Dynamics of Localized Carriers in III-V Nitride Compound Semiconductors

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Abstract

Dynamics of localized carriers in III-V nitride compound semiconductors was studied in this thesis. In the In$_x$Ga$_{1-x}$N ternary alloy system, exciton localization due to alloy disorder effect can be observed through the broadening of the optical spectra. The stimulated emission and anti-Stokes photoluminescence (PL), which are related to the exciton localization, can be also observed. The exciton localization and its related phenomena in In$_x$Ga$_{1-x}$N ternary alloy system were studied from the viewpoint of carrier dynamics.

At first, the exciton localization in single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N multiple quantum wells was studied. The PL spectra of In$_x$Ga$_{1-x}$N ternary alloy system showed Stokes shift and the broadening at the lower photon energy side. The absorption spectra were also broadened. Site-selectively excited PL measurement determined the mobility edge, which is a boundary to determine whether the carriers are localized or not. The carrier relaxation process was studied by means of the time-resolved PL measurement. The PL decay time increased with the decrease of the detection photon energy. It indicated the dynamical feature of the exciton localization.

Next, the stimulated emission from In$_x$Ga$_{1-x}$N ternary alloy system was studied. The stimulated emission was located below the mobility edge, indicating that the stimulated emission was related to the localized states. The lifetime of the stimulated emission was short within few tens picoseconds. Fast carrier relaxation process, which is the dynamical gain formation process, was analyzed by means of the time-resolved pump-and-probe measurement. The photoexcited electron-hole pairs relaxed into the localized states through the delocalized states, and localized excitons were formed. Under the excitation energy density above stimulation threshold, the localized states were saturated, and many
electron-hole pairs were present at the delocalized states. The optical gain was possible in terms of stimulated emission process from the localized states. The phenomenological model for the inhomogeneously broadened system was introduced and the calculated optical gain spectra were presented. The results agreed with the experiment results. As a result, the stimulated emission was related to the filling of the localized states.

Finally, anti-Stokes PL in In$_x$Ga$_{1-x}$N/GaN quantum well structures was studied. Ultraviolet anti-Stokes PL was observed. It was located at 3.49 eV, which is the highest photon energy of anti-Stokes PL in semiconductors. The observed anti-Stokes PL exhibited quadratic dependence on the excitation energy density. Anti-Stokes PL excitation spectrum was proportional to the optical absorption spectrum of the In$_x$Ga$_{1-x}$N quantum wells. These results indicated that the real states (localized states) in In$_x$Ga$_{1-x}$N quantum wells influenced carrier excitation process. Time-resolved PL measurement showed that a decay time of the anti-Stokes PL was slower than that of the GaN PL under the excitation photon energy above the GaN band gap. The decay time of the anti-Stokes PL was almost half the time constant of the In$_x$Ga$_{1-x}$N PL decay. The photon absorption for the second absorption step in anti-Stokes PL was directly observed by means of the two-color pump-and-probe experiment. These results indicated that the anti-Stokes PL was caused by two-step two-photon absorption process involving the localized states in In$_x$Ga$_{1-x}$N quantum wells, and that the second absorption step was provided by the photon recycling of the In$_x$Ga$_{1-x}$N PL.
# Table of Contents

1. Introduction ................................................................................................................................. 1  

2. Fundamentals .................................................................................................................................... 8  
   2.1 Crystal Structures ......................................................................................................................... 8  
   2.2 Crystal Growth .............................................................................................................................. 8  
   2.3 Band Structures ............................................................................................................................ 9  
   2.4 Theoretical Model of Alloy Broadening ....................................................................................... 10  

3. Exciton Localization in Single-Layer In\(_x\)Ga\(_{1-x}\)N and In\(_x\)Ga\(_{1-x}\)N Multiple Quantum Wells ................................................................................................................................. 22  
   3.1 Introduction .................................................................................................................................... 22  
   3.2 Experimental Procedure ............................................................................................................... 23  
      3.2.1 Samples .................................................................................................................................. 23  
      3.2.2 Experimental setup ................................................................................................................ 23  
   3.3 Experimental Results and Discussion .......................................................................................... 24  
      3.3.1 Broadening of optical spectra in single-layer In\(_x\)Ga\(_{1-x}\)N .................................................. 24  
      3.3.2 Broadening of optical spectra in In\(_x\)Ga\(_{1-x}\)N multiple quantum wells ............................. 24  
      3.3.3 Relaxation process of localized excitons .............................................................................. 24  
   3.4 Summary ...................................................................................................................................... 29  

4. Stimulated Emission from Single-Layer In\(_x\)Ga\(_{1-x}\)N and In\(_x\)Ga\(_{1-x}\)N Multiple Quantum Wells ................................................................................................................................. 41  
   4.1 Introduction .................................................................................................................................... 41  
   4.2 Experimental Procedure ............................................................................................................... 42  
   4.3 Experimental Results and Discussion .......................................................................................... 42
4.3.1 Stimulated emission from single-layer $\text{In}_x\text{Ga}_{1-x}\text{N}$

4.3.2 Stimulated emission from $\text{In}_x\text{Ga}_{1-x}\text{N}$ multiple quantum wells

4.3.3 Mechanism of stimulated emission

4.3.4 Nonlinear luminescence of $\text{In}_x\text{Ga}_{1-x}\text{N}$ multiple quantum wells

4.4 Summary ........................................................................................................................................47

5. Dynamical Gain Formation Process in $\text{In}_x\text{Ga}_{1-x}\text{N}$ Multiple Quantum Wells ..........56

5.1 Introduction ................................................................................................................................56

5.2 Experimental Procedure ..............................................................................................................57

5.3 Experimental Results and Discussion ........................................................................................57

5.3.1 Time-resolved differential absorption spectra

5.3.2 Fast relaxation process of stimulated emission

5.3.3 Optical gain spectra

5.3.4 Induced absorption

5.4 Summary ........................................................................................................................................62

6. Ultraviolet Anti-Stokes Photoluminescence in $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ Quantum Well Structures ........................................................................................................69

6.1 Introduction ..................................................................................................................................69

6.2 Experimental Procedure ..............................................................................................................70

6.2.1 Sample

6.2.2 Experimental setup

6.3 Experimental Results and Discussion ........................................................................................71

6.3.1 Ultraviolet anti-Stokes photoluminescence spectra from GaN barrier

6.3.2 Dynamical carrier generation for anti-Stokes photoluminescence process

6.4 Summary ........................................................................................................................................77
7. Conclusions

Acknowledgments

List of Publications
CHAPTER 1
Introduction

Semiconductor lasers have been studied intensively because they are both physically interesting and technologically important. The fabrication of semiconductor lasers have developed on III-V compound semiconductors such as GaAs, AlAs, and related compounds as a result of the development of new techniques for crystal growth namely molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD). GaAs based laser diodes (LDs) are operating in the red and infrared spectral regions. The commercially available LDs and light emitting diodes (LEDs) operating in the blue and green spectral regions have been required for use in full-color displays, full-color indicators, and light source with high efficiency, high reliability, quick response time, and long lifetime. II-VI compound semiconductors and III-V nitride compound semiconductors provide an attractive opportunity to produce such LDs and LEDs, and have been investigated intensively. Recently, much progress has been made in II-VI compound semiconductors in which first blue-green [1] and blue [2] injection LDs as well as high efficient blue LEDs [3] have been demonstrated. However, the short lifetimes prevent II-VI based devices from commercialization at present. While, III-V nitride compound semiconductors have been paid much attention as very important materials for fabricating short-wavelength-emitting devices because of the successes in fabrication and commercialization of GaN based LEDs in the early 1990’s.

III-V nitride compound semiconductors such as AlN, GaN, and InN have wurtzite crystal structure and direct energy transition type band structure. The band gap energy of III-V nitride compound semiconductors varies between 1.95 (band gap of InN) and 6.2 eV
(band gap of AlN) depending on the alloy composition at room temperature. Therefore, III-V nitride compound semiconductors are particularly useful for the short-wavelength-emitting devices. In$_x$Ga$_{1-x}$N ternary alloy is a candidate for the active layer of blue emitting devices because its band gap varies from 1.95 to 3.4 eV depending on the indium concentration [4]. In$_x$Ga$_{1-x}$N/Al$_x$Ga$_{1-x}$N heterostructures, In$_x$Ga$_{1-x}$N single quantum well and multiple quantum wells (MQWs) have already been used as the active layer of blue-green LEDs and blue LDs [5]. However, the optical properties of In$_x$Ga$_{1-x}$N ternary alloy system are still unclear.

Recently, it has been reported that the localized excitons play an important role in the spontaneous emission mechanism in In$_x$Ga$_{1-x}$N ternary alloy system [6-9], and the possibility of the contribution of the localized excitons to the lasing mechanism has been proposed. Smith et al. have suggested that the photoluminescence (PL) in In$_x$Ga$_{1-x}$N epilayers results primarily from localized exciton recombination by means of the time-resolved PL measurement [6]. Chichibu et al. have reported that the static electroluminescence peak is assigned to the recombination of the excitons localized at certain potential minima in quantum well [7]. Narukawa et al. have reported the exciton localization in In$_x$Ga$_{1-x}$N MQWs by means of transmittance, electoreflectance, PL excitation, and time-resolved PL spectroscopy [8]. They have also reported that the exciton localization at the In-rich regions acting as quantum dots by studying cross-sectional transmission electron microscopy (TEM) and energy-disperse x-ray microanalysis (EDX) [9].

The carrier localization has been reported in many mixed crystals [10-22]. Mixed crystals of semiconductors are very interesting materials. One of the reasons of interest is that mixed crystals are convenient model systems for the study of the general properties of disordered systems. The potential fluctuations of the crystal caused by the isoelectronic substitution of components have a short-range nature. Other reason is that mixed crystals are
important materials for modern electronics. Their band structure can vary smoothly with a change in the composition in mixed crystal. There are many technical applications of semiconductor mixed crystals such as LEDs and semiconductor lasers.

In mixed crystals, the effect of disorder causes the localization of excitons or carriers, leading to modification of the density of states and the dynamical properties of carriers near the band edge. The studies of the broadening of optical spectra due to disorder effect and the dynamical properties of the localized carriers have been reported in III-V [10-14] and II-VI compound semiconductors [15-19]. Moreover, it has been reported that the localized excitons can contribute to the optical gain in II-VI compound semiconductors because of the saturation of the low density of tail states by moderate pumping [20-22].

Furthermore, carrier localization causes interesting phenomena. Recently, anti-Stokes PL phenomenon has been observed in heterostructures and quantum well structures of semiconductors [23-30]. It has been reported that the carrier excitation mechanism in anti-Stokes PL is Auger process or two-step two-photon absorption process. In the Auger process, nonradiative recombination of carriers in narrow-gap material excites carriers into the wide-gap material. On the other hand, in the two-step two-photon absorption process, carriers in a narrow-gap material are excited into a wide-gap material by second photons such as luminescence from narrow-gap material. In both processes, the carrier localization in a narrow-gap material plays an important role in carrier excitation process for anti-Stokes PL phenomenon.

In this thesis, we have studied and discussed four issues: (i) exciton localization in In$_x$Ga$_{1-x}$N ternary alloy system, (ii) optical properties of stimulated emission from In$_x$Ga$_{1-x}$N ternary alloy system, (iii) optical gain formation process in In$_x$Ga$_{1-x}$N MQWs, and (iv) anti-Stokes PL phenomenon in In$_x$Ga$_{1-x}$N/GaN quantum well structures, from the viewpoint of
carrier dynamics. The layout of this thesis is as follows:

Chapter 2: The exciton localization in single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N MQWs is studied.

The broadening of the optical spectra is presented and explained by the alloy disorder. The mobility edge is determined by means of a site-selectively excited PL measurement. The determination of the mobility edge is important to determine whether the carriers are localized or not. The carrier relaxation process is studied by means of a time-resolved PL measurement.

Chapter 3: The stimulated emission from single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N MQWs is observed in the surface-emitting configuration. The optical properties of the stimulated emission are studied by means of a time-resolved PL measurement and a nonlinear luminescence measurement. The lifetime of the stimulated emission is short within few tens picoseconds.

Chapter 4: The dynamical gain formation process, which is lasing mechanism, in In$_x$Ga$_{1-x}$N MQWs is analyzed. The phenomenological model for the inhomogeneously broadened system is introduced. The optical gain spectra are presented by means of a time-resolved pump-and-probe measurement with white-light subpicosecond pulses. It is found that the formation of the optical gain comes from the filling of the localized states.

Chapter 5: Ultraviolet anti-Stokes PL in In$_x$Ga$_{1-x}$N/GaN quantum well structures is presented at 77 K and its mechanism is discussed. The carrier generation process for the
anti-Stokes PL is studied by means of a time-resolved PL measurement and a two-color pump-and-probe experiment. It is found that the localized states in In$_x$Ga$_{1-x}$N quantum wells play an important role in this mechanism and that photon recycling occurs for the second step absorption.

Chapter 6: Conclusion of this thesis.

References

R4375 (1997).


CHAPTER 2
Fundamentals

2.1 Crystal Structures

III-V nitride compound semiconductors have the zincblende as well as the wurtzite structures, but the thermodynamically stable phase is the wurtzite structure. The zincblende structure is metastable and may be stabilized only by heteroepitaxial growth on substrates reflecting topological compatibility.

The wurtzite structure has a hexagonal unit cell with two lattice parameters $a$ and $c$ in ratio $c/a = \sqrt{8/3} \approx 1.633$. Figure 2.1 shows the wurtzite crystal structure. This structure is composed of two hexagonal close-packed (hcp) sublattices, which are shifted with respect to each other along the $c$ axis by amount of $u = 3/8$. Both sublattices are occupied by one atomic species only, resulting in four atoms/unit cell. The space group of the wurtzite structure is $C_{6v}^4$ (P6$_3$mc). There are atoms of one species both at (0, 0, 0) and (2/3, 1/3, 1/2), while there are atoms of other species at (0, 0, $u$) and (2/3, 1/3, 1/2+$u$). Table I shows the crystal lattice parameters for AlN, GaN, and InN.

2.2 Crystal Growth

Wurtzite GaN is grown on (0001) orientated hexagonal sapphire substrates by metal-organic chemical vapor deposition (MOCVD). The lattice mismatch between GaN and sapphire lattices is given by $(a_{\text{sapphire}} - a_{\text{GaN}})/a_{\text{sapphire}} = 0.33$. The actual epitaxial relationship between GaN and sapphire is characterized by

$$(0001)\ \text{GaN} \parallel (0001)\ \text{sapphire \ with \ [2\bar{1}\bar{1}0] \ GaN \parallel [1\bar{1}00] \ sapphire}$$
as shown in Fig. 2.2. The 30° rotation of both lattices against each other leads to a reduction of lattice mismatch to 16%.

In\textsubscript{x}Ga\textsubscript{1-x}N crystal growth was originally conducted at low-temperature (about 500 °C) to prevent InN dissociation during growth, by means of MOCVD [3]. Recently, relative high-quality In\textsubscript{x}Ga\textsubscript{1-x}N films were obtained on (0001) sapphire substrate using a high growth temperature (800 °C) and a high indium mole fraction flow rate [4]. However, the crystal quality of the In\textsubscript{x}Ga\textsubscript{1-x}N films was still insufficient to realize blue LDs. It was reported that the crystal quality of the In\textsubscript{x}Ga\textsubscript{1-x}N films grown on GaN films was much improved in comparison with those grown directly on sapphire substrates, because GaN has a lattice constant between that of In\textsubscript{x}Ga\textsubscript{1-x}N and that of sapphire [5].

2.3 Band Structures

The calculated band structures of wurtzite AlN, GaN and InN are shown in Figs. 2.3, 2.4 and 2.5, respectively. The schematic illustration of near band gap electronic structure of the wurtzite GaN is shown in Fig. 2.6. The valence band is characterized by strongly coupled $\Gamma_9$, upper $\Gamma_7$ and lower $\Gamma_7$ levels. The holes or associated excitons in the three valence bands are conventionally called A- B- and C-type holes or excitons. The interband transitions and their temperature dependence have recently been studied by means of photoluminescence and photoreflectance measurements [9]. The temperature variations of A- $(\Gamma^*_9 - \Gamma^*_7)$ , B-$(\Gamma^*_7 - \Gamma^*_5)$ and C-$(\Gamma^*_7 - \Gamma^*_5)$ interband transition energy for GaN are shown Fig. 2.7. There are still substantial variations of band gap energies and splitting energies determined or predicted by different experimental or theoretical methods. For the splitting between A and C valence band $(E_{AC})$, values of 18, 22, 24, and 28 meV have been published [10-13]. For the $E_{AB}$ gap, value of 6 meV has been published [10-13]. Thus, there is a necessity for more
electronic band structure work to obtain more complete and more reliable set of band parameters.

2.4 Theoretical Model of Alloy Broadening [14,15]

The model assumes the In$_x$Ga$_{1-x}$N ternary alloy where In- and Ga-atoms are randomly distributed over the lattice site. It is not taken into account macroscopic inhomogeneity in lateral as well as in growth direction of the epitaxial layer. In a certain volume $V$, there is a finite number, $KV$, of group-III elements, where $K$ is the density of cations in the crystal. The cation density in the wurtzite lattice is given by

$$K = \frac{2}{V_0},$$

(2.1)

because there are two cations in the unit cell with volume $V_0$. The probability of $n$ In-atoms in a volume $V$ is given by the binomial distribution

$$p(n) = \binom{KV}{n} x^n (1-x)^{KV-n}.$$  

(2.2)

The distribution has the mean value $\mu = xKV$ and the variance $\sigma^2 = KVx(1-x)$. The broadening of optical spectra is caused by the statistical distribution of the two kind of group-III elements. Now, we consider an excitonic volume $V_{exc}$, which results from the hydrogen model,

$$V_{exc} = \frac{4}{3} \pi a_B^3,$$

(2.3)

where $a_B$ is the exciton Bohr radius. In this case, the standard deviation of the alloy composition is given by

$$\sigma_x = \sqrt{\frac{x(1-x)}{KV_{exc}}}$$

(2.4)
Therefore, the standard deviation of the band gap is obtained by
\[
\sigma_E = \frac{dE_g}{dx} \left[ \frac{x(1-x)}{KV_{exc}} \right]^{1/2}.
\] (2.5)

The binomial distribution can be approximated to be a Gaussian distribution. The full width at half-maximum of Gaussian distribution is \(2\sqrt{2\ln(2)} \approx 2.36\) times of its standard deviation.

The band gap of In\(_x\)Ga\(_{1-x}\)N ternary alloy varies with the alloy composition \(x\) and is given by
\[
E_{InGaN}(x) = (1-x)E_{GaN} +xE_{InN} - bx(1-x),
\] (2.6)
where \(E_{InGaN}\), \(E_{GaN}\), and \(E_{InN}\) are the band gaps of In\(_x\)Ga\(_{1-x}\)N, GaN, and InN, respectively. \(b\) is known as a bowing parameter. The bowing parameter has a large value of \(b=3.2\) eV for the In\(_x\)Ga\(_{1-x}\)N ternary alloy with \(x<0.2\) [16]. Consequently, calculated alloy broadening in In\(_x\)Ga\(_{1-x}\)N is shown in Fig. 2.8. However, this calculated linewidth is smaller than that of the photoluminescence. This indicates that the macroscopic inhomogeneity is present in In\(_x\)Ga\(_{1-x}\)N ternary alloy.

References


Table I  Lattice constants and unit cell parameters for AlN, GaN, and InN with lattice constant for sapphire (from Ref. 2).

<table>
<thead>
<tr>
<th></th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
<th>sapphire</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>3.091 Å</td>
<td>3.174 Å</td>
<td>3.538 Å</td>
<td>4.758 Å</td>
</tr>
<tr>
<td></td>
<td>(3.111 Å)</td>
<td>(3.189 Å)</td>
<td>(3.544 Å)</td>
<td></td>
</tr>
<tr>
<td>$c$</td>
<td>4.954 Å</td>
<td>5.169 Å</td>
<td>5.707 Å</td>
<td>12.991 Å</td>
</tr>
<tr>
<td></td>
<td>(4.978 Å)</td>
<td>(5.185 Å)</td>
<td>(5.718 Å)</td>
<td></td>
</tr>
<tr>
<td>$u$</td>
<td>0.3815</td>
<td>0.3768</td>
<td>0.3792</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>(0.382)</td>
<td>(0.377)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2.1 The wurtzite crystal structure: atoms of one species are black, those of other species are white, the unit cell is shaded (from Ref. 1).
Fig. 2.2  Schematic illustration of GaN growth on sapphire surface (0001).
Fig. 2.3 Calculated band structure of wurtzite AlN (from Ref. 6).
Fig. 2.4 Calculated band structure of wurtzite GaN (from Ref. 7).
Fig. 2.5  Calculated band structure of wurtzite InN (from Ref. 8).
Fig. 2.6 Schematic illustration of near band gap electronic structure of the wurtzite GaN.
Fig. 2.7 Temperature dependence of A-, B- and C- transition energies of GaN grown on sapphire (from Ref. 9).
Fig. 2.8 Theoretical values of alloy broadening in In$_x$Ga$_{1-x}$N ternary alloy.
CHAPTER 3

Exciton Localization in Single-Layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N Multiple Quantum Wells

3.1 Introduction

The carrier localization has been reported in many mixed crystals [1-9]. In mixed crystals, the effect of disorder on electronic states of materials can be observed in the band edge region through the broadening of the optical spectra due to the formation of the band tail states. The density of states for the localized carriers has the form of an exponential tail extending down to the forbidden gap by few tens of meV [1,3,9]. In the In$_x$Ga$_{1-x}$N ternary alloy system, several origins of the carrier localization have been reported: random well width variations, spatial compositional fluctuations, and complete phase separation. The potential inhomogeneity caused by such effects has been known. Transmission electron microscopy indicates the presence of In-rich region acting as quantum dots [10], and cathodoluminescence spectra mapping indicates that the In-rich area is smaller than 60 nm in diameter [11]. The localized states strongly influence the recombination properties and the process of the carrier migration.

In this chapter, we study exciton localization in single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N multiple quantum wells (MQWs) grown by a metal-organic chemical vapor deposition (MOCVD), and discuss the exciton relaxation process. We perform a site-selectively excited photoluminescence (PL) measurement at 2 K and determine the mobility edge. The energy- and time-resolved PL charts are measured by means of a time-resolved PL measurement. These results indicate the dynamical feature of the exciton localization.
3.2 Experimental Procedure

3.2.1 Samples

We prepared two single-layer \( \text{In}_x\text{Ga}_{1-x}\text{N} \) \((x=0.07\) and \(0.1)\) and an \( \text{In}_x\text{Ga}_{1-x}\text{N} \) MQWs. The samples were grown on (0001) orientated sapphire substrates with GaN buffer layers by MOCVD. Trimethylgallium (TMG), trimethylindium (TMIn) and ammonia (\(\text{NH}_3\)) were used as Ga, In and N sources, respectively. Undoped single-layer \( \text{In}_{0.07}\text{Ga}_{0.93}\text{N} \) was 360 nm thick grown on a GaN layer 1 \(\mu\text{m}\) thick and covered by a GaN cap layer 50 nm thick. Undoped single-layer \( \text{In}_{0.1}\text{Ga}_{0.9}\text{N} \) was 200 nm thick grown on a GaN layer 1.5 \(\mu\text{m}\) thick. The indium concentrations were estimated by means of a x-ray diffraction measurement. The MQWs sample consisted of an undoped GaN layer 1.5 \(\mu\text{m}\) thick, a Si-doped GaN layer 20 nm thick, a Si-doped \( \text{In}_x\text{Ga}_{1-x}\text{N} \) MQWs and a Si-doped GaN layer 80 nm thick. The \( \text{In}_x\text{Ga}_{1-x}\text{N} \) MQWs was 25 periods of a 2-nm-thick \( \text{In}_{0.11}\text{Ga}_{0.89}\text{N} \) quantum well and a 4-nm-thick \( \text{In}_{0.03}\text{Ga}_{0.97}\text{N} \) barrier. The average indium concentration of the MQWs and the period of MQWs were evaluated by means of the x-ray diffraction measurement. The diffraction lines of GaN \((0004)\), \( \text{In}_x\text{Ga}_{1-x}\text{N} \), and its satellite peaks were measured by the \( \theta-2\theta \) scan. We estimated the average indium concentration to be \(x=0.057\) from the peak position of the \( \text{In}_x\text{Ga}_{1-x}\text{N} \) line, by taking into account of the strain in the same way that was used in Ref. 12. The spectrum clearly showed higher-order peaks, indicating the high interface quality and uniformity of the thickness.

3.2.2 Experimental setup

Site-selectively excited PL measurement was performed by using second harmonic pulses of a mode-locked Ti:sapphire laser pumped by a continuous wave (cw) \( \text{Ar}^+ \) laser. The pulse duration and the repetition rate were about 2 ps and 82 MHz, respectively. It was
possible to turn photon energy of the laser output from 1.5 to 1.7 eV, and to give second harmonic pulses ranging from 3.0 to 3.4 eV. For a time-resolved PL measurement, a synchroscan streak camera connected to a 25-cm subtractive dispersion double monochromator was used. The time resolution was about 30 ps. The laser source was a mode-locked Ti:sapphire laser (2 ps, 82 MHz) or a Ti:sapphire regenerative amplifier. The amplifier output pulses had the pulse duration of 300 fs and the repetition rate of 200 kHz. The second harmonic pulses of the laser output were used as the excitation source. The excitation photon energy was lower than the band gap of the GaN layer in order to study the carrier dynamics only in the In$_x$Ga$_{1-x}$N layer. The samples were directly immersed in superfluid liquid helium at 2 K.

3.3 Experimental Results and Discussion

3.3.1 Broadening of optical spectra in single-layer In$_x$Ga$_{1-x}$N

In mixed crystals, the carriers can be localized at certain potential minima due to spatial compositional fluctuations. The density of localized states is approximated to be an exponential tail [1-9]. In the In$_x$Ga$_{1-x}$N ternary alloy system, it has been proposed that the spontaneous emission from the In$_x$Ga$_{1-x}$N layer is attributed to the localized excitons. However, the mobility edge is not determined experimentally and this weakens validity of the proposal. We determine the mobility edge of the samples by means of the site-selectively excited PL measurement. Figure 3.1 shows the PL spectra of the single-layer In$_{0.07}$Ga$_{0.93}$N measured at different excitation photon energies ranging from 3.122 to 3.305 eV. The PL peak position depends on the excitation photon energy, as shown in the inset of Fig. 3.1. Above the excitation at 3.175 eV, the PL peak position does not move with the change of the excitation photon energy. Below the excitation at 3.175 eV, the peak shows a redshift with the decrease
of the excitation photon energy. We can determine the mobility edge from the results of Fig. 3.1 and it is located at 3.175 eV. In the same way, the mobility edge of the single-layer In$_{0.1}$Ga$_{0.9}$N is determined to be 3.07 eV.

Figure 3.2 shows the absorption spectrum (dashed line) and the PL spectrum (solid line) of the single-layer In$_{0.07}$Ga$_{0.93}$N at 2 K. These spectra were modulated by Fabry-Perot interference effects of thin films, but we got rid of the Fabry-Perot modes and restored to the intrinsic spectra by calculation. The PL peak is located at 3.13 eV, which shows a Stokes shift from the absorption band. The PL spectrum is broadened toward the lower photon energy side, and a full width at half-maximum (FWHM) is about 95 meV. We can observe the lower-energy tail states at the absorption spectrum. Below the mobility edge ($E_{me}$), the absorption spectrum is considered by

$$D(E) = A \exp \left( \frac{E - E_{me}}{\epsilon} \right),$$

(3.1)

where $D(E)$ is the optical density spectrum and $\epsilon$ is the characteristic energy indicating the broadening of the tail states. The absorption tail is well fitted by this equation. The fitting parameters are $A=0.31$ and $\epsilon=21$ meV.

Figure 3.3 shows the absorption spectrum (dashed line) and the PL spectrum (solid line) of the single-layer In$_{0.1}$Ga$_{0.9}$N. The PL peak is located at 2.98 eV and FWHM is about 200 meV. The PL spectrum is broadened toward the lower photon energy side. We can also observe the lower-energy tail states at the absorption spectrum, and the absorption tail is fitted by the Eq. (3.1). The fitting parameters are $A=0.51$ and $\epsilon=93$ meV.

When the indium concentration $x$ increases, the band gap is expected to become smaller and the spectral broadening is expected to become larger due to the alloy broadening effects [13]. The band gap of In$_x$Ga$_{1-x}$N ternary alloy is given by
where $E_{InGaN}$, $E_{GaN}$, and $E_{InN}$ are the band gaps of In$_x$Ga$_{1-x}$N, GaN, and InN, respectively. $b$ is known as a bowing parameter. The bowing parameter has a large value of $b=3.2$ eV for the In$_x$Ga$_{1-x}$N ternary alloy with $x<0.2$ [12]. The band gaps of the In$_{0.07}$Ga$_{0.93}$N ternary alloy and the In$_{0.1}$Ga$_{0.9}$N ternary alloy are obtained to be 3.19 and 3.06 eV from Eq. (3.2). In our experiments, the mobility edge of the single-layer In$_{0.1}$Ga$_{0.9}$N is lower than that of the single-layer In$_{0.07}$Ga$_{0.93}$N. The PL peak of the single-layer In$_{0.1}$Ga$_{0.9}$N is also located at lower photon energy side than that of the single-layer In$_{0.07}$Ga$_{0.93}$N. Furthermore, the PL spectrum of the single-layer In$_{0.1}$Ga$_{0.9}$N is broader than that of the single-layer In$_{0.07}$Ga$_{0.93}$N, and the characteristic energy $\varepsilon$ of the single-layer In$_{0.1}$Ga$_{0.9}$N is also larger than that of the single-layer In$_{0.07}$Ga$_{0.93}$N. These optical properties of the single-layer In$_x$Ga$_{1-x}$N are consistent with the compositional disorder model. The exciton localization is caused by the compositional fluctuation in the In$_x$Ga$_{1-x}$N ternary alloy system.

### 3.3.2 Broadening of optical spectra in In$_x$Ga$_{1-x}$N multiple quantum wells

Figure 3.4 shows the PL spectra of In$_x$Ga$_{1-x}$N MQWs measured at different excitation photon energies ranging from 3.005 to 3.305 eV. The PL peak position depends on the excitation photon energy, as shown in the inset of Fig. 3.4. Above the excitation at 3.178 eV, the PL peak position does not move with the change of the excitation photon energy. Below the excitation at 3.178 eV, the peak shows a redshift with the decrease of the excitation photon energy. We can also determine the mobility edge from the results of Fig. 3.4 and it is located at 3.178 eV in the same manner that was used in the single-layer In$_x$Ga$_{1-x}$N.

The band gap of the In$_{0.11}$Ga$_{0.89}$N ternary alloy is obtained to be 3.02 eV from Eq. (3.2). In the two-dimensional system, the transition energy between quantum levels in the
In$_x$Ga$_{1-x}$N quantum wells should be shifted to higher energy from the band gap due to the confinement effects. We estimate the lowest quantized energy transition ($n=1$) in the In$_{0.11}$Ga$_{0.89}$N (2 nm)/In$_{0.03}$Ga$_{0.97}$N (4 nm) MQWs by using the finite potential well model. The lowest quantized energy transition ($n=1$) at 2 K is estimated to be about 3.18 eV. In this calculation, the band-offset ratio of 4:1 for the conduction and valence bands is assumed [14]. The effective electron and hole masses of the In$_{0.11}$Ga$_{0.89}$N quantum wells are 0.19$m_0$ and 0.77$m_0$, respectively, which are estimated by linear extrapolation from the effective electron and hole masses in GaN, 0.2$m_0$ and 0.8$m_0$ [15,16], and those in InN, 0.12$m_0$ and 0.5$m_0$ [17] respectively. Because the calculated band gap of the In$_{0.11}$Ga$_{0.89}$N is lower than the mobility edge and the calculated lowest quantized energy transition is very close to the mobility edge, the two-dimensional confinement effects are considered to be present in this sample.

Figure 3.5 shows the absorption spectrum (dashed line) and the PL spectrum (solid line) of the In$_x$Ga$_{1-x}$N MQWs. The PL spectrum has a broad emission band with FWHM of about 185 meV. The PL peak is located at 3.06 eV, which shows a Stokes shift. We can also observe the lower-energy tail states at the absorption spectrum. The optical density spectrum $D(E)$ in Eq. (3.1) is considered as the areal density of states in the two-dimensional system, and the absorption tail is well fitted in the same way that was used in the single-layer In$_x$Ga$_{1-x}$N. The fitting parameters are $A=1.87\times10^{13}$ eV$^{-1}$ cm$^{-2}$ and $\varepsilon=83$ meV.

### 3.3.3 Relaxation process of localized excitons

The PL decay profiles of the single-layer In$_{0.07}$Ga$_{0.93}$N are shown in Fig. 3.6. The PL decay can be described by nearly a single exponential decay function, and the decay time increases with the decrease of the detection photon energy. The decay time of the various observed photon energies is shown with the time-integrated PL spectrum in the Fig. 3.7(b).
Figure 3.7(a) shows the energy- and time-resolved PL of the single-layer In$_{0.07}$Ga$_{0.93}$N. This figure is constructed from spectrally resolved temporal changes of the PL. The open squares in Fig. 3.7(a) indicate the temporal change of the center of gravity of the PL, which is defined by

$$\langle E(t) \rangle = \left( \sum_i E_i f(E_i, t) \right) / \left( \sum_i f(E_i, t) \right),$$  \hspace{1cm} (3.3)

where $f(E_i, t)$ is the spectrally resolved temporal change of the PL, and $E_i$ corresponds to the observed photon energies. As time passes, the center of gravity of the PL shifts toward lower photon energy. It is well fitted by

$$\langle E(t) \rangle = 3.097 + 0.019 \times \exp \left( -\frac{t}{812 \text{ ps}} \right) \text{ (eV)},$$  \hspace{1cm} (3.4)

and the decrease rate of its energy is $1 \times 10^7$ eV/s, as shown by the solid line in Fig. 3.7(a).

Figure 3.8 shows the PL decay profiles of the In$_x$Ga$_{1-x}$N MQWs. The PL decay shows nearly a single exponential decay function, and the decay time increases with the decrease of the detection photon energy, similarly to what happens in the single-layer In$_{0.07}$Ga$_{0.93}$N. The decay time of the various observed photon energies is shown with the time-integrated PL spectrum in the Fig. 3.9(b). Figure 3.9(a) shows the energy- and time-resolved PL of the In$_x$Ga$_{1-x}$N MQWs. This figure is constructed in the same manner that was used in the single layer In$_{0.07}$Ga$_{0.93}$N. The open squares in Fig. 3.9(a) indicate the temporal change of the center of gravity of the PL, and the decrease rate of its energy is $3 \times 10^7$ eV/s. It is also well fitted by

$$\langle E(t) \rangle = 3.037 + 0.05 \times \exp \left( -\frac{t}{896 \text{ ps}} \right) \text{ (eV)}. \hspace{1cm} (3.5)$$

It seems that similar relaxation process takes place in the single-layer In$_x$Ga$_{1-x}$N and the In$_x$Ga$_{1-x}$N MQWs.
The observed slow energy-loss rate is interpreted on the energy relaxation model for the exciton localization. The relaxation process of localized excitons is explained as follows. The electron-hole pairs are generated by the excitation in the delocalized states and have a kinetic energy far exceeding the amplitude of potential fluctuations. The electron-hole pairs have a high probability of the spatial migration, and lose their energy quickly via acoustic-phonon interactions. After most of the kinetic energy is lost, electrons or holes are captured at the localized states, and the localized excitons are formed, where the relaxation process is mainly due to the spatial migration between the localized states with the emission of acoustic phonons. The relaxation rate of such process depends on the density of the available final states at the lower energy. The relaxation rate of the localized states is expressed by the relaxation rate to the lower-energy states minus that from the higher-energy states into the localized states, plus the radiative recombination rate. Therefore, the decay time increases with the decrease of the detection energy, and the center of gravity of the PL shifts toward the lower photon energy as time passes.

3.4 Summary

Exciton localization in single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N MQWs grown by MOCVD was studied at 2 K. The mobility edge of samples is determined to be 3.175 eV for the single-layer In$_{0.07}$Ga$_{0.93}$N, 3.07 eV for the single-layer In$_{0.1}$Ga$_{0.9}$N, and 3.178 eV for the In$_x$Ga$_{1-x}$N MQWs, respectively, by means of the site-selectively excited PL measurement. The exciton relaxation process was studied by means of the time-resolved PL measurement. The PL decay time increased with the decrease of the detection photon energy, indicating the dynamical feature of the exciton localization.
References


Fig. 3.1  PL spectra of single-layer In$_{0.07}$Ga$_{0.93}$N obtained under the site-selective excitation ranging from 3.122 to 3.305 eV. Closed circles show the PL peaks. The inset shows the PL peak photon energy as a function of the excitation photon energy. The mobility edge is obtained from the kink point.
Fig. 3.2 Absorption (dashed line) and PL (solid line) spectra of single-layer In$_{0.07}$Ga$_{0.93}$N. They are gotten rid of Fabry-Perot modes and are restored by calculation. The absorption tail is fitted by Eq. (3,1) in the text.
Fig. 3.3 Absorption (dashed line) and PL (solid line) spectra of single-layer In$_{0.1}$Ga$_{0.9}$N. They are gotten rid of Fabry-Perot modes and are restored by calculation. The absorption tail is fitted by Eq. (3,1) in the text.
Fig. 3.4 PL spectra of In$_x$Ga$_{1-x}$N MQWs obtained under the site-selective excitation ranging from 3.005 to 3.305 eV. The inset shows the PL peak photon energy as a function of the excitation photon energy. The mobility edge is obtained from the kink point.
Fig. 3.5  Absorption (dashed line) and PL (solid line) spectra of In$_{x}$Ga$_{1-x}$N MQWs. The absorption tail is fitted by Eq. (3.1) in the text. The closed circle and triangle show the band gap of the In$_{0.11}$Ga$_{0.89}$N ternary alloy $E_g$ and the lowest energy transition $n=1$ in the In$_{0.11}$Ga$_{0.89}$N (2 nm)/In$_{0.03}$Ga$_{0.97}$N (4 nm) MQWs obtained by calculation.
Fig. 3.6 Time-resolved PL of single-layer In$_{0.07}$Ga$_{0.93}$N obtained at 3.08, 3.12, 3.16, and 3.20 eV.
Fig. 3.7  (a) Contour map of energy- and time-resolved PL intensity of single-layer In$_{0.07}$Ga$_{0.93}$N. The excitation photon energy is 3.382 eV. The open squares show the PL center of gravity as a function of time. (b) Time-integrated PL spectrum. The open circles show the decay time observed at various photon energies.
Fig. 3.8  Time-resolved PL of In$_x$Ga$_{1-x}$N MQWs obtained at 2.99, 3.04, 3.10, and 3.22 eV.
Fig. 3.9  (a) Contour map of energy- and time-resolved PL intensity of In$_x$Ga$_{1-x}$N MQWs. The excitation photon energy is 3.323 eV. The open squares show the PL center of gravity as a function of time. (b) Time-integrated PL spectrum. The open circles show the decay time observed at various photon energies.
CHAPTER 4
Stimulated Emission from Single-Layer In$_x$Ga$_{1-x}$N and
In$_x$Ga$_{1-x}$N Multiple Quantum Wells

4.1 Introduction

Recently, it has been reported that spontaneous emission from In$_x$Ga$_{1-x}$N ternary alloy system is related to the radiative recombination of excitons localized at certain minima in In$_x$Ga$_{1-x}$N layers [1-4]. It is possible that the exciton localization contributes to the optical gain, because the low-density tail states are easily occupied by moderate pumping, which has been reported in II-VI compound semiconductors [5-7]. However, the origin of the stimulated emission from the In$_x$Ga$_{1-x}$N ternary alloy system has not been clarified yet. Although it has been proposed that the exciton localization is related to the lasing mechanism for In$_x$Ga$_{1-x}$N laser diodes [1-3], there is so far no direct experimental support for this claim. Therefore, it is necessary to study the optical properties of the stimulated emission from In$_x$Ga$_{1-x}$N ternary alloy system.

In this chapter, we study the optical properties of the stimulated emission from single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N multiple quantum wells (MQWs) used in Chapter 3. Under the high-density excitation, the stimulated emission is observed in surface-emitting configuration. The excitation energy density dependence of the photoluminescence (PL) intensity provides the stimulation threshold density. The lifetime of the stimulated emission is measured by means of a time-resolved PL measurement and a nonlinear luminescence measurement. The nonlinear luminescence measurement provides the detailed characters of the stimulated emission [8-10].
4.2 Experimental Procedure

In this chapter, the samples were single-layer $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$ and $\text{In}_x\text{Ga}_{1-x}\text{N}$ MQWs used in Chapter 3. In order to make assignment of emission under high-density excitation, the second harmonic pulses of Ti:sapphire regenerative amplifier output were used as excitation source. The pulse duration and the repetition rate were 300 fs and 200 kHz, respectively. Time-resolved PL profiles were measured by using a synchroscan streak camera in connected to a 25-cm subtractive dispersion double monochromator. The time resolution was about 30 ps. Nonlinear luminescence was dispersed by a 25-cm monochromator and detected by a photomultiplier tube. The excitation beam is divided into two beams of the equal intensity. The two beams were modulated the amplitude at different frequencies by a mechanical chopper, and focused at the same spot on the sample with time delay. The differential frequency component of the PL was detected by a lock-in detection technique.

4.3 Experimental Results and Discussion

4.3.1 Stimulated emission from single-layer $\text{In}_x\text{Ga}_{1-x}\text{N}$

Under the high-density excitation, we can observe stimulated emission in the surface-emitting configuration. Figure 4.1 shows the PL spectra of the single-layer $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$ at 2 K under the excitation energy densities of 2.5, 25, and 50 µJ/cm$^2$, respectively. The excitation photon energy is 3.323 eV. The PL spectra were modulated by Fabry-Perot interference effect, but we got rid of the Fabry-Perot modes and restored to the intrinsic spectra by calculation. Under the excitation energy density of 2.5 µJ/cm$^2$, the PL spectrum has a broad emission band with a full width at half-maximum (FWHM) of about 200 meV. Increasing the excitation energy density, the PL intensity increases linearly below the stimulation threshold. While, above the stimulation threshold, a superlinearly grown sharp
emission band appeared. The sharp emission peak is located at 3.03 eV, which is just below the mobility edge, and FWHM is about 30 meV under the excitation energy density of 25 \( \mu J/cm^2 \). The stimulation threshold is 10.5 \( \mu J/cm^2 \) obtained from the excitation energy density dependence of the PL intensity, as shown in the inset of Fig. 4.1.

Figure 4.2 shows the PL decay profiles at 2 K under the excitation energy densities of (a) 2.5 and (b) 25 \( \mu J/cm^2 \), respectively. Under the excitation energy density of 2.5 \( \mu J/cm^2 \), the PL decay is nearly a single exponential decay. The decay time of the PL increases with the decrease of the detection photon energy: 302 ps detected at 3.08 eV and 576 ps detected at 2.93 eV. Under the excitation energy density of 25 \( \mu J/cm^2 \), the decay time of the sharp emission is less than 30 ps, which is the time resolution of the experiment. The temporal trace at 3.04 eV indicates a transformation the stimulated emission to the spontaneous emission.

### 4.3.2 Stimulated emission from In\(_x\)Ga\(_{1-x}\)N multiple quantum wells

The stimulated emission from In\(_x\)Ga\(_{1-x}\)N MQWs can be also observed at 2 K and room temperature. Figure 4.3 shows the PL spectra at 2 K under the excitation energy densities of 5 (dotted line) and 25 \( \mu J/cm^2 \) (solid line), respectively. A dashed line shows the absorption spectrum. The excitation photon energy is 3.323 eV. Under the excitation energy density of 5 \( \mu J/cm^2 \), the PL spectrum has a broad spontaneous emission with FWHM of about 185 meV. The peak position of the spontaneous emission is located at 3.06 eV. The spontaneous emission shows nearly a single exponential decay and the decay time increases with the decrease of the detection photon energy, as shown in Fig. 4.5(a). Under the excitation energy density of 25 \( \mu J/cm^2 \), we can observe a sharp stimulated emission at the higher-energy side of the spontaneous emission. The peak position of the stimulated emission is located at 3.16 eV, which is just below the mobility edge. The FWHM of the stimulated emission is
about 20 meV. The stimulation threshold is 17 $\mu$J/cm$^2$ obtained from the excitation energy density dependence of the PL intensity. The decay time of the stimulated emission is less than 30 ps, as shown in Fig. 4.5(b). The temporal trace at 3.16 eV indicates a transformation from the stimulated emission to the spontaneous emission.

The PL spectra at room temperature are shown in Fig. 4.4. The excitation photon energy is 3.287 eV. The excitation energy densities are 35 (dotted line) and 100 $\mu$J/cm$^2$ (solid line), respectively. The peak position of the spontaneous emission is located at 3.01 eV with FWHM of about 185 meV. Above the stimulation threshold, we can observe the stimulated emission even at room temperature. The peak position of the stimulated emission is located at 3.14 eV. The temporal traces of the PL at room temperature are shown in Figs. 4.5(c) and 4.5(d). The spontaneous emission shows nearly a single exponential decay. The decay time increases with the decrease of the detection photon energy, similar to what happens at 2 K. The decay time of the stimulated emission is less than 30 ps, similar to what happens at 2 K.

### 4.3.3 Mechanism of stimulated emission

The observed properties of the stimulated emission from the single-layer In$_x$Ga$_{1-x}$N are similar to those of the stimulated emission from the In$_x$Ga$_{1-x}$N MQWs, such as the location of the stimulated emission just below the mobility edge and the fast decay time constant less than 30 ps. We consider that the physical mechanisms of the stimulated emission from the single-layer In$_x$Ga$_{1-x}$N and the In$_x$Ga$_{1-x}$N MQWs are the same mechanism. Therefore, we discusses the mechanism mainly as the results of the In$_x$Ga$_{1-x}$N MQWs in the following.

We consider that the stimulated emission can be attributed to the localized excitons because the stimulated emission is just below the mobility edge. The optical gain for mixed crystals is due simply to the filling of the localized states and the gain peak can be observed at
the highest density [5]. In the InₓGa₁₋ₓN MQWs, the stimulation threshold is 17 µJ/cm² at 2 K. The areal density of the photogenerated carrier at the stimulation threshold (17 µJ/cm²) is estimated to be \( n = 2.5 \times 10^{12} \) cm² at the first layer in the InₓGa₁₋ₓN MQWs (\( n = 1.1 \times 10^{12} \) cm² is the average areal density). This value is below the density necessary for the formation of an electron-hole plasma, which is given in the first approximation by \( n_p = \frac{1}{\pi} (a_B^{_{2D}})^2 = 9.8 \times 10^{12} \) cm⁻² for the parameters in GaN, where \( a_B^{_{2D}} = 1.8 \) nm is the two-dimensional (2D) Bohr radius of the exciton estimated by the theoretical value of \( a_B^{_{3D}}/2 \) [11]. In addition, it has been known that the many-body effects are reduced as long as the carriers are localized in mixed crystals [12]. Under the quasi-steady state condition, the delocalized states are occupied only when the total density of the electron-hole pairs exceeds the density of the localized states under the strong excitation. The total areal density of the localized states is estimated to be an order of \( 10^{12} \) cm⁻² in the sample from the absorption spectrum. This means that the localized states are able to accommodate all carriers produced by the excitation. Therefore, the possibility of the electron-hole plasma formation can be ruled out in the stimulation mechanism in the InₓGa₁₋ₓN MQWs.

The reason why the stimulated emission is located just below the mobility edge can be explained as follows. When the excitation photon energy is above the mobility edge, the photogenerated electron-hole pairs lose their energy quickly. This is because the electron-hole pairs can find easily the lower-energy states by their migration. After their energy is lost electrons or holes are captured at the localized states, and localized excitons are formed. In the localized states, the exciton energy relaxation becomes slow, because the energy relaxation mode turns to the migration between the low-density localized states. The potential depth and barrier depend on the concentration of indium and/or the width of the InₓGa₁₋ₓN quantum well, which change with the change of spatial position. The excitons are localized at the positions
where the exciton energy decreases and passes through the mobility edge. As a result, the localized excitons occupy every localized state equally. As the first approximation, the energy distribution function of exciton is neither represented by Fermi distribution function nor by the Boltzmann function, but by a constant. The density of the localized states is considered as an exponential tail. Then, the optical gain has the maximum value just below the mobility edge. The observed features are well understood by the scenario mentioned above.

### 4.3.4 Nonlinear luminescence of $\text{In}_x\text{Ga}_{1-x}\text{N}$ multiple quantum wells

The nonlinear luminescence measurement provides more understanding of the detailed characters of the stimulated emission. Figure 4.6(a) shows the nonlinear luminescence spectra as a function of time delay $\tau$ between two excitation beams. In this figure, the upward direction (positive value) on the vertical axis means superlinear dependence of the excitation energy density and the downward direction (negative value) means sublinear dependence of the excitation energy density. The excitation photon energy is 3.323 eV. The total excitation energy density is 40 $\mu$J/cm$^2$. The time-integrated PL spectrum obtained at the same condition is shown in Fig. 4.6(b).

The nonlinear luminescence spectrum obtained at the time delay $\tau=0$ ps shows two resolved peaks of the positive signal, although the time-integrated PL shows an asymmetric peak of the stimulated emission. They are located at 3.162 and 3.193 eV, respectively. The lower photon energy peak is the same photon energy position of the time-integrated PL peak and does not move with the increase of the time delay. The peak is attributed to the localized exciton because it is observed below the mobility edge. The higher photon energy peak, which is observed above the mobility edge at the time delay $\tau=0$ ps, shifts toward the lower photon energy side as the time delay increases. The peak is located on the mobility edge at the time
delay $\tau=20$ ps. It seems reasonable to suppose that the peak is related to the energy relaxation of mobile excitons. On the other hand, the broad negative signal is observed. It is due to the saturation of the localized states.

The time-correlation trace of the nonlinear luminescence at 3.170 eV is shown in Fig. 4.7. The time-correlation trace is symmetric as against at the time delay $\tau=0$ ps and has two decay components. The time constant of the faster decay is 9 ps and that of slower decay is 320 ps, respectively. The stimulated emission occurs when the stimulation threshold is achieved by second excitation beam before the annihilation of the carriers created by the first excitation beam. In this case, the decay time constant for the time-correlation trace means the carrier lifetime: the time constant of the faster decay is attributed to the radiative lifetime of the stimulated emission.

4.4 Summary

We observed the stimulated emission from single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N MQWs at 2 K in the surface-emitting configuration. The stimulation threshold of the single-layer In$_{0.1}$Ga$_{0.9}$N and the In$_x$Ga$_{1-x}$N MQWs were 10.5 and 17 $\mu$J/cm$^2$, respectively. The stimulated emission was located below the mobility edge. We suggested that the stimulated emission is attributed to the localized states. In the In$_x$Ga$_{1-x}$N MQWs, the stimulated emission was observed even at room temperature. The time-resolved PL showed a transformation from the stimulated emission to the spontaneous emission. The detailed optical properties of the stimulated emission were studied by means of the nonlinear luminescence measurement. The lifetime of the stimulated emission was 9 ps in In$_x$Ga$_{1-x}$N MQWs.
References


Fig. 4.1  PL spectra of single-layer In$_{0.1}$Ga$_{0.9}$N at 2 K under the excitation energy densities of 2.5, 25, and 50 $\mu$J/cm$^2$, respectively. The excitation photon energy is 3.323 eV. The Fabry-Perot modes are eliminated by calculation. The inset shows the excitation energy density dependence of the PL intensity. The stimulation threshold is 10.5 $\mu$J/cm$^2$. 
Fig. 4.2  Time-resolved PL at 2 K obtained under the excitation energy densities of (a) 2.5 and (b) 25 $\mu$J/cm$^2$, respectively. The detection photon energies are 2.93, 2.97, 3.00, 3.04, and 3.08 eV, respectively. The decay of the stimulated emission is observed at 3.04 eV in (b).
Fig. 4.3  PL spectra and absorption spectrum (dashed line) of In$_{x}$Ga$_{1-x}$N MQWs at 2 K. The excitation energy densities are 5 (dotted line) and 25 $\mu$J/cm$^2$ (solid line), respectively. The excitation photon energy is 3.323 eV.
Fig. 4.4 PL spectra and absorption spectrum (dashed line) at room temperature. The excitation energy densities are 35 (dotted line) and 100 μJ/cm² (solid line), respectively. The excitation photon energy is 3.287 eV.
Fig. 4.5  Time-resolved PL at 2 K obtained under the excitation energy densities of (a) 5 and (b) 25 \( \mu \text{d/cm}^2 \), respectively. The detection photon energies are 2.99, 3.04, 3.10, 3.16, and 3.22 eV, respectively. The decay of the stimulated emission is observed at 3.16 eV in (b). Time-resolved PL at room temperature obtained under the excitation energy densities of (c) 35 and (d) 100 \( \mu \text{d/cm}^2 \), respectively. The detection photon energies are 2.97, 3.02, 3.08, 3.14, and 3.20 eV, respectively. The decay of the stimulated emission is observed at 3.14 eV in (d).
Fig. 4.6  (a) Nonlinear luminescence spectra of In$_x$Ga$_{1-x}$N MQWs as a function of delay time between two excitation beams. The total excitation energy density is 40 $\mu$J/cm$^2$.

(b) Time-integrated PL spectrum obtained under the excitation energy density of 40 $\mu$J/cm$^2$. The excitation photon energy is 3.323 eV.
Fig. 4.7  Time-correlation trace of nonlinear luminescence obtained at 3.170 eV.
CHAPTER 5

Dynamical Gain Formation Process in In$_x$Ga$_{1-x}$N Multiple Quantum Wells

5.1 Introduction

The dynamical optical properties of In$_x$Ga$_{1-x}$N ternary alloy system have been reported by means of the time-resolved luminescence measurement [1-3]. Most reports are the studies of the spontaneous emission, and there have been few reports on the stimulated emission. The lifetime of the spontaneous emission from the In$_x$Ga$_{1-x}$N ternary alloy system ranges from hundreds of picoseconds to a few nanoseconds, while that of the stimulated emission is less than tens of picoseconds [3]. The fact indicates that the stimulated emission process is completed within tens of picoseconds.

The reports on the optical gain spectra have been presented by means of the variable excitation-stripe length method [4-6] and the nanosecond nondegenerate optical pump-and-probe experiment [7]. In these methods, a dynamic phenomenon cannot be observed although a static phenomenon can be observed. Because the stimulated emission process in the In$_x$Ga$_{1-x}$N ternary alloy system is completed within tens of picoseconds, it is very important to know the dynamical formation gain process. The time-resolved pump-and-probe method provides direct information on the photoexcited carrier dynamics in semiconductor materials, because it can observe the distribution of the photoexcited carriers [8]. Hence, this method is useful for the investigation of the gain formation dynamics and the stimulation mechanism.

In this chapter, we study dynamical gain formation process of In$_x$Ga$_{1-x}$N multiple quantum wells (MQWs). The stimulated emission process is found to be fast within tens of
picoseconds from the time-resolved photoluminescence (PL) measurement in Chapter 4. To
directly observe the exciton relaxation and to discuss the dynamical gain formation process,
we performed a time-resolved pump-and-probe measurement employing white-light pulses.

5.2 Experimental Procedure

The sample of In$_x$Ga$_{1-x}$N MQWs used in Chapters 3 and 4 was used in the study of
this chapter. For a time-resolved pump-and-probe measurement employing white-light pulses,
the laser source was a Ti:sapphire regenerative amplifier whose output pulses had the pulse
duration of 300 fs and the repetition rate of 1 kHz. The second harmonic pulses of the
amplified laser output were used as the pump beam. A part of the amplified laser output was
focused in pure water to produce white-light pulses, which were used as the probe beam. The
transient absorption spectra were recorded by a 25-cm monochromator and a liquid-nitrogen
cooled charge-coupled-device multichannel detector.

5.3 Experimental Results and Discussion

5.3.1 Time-resolved differential absorption spectra

Figure 5.1(a) shows the absorption spectrum (dashed line) without pump beam and
the PL spectra (solid lines) at 2 K under the excitation energy densities of 10 (open circles)
and 60 $\mu$J/cm$^2$ (open squares), respectively. The excitation photon energy is 3.323 eV. Figures
5.1(b) and 5.1(c) show the temporal changes of the differential absorption spectra under the
excitation energy densities of 10 and 60 $\mu$J/cm$^2$, respectively. The upward vertical direction
means the bleaching of the absorption. Under both the excitation energy densities, the
differential absorption spectra show the negative signals at the lower-energy tail states
(localized states) and the signals are almost proportional to the state density below the photon
energy of 3.16 eV. The signal hardly changes within 100 ps because the relaxation at the localized states is very slow. Under the excitation energy density of 10 $\mu J/cm^2$, the positive signal, that is the induced absorption, is clearly observed above the photon energy of 3.3 eV. On the other hand, above the stimulation threshold, the signals at the higher-energy states (delocalized states) have drastic changes within 20 ps. After 20 ps, the signals are comparable to the signals below the stimulation threshold.

Similar results are obtained at room temperature. Figure 5.2(a) shows the absorption spectrum (dashed line) and the PL spectra (solid lines) at room temperature under the excitation energy densities of 25 (open circles) and 100 $\mu J/cm^2$ (open squares), respectively. The excitation photon energy is 3.278 eV. The differential absorption spectra are shown in Figs. 5.2(b) and 5.2(c). Below the stimulation threshold, the negative signals hardly change. Above the stimulation threshold, the drastic changes are observed at the delocalized states within 20 ps. This behavior of the signals at room temperature is similar to that of the signals at 2 K. Therefore, we can conclude from the results that the optical gain is formed by the same mechanism at 2 K and room temperature.

5.3.2 Fast energy relaxation process of stimulated emission

Comparing the temporal change of the differential absorption with that of the PL, which is shown in Fig. 4.5 in Chapter 4, we note that the rapid decay observed in the stimulated emission by the time-resolved PL measurement is not repeated at the same position by the time-resolved pump-and-probe measurement. The result of the differential absorption spectra indicates that the localized states are saturated and that many electron-hole pairs are present in the delocalized states. The optical gain is possible due to the localized states, and the electron-hole pairs are supplied to the localized states from the delocalized states.
We explain the fast energy relaxation concerned with the stimulation process by using a simplified three-energy-level scheme, as shown in Fig. 5.3. Now we consider a delocalized site $|1\rangle$, a localized site $|2\rangle$, and the ground state $|0\rangle$. The actual delocalized and localized sites cause the energy distribution, and form the bands, respectively. The photogenerated electron-hole pairs diffuse and relax rapidly into the delocalized site, and then relax into the localized site, and then the localized excitons are formed. Since the filling of the localized site prevents the relaxation from delocalized site to the localized site, the relaxation rate depends on the occupation probability of the localized site. As a result of a filling of the localized states, the optical gain is possible from the localized site due to the stimulated emission process, and some excitons emit photons as the lasing mode. Some excitons recombine radiatively or nonradiatively, including the spatial migration mode between the localized states. Then the rate equations in this model are given by

\[
\frac{dN_1}{dt} = -\frac{N_1}{\tau_{r1}} - \frac{N_1}{\tau_D}, \quad (5.1)
\]

\[
\frac{dN_2}{dt} = \frac{N_1}{\tau_D} - \frac{N_2}{\tau_{r2}} - \alpha S, \quad (5.2)
\]

Here $N_1$ is the number of the electron-hole pair at the delocalized site, $N_2$ is that of excitons at the localized site and $S$ is given by $S = N_2 - N_{th}$, where $N_{th}$ is the threshold number of the excitons. $\tau_{r1}$ is the recombination rate at the delocalized site, $\tau_{r2}^{-1}$ is that at the localized site, $\alpha$ is that via the stimulation mode, and $\tau_D^{-1}$ is the relaxation rate derived from the delocalized site to the localized site given by $\tau_D^{-1} = \tau_0^{-1}(1 - N_2/N_{2\text{max}})$, where $N_{2\text{max}}$ is the maximum number of the excitons in the localized site and $\tau_0^{-1}$ is the relaxation rate in the unoccupied localized state.

Now we consider the condition $\tau_{r2}^{-1} < \tau_{r1}^{-1} << \tau_0^{-1} < \alpha$. In this condition, the temporal
change of the electron-hole pair at the delocalized site has a rapid decay $\tau_D$, and that at the localized site has a rapid rise time $\tau_D$ and a slow radiative decay time $\tau_r$ below the stimulation threshold. Above the stimulation threshold, the temporal change of the excitons at the localized site has a rapid decay and a slow decay. Figure 5.4 shows the calculations of the temporal changes of the number of the excitons by using the parameters $\tau_1=100$ ps, $\tau_2=500$ ps, $\tau_0=1$ ps, and $\alpha^{-1}=1$ ps. The calculations explain the temporal changes of the excitons well, adjusting the ratio of the delocalized states and the localized states at the different photon energies. Thus, the optical gain is possible from the localized states as a result of a filling of the localized states. The electron-hole pairs are supplied to the localized states from the delocalized states.

### 5.3.3 Optical gain spectra

We analyze the optical gain spectra for In$_x$Ga$_{1-x}$N MQWs by using the phenomenological model for the inhomogeneously broadened system, which is proposed in II-VI compound semiconductors [9]. The excitons are localized due to the alloy compositional fluctuation and random well width variations, which leads to the inhomogeneously broadened absorption profile. The population inversion condition is decided on the occupancy probability of the localized site. If the localized site is occupied, the contribution is positive (gain). On the other hand, if it is unoccupied, the contribution is negative (absorption). In the simplified three-energy-level model, the exciton relaxation occurs from the initial higher-energy states (delocalized states) to the lower-energy states (localized states), from which the optical gain is possible due to stimulated emission to the ground state. In the extreme inhomogeneous broadening system, the gain/absorption coefficient can be written as

$$g(E) = D_r(E) \left[ 2f(E) - 1 \right],$$

(5.3)
where $D_i(E)$ is the inhomogeneous line-shape function and $f(E)$ is the energy distribution function. If all the states are empty, the absorption profile is obtained as $-D_i(E)$.

The calculated gain spectra for In$_x$Ga$_{1-x}$N MQWs at 2 ps under the excitation energy density of 20 $\mu$J/cm$^2$ are shown in Fig. 5.5(a), in which we took account of the depth profile of the carrier density obtained by the absorption coefficient and the structure of the sample. We assumed the energy distribution function to be

$$f(E) = \frac{a}{\exp \left( \frac{E - b}{\epsilon} \right) + 1}. \quad (5.4)$$

Here $a$, $b$ and $\epsilon$ are the calculation parameters, which are chosen so as to reproduce the differential absorption spectra. The reproduced differential absorption spectra at 2 and 100 ps are shown in Fig. 5.5(b). The energy position of the maximum gain obtained by the calculation agrees with the stimulated emission peak observed by the experiment. Thus, the phenomenological model for the inhomogeneously broadened system can explain the optical gain formation process.

### 5.3.4 Induced absorption

In the differential absorption spectra, we observe the induced absorption. One explanation for the induced absorption may be that the redshift of the absorption spectrum. The induced absorption measured at 3.35 eV is $\Delta \alpha = 0.03$, which may correspond to the redshift of 5 meV of the absorption spectrum. We think that the induced absorption is not due to the band gap renormalization effect, because the induced absorption can be also observed in this sample under low-density excitation at 100 nJ/cm$^2$ by means of the one-beam pump-and-probe measurement. Another explanation may be the presence of the intermediate states such as localized states and trap states [10,11]. In this case, the induced absorption can
be observed at the wide range of the photon energy, but it is inconspicuous due to the large contribution of the band filling effect in this experiment. However, the induced absorption can be observed at red color regions (below the band gap of the In$_x$Ga$_{1-x}$N) by means of a two-color pump-and-probe measurement.

5.4 Summery

We studied the dynamical gain formation process in In$_x$Ga$_{1-x}$N MQWs by means of the time-resolved pump-and-probe measurement. The photoexcited electron-hole pairs relaxed into the localized states through the delocalized states. The localized excitons were formed in a few picoseconds. Over the stimulation threshold, the localized states were saturated, and then many electron-hole pairs could be present in the delocalized states within a few tens of picoseconds. The optical gain was possible in terms of the stimulated emission process from the localized states, and then the fast relaxation from the delocalized states to the localized states occurred. The stimulated emission was related to the filling of the localized states.

References


Fig. 5.1 The pump-and-probe measurement at 2 K. (a) The dashed line shows the absorption spectrum. The solid lines show the PL spectra under the excitation energy densities of 10 (open circles) and 60 $\mu J/cm^2$ (open squares), respectively. The excitation photon energy is 3.323 eV. The time-resolved differential absorption spectra under the excitation energy densities of (b) 10 and (c) 60 $\mu J/cm^2$, respectively.
Fig. 5.2 The pump-and-probe measurement at room temperature. (a) The dashed line shows the absorption spectrum. The solid lines show the PL spectra under the excitation energy densities of 25 (open circles) and 100 $\mu J/cm^2$ (open squares), respectively. The excitation photon energy is 3.278 eV. The time-resolved differential absorption spectra under the excitation energy densities of (b) 25 and (c) 100 $\mu J/cm^2$, respectively.
Fig. 5.3  Schematic illustration of the relaxation model.
Fig. 5.4 Temporal changes of the differential absorption obtained under the excitation energy densities of (a) 10 and (b) 60 $\mu J/cm^2$ at 2 K. The bold solid lines are calculated by the three-energy level scheme.
Fig. 5.5  (a) The calculated optical gain spectra at each quantum well in the In$_x$Ga$_{1-x}$N MQWs under the excitation energy density of 20 $\mu$d/cm$^2$ at 2 ps. These are calculated by taking account of the depth profile of the carrier density. (b) The differential absorption spectra under the excitation energy density of 20 $\mu$d/cm$^2$ with the time-integrated PL spectrum at 2 K. The solid lines show the differential absorption spectra at 2 (open circles) and 100 ps (open triangles). The dashed lines show the reproduced differential absorption spectra.
CHAPTER 6
Ultraviolet Anti-Stokes Photoluminescence in In$_x$Ga$_{1-x}$N/GaN Quantum Well Structures

6.1 Introduction

Anti-Stokes photoluminescence (PL) or up-converted PL is a phenomenon in which photon energy of PL is higher than the excitation photon energy. Generally, the energy up-conversion in bulk semiconductors is achieved by a momentum converting Auger process [1-3], thermal population of phonon modes as observed anti-Stokes Raman lines [4,5], or nonlinear mechanisms such as second harmonic generation, optical parametric oscillation, and two-photon absorption (TPA) processes [6-8]. The TPA processes are distinguished by two mechanisms. One is a coherent TPA, where the intermediate states are virtual states. Another is a two-step TPA, where the intermediate states are real states.

Recently, efficient anti-Stokes PL has been observed in heterostructures and quantum wells (QWs) of semiconductors [9-16]. It has been proposed that the carrier excitation mechanisms in anti-Stokes PL are cold Auger process for InP/Al$_x$In$_{1-x}$As type-II heterojunctions [9], two-step TPA for CdTe/Cd$_x$Mn$_{1-x}$Te QWs [10], and cold Auger process and/or two-step TPA for GaAs/(Al,Ga)InP$_2$ heterostructures [11-16]. In these cases, the samples consist of stacked narrow gap and wide gap semiconductors. It has been argued that anti-Stokes PL is caused by a radiative recombination in the wide gap material, into which carriers are excited from the narrow gap material. Hellmann et al. have proposed that the anti-Stokes PL in the CdTe/Cd$_x$Mn$_{1-x}$Te QWs is due to the two-step TPA process involving localized or impurity bound exciton state as the intermediate state. The photons for the second
absorption step can be provided by the photon recycling of the exciton recombination in the QWs [10]. Driessen et al. have proposed that the anti-Stokes PL in GaAs/GaInP$_2$ QWs is due to the cold Auger process via interface states. They have shown the temperature dependence of the anti-Stokes PL intensity and that the results of a collinear double-beam experiment agree with their assignment [11].

In this chapter, we report on the observation of ultraviolet anti-Stokes PL in In$_x$Ga$_{1-x}$N/GaN quantum well structures. This anti-Stokes PL (3.49 eV) is the highest photon energy in semiconductors to our knowledge. The anti-Stokes PL of the GaN barrier exhibits a superlinear dependence on the excitation energy density. We demonstrate that the anti-Stokes PL in the In$_x$Ga$_{1-x}$N/GaN quantum well structures is due to the two-step TPA process by means of time-resolved PL measurement and two-color pump-and-probe experiment.

6.2 Experimental Procedure

6.2.1 Sample

The sample used in this chapter was Si-doped In$_x$Ga$_{1-x}$N/GaN multiple quantum wells (MQWs) grown on a (0001) orientated sapphire substrate by a metal-organic chemical vapor deposition. The In$_x$Ga$_{1-x}$N/GaN MQWs consisted of 3 periods of a 3.5-nm-thick In$_x$Ga$_{1-x}$N quantum well separated by a 7-nm-thick GaN barrier. The indium concentration of the well was 6.2-7.4% estimated by a x-ray diffraction measurement. The sample consisted of a GaN buffer layer, an undoped GaN layer 1.2 $\mu$m thick, a Si-doped GaN 0.8 $\mu$m thick, Si-doped In$_x$Ga$_{1-x}$N/GaN MQWs and a Si doped GaN layer 100 nm thick. The doping density was about $2 \times 10^{19}$ cm$^{-3}$. 
6.2.2 Experimental setup

For optical experiments, the excitation laser source was a mode-locked Ti:sapphire laser (2 ps, 82 MHz) or an optical parametric amplification (OPA) with a Ti:sapphire regenerative amplifier (300 fs, 200 kHz). The excitation for the anti-Stokes PL measurements was performed by a frequency doubled Ti:sapphire laser output. Under the excitation above a band gap of a GaN barrier, a frequency doubled OPA output was used. The anti-Stokes PL spectra were dispersed by a 0.6-m triple spectrometer and detected by liquid nitrogen cooled charge-coupled-device multichannel detector. Time-resolved PL profiles were measured by using a synchroscan streak camera in connected to a 25-cm subtractive dispersion double monochromator. The time resolution was about 30 ps. Two-color pump-and-probe experiment was performed in the transmission geometry. A part of Ti:sapphire laser pulses was used as the probe beam and the frequency doubled Ti:sapphire laser pulses were used as the pump beam. The amplitude modulation of the pump and probe beams at different frequencies (1.5 MHz, 200 Hz) was made by an acousto-optical modulator and a mechanical chopper, respectively. A double lock-in detection of the signal modulated at the different frequency allowed us to reduce noise from the scattered light and to achieve highly sensitive detection of nonlinear transmission. The time dependence of the pump-and-probe signal was measured by scanning the optical delay line. The sample was directly immersed in liquid nitrogen at 77 K.

6.3 Experimental Results and Discussion

6.3.1 Ultraviolet anti-Stokes photoluminescence spectra from GaN barrier

Figure 6.1 shows the PL spectra of the In$_x$Ga$_{1-x}$N/GaN MQWs at 77 K for the excitation above (a) and below (b) the band gap of the GaN barrier. Under the excitation photon energy at 3.756 eV, we can observe two emission bands. The emission with the peak at
3.18 eV is due to the radiative recombination in the In\textsubscript{x}Ga\textsubscript{1-x}N QWs, while the emission with the peak at 3.49 eV is due to that in GaN barrier layers. It is a typical PL spectrum of the In\textsubscript{x}Ga\textsubscript{1-x}N/ GaN MQWs system. It has been reported that the In\textsubscript{x}Ga\textsubscript{1-x}N PL is attributed to the recombination of the excitons localized at certain potential minima in the In\textsubscript{x}Ga\textsubscript{1-x}N layers [17-20]. The PL intensity of the GaN barrier is smaller than that of the In\textsubscript{x}Ga\textsubscript{1-x}N QWs, indicating efficient carrier transfer from the GaN barrier into the In\textsubscript{x}Ga\textsubscript{1-x}N QWs. Under the excitation photon energy at 3.305 eV, a similar In\textsubscript{x}Ga\textsubscript{1-x}N PL is observed and an anti-Stokes PL of the GaN barrier can be observed clearly even under the excitation below the band gap of the GaN barrier. The excitation energy density dependencies of the anti-Stokes PL and the In\textsubscript{x}Ga\textsubscript{1-x}N PL intensities excited at 3.305 and 3.228 eV are shown in Figs 6.2 and 6.3, respectively. The anti-Stokes PL exhibits a superlinear dependence on the excitation energy density, while the In\textsubscript{x}Ga\textsubscript{1-x}N PL exhibits a linear dependence.

The dependencies of the anti-Stokes PL and the In\textsubscript{x}Ga\textsubscript{1-x}N PL intensities on the excitation photon energy, i.e., the PL excitation (PLE) spectra detected at the anti-Stokes GaN PL band (3.49 eV) and the In\textsubscript{x}Ga\textsubscript{1-x}N PL band (3.10 eV), are shown as open circles and closed squares in Fig. 6.4, respectively. The excitation energy density is fixed at 0.488 \( \mu \)J/cm\(^2\). Because the PLE spectrum is almost proportional to the joint density of states in the direct energy transition type semiconductors and the absorption of In\textsubscript{x}Ga\textsubscript{1-x}N ternary alloy system is broadened due to the formation of the tail states [20], the In\textsubscript{x}Ga\textsubscript{1-x}N PLE spectrum is fitted by the error function

\[
D(E) = \frac{1}{0.05\sqrt{\pi}} \frac{m_r}{\hbar^2} \int_{-\infty}^{\infty} \exp\left(-\frac{(E-t)^2}{0.05^2}\right) \Theta(t - 3.294) dt
\]

\[
= \frac{1}{0.05\sqrt{\pi}} \frac{m_r}{\hbar^2} \int_{-\infty}^{\infty} \exp\left(-\frac{(t - 3.294)^2}{0.05^2}\right) dt.
\]

(6.1)

Here, \( m_r \) is a reduced mass of the electron-hole pair and \( m_r/\hbar^2 \Theta(E - 3.294) \) is a step function.
function, indicating two-dimensional joint density of states in the $\text{In},\text{Ga}_{1-x}\text{N}/\text{GaN}$ MQWs. The fitting parameter of 3.294 eV is almost consistent with the calculated value of the lowest quantized energy transition in the $\text{In},\text{Ga}_{1-x}\text{N}/\text{GaN}$ MQWs by using the finite potential well model. The intensity of anti-Stokes PL excited above 3.27 eV increases drastically with the increase of the excitation photon energy like that of the $\text{In},\text{Ga}_{1-x}\text{N}$ PL. This result indicates that the anti-Stokes PL mechanism is related to the real states in the $\text{In},\text{Ga}_{1-x}\text{N}$ QWs. On the other hand, under the excitation below 3.23 eV, the anti-Stokes PL can be observed unless the $\text{In},\text{Ga}_{1-x}\text{N}$ PL becomes weak. The anti-Stokes PL excited at 3.228 eV also exhibits a quadratic dependence on the excitation energy density, as shown in Fig. 6.3. It seems that the coherent TPA process or the process related to deeper states such as deep acceptor states causes the anti-Stokes PL excited below 3.23 eV.

Considering that the anti-Stokes PL depends on the excitation energy density quadratically and is related to the real states of the $\text{In},\text{Ga}_{1-x}\text{N}$ QWs, we presume a main mechanism of the anti-Stokes PL to be the two-step TPA process via the localized states in the $\text{In},\text{Ga}_{1-x}\text{N}$ QWs. We explain the two-step TPA process as follows. After the initial excitation process, the electron-hole pairs are generated in the $\text{In},\text{Ga}_{1-x}\text{N}$ QWs. They lose their energy quickly, electrons or holes are captured at certain potential minima and localized excitons are formed, as schematically shown on the left side of Fig. 6.5. Since the localized states have a very limited spatial extension, the wave function of the localized exciton has contributions from all $k$ states in the Brillouin zone. Therefore, high-energetic electron-hole pairs can be directly created by second photon absorption without phonon participation, as shown on the right side of Fig. 6.5. After the second excitation process, the electron-hole pairs with the energy higher than the band gap of the GaN barrier relax into the GaN barrier states or are localized again in the $\text{In},\text{Ga}_{1-x}\text{N}$ QWs. The electron-hole pairs recombine radiatively like the
excitation above the band gap of the GaN barrier. This radiative recombination in the GaN barrier gives rise to the observed anti-Stokes PL.

6.3.2 Dynamical carrier generation for anti-Stokes photoluminescence process

Time-resolved PL measurement provides the carrier dynamics of the In$_x$Ga$_{1-x}$N/GaN MQWs and shows that the second absorption step is mainly induced by photon recycling, i.e., the photons stem from radiative recombination process of the In$_x$Ga$_{1-x}$N QWs. Figures 6.6(a) and 6.6(b) show the PL decay profiles under the excitation above (at 3.756 eV) and below (at 3.305 eV) the band gap of the GaN barrier. Solid lines show the fittings of single or double exponential functions convoluted by the excitation laser profile. The decay profiles of the In$_x$Ga$_{1-x}$N PL (squares) are detected at 3.18 eV, while the decay profiles of the GaN PL (circles) are detected at 3.49 eV. Under the excitation at 3.756 eV, the GaN PL shows a single exponential decay, whose decay time constant is 72.1 ps. While, the In$_x$Ga$_{1-x}$N PL shows 72.1 ps rise and 693 ps decay. The In$_x$Ga$_{1-x}$N PL excited at 3.305 eV shows a single exponential decay, whose decay time constant is 800 ps. The decay time of the In$_x$Ga$_{1-x}$N PL increases with the decrease of the detected photon energy (0.4 ns detected at 3.3 eV, 0.9 ns detected at 3.1 eV), indicating a typical dynamical feature of the exciton localization in In$_x$Ga$_{1-x}$N ternary alloy system [19,20]. The rise cannot be observed under the excitation below the band gap of the GaN barrier, unless the rise is clearly observed under the excitation above the band gap of the GaN barrier. This result indicates that the photogenerated electron-hole pairs transfer from the GaN barrier into the In$_x$Ga$_{1-x}$N QWs.

The anti-Stokes PL of GaN excited at 3.305 eV shows a single exponential decay. Its time constant is 425 ps, which is longer than that of normal GaN decay. This indicates that the carrier generation process is slower than the relaxation process in the GaN barrier—if the
carrier generation is fast, such as the coherent TPA process or the two-step TPA process where the second absorption step is caused by laser photons, the relaxation process for the anti-Stokes PL should be completed within 72 ps. The notable point is that the decay time of the anti-Stokes PL is almost half the time constant of the In$_x$Ga$_{1-x}$N PL decay. In the two-step TPA process, the intensity of the anti-Stokes PL is proportional to the population $N_{\text{InGaN}}(t)$ of the localized states in the In$_x$Ga$_{1-x}$N QWs and to the number of photons responsible for the second absorption step. If the second absorption step is caused by the photons of the In$_x$Ga$_{1-x}$N PL, the number of photons is directly proportional to the population $N_{\text{InGaN}}(t)$ of the localized states in the In$_x$Ga$_{1-x}$N QWs: the intensity of the anti-Stokes PL is proportional to the square of the population of the localized states in the In$_x$Ga$_{1-x}$N QWs. After all, the second photons for the two-step TPA process are provided by photon recycling. This can explain notable characteristics of the decay time of the anti-Stokes PL.

We have presumed that the second absorption step is caused by the photon process. However, it is difficult to distinguish between two-step TPA process provided by photon recycling and Auger process: the energy transfer due to radiative or nonradiative recombination in the In$_x$Ga$_{1-x}$N QWs. We performed two-color pump-and-probe experiment to discuss the second absorption process. In this experiment, the localized excitons generated in the In$_x$Ga$_{1-x}$N QWs by pump beam (photon energy below the GaN band gap), and the second photons are supplied by probe beam (photon energy below the In$_x$Ga$_{1-x}$N band gap). Figure 6.7 shows a temporal change of a differential transmission. The photon energy and the excitation energy density of the pump beam are 3.311 eV and 0.244 $\mu$J/cm$^2$, respectively. These of the probe beam are 1.656 eV and 0.049 $\mu$J/cm$^2$, respectively. The signal indicates an induced absorption and its decay time is 802 ps, which is comparable to that of the In$_x$Ga$_{1-x}$N PL. The signal is proportional to the intensity of the pump beam. This is the direct observation
of the two-step TPA process. This decay profile also assures that the intermediate states are the localized states in the In$_x$Ga$_{1-x}$N QWs. The inset of Fig. 6.7 shows the anti-Stokes PL spectra excited at 3.311 eV with (solid line) or without (dashed line) an additional pumping at 1.656 eV. The excitation energy densities are 0.146 µJ/cm$^2$ for the first pumping and 0.244 µJ/cm$^2$ for the additional pumping, respectively. It is clearly seen that the anti-Stokes PL intensity increases by the additional pumping. This result is a positive proof that the anti-Stokes PL can be caused by photon absorption.

We discuss the efficiency of the photon absorption. The dynamics of the anti-Stokes PL process is described by the rate equations

$$\frac{dN_{\text{GaN}}}{dt} = -\frac{N_{\text{GaN}}}{\tau_{\text{GaN}}} - \frac{N_{\text{GaN}}}{\tau_D} + \frac{\alpha N_{\text{InGaN}}^2}{\tau_{\text{InGaN}}} + \beta N_{\text{InGaN}} I_{\text{exc}}(t), \quad (6.2)$$

$$\frac{dN_{\text{InGaN}}}{dt} = -\frac{N_{\text{InGaN}}}{\tau_{\text{InGaN}}} + \frac{N_{\text{GaN}}}{\tau_D} - \frac{\alpha N_{\text{InGaN}}^2}{\tau_{\text{InGaN}}} - \beta N_{\text{InGaN}} I_{\text{exc}}(t), \quad (6.3)$$

and they can explain our experimental results well. In each equation, the first term means the main relaxation term including the radiative recombination. The second term is relaxation from the GaN barrier to the In$_x$Ga$_{1-x}$N QWs. The third and fourth terms are the photon absorption by the In$_x$Ga$_{1-x}$N PL ($N_{\text{InGaN}}/\tau_{\text{InGaN}}$) and excitation laser ($I_{\text{exc}}$), respectively. The absorption efficiency by the In$_x$Ga$_{1-x}$N PL photons ($\alpha N_{\text{InGaN}}$) is guessed by the ratio of the time-integrated In$_x$Ga$_{1-x}$N PL to that of anti-Stokes PL. We estimate the coefficient for PL photons $\alpha$ to be $4 \times 10^{-15}$ cm$^2$. While, the absorption efficiency by laser photons ($\beta N_{\text{InGaN}}$) is directly measured by the two-color pump-and-probe experiment. We estimate the coefficient for laser photons $\beta$ to be $1.77 \times 10^{-17}$ cm$^2$. The coefficient for PL photons $\alpha$ is $10^2$ times larger than that for laser photons $\beta$. The main reason is ascribed to the different geometric factor, shown in the following. The intermediate states present in the In$_x$Ga$_{1-x}$N QWs at the areal
range of the spot size of the initial excitation. The PL photons emit in all the directions. If the condition of total reflection is satisfied, the emission goes back and forth in the lateral direction of the sample. The critical angle for the interface with the GaN buffer and the sapphire substrate is about 41°. Considering the width of the sample (a few µm) and the spot size (a few hundred µm), the difference of the coefficients for the PL and laser photons is reasonable.

6.4 Summary

We presented detailed experimental studies of ultraviolet anti-Stokes PL in In$_x$Ga$_{1-x}$N/ GaN MQWs. We directly observed second step photon absorption for anti-Stokes PL by means of two-color pump-and-probe experiment. We concluded that this anti-Stokes PL is mainly caused by two-step TPA process via localized states of the In$_x$Ga$_{1-x}$N QWs and that the second absorption step can be provided by photon recycling of the In$_x$Ga$_{1-x}$N PL.

References

Fig. 6.1  PL spectra of the In$_x$Ga$_{1-x}$N/GaN MQWs excited above (a) and below (b) the band gap of the GaN barrier, respectively. The In$_x$Ga$_{1-x}$N PL is located at 3.18 eV and the GaN PL is located at 3.49 eV.
Fig. 6.2  Excitation energy density dependencies of the In$_x$Ga$_{1-x}$N PL (squares) and GaN anti-Stokes PL intensities (circles), respectively. The excitation photon energy is 3.305 eV.
Fig. 6.3 Excitation energy density dependencies of the In$_x$Ga$_{1-x}$N PL (squares) and GaN anti-Stokes PL intensities (circles), respectively. The excitation photon energy is 3.228 eV.
Fig. 6.4  Excitation photon energy dependencies of the In$_x$Ga$_{1-x}$N PL (closed squares) and GaN anti-Stokes PL intensities (open circles), respectively. The excitation energy density is fixed at 0.488 $\mu$J/cm$^2$. A solid line is a fitting by Eq. (6,1) in the text.
Fig. 6.5  Schematic illustration of a two-step TPA process for anti-Stokes PL.
Fig. 6.6 Temporal changes of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ PL and the GaN PL excited above (a) and below (b) the band gap of the GaN barrier. These decay profiles are fitted by single or double exponential functions convoluted by the excitation laser profile.
Fig. 6.7 Temporal change of the differential transmission by means of two-color pump-and-probe experiment. The photon energies of pump and probe beams are 3.311 and 1.656 eV, respectively. The inset shows anti-Stokes PL spectra excited at 3.311 eV with (solid line) or without (dashed line) an additional pumping at 1.656 eV.
CHAPTER 7

Conclusions

In this thesis, exciton localization and its related phenomena in III-V nitride compound semiconductors were studied from the viewpoint of carrier dynamics. We used single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N multiple quantum wells (MQWs) grown by metal-organic chemical vapor deposition. In the In$_x$Ga$_{1-x}$N ternary alloy system, exciton localization was caused by alloy disorder and was observed through the broadening of the optical spectra. We also observed its related phenomena: stimulated emission and anti-Stokes photoluminescence (PL), and studied these phenomena. The results and conclusions are summarized as follows.

Exciton localization in single-layer In$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N MQWs was observed. The mobility edge of the samples was determined by means of a site-selectively excited PL measurement. The determination of the mobility edge is important to determine whether the carriers are localized or not. The expected optical broadening due to the alloy disorder was observed by variation of the composition fraction of indium $x$. The decay of the spontaneous emission from In$_x$Ga$_{1-x}$N layers showed the dynamical feature of the exciton localization.

Next, the stimulated emission from In$_x$Ga$_{1-x}$N ternary alloy system was studied. The stimulated emission from single-layer In$_x$Ga$_{1-x}$N was observed in the surface-emitting configuration at 2 K. The stimulated emission from In$_x$Ga$_{1-x}$N MQWs was also observed at 2 K and room temperature. The stimulated emission was located below the mobility edge, indicating that the stimulated emission was related to the localized states. The lifetime of the stimulated emission is short within few tens picoseconds. Fast relaxation process was studied
by means of a time-resolved pump-and-probe measurement, and the optical gain spectra were presented. These results indicated that the saturation of the localized states played important role in the optical gain formation. The phenomenological model for the inhomogeneously broadened system was introduced. The photoexcited carriers relax from the delocalized states into the localized states, and the saturation of the localized states takes place. The optical gain from the localized states is possible in terms of stimulated emission to the ground states. This analysis was found to be in good agreement with experimental results. As a result, the formation of the optical gain in In$_x$Ga$_{1-x}$N ternary alloy system comes from the filling of the localized states.

Finally, anti-Stokes PL in In$_x$Ga$_{1-x}$N/GaN MQWs was studied. Ultraviolet anti-Stokes PL was observed at 3.49 eV, which is the highest photon energy of anti-Stokes PL in semiconductors to our knowledge. The anti-Stokes PL intensity exhibited a quadratic dependence on the excitation energy density. The PL excitation spectrum showed that the real states (localized states) in In$_x$Ga$_{1-x}$N quantum wells influenced the carrier excitation process. The time-resolved PL measurement showed that a decay time of the anti-Stokes PL was slower than that of the GaN PL under the excitation above the band gap of the GaN, and its time constant was half that of the InGaN PL decay. Two-step photon absorption was directly observed by means of a two-color pump-and-probe experiment. These results indicated that anti-Stokes PL was caused by two-step two-photon absorption process via localized states of the In$_x$Ga$_{1-x}$N quantum wells and that the second step carrier excitation was provided by photon recycling of the In$_x$Ga$_{1-x}$N PL.
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List of Publications

1. “Localized exciton and its stimulated emission in surface mode from single-layer $\text{In}_x\text{Ga}_{1-x}\text{N}$”,
   Akihiro Satake, Yasuaki Masumoto, Takao Miyajima, Tsunenori Asatsuma, Fumihiko Nakamura, and Masao Ikeda,

2. “Localized exciton and its stimulated emission in InGaN multiple quantum wells”,
   Akihiro Satake, Yasuaki Masumoto, Takao Miyajima, Tsunenori Asatsuma, and Masao Ikeda,

3. “Dynamical gain formation processes in InGaN multiple quantum wells”,
   Akihiro Satake, Yasuaki Masumoto, Takao Miyajima, Tsunenori Asatsuma, and Masao Ikeda,
   Proceedings of the 24th International Conference on Physics of Semiconductors,

4. “Two-dimensional exciton dynamics and gain formation processes in $\text{In}_x\text{Ga}_{1-x}\text{N}$ multiple quantum wells”,
   Akihiro Satake, Yasuaki Masumoto, Takao Miyajima, Tsunenori Asatsuma, and Masao Ikeda,
Other Fields

1. “Exciton localization and decomposition dynamics in cuprous halide nanocrystals”,
   Tsuyoshi Okuno, Hiroshi Miyajima, Akihiro Satake, and Yasuaki Masumoto,

2. “Reconsideration of relaxation processes of excitons in CuCl nanocrystals”,
   Tsuyoshi Okuno, Akihiro Satake, and Yasuaki Masumoto,