surface normal, and PL signals were detected from the surface normal. The PL spectra of the as-grown and as-implanted samples at 11 K are shown in Fig. 6.6(a), and the respective spectra are depicted as a broken line and a solid line. For the emission from the as-implanted sample, three distinct peaks are mainly observed. The dominant highest-energy peak may be a mixed peak with α and FX. As we described in Chap. 2, the origin of the α peak is under debate, whereas that of the FX peak is assigned as a free exciton with I_1 [18, 19], and that of the Si⁰X peak is assigned as a silicon donor-bound exciton of the FX peak [20]. The lowest-energy peak emitting at 6.0080 eV (O⁰X) may be derived from an oxygen donor-bound exciton [21]. For the as-grown sample, Si⁰X peak is quite strong and other peaks are confirmable only in the log scale (see Chap. 2). The PL spectra of the as-grown and after-annealing samples at 11 K are shown in Fig. 6.6(b), and the respective spectra are depicted as a broken line and a solid line. For the after-annealing sample, Si⁰X peak is dominant similarly to the as-grown sample. However, the α and O⁰X peaks can be clearly observed even in the linear scale.

We predict the Al ion implantation effects on the crystalline quality from the differences of the PL spectra. Figures 6.7(a)–(c) show the schematic images of predicted atomic ar-

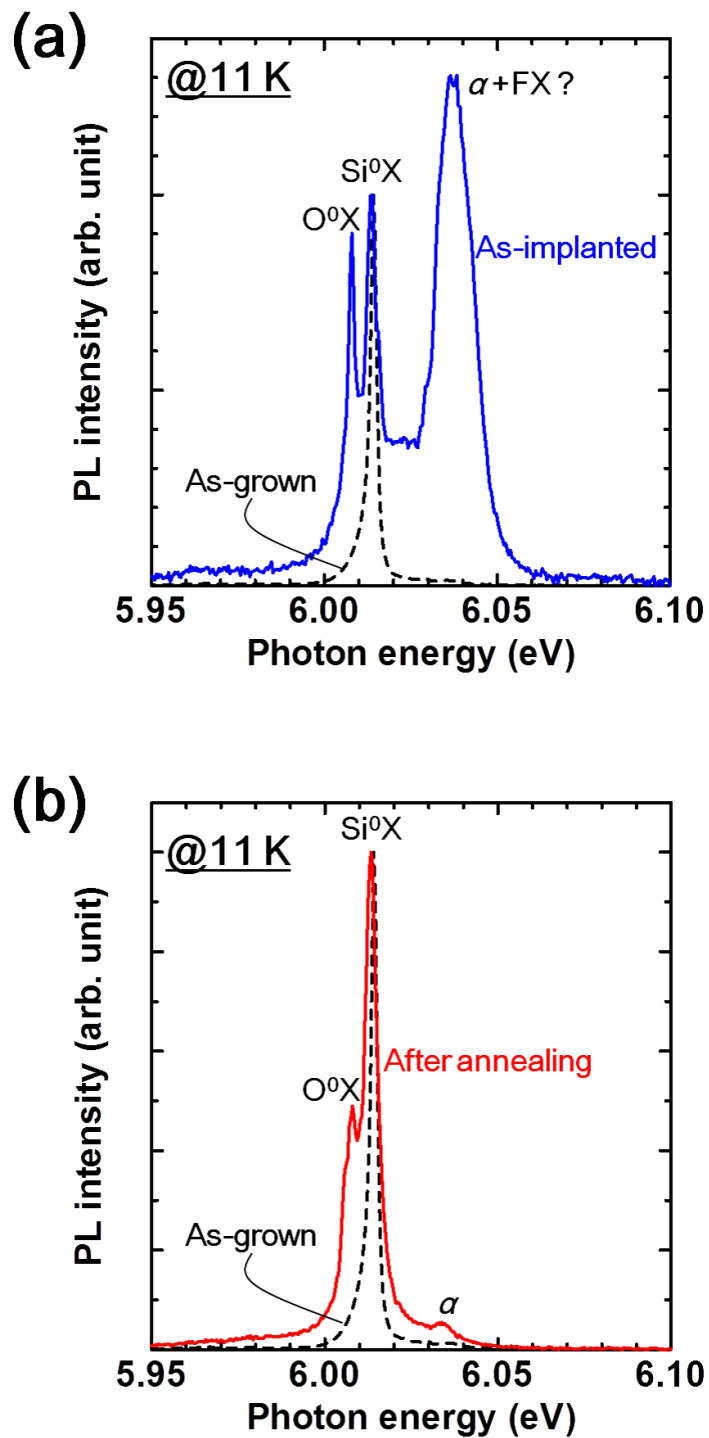
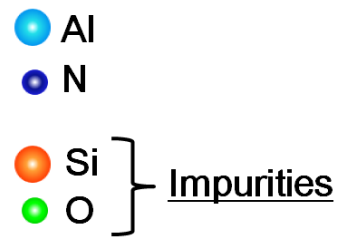
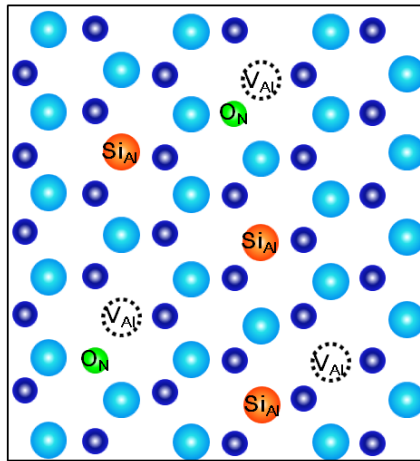
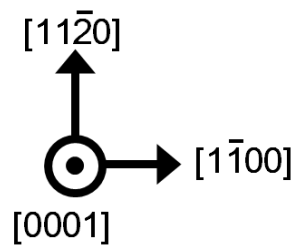
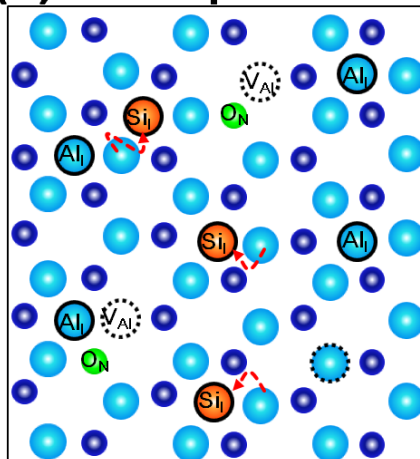


Figure 6.6: (a) PL spectra of as-grown and as-implanted AlN films at 11 K. The respective spectra are depicted as a broken line and a solid line. (b) PL spectra of as-grown and after-annealing AlN films at 11 K. The respective spectra are depicted as a broken line and a solid line.

(a) As-grown



(b) As-implanted



(c) After annealing

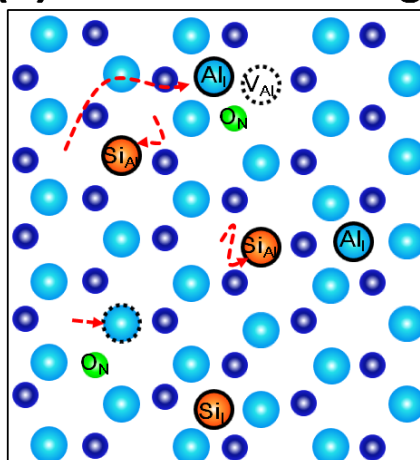


Figure 6.7: Schematic images of predicted atomic arrangements for (a) as-grown, (b) as-implanted, and (c) after-annealing AlN films.

rangements for the as-grown, as-implanted, and after-annealing samples, respectively. In the as-grown sample, silicon and oxygen impurities are incorporated in the epilayer due to the high pressure growth as described in Chap. 2. Considering the strong Si^0X emission, most of the Si impurities may be substituted into Al atom sites (Si_{Al}), and parts of O impurities may be also substituted into N atom sites (O_{N}). These impurities act as donor-like defects in AlN films. Due to the Al ion implantation, parts of the Si_{Al} are pushed out from the Al sites and become interstitials (Si_{I}). Furthermore, parts of the V_{Al} may be eliminated by the recombination with the implanted Al atoms. On the other hand, O_{N} defects are unchanged by the implantation because they are not in the Al sites but in N sites. As a consequence of the variation of the atomic arrangement in the as-implanted sample, the Si^0X emission was suppressed by the reduction of Si_{Al} , and the O^0X peak became relatively strong due to the remaining O_{N} as shown in Fig. 6.6(a). In the as-implanted sample, however, a lot of Al interstitials (Al_{I}) should also exist by the implantation.

In the after-annealing sample, parts of the Al_{I} thermally diffuse and may recombine with the V_{Al} . Moreover, parts of the Si_{I} are changed to Si_{Al} again. As a result, the Si^0X peak became dominant again similarly to the as-grown sample, whereas the α and O^0X peaks could be clearly observed [see Fig. 6.6(b)] because parts of the Si_{I} remained in the AlN film.

To compare the emission intensities of these samples with each other, temperature dependent PL measurements were performed. Figure 6.8 shows the temperature dependence of the integrated PL intensities of the as-grown, as-implanted, and after-annealing samples. The thermal quenching of the as-implanted sample is much stronger than those of the as-grown sample. We consider that this may be because many Si_{I} and Al_{I} in the as-implanted sample form a lot of deep levels as shown in Fig. 6.7(b). In fact, we can confirm the improvement of thermal quenching for the after-annealing sample due to the reduction of such interstitials. Moreover, the thermal quenching below 100 K for the both as-implanted and after-annealing samples is weaker than that of the as-grown sample even under weaker excitation conditions.³ This may be caused by the reduction of P1-type defects due to the Al ion implantation, which means that P1 may be also V_{Al} -related PD similar to P2. However, in both of the as-implanted and after-annealing samples, the integrated PL intensities at room temperature are weaker than that of the as-grown sample. The additional annealing and adjustment of implantation conditions are therefore needed. On the other hand, the ion-implanted samples should suffer from the implantation damages to some content, and the actual impacts of the Al ion implantation on the PD reduction are under consideration.

6.2.2.2 Al dip

Although the aforementioned Al-ion-implantation method may damage samples, we present a damage-free “*ex-situ*” approach to reduce PD here.

³In Chap. 3, we confirmed that stronger excitation conditions lead to weaker thermal quenching, which is due to the occupation of P1 and P2 defects by photo-excited carriers.

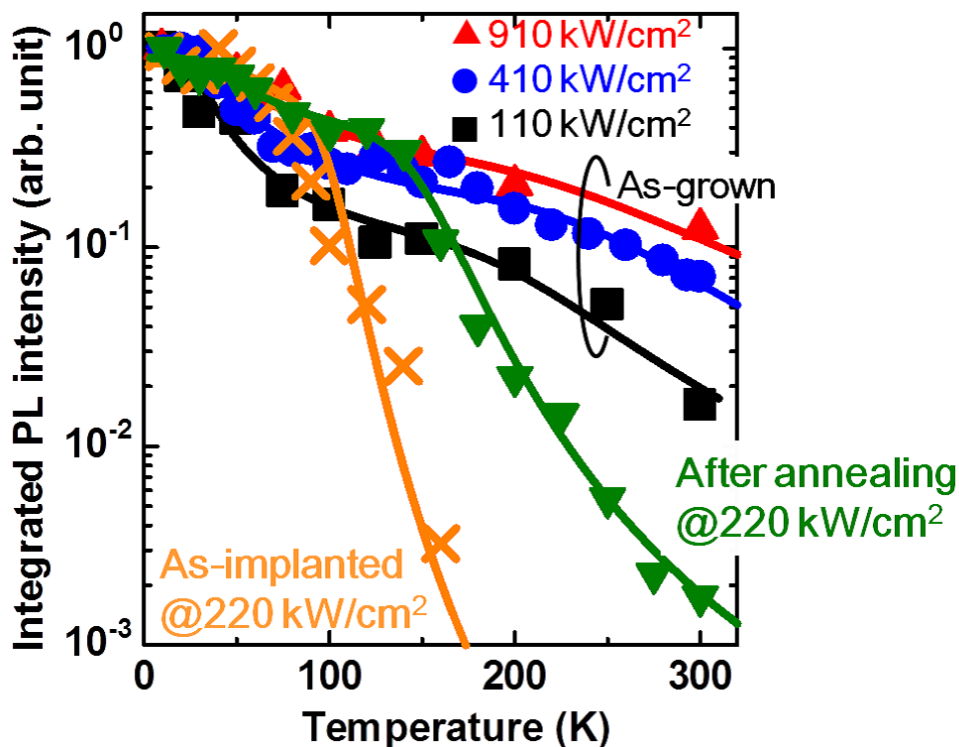


Figure 6.8: Temperature dependence of the integrated PL intensities of the as-grown, as-implanted, and after-annealing AlN films.

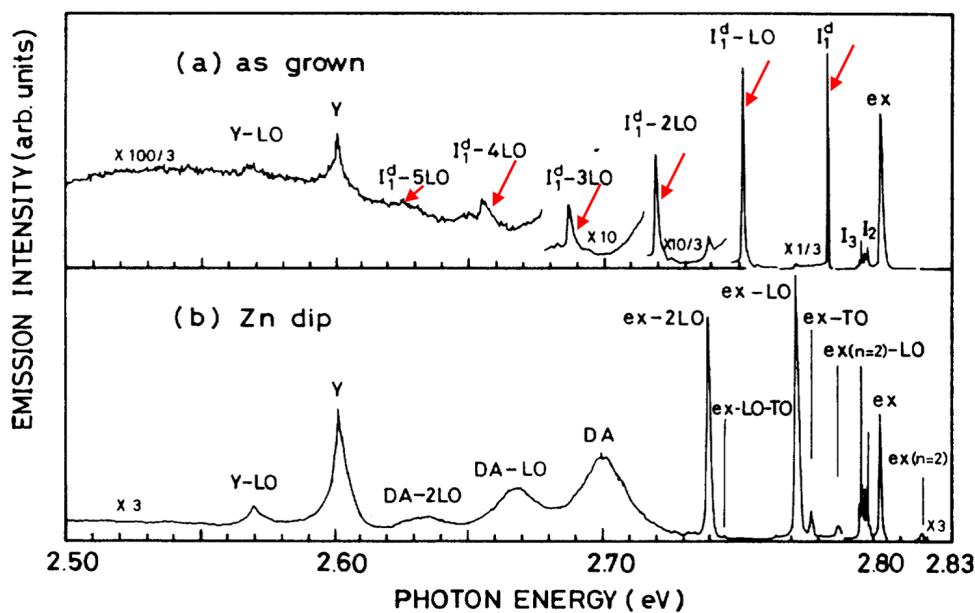


Figure 6.9: PL spectra measured on (a) the as-grown ZnSe single crystal and (b) Zn-dip treated crystal. The figure is taken from Ref. [22]

In ZnSe, Zn vacancies in the crystal decrease the recombination lifetime and suppress the emission intensity by free-exciton [22]. In the previous works, the treatment in liquid or gaseous Zn was performed at high temperature (700–1000°C) in a vacuum-sealed quartz ampule to reduce the Zn vacancies, and the treatment was called as Zn-dip [22–24]. Figure 6.9 shows the PL spectra of ZnSe, which are reported in Ref. [22], measured on the as-grown ZnSe single crystal and Zn-dip treated crystal. The I_1^d line derived from Zn vacancies and the LO phonon replicas are disappeared by Zn-dip treatment (the emission lines are marked by the arrows in Fig. 6.9). The experimental results indicate that the Zn-dip treatment can reduce the density of Zn vacancies and enhance the free-exciton emissions. Then, we suggest that Al-dip treatment for AlN or Al-rich AlGaN materials may be effective to reduce V_{Al} -related PDs. Furthermore, the Al-dip treatment will not give obvious damages on the samples in contrast to the Al ion implantation.

6.2.3 ML-thick GaN/AlN QW

In the previous sections, we introduced some ideas to reduce V_{Al} -related PDs. As we described in Chap. 3, the theoretically calculated formation energy of V_{Ga} in GaN is much larger than that of V_{Al} in AlN [5]. Therefore, the impacts of V_{Ga} -related PDs in GaN films on the efficiency degradations should be smaller than those of V_{Al} -related PDs in AlN films. Then, we present DUV emitters using GaN well layers without any Al atoms to avoid the high density of vacancies.

To use GaN as active layers for DUV emitters, ultra-thin GaN wells, which can make use of strong quantum confinement effects, are needed considering the narrow bandgap energy. In such a case, we have to control the well width at the ML-level. For InN/GaN QWs, 1 ML-thick well layers have been realized by several groups [25, 26]. In particular, T. Akasaka *et al.* fabricated InN/GaN SQW with a 1 ML-thick well layer using MOVPE method, and they confirmed the violet PL emission from the QW. Because the growth rate of InN is generally quite slow, such an ultra-thin QW can be obtained even by MOVPE. However, the growth rate of GaN is relatively fast and the well width control at the ML-level is not easy.

On the other hand, atomic layer epitaxy (ALE) using MOVPE was developed for GaAs-related materials [27–30]. ALE for GaAs was firstly reported by J. Nishizawa *et al.* using TMG and arsine as the precursors [27]. This was followed by ALE growths for GaAs in MOVPE reactors. ALE is a self-limiting ML growth utilizing an alternate supply of precursors, and it is realized by appropriately adjusting the growth temperature and precursor supply. Then, we propose GaN/AlN QWs with ML-thick well layers grown by ALE.

Figure 6.10 shows the schematic image of the crystal growth of a GaN layer on an AlN template. The lifetime of Ga adatoms (τ_{Ga}) can be expressed as

$$\frac{1}{\tau_{Ga}} = \frac{1}{\tau_{eva}} + \frac{1}{\tau_{nuc}} + \frac{1}{\tau_{cap}}, \quad (6.2)$$

where τ_{eva} , τ_{nuc} , and τ_{cap} are the lifetimes for the evaporation, nucleation with a N atom, and capture by GaN growth islands, respectively. Therefore, the lifetime for the crystallization (τ_{cryst}) is given by

$$\frac{1}{\tau_{\text{cryst}}} = \frac{1}{\tau_{\text{nuc}}} + \frac{1}{\tau_{\text{cap}}}. \quad (6.3)$$

In the case of $\tau_{\text{cryst}} < \tau_{\text{eva}}$, GaN crystal growth proceeds, whereas etchings occur for $\tau_{\text{cryst}} > \tau_{\text{eva}}$. Thus, ALE of GaN may be realized by adjusting the lifetimes to be $\tau_{\text{cryst}} \approx \tau_{\text{eva}}$. In theory, high growth temperature promotes the evaporation of Ga and high V/III ratio cause the short τ_{nuc} . Adjusting the growth conditions, which are varied from an ordinary growth conditions for GaN epitaxy, we tried to realize ALE of GaN. In general, several thousand V/III ratio and growth temperature of $\sim 1000^\circ\text{C}$ are used for the GaN epitaxy, and $\tau_{\text{cryst}} < \tau_{\text{eva}}$ is satisfied in such conditions. We adopted higher growth temperature and lower V/III ratio to make the condition close to the relation $\tau_{\text{cryst}} \approx \tau_{\text{eva}}$.

GaN/AlN QWs were fabricated at 500 Torr on AlN homoepitaxial films grown on *r*-plane AlN substrates. TMG, TMA, and NH_3 were used as the precursors for Ga, Al, and N, respectively. The TMG and NH_3 fluxes were adjusted to 8.18 and 893 $\mu\text{mol}/\text{min}$, which realized low V/III ratio of 109. The growth temperature was adjusted from 1000 to 1115°C . Figure 6.11 shows the QW-growth time dependence of the PL peak energies of fabricated GaN/AlN QWs at 10 K ⁴. For the GaN/AlN QWs grown at 1115°C , the PL peak energies are completely independent of the growth time, and we estimated the well widths to be ~ 1 ML from the energies. This indicates that 1 ML-thick GaN layers are self-limitedly grown on AlN due to the balance of the evaporation and crystallization ($\tau_{\text{cryst}} \approx \tau_{\text{eva}}$). Furthermore, adjusting the growth temperatures to 1000°C , the PL peak energies of GaN/AlN QWs slightly become lower than those of QWs grown at 1115°C . From the PL peak energies, we estimated the well widths to be ~ 2 ML, and the well widths of the QWs were also independently of the growth time. Therefore, we conclude that ALE of GaN well layers using MOVPE method can be realized by the growth conditions. As a consequence, ultra-thin GaN/AlN QWs emitting at DUV region (210–240 nm) were achieved. Toward actual device applications, further investigations such as optimization of structure and growth conditions are required.

6.2.4 AlGaN quantum wire

Finally, we introduce the unique quantum structure for highly efficient UV emitters. Quantum wires (QWRs) are promising quantum structures to enhance IQE, because the lower dimensionality for exciton confinement compared with typical QWs can suppress the exciton thermal distribution and can enhance the radiative recombination probabilities at room temperature. In theory, the radiative recombination lifetimes in QWRs are pro-

⁴The obtained PL spectra were depicted in Chap. 5.

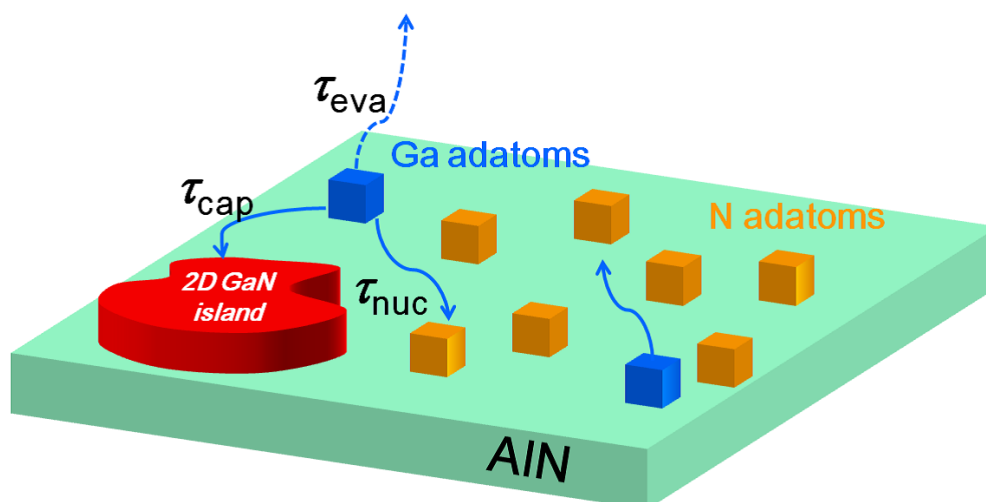


Figure 6.10: Schematic image of the crystal growth of a GaN layer on an AlN template.

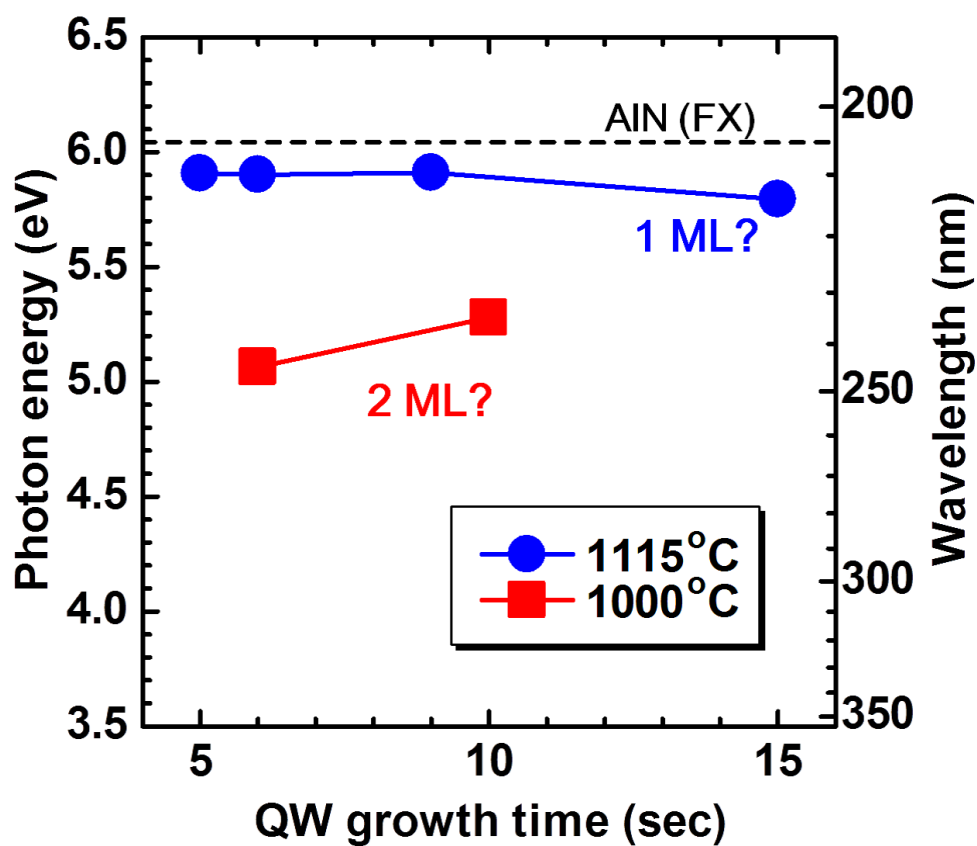


Figure 6.11: QW-growth time dependence of the PL peak energies of fabricated *r*-plane GaN/AlN QWs at 10 K.

portional to the square root of temperature, whereas those in QWs are proportional to temperature [31]. In GaAs-related materials, the superior properties of QWRs have been experimentally confirmed [31, 32]. In particular, GaAs QWRs were easily formed at the step-edges of underlying AlGaAs bunched steps grown on vicinal GaAs substrates by the MOVPE method [33, 34]. Similarly, we have also fabricated AlGaN QWRs at the bunched step-edges of AlN grown on vicinal sapphire (0001) substrates [35]. Figure 6.12 shows the cross sectional HAADF-STEM (High-angle annular dark field scanning TEM) image of a AlGaN/AlN QWR fabricated on a vicinal sapphire (0001) substrate. In general, heavier atoms provide brighter contrast in HAADF-STEM, and Fig. 6.12 indicates the higher Ga composition at the step-edge compared with the terrace area. The higher Ga compositions at the step-edges form QWR structures.

Figure 6.13 shows the SEM image and CL map at room temperature of AlGaN/AlN QWRs fabricated on the step-bunched surface of an AlN film grown on a vicinal *c*-plane AlN substrate. The SEM image and CL map were obtained at the same area. We found that the CL intensity is enhanced along the macro-steps, and the result indicates the existence of AlGaN QWR structures. It was also elucidated that the thermal quenching of AlGaN QWRs is much weaker than that of typical AlGaN QWs in Ref. [35]. Although the detailed optical properties and appropriate structures have yet to be clarified, the superior properties of AlGaN QWRs will be proved near future.

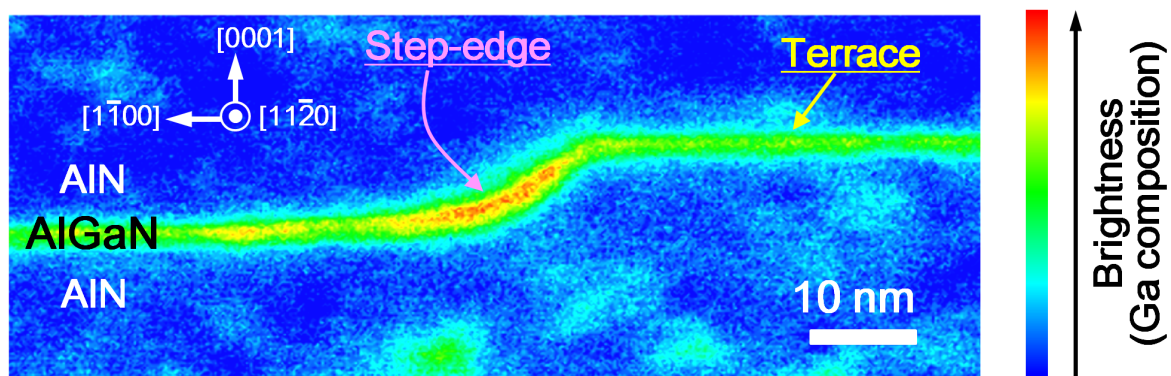
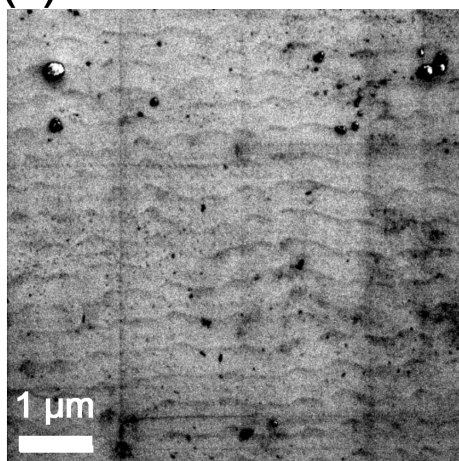


Figure 6.12: Cross sectional HAADF-STEM image of an AlGaN/AlN QWR fabricated on a vicinal sapphire (0001) substrate [35].

(a) SEM



(b) CL map @RT

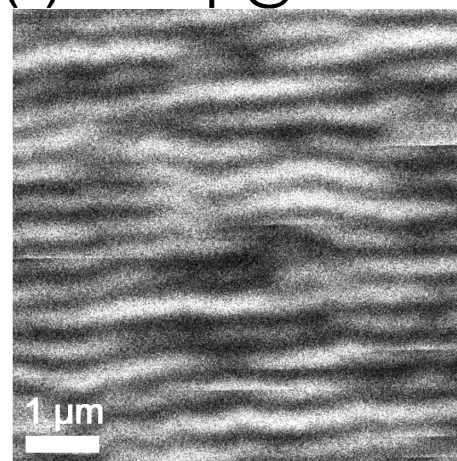


Figure 6.13: (a) SEM image and (b) CL map at room temperature of AlGaN/AlN QWRs fabricated on the step-bunched surface of an AlN film grown on a vicinal *c*-plane AlN substrate. The SEM image and CL map were obtained at the same area.

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Appendix A

Material parameters

• Material parameters of AlN and GaN

The material parameters of AlN and GaN used in this study are introduced. Table A.1 lists the material parameters used for the calculations of the strains and the internal electric fields. These parameters were used in Chaps. 2, 4, and 5. Table A.2 lists the parameters for the band structure calculations, which was used in Chap. 5. Note that the exciton deformation potentials (C_i) and the effective mass parameters for valence bands (A_i) are appropriately chosen reflecting the results in Chap. 5. The superscripts or subscripts of “||” and “ $\perp$ ” mean the parameters along the directions parallel and perpendicular to c -axis, respectively.

• Bowing parameters for AlGaN

Material parameters of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ are basically estimated by the linear interpolation between the parameters of AlN and GaN listed in Tabs. A.1 and A.2. Thus, the material parameters (M) of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ except for the spontaneous polarizations and energy bandgaps are given by

$$M_{\text{AlGaN}} = x \cdot M_{\text{AlN}} + (1 - x) \cdot M_{\text{GaN}}. \quad (\text{A.1})$$

The relation is called as Vegard’s law. However, the relation is not satisfied for some parameters, and we used the bowing parameters (M^{bow}) for such parameters. The material parameters considering the bowing parameters are obtained as

$$M_{\text{AlGaN}} = x \cdot M_{\text{AlN}} + (1 - x) \cdot M_{\text{GaN}} - x(1 - x) \cdot M^{\text{bow}}. \quad (\text{A.2})$$

In this study, the spontaneous polarization and the bandgap energy of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ are estimated by Eq. (A.2). The respective bowing parameters are listed in Tab. A.3.

Table A.1: Material parameters of AlN and GaN used for the calculations of the strains and the internal electric fields in this study.

Parameters		AlN	GaN
Lattice constant at 300 K (nm)	a	0.3112 [1, 2]	0.3189 [1, 2]
	c	0.4982 [1, 2]	0.5185 [1, 2]
Elastic stiffness constant (GPa)	C_{11}	396 [1, 2]	390 [1, 2]
	C_{12}	137 [1, 2]	145 [1, 2]
	C_{13}	108 [1, 2]	106 [1, 2]
	C_{33}	373 [1, 2]	398 [1, 2]
	C_{44}	116 [1, 2]	105 [1, 2]
Piezoelectric constant (C/m ²)	e_{15}	-0.48 [3]	-0.33 [4]
	e_{31}	-0.58 [3]	-0.33 [4]
	e_{33}	1.55 [3]	0.65 [4]
Permittivity (ϵ_0)	$\epsilon_{\parallel}^p$	9.32 [5]	10.4 [6]
	$\epsilon_{\perp}^p$	7.76 [5]	9.5 [6]
Spontaneous polarization (C/m ²)	P^{sp}	-0.090 [1, 2]	-0.034 [1, 2]

Table A.2: Material parameters of AlN and GaN used for the band structure calculations in this study.

Parameters		AlN	GaN
Bandgap energy at 0 K (eV)	E_g	6.10 [1]	3.510 [1]
Crystal-field splitting energy (meV)	Δ_1	-211.5 [7]	12.3 [8]
Spin-orbit interaction $\parallel c$ (meV)	Δ_2	6.0 [7]	5.2 [8]
Spin-orbit interaction $\perp c$ (meV)	Δ_3	6.5 [7]	5.9 [8]
Exciton deformation potential (eV)	C_1	4.3 [7]	6.5 [8]
	C_2	11.5 [7]	11.2 [8]
	C_3	6.8 [7]	4.9 [8]
	C_4	-3.6 [7]	-5.0 [8]
	C_5	-2.8 [7]	-2.8 [8]
	C_6	-4.5 [7]	-3.1 [8]
Electron effective mass (m_0)	$m_e^{\parallel}$	0.32 [1]	0.21 [1]
	$m_e^{\perp}$	0.30 [1]	0.20 [1]
Effective mass parameter for valence band	$A_1 (\hbar^2/2m_0)$	-3.86 [1, 2]	-7.21 [1, 2]
	$A_2 (\hbar^2/2m_0)$	-0.25 [1, 2]	-0.44 [1, 2]
	$A_3 (\hbar^2/2m_0)$	3.58 [1, 2]	6.68 [1, 2]
	$A_4 (\hbar^2/2m_0)$	-1.32 [1, 2]	-3.46 [1, 2]
	$A_5 (\hbar^2/2m_0)$	-1.47 [1, 2]	-3.40 [1, 2]
	$A_6 (\hbar^2/2m_0)$	-1.64 [1, 2]	-4.90 [1, 2]

Table A.3: Bowing parameters for AlGa_N used in this study.

Bowing parameters for AlGa _N		
Spontaneous polarization (C/m ²)	$P_{\text{bow}}^{\text{sp}}$	-0.021 [1, 2]
Bandgap energy (eV)	E_g^{bow}	0.8 [1]

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Appendix B

Finite-difference method

Effective-mass equations can be solved by a finite-difference method [1, 2]. Here, we explain the finite-difference method which was used to derive Hamiltonian for the QW in Chap. 5.

For QW structures, the wave number ($k_{z'}$) along the growth direction (z' direction) is discretized and $k_{z'}$ is substituted by $-i\partial/\partial z'$. Using Hamiltonian for the valence band, simultaneous Schrödinger equations for holes are expressed in Eq. (5.8). The matrix elements of the Hamiltonian for QW can be written as

$$\left\{ \begin{array}{l} F^{z'z'} = -\{(A_1 + A_3)\cos^2\theta + (A_2 + A_4)\sin^2\theta\} \frac{\partial^2}{\partial z'^2}, \\ \Lambda^{z'z'} = -(A_1\cos^2\theta + A_2\sin^2\theta) \frac{\partial^2}{\partial z'^2}, \\ K^{z'z'} = -(A_5\sin^2\theta) \frac{\partial^2}{\partial z'^2}, \\ H^{z'z'} = -(A_6\sin\theta\cos\theta) \frac{\partial^2}{\partial z'^2}, \end{array} \right. \quad (\text{B.1})$$

$$\left\{ \begin{array}{l} F^{z'} = -i\{(-A_1 + A_2 - A_3 + A_4)k'_x\sin 2\theta\} \frac{\partial}{\partial z'}, \\ \Lambda^{z'} = -i\{(-A_1 + A_2)k'_x\sin 2\theta\} \frac{\partial}{\partial z'}, \\ K^{z'} = -i\{2A_5(k'_x\cos\theta + ik'_y)\sin\theta\} \frac{\partial}{\partial z'}, \\ K^{*z'} = -i\{2A_5(k'_x\cos\theta - ik'_y)\sin\theta\} \frac{\partial}{\partial z'}, \\ H^{z'} = -i\{A_6(k'_x\cos 2\theta + ik'_y\cos\theta)\} \frac{\partial}{\partial z'}, \\ H^{*z'} = -i\{A_6(k'_x\cos 2\theta - ik'_y\cos\theta)\} \frac{\partial}{\partial z'}, \end{array} \right. \quad (\text{B.2})$$

$$\left\{ \begin{array}{l} F^t = \{ (A_1 + A_3) \sin^2 \theta + (A_2 + A_4) \cos^2 \theta \} k_x'^2 + (A_2 + A_4) k_y'^2, \\ \Lambda^t = (A_1 \sin^2 \theta + A_2 \cos^2 \theta) k_x'^2 + A_2 k_y'^2, \\ K^t = A_5 (k_x'^2 \cos^2 \theta - k_y'^2 + 2i k_x' k_y' \cos \theta), \\ K^{*t} = A_5 (k_x'^2 \cos^2 \theta - k_y'^2 - 2i k_x' k_y' \cos \theta), \\ H^t = -A_6 k_x' \sin \theta (k_x' \cos \theta + i k_y'), \\ H^{*t} = -A_6 k_x' \sin \theta (k_x' \cos \theta - i k_y'), \end{array} \right. \quad (\text{B.3})$$

$$\left\{ \begin{array}{l} K_\epsilon = D_5 (\epsilon_{xx} - \epsilon_{yy} + 2i\epsilon_{xy}), \\ H_\epsilon = D_6 (\epsilon_{xz} + i\epsilon_{yz}), \\ V_1 = \Delta_1 + \Delta_2 + \Lambda_\epsilon + \Theta_\epsilon + e_0 E_{\text{int}} z' + E_v^{(0)}, \\ V_2 = \Delta_1 - \Delta_2 + \Lambda_\epsilon + \Theta_\epsilon + e_0 E_{\text{int}} z' + E_v^{(0)}, \\ V_3 = \Lambda_\epsilon + e_0 E_{\text{int}} z' + E_v^{(0)}. \end{array} \right. \quad (\text{B.4})$$

Here, we omit $(\hbar^2/2m_0)$ before the A_i for the simplicity. In this study, we used the following finite-difference formulae [3],

$$\begin{aligned} X^{z'z'} &= X(z') \frac{\partial^2 g}{\partial z'^2} \rightarrow \frac{d}{dz'} \left(X(z') \frac{dg}{dz'} \right) \Big|_{z'=z'_j} \\ &\simeq \frac{X_{j+1} + X_j}{2(\Delta z')^2} g_{j+1} - \frac{X_{j+1} + 2X_j + X_{j-1}}{2(\Delta z')^2} g_j + \frac{X_j + X_{j-1}}{2(\Delta z')^2} g_{j-1} \\ &\equiv X_j^{z'z'(+1)} g_{j+1} + X_j^{z'z'(0)} g_j + X_j^{z'z'(-1)} g_{j-1}, \end{aligned} \quad (\text{B.5})$$

$$\begin{aligned} Y^{z'} &= Y(z') \frac{\partial g}{\partial z'} \rightarrow \frac{1}{2} \left(Y(z') \frac{dg}{dz'} + \frac{d(Bg)}{dz'} \right) \Big|_{z'=z'_j} \\ &\sim \frac{Y_{j+1} + Y_j}{4\Delta z'} g_{j+1} - \frac{Y_j + Y_{j-1}}{4\Delta z'} g_{j-1} \\ &\equiv Y_j^{z'(+1)} g_{j+1} + Y_j^{z'(-1)} g_{j-1}. \end{aligned} \quad (\text{B.6})$$

where X (Y) corresponds with F , Λ , K , and H (K^* and H^*). Here, we define $\Delta z' = z'_{j+1} - z'_i = z'_i - z'_{i-1}$, $X(z'_j) = X_j$, and $g(z'_j) = g_j$ for the following discussions. From

Eqs. (B.5) and (B.6), we have

$$\begin{cases} X_j^{z'z'+1} = X_{j+1}^{z'z'(-1)}, \\ Y_j^{z'+1} = -Y_{j+1}^{z'(-1)}. \end{cases} \quad (\text{B.7})$$

We define the local operators $\mathbf{M}_{j,j}$ obtained by gathering the coefficients of the wavefunctions g_j at $z = z_j$ as

$$\mathbf{M}_{j,j} = \mathbf{M}_{j,j}^{z'z'} + \mathbf{M}_{j,j}^t + \mathbf{M}_{j,j}^{\text{const.}}, \quad (\text{B.8})$$

where

$$\mathbf{M}_{j,j}^{z'z'} = \begin{bmatrix} F_j^{z'z'(0)} & -K_j^{z'z'(0)} & -H_j^{z'z'(0)} & & & \\ -K_j^{z'z'(0)} & F_j^{z'z'(0)} & H_j^{z'z'(0)} & & & \\ -H_j^{z'z'(0)} & H_j^{z'z'(0)} & \Lambda_j^{z'z'(0)} & & & \\ & & & F_j^{z'z'(0)} & -K_j^{z'z'(0)} & H_j^{z'z'(0)} \\ & & & -K_j^{z'z'(0)} & F_j^{z'z'(0)} & -H_j^{z'z'(0)} \\ & & & H_j^{z'z'(0)} & -H_j^{z'z'(0)} & \Lambda_j^{z'z'(0)} \end{bmatrix}, \quad (\text{B.9})$$

$$\mathbf{M}_{j,j}^t = \begin{bmatrix} F_j^t & -K_j^{*t} & -H_j^{*t} & & & \\ -K_j^t & F_j^t & H_j^t & & & \\ -H_j^t & H_j^{*t} & \Lambda_j^t & & & \\ & & & F_j^t & -K_j^t & H_j^t \\ & & & -K_j^{*t} & F_j^t & -H_j^{*t} \\ & & & H_j^{*t} & -H_j^t & \Lambda_j^t \end{bmatrix}, \quad (\text{B.10})$$

$$\mathbf{M}_{j,j}^{\text{const.}} = \begin{bmatrix} V_{1,j} & -K_{\epsilon,j} & -H_{\epsilon,j} & & & \\ -K_{\epsilon,j} & V_{2,j} & H_{\epsilon,j} & & & \Delta_j \\ -H_{\epsilon,j} & H_{\epsilon,j} & V_{3,j} & & & \Delta_j \\ & & & V_{1,j} & -K_{\epsilon,j} & H_{\epsilon,j} \\ & & & \Delta_j & -K_{\epsilon,j} & V_{2,j} & -H_{\epsilon,j} \\ & & & & & & \Delta_j \\ & & & & & & H_{\epsilon,j} & -H_{\epsilon,j} & V_{3,j} \end{bmatrix}. \quad (\text{B.11})$$

Furthermore, we define the nonlocal operators $\mathbf{M}_{j,j\pm 1}$ obtained by gathering the coefficients

of the wavefunctions $g_{j\pm 1}$ as

$$\mathbf{M}_{j,j\pm 1} = \mathbf{M}_{j,j\pm 1}^{z'z'} + \mathbf{M}_{j,j\pm 1}^{z'}, \quad (\text{B.12})$$

where

$$\mathbf{M}_{j,j\pm 1}^{z'z'} = \begin{bmatrix} F_j^{z'z'(\pm 1)} & -K_j^{z'z'(\pm 1)} & -H_j^{z'z'(\pm 1)} & & & \\ -K_j^{z'z'(\pm 1)} & F_j^{z'z'(\pm 1)} & H_j^{z'z'(\pm 1)} & & & \\ -H_j^{z'z'(\pm 1)} & H_j^{z'z'(\pm 1)} & \Lambda_j^{z'z'(\pm 1)} & & & \\ & F_j^{z'z'(\pm 1)} & -K_j^{z'z'(\pm 1)} & H_j^{z'z'(\pm 1)} & & \\ & -K_j^{z'z'(\pm 1)} & F_j^{z'z'(\pm 1)} & -H_j^{z'z'(\pm 1)} & & \\ & H_j^{z'z'(\pm 1)} & -H_j^{z'z'(\pm 1)} & \Lambda_j^{z'z'(\pm 1)} & & \end{bmatrix}, \quad (\text{B.13})$$

$$\mathbf{M}_{j,j\pm 1}^{z'} = \begin{bmatrix} F_j^{z'(\pm 1)} & -K_j^{*z'(\pm 1)} & -H_j^{*z'(\pm 1)} & & & \\ -K_j^{z'(\pm 1)} & F_j^{z'(\pm 1)} & H_j^{z'(\pm 1)} & & & \\ -H_j^{z'(\pm 1)} & H_j^{*z'(\pm 1)} & \Lambda_j^{z'(\pm 1)} & & & \\ & F_j^{z'(\pm 1)} & -K_j^{z'(\pm 1)} & H_j^{z'(\pm 1)} & & \\ & -K_j^{*z'(\pm 1)} & F_j^{z'(\pm 1)} & -H_j^{*z'(\pm 1)} & & \\ & H_j^{*z'(\pm 1)} & -H_j^{*z'(\pm 1)} & \Lambda_j^{z'(\pm 1)} & & \end{bmatrix}. \quad (\text{B.14})$$

Thus, using $\mathbf{M}_{j,j}$ and $\mathbf{M}_{j,j\pm 1}$, $6N \times 6N$ Hamiltonian for the QW is given by

$$\mathbf{H}_{\text{QW}} = \begin{bmatrix} \mathbf{M}_{1,1} & \cdots & & 0 & & \cdots & 0 \\ \vdots & \ddots & & \vdots & & & \vdots \\ & & \mathbf{M}_{j-1,j-1} & \mathbf{M}_{j-1,j} & 0 & & \\ 0 & \cdots & \mathbf{M}_{j,j-1} & \mathbf{M}_{j,j} & \mathbf{M}_{j,j+1} & \cdots & 0 \\ & & 0 & \mathbf{M}_{j+1,j} & \mathbf{M}_{j+1,j+1} & & \\ \vdots & & & \vdots & & \ddots & \vdots \\ 0 & \cdots & & 0 & & \cdots & \mathbf{M}_{N,N} \end{bmatrix}. \quad (\text{B.15})$$

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Appendix C

Optical polarization of $(11\bar{2}2)$ AlGa_N/AlN QW

C.1 Introduction

In Chap. 5, we demonstrated stimulated emissions at 250 nm from semipolar r -plane AlGa_N/AlN QWs for the first time. However, comparing the threshold power density with the reported values, our experimental result is neither better nor worse than the previous works in spite of the superior optical properties to conventional c -plane QWs such as high IQE and strongly polarized emissions. We think that the large mirror loss of the r -plane sample may be one of the reason why the superior optical property cannot well be utilized for a lower threshold power density. In most cases of the previous reports on optical pumping measurements using c -plane AlGa_N QWs, m -planes were used for the cavity mirrors. Although a -planes should be used for the cavity mirrors in semipolar-plane QWs with the off-angles along the $[1\bar{1}00]$ directions such as r -plane QWs, the cleavability of a -planes is generally worse than that of m -planes. As a consequence, the r -plane QW may have a larger mirror loss compared to the reported samples. Then, we suggested the 10 pairs of HfO₂/SiO₂ DBR, which can realize the high reflectance beyond 99% at 250 nm to reduce the threshold pumping power density of the fabricated r -plane Al_{0.5}Ga_{0.5}N/AlN MQW in Chap. 5.

On the other hand, because m -planes can be used as cavity mirrors, semipolar QWs with the off-angles toward $[11\bar{2}0]$ directions such as $(11\bar{2}2)$ QWs may be attractive to suppress the mirror loss. Furthermore, we clarified that $(11\bar{2}2)$ AlGa_N/AlN QWs with high IQE (described in Chap. 2) have a lot of flexibility in designing QWs considering the critical thickness calculated in Chap. 4. To use m -planes as cavity mirrors for $(11\bar{2}2)$ QWs, the in-plane optical polarization should be controlled as mentioned in Chap. 5. In this chapter, we discuss the optical polarization of $(11\bar{2}2)$ AlGa_N/AlN QWs comparing with those of r -plane QWs toward practical DUV devices.

C.2 In-plane polarization degree

At first, we calculated the in-plane polarization degrees of (11 $\bar{2}2$) AlGa N /Al N QWs as functions of well width and Al composition. For the following calculations, we used the exciton deformation potentials and effective mass parameters for valence bands reported in Refs. [1, 2] and [3], respectively, which are appropriately chosen in Chap 5. Moreover, the definition of the coordinate (x', y', z') is the same as in Chap. 5.

In order to use nonpolar planes as cavity mirrors for semipolar QWs, the emissions strongly polarized along $\mathbf{E}||x'$ are desired. Thus, defining the in-plane polarization degree as

$$\rho_{\text{in}} = \frac{I_{y'} - I_{x'}}{I_{y'} + I_{x'}}, \quad (\text{C.1})$$

$\rho_{\text{in}} < 0$ is needed for LDs, where I_i means the surface emission intensity polarized along the i direction.

Figure C.1(a) and (b) show the calculated in-plane polarization degrees of the (11 $\bar{2}2$) and r -plane AlGa N /Al N QWs. The calculation results are based on the finite-potential-barrier calculations. For the negative ρ_{in} of the r -plane QWs, we have to design the QW structures to have Al compositions more than 0.2. In the case of the (11 $\bar{2}2$) AlGa N /Al N QWs, on the other hand, we found that the relation $\rho_{\text{in}} < 0$ can be obtained for almost all the QW structures as shown in Fig. C.1(a). The result indicates that LDs based on (11 $\bar{2}2$) AlGa N /Al N QWs can use m -planes, which have high cleavability, as cavity mirrors, and we can expect the reduction of the threshold power density using the QWs.

C.3 Out-of-plane polarization degree

Subsequently, we discuss the out-of-plane polarization degree, which plays an important role in LEE of the LED structures, of AlGa N /Al N QWs based on the calculation results. Here, we define the out-of-plane polarization degree as

$$\rho_{\text{out}} = \frac{I_{x'} + I_{y'} - I_{z'}}{I_{x'} + I_{y'} + I_{z'}}, \quad (\text{C.2})$$

where I_i means the emission intensity polarized along the i direction, and $\rho_{\text{out}} > 0$ is needed for LEDs.

Figure C.2(a) and (b) show the calculated out-of-plane polarization degrees of the (11 $\bar{2}2$) and r -plane AlGa N /Al N QWs, respectively, as functions of well width and Al composition. The calculation results are based on the finite-potential-barrier calculations. For the (11 $\bar{2}2$) QWs, positive ρ_{out} are realized in any structures independently of Al compositions and well widths. Furthermore, the ρ_{out} of (11 $\bar{2}2$) QWs are larger than those of the r -plane QWs, which are superior to conventional c -plane QWs (as described in Chap. 5). Therefore, it

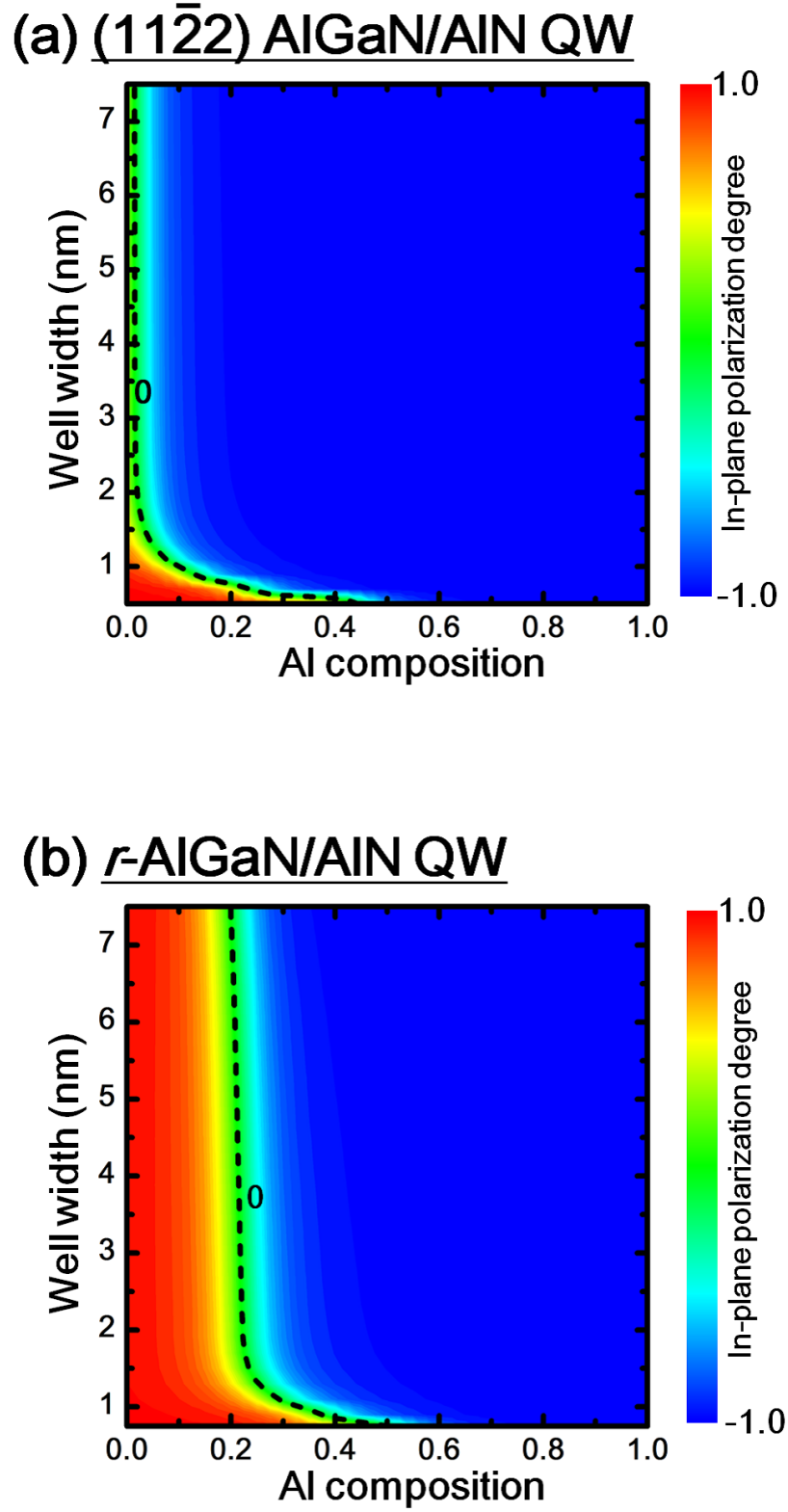


Figure C.1: Calculated results of “in-plane” polarization degree as functions of well width and Al composition assuming the finite potential barriers. The calculation results are for (a) $(11\bar{2}2)$ plane and (b) r -plane AlGa_N/AlN QWs.

was clarified that the (11 $\bar{2}2$) AlGa N /Al N QWs are quite attractive structures to achieve highly efficient LEDs in terms of the LEE in addition to the high IQE.

C.4 Summary

In this chapter, we discussed the availability of (11 $\bar{2}2$) AlGa N /Al N QWs toward DUV devices focusing on the optical polarization degrees. From the calculation results of the in-plane polarization degree, we found that the relation $\rho_{\text{in}} < 0$ can be obtained for almost all the QW structures, which indicates that m -plane cavity mirrors can be used for (11 $\bar{2}2$) AlGa N /Al N QWs. Therefore, we can expect the lower threshold power density compared with the r -plane QWs discussed in Chap. 5.

Furthermore, the calculated out-of-plane polarization degrees of (11 $\bar{2}2$) AlGa N /Al N QWs clarified that positive ρ_{out} are realized in any structures independently of Al compositions and well widths. These results indicate that the LEDs and LDs based on (11 $\bar{2}2$) AlGa N /Al N QWs are very attractive from the perspective of the LEE and mirror loss (cleavage). However, the large-scaled (11 $\bar{2}2$) Al N bulk substrates are not currently obtained in contrast to r -plane Al N substrates [4] because the (11 $\bar{2}2$) surfaces are given by slicing bulk crystals grown on c -plane templates. Practically, we should therefore consider the both availability of the substrates and optical (and structural) properties.

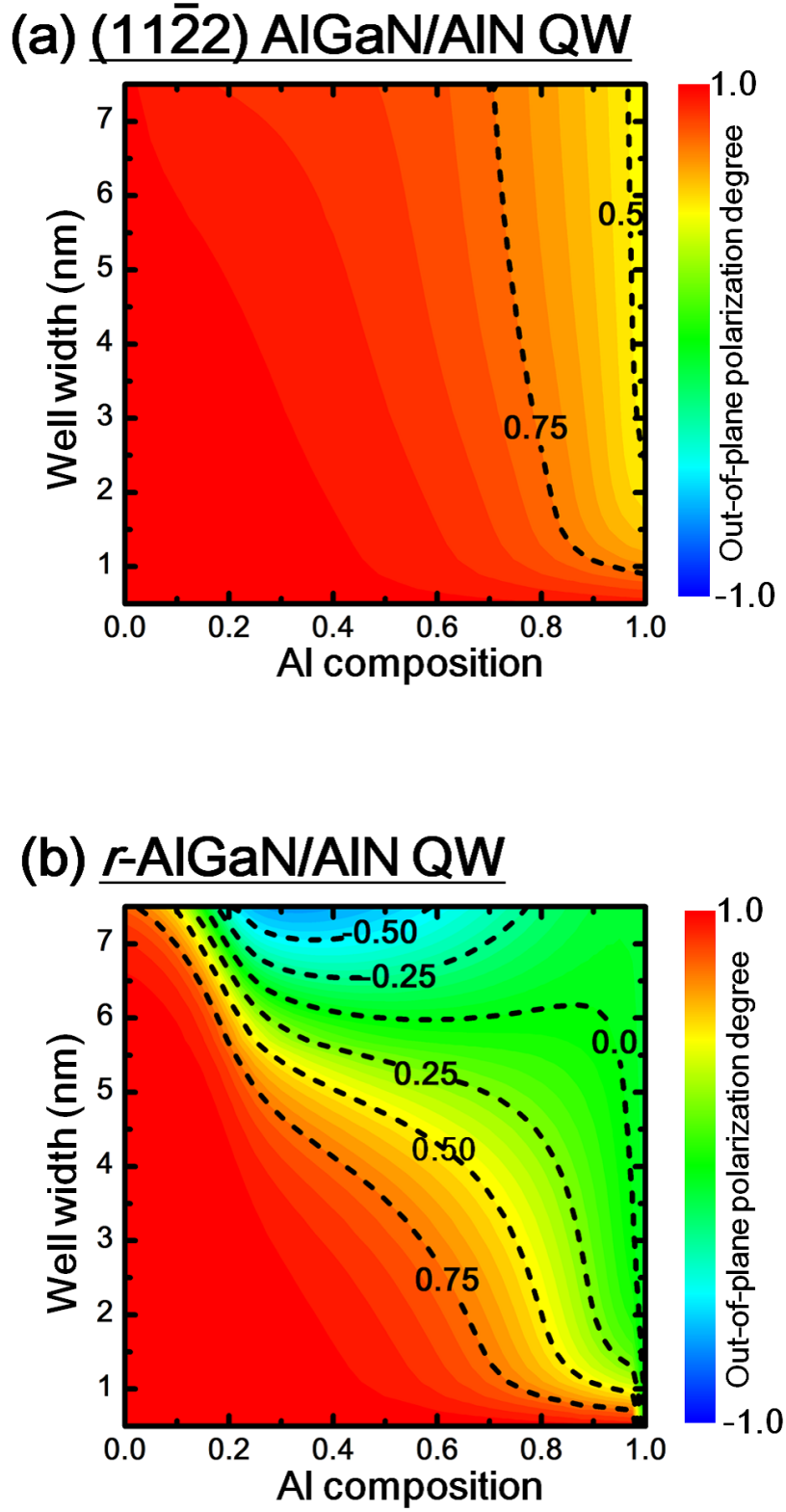


Figure C.2: Calculated results of “out-of-plane” polarization degree as functions of well width and Al composition assuming the finite potential barriers. The calculation results are for (a) $(11\bar{2}2)$ plane and (b) r -plane AlGa_N/AlN QWs.

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List of Publications

A. Full Length Papers and Letters

1. S. Ichikawa, K. Kawahara, J. Suda, and T. Kimoto,
“Carrier Recombination in n-Type 4H-SiC Epilayers with Long Carrier Lifetimes,”
Appl. Phys. Express **5**, 10301 (2012).
2. T. Kimoto, J. Suda, G. Feng, H. Miyake, K. Kawahara, H. Niwa, T. Okuda,
S. Ichikawa, and Y. Nishi,
“Defect Electronics in SiC and Fabrication of Ultrahigh-Voltage Bipolar Devices,”
ECS Transactions **50**, 25 (2012).
3. S. Ichikawa, Y. Iwata, M. Funato, S. Nagata, and Y. Kawakami,
“High quality semipolar (1 $\bar{1}$ 02) AlGaN/AlN quantum wells with remarkably enhanced
optical transition probabilities,”
Appl. Phys. Lett. **104**, 252102 (2014).
4. Y. Iwata, R. G. Banal, S. Ichikawa, M. Funato, and Y. Kawakami,
“Emission mechanisms in Al-rich AlGaN/AlN quantum wells assessed by excitation
power dependent photoluminescence spectroscopy,”
J. Appl. Phys. **117**, 075701 (2015).
5. S. Ichikawa, M. Funato, and Y. Kawakami,
“Highly efficient UV emission with semipolar quantum wells,”
SPIE Newsroom Lasers & Sources **2 February 2016** (2016).
6. S. Ichikawa, M. Funato, and Y. Kawakami,
“Approaches to highly efficient UV emitters based on AlGaN quantum wells,”
Proc. of SPIE **9748**, 97480U (2016).
7. M. Hayakawa, Y. Hayashi, S. Ichikawa, M. Funato, and Y. Kawakami,
“Enhanced radiative recombination probability in AlGaN quantum wires on (0001)
vicinal surface,”
Proc. of SPIE **9926**, 99260S (2016).

8. M. Funato, S. Ichikawa, K. Kumamoto, and Y. Kawakami,
“Design of Al-rich AlGa_N quantum well structures for efficient UV emitters,”
Proc. of SPIE (in press).
9. S. Ichikawa, M. Funato, and Y. Kawakami,
“Clarification of dominant nonradiative recombination paths and their activation
processes in Al_xGa_{1-x}N-related materials,”
to be submitted to *Phys. Rev. B*.
10. S. Ichikawa, K. Kumamoto, M. Funato, and Y. Kawakami,
“Latent critical thickness of (0001) AlGa_N heterostructures and their novel slip
systems,”
in preparation.
11. S. Ichikawa, M. Funato, and Y. Kawakami,
“Optimal growth conditions and growth mechanisms for high quality semipolar AlN
epitaxial films,”
in preparation.
12. S. Ichikawa, M. Funato, and Y. Kawakami,
“Short radiative recombination lifetimes and suppressed potential fluctuations in
semipolar AlGa_N/AlN quantum wells,”
in preparation.
13. S. Ichikawa, M. Funato, and Y. Kawakami,
“Optical polarization controls in semipolar (1 $\bar{1}$ 02) AlGa_N/AlN quantum wells,”
in preparation.
14. S. Ichikawa, M. Funato, and Y. Kawakami,
“Stimulated emission at 250 nm from optically-pumped semipolar (1 $\bar{1}$ 02) AlGa_N/AlN
quantum well,”
in preparation.

B. International Conferences

1. T. Kimoto, K. Kawahara, B. Zippelius, S. Ichikawa, and J. Suda,
“Generation and elimination of the Z1/2 center in 4H-SiC,” **(Invited)**
Materials Research Society Spring Meeting 2012, San Francisco, USA, H1.1,
(Apr. 2012), oral.

2. T. Kimoto, J. Suda, K. Kawahara, H. Niwa, T. Okuda, N. Kaji, and S. Ichikawa,
 “Defect Electronics toward Ultrahigh-Voltage SiC Bipolar Devices,” **(Invited)**
9th European Conference on Silicon Carbide and Related Materials, St. Petersburg,
 Russia, We6-1, (Sep. 2012), oral.

3. T. Kimoto, J. Suda, G. Feng, H. Miyake, K. Kawahara, H. Niwa, T. Okuda,
S. Ichikawa, and Y. Nishi,
 “Defect Electronics in SiC and Fabrication of Ultrahigh-Voltage Bipolar Devices,”
(Plenary)
222nd Electrochemical Society Fall Meeting 2012, Honolulu, USA, II-1, (Oct. 2012),
 oral.

4. S. Ichikawa, M. Funato, S. Nagata, and Y. Kawakami,
 “Optimal Growth Pressure for High Quality Semipolar (1 $\bar{1}$ 02) AlN Homoepitaxial
 Films,”
40th International Symposium of Compound Semiconductors, Kobe, Japan, MoA4-3,
 (May 2013), oral.

5. S. Ichikawa, M. Funato, S. Nagata, and Y. Kawakami,
 “Mechanism of Pit Generation and Elimination of Semipolar (1 $\bar{1}$ 02) AlN
 Homoepitaxial Films,”
10th International Conference on Nitride Semiconductors, Washington DC, USA,
 A5.05, (Aug. 2013), oral.

6. S. Ichikawa, M. Funato, S. Nagata, and Y. Kawakami,
 “Homoepitaxy of AlN on Semipolar (1 $\bar{1}$ 02) Substrates Grown by Physical Vapor
 Transport Method,”
2013 JSAP-MRS Joint Symposia, Kyoto, Japan, 18a-M6-7, (Sep. 2013), oral.

7. S. Ichikawa, M. Funato, and Y. Kawakami,
 “High quality semipolar AlGaN/AlN quantum wells for deep ultraviolet emitters,”
Swiss-Kyoto Symposium 2013, Zurich, Switzerland, Ops5, (Nov. 2013), oral.

8. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
 “Fabrication of High Quality Semipolar AlGaN/AlN Quantum Wells with Remarkably
 Short Radiative Recombination Lifetimes,”
International Workshop on Nitride Semiconductors 2014, Wrocław, Poland, WeGO22,
 (Aug. 2014), oral.

9. S. Ichikawa, M. Funato, Y. Iwasaki, and Y. Kawakami,
 “Dominant nonradiative recombination paths in Al-rich AlGaN related structures,”
11th International Conference on Nitride Semiconductors, Beijing, China, MoBO12,
 (Aug. 2015), oral.

10. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
 “Optically determined critical thickness of AlGa_N/AlN heterostructures,”
6th International Symposium on Growth of III-Nitrides, Hamamatsu, Japan, Tu-B-39,
 (Nov. 2015), short presentation and poster.
11. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Approaches to highly efficient UV emitters based on AlGa_N quantum wells,”
(Invited)
SPIE Photonics West 2016, San Francisco, USA, 9748-29, (Feb. 2016), oral.
12. M. Hayakawa, Y. Hayashi, S. Ichikawa, M. Funato, and Y. Kawakami,
 “Enhanced radiative recombination probability in AlGa_N quantum wires on (0001)
 vicinal surface,”
SPIE Optics+Photonics 2016, San Diego, USA, 9926-28, (Aug. 2016), oral.
13. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Stimulated Emission at 250 nm from Optically-pumped Semipolar (1 $\bar{1}$ 02)
 AlGa_N/AlN Quantum Wells,”
11th International Conference on Nitride Semiconductors, Beijing, China, MoBO12,
 (Aug. 2015), oral.
14. S. Ichikawa, M. Funato, Y. Iwasaki, and Y. Kawakami,
 “Dominant nonradiative recombination paths in Al-rich AlGa_N related structures,”
International Workshop on Nitride Semiconductors 2016, Orlando, USA, B2.3.04,
 (Oct. 2016), oral.
15. M. Funato, S. Ichikawa, K. Kumamoto, and Y. Kawakami,
 “Design of Al-rich AlGa_N quantum well structures for efficient UV emitters,”
(Invited)
SPIE Photonics West 2017, San Francisco, USA, 10104-16, (Jan. 2017), oral.

C. Domestic Conferences

1. S. Ichikawa, J. Suda, and T. Kimoto,
 “Dominant Carrier Recombination Process in n-type SiC Epilayers with Long Carrier
 Lifetime,”
59th Japan Society of Applied Physics Spring Meeting, 17p-A8-12, Waseda Univ.,
 (Mar. 2012), oral.

2. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Generation and Elimination of Surface Nanopits on Semipolar (1 $\bar{1}$ 02) AlN Homoepitaxial Films,” (**Excellent Paper Award**)
5th Integrated Nanotechnology Foundation Research Report Meeting, 10, Kyoto Univ., (Mar. 2013), oral.
3. S. Ichikawa, M. Funato, S. Nagata, and Y. Kawakami,
 “Optimal Growth Pressure for High Quality Semipolar AlN (1 $\bar{1}$ 02) Homoepitaxial Films,”
60th Japan Society of Applied Physics Spring Meeting, 29a-G21-6, Kanagawa Institute Technology, (Mar. 2013), oral.
4. S. Ichikawa, M. Funato, S. Nagata, and Y. Kawakami,
 “Remarkable Surface Morphology Improvement of Semipolar (1 $\bar{1}$ 02) AlN Homoepitaxial Films by Nucleation Control Growth,”
32nd Electronic Materials Symposium, Th3-6, Laforet Biwako, (Jul. 2013), short presentation and poster.
5. S. Ichikawa, M. Funato, S. Nagata, and Y. Kawakami,
 “Fabrication of Semipolar (1 $\bar{1}$ 02) AlGa $\bar{\text{N}}$ /AlN Quantum Wells on AlN Substrates,”
74th Japan Society of Applied Physics Fall Meeting, 19p-B5-10, Doshisha Univ., (Sep. 2013), oral.
6. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
 “Remarkably Short Radiative Recombination Lifetime of High Quality Semipolar AlGa $\bar{\text{N}}$ /AlN Quantum Wells due to Suppression of Internal Electric Field,”
61st Japan Society of Applied Physics Spring Meeting, 19a-E13-4, Aoyama Gakuin Univ., (Mar. 2014), oral.
7. S. Ichikawa, R. Ishii, M. Funato, and Y. Kawakami,
 “In-plane Polarization Control of Semipolar AlGa $\bar{\text{N}}$ /AlN Quantum Wells,”
61st Japan Society of Applied Physics Spring Meeting, 19a-E13-5, Aoyama Gakuin Univ., (Mar. 2014), oral.
8. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
 “Strong Emissions from Semipolar AlGa $\bar{\text{N}}$ /AlN Quantum Wells with Fast Radiative Recombination Lifetimes,” (**EMS Award**)
33rd Electronic Materials Symposium, Fr1-10, Laforet Shuzenji, (Jul. 2014), short presentation and poster.

9. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
“Strong Emissions and Short Radiative Recombination Lifetimes of Semipolar AlGa_N/AlN Quantum Wells,” **(Young Scientist Presentation Award)**
6th Growth of III-Nitrides Meeting, Fr-8, Meijo Univ., (Jul. 2014), short presentation and poster.
10. S. Ichikawa, M. Funato, Y. Iwasaki, and Y. Kawakami,
“Direct Observation of Dominant Nonradiative Recombination Path in AlGa_N-related Structures using Cathodoluminescence Mapping,”
(Young Scientist Presentation Award)
75th Japan Society of Applied Physics Fall Meeting, 18a-C5-12, Hokkaido Univ., (Sep. 2014), oral.
11. Y. Iwata, S. Ichikawa, M. Funato, and Y. Kawakami,
“Well-defined LO Phonon Replicas for Homo-epitaxial AlGa_N/AlN Quantum Wells Observed by Microscopic PL Measurements,”
75th Japan Society of Applied Physics Fall Meeting, 20p-C5-8, Hokkaido Univ., (Sep. 2014), oral.
12. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
“Optimization of Growth Conditions for Semipolar AlGa_N/AlN Quantum Wells and Their Strong Emissions,” **(Invited)**
44th National Conference on Crystal Growth, 06pB07, Gakushuin Univ., (Nov. 2014), oral.
13. S. Ichikawa, M. Funato, Y. Iwasaki, and Y. Kawakami,
“Variation of Dominant Nonradiative Recombination Paths in AlGa_N-related Structures due to Temperature,” **(Invited)**
62nd Japan Society of Applied Physics Spring Meeting, 11p-B1-13, Tokai Univ., (Mar. 2015), oral.
14. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
“Investigation of Critical Thickness for AlGa_N/AlN Heterostructures using Time-resolved Photoluminescence Spectroscopy,”
62nd Japan Society of Applied Physics Spring Meeting, 14p-B1-4, Tokai Univ., (Mar. 2015), oral.
15. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
“Critical Thickness of AlGa_N/AlN Quantum Wells and Variation of Recombination Lifetimes,”
7th Growth of III-Nitrides Meeting, Fr-20, Tohoku Univ., (May 2015), short presentation and poster.

16. S. Ichikawa, M. Funato, Y. Iwasaki and Y. Kawakami,
 “Nonradiative Recombination Paths in AlGa_N-related Structures and their Temperature Dependence,”
34th Electronic Materials Symposium, Th3-2, Laforet Biwako, (Jul. 2015), short presentation and poster.
17. S. Ichikawa, M. Funato, Y. Iwasaki, and Y. Kawakami,
 “Design of Semipolar AlGa_N/Al_N Quantum Wells for Stimulated Emissions,”
(Notable presentation)
76th Japan Society of Applied Physics Fall Meeting, 13p-1D-14, Nagoya Congress Center, (Sep. 2015), oral.
18. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Optical Properties of Semipolar AlGa_N Quantum Wells Grown by MOVPE on Al_N Bulk Substrates,” **(Invited)**
76th Japan Society of Applied Physics Fall Meeting, 15p-1D-8, Nagoya Congress Center, (Sep. 2015), oral.
19. S. Ichikawa, Y. Iwata, M. Funato, and Y. Kawakami,
 “Identification of Nonradiative Recombination Paths in AlGa_N-related Structures toward Highly Efficient Deep-UV Emitters,”
8th Photon Frontier Network Symposium, 10, Osaka Univ., (Jan. 2016), short presentation and poster.
20. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Slip System and Lattice Relaxation Model of (0001) AlGa_N/Al_N Heterostructures,”
63rd Japan Society of Applied Physics Spring Meeting, 22a-H121-1, Tokyo Institute of Technology, (Mar. 2016), oral.
21. S. Ichikawa, K. Kumamoto, M. Funato, and Y. Kawakami,
 “Control of Lattice Relaxation Position in AlGa_N Heterostructures for Strong Emissions,”
63rd Japan Society of Applied Physics Spring Meeting, 22a-H121-2, Tokyo Institute of Technology, (Mar. 2016), oral.
22. M. Hayakawa, Y. Hayashi, S. Ichikawa, M. Funato, and Y. Kawakami,
 “Enhanced Radiative Recombination Processes in AlGa_N Quantum Wires Fabricated on Sapphire (0001) Vicinal Substrates,”
63rd Japan Society of Applied Physics Spring Meeting, 21p-H121-10, Tokyo Institute of Technology, (Mar. 2016), oral.

23. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Possibility of c -plane Slips for c -plane AlGa_N/AlN Heterostructures due to Unintentional Off-angles,”
8th Growth of III-Nitrides Meeting, Mo-22, Kyoto Univ., (May 2016), short presentation and poster.
24. M. Hayakawa, Y. Hayashi, S. Ichikawa, M. Funato, and Y. Kawakami,
 “Suppression of Thermal Quenching in AlGa_N Quantum Wires Fabricated on Macro Step Structures,”
8th Growth of III-Nitrides Meeting, Mo-23, Kyoto Univ., (May 2016), short presentation and poster.
25. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Stimulated Emission from Optically-pumped Semipolar AlGa_N/AlN Quantum Well,”
35th Electronic Materials Symposium, Th1-14, Laforet Biwako, (Jul. 2016), short presentation and poster.
26. S. Ichikawa, M. Funato, and Y. Kawakami,
 “Suppression of Potential Fluctuations in Semipolar AlGa_N/AlN Quantum Wells,”
77th Japan Society of Applied Physics Fall Meeting, 13p-1D-14, TOKI MESSE (Niigata City), (Sep. 2016), oral.
27. Y. Kawakami, S. Ichikawa, and M. Funato,
 “Radiative and Non-radiative Recombination Processes in Al-rich AlGa_N Quantum Wells,” **(Invited)**
64th Japan Society of Applied Physics Spring Meeting, 14p-503-2, PACIFICO YOKOHAMA, (Mar. 2017), oral.

D. Awards

1. Excellent Paper Award
 (5th Integrated Nanotechnology Foundation Research Report Meeting)
2. EMS Award
 (33rd Electronic Materials Symposium)
3. Young Scientist Presentation Award
 (6th Growth of III-Nitrides Meeting)
4. Young Scientist Presentation Award
 (75th Japan Society of Applied Physics Fall Meeting)

E. Research Grants

1. Grant-in-Aid for JSPS Research Fellow (DC1)
2. Grant for Young Scientist in 2014 (Photonics and Electronics Science and Engineering COE of Kyoto Univ.)