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**Study on optical properties of semiconductor
nanostructures created using designable nanofabrication
processes**

設計可能なナノ加工プロセスを用いて作製した
半導体ナノ構造の光学特性に関する研究

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February 2020

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Chapter 1 Introduction

1.1 Background

Nanotechnology is set up slightly above atoms and molecules, and is an advanced technology that has recently attracted much attention. Furthermore, semiconductor quantum nanodots (QD) are one of the central topics that have received much attention in semiconductor nanotechnology. As we know, QDs with sizes less than several tens nanometers can strongly confine an exciton in three dimensions, hence are also called a zero-dimensional nanostructure. There are many interesting properties in QDs: designable emission spectrum by changing the size and chemical composition, high oscillator strength (high optical gain) good photo-stability and so on. In addition, the strong quantum confinement in QDs contributes to the quantum size effect, surface effect, dielectric confinement, quantum tunneling, coulomb blocking and so on. According to these properties and effects, QDs can be applied to semiconductor optical devices, such as a solar cell, light emitting diode, laser, display, photodetector and so on.

Semiconductor QD growth methods and characteristics are hot topics in current research. The most commonly used method is a self-assembled growth mode because of its smaller size, higher density, and less defect than other early growth methods. However, the inhomogeneities in the size and shape make it difficult to control quantum confinement, thus making it difficult to accurately design and control the energy of the confined carriers. In an early research stage, a selective area growth method and combined fabrication method using lithography and etching were utilized to fabricate QD nanostructures. These methods enabled one to design the QD structure. However, according to the manufacturing processes of both methods, a sufficiently small size was not obtained. Moreover, serious damages occurred, leading to defects, carrier trap sites, and non-luminescent centers. Nevertheless, these early growth methods by the intentional design are worth studying if they can improve their disadvantages because they are likely to produce QDs with uniform size and distribution.

1.2 Semiconductor nanostructure growth methods

1.2.1 Selective area growth

In the early 1960s, Joyce, B.D. et al. [1] developed a selective area growth (SAG) technique in a silicon material. Then SAG began to be used for III-V compound semiconductors [2, 3]. This SAG is a template growth technique that involves lithography and epitaxial growth. First, for this SAG approach, a mask pattern, usually using amorphous film (such as SiO_2 , SiN_x), is prepared on a substrate surface by chemical dry or wet etching. Subsequently, nanostructures (nanowire or quantum dot) can be grown by metal organic vapor-phase epitaxy (MOVPE) or metal organic chemical vapor deposition (MOCVD) according to the mask pattern. The growth process is outlined in figure 1.1 [4]. This SAG cannot result in some significant damage due to the direct growth of nanostructures after the etching of mask pattern. However, the other approach without a mask pattern is direct irradiation on the surface of sample by a strong laser beam or electron beam, followed by an epitaxial growth of nanostructure. Surface damages originating from the etching process used for the SAG can degrade optical properties or performances of the nanostructure.

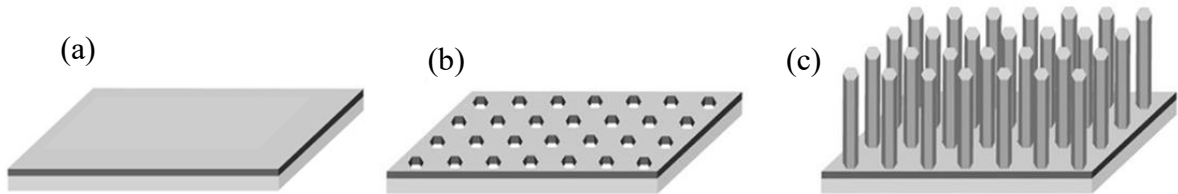


Figure 1.1| Fabrication process for selective area growth. [4] (a) Deposition of an amorphous film, (b) Formation of holes formed by lithography and etching, (c) nanostructure (nanowires) growth.

1.2.2 Self-assembled growth

Self-assembled growth of nanostructure was based on a theoretical study of thin film formation. As we know, hetero-epitaxial layers can be formed by depositing two different materials usually with different lattice constants. In addition, different surface morphologies of the hetero-epitaxial layers can be generated according to different amount of strain due to the lattice mismatch. There are three main growth modes: Frank Van-der-Merwe growth mode (layer-by-layer mode) [5], Stranski-Krastanow (SK) growth mode (layer-plus-island mode) [6], and Volmer-Weber growth mode (island mode) [7]. These three modes are

schematically shown in figure 1.2. In 1985, L. Goldstein et al. observed the first island nanostructure with the Stranski-Krastanow mode, i.e. self-assembled growth [8].

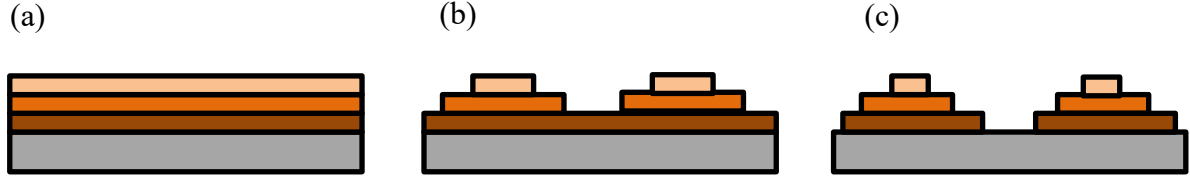


Figure 1.2| Schematics of three growth modes. (a) The layer-by-layer mode, (b) The Stranski-Krastanow (SK) growth mode (layer-plus-island mode), (c) The Volmer-Weber growth mode (island mode).

So far, the self-assembled growth of the nanostructure (i.e. QD) follows the SK growth mode, which can be applied to many crystal growth processes such as molecular beam epitaxy (MBE), MOCVD, atomic layer epitaxy (ALE), low pressure chemical vapor deposition (LPCVD) and so on. And, using this SK mode, many semiconductor QD nanostructures of III-V group, II-VI group, and IV group materials could be grown.

If we realize the self-assembled growth of QD, it is necessary that the growth structure should have a moderate (several %) lattice mismatch with the substrate. First, the fabrication should be begun by the layer growth mode, until the thickness of the layer exceeds a certain critical value. When this layer (the infiltration/wetting layer) is completed, the fabrication process is no longer two-dimensionally uniform, like a non-uniform three-dimensional island growth. Finally, the SK mode (layer-plus-island mode) of QD can be completed. In addition, we can control the size and density of the island-like nanostructure primarily by changing with the deposition temperature and growth rate, reported by the previous literatures [9-13]. The density of QDs can be increased with increasing the deposition rate but decreased by increasing the growth temperature. An increase in QD size can be affected by a decrease in the density, because the deposited material is distributed according to stable growth nuclei [14]. One can add an annealing process after deposition of the QDs material to improve the size homogeneity [15]. However, the QD size of the QDs can be decreased and the material composition also can be varied by mixing of the QDs and wetting layer during longer annealing periods.

Such self-organized growth has allowed the nanostructure size to be sufficiently small and the number of defects in the formed nanostructure to be reduced compared to the previous SAG technology. However, size and distribution inhomogeneities still exist in this self-assembled nanostructure.

1.2.3 Lithography

Lithography is one of the important fabrication process of semiconductor devices. Compared with the above SAG technique and self-assembled growth, this lithography has the following advantages; including high controllability of size and shape, high uniformity, short fabrication period and so on. From the strong demand for ultra-miniaturized semiconductor devices, advanced lithography processes need to be developed. For instance, optical lithography in the new generation makes a use of X-ray [16], extreme UV [17], or charge particles [18]. Lithography using both of electrons and ion beams also is included [19]. Furthermore, nano-scale lithography is introduced, which utilizes proximal probe nanolithography [20], such as scanning tunnel microscope (STM)- or atomic force microscope (AFM)-based nanolithography. There are some other lithography processes, including plasmonic-assisted lithography [21], chemistry-based nanofabrication [22], laser interference lithography [23], nanosphere lithography [24], nanoimprint (nano-scale mold) lithography [25], dip pen lithograph with AFM [26] and so on. All these advanced lithography procedures can be applied to the fabrication of nanostructure.

One of these advanced lithography procedures: a basic photolithography process to fabricate a QDs-like nanostructure is shown in figure 1.3 [27]. After cleaning of a sample, the photoresist layer is spin coated on a surface of sample and then exposed to ultraviolet (UV) radiation through a patterned mask. At last, a QD-like nanostructure is etched by a reactive ion etching (RIE) process with protecting the residual resist in the resist development. Although this process is just one of the photolithographic procedures, but it becomes the basic process for most advanced lithography procedures and can prepare a mask for lithography, where most of the advanced lithography procedures are devoted to make a nanoscale mask. However, industry has very recently announced a 10 nm-scale lithography process, but with extremely high cost. Moreover, significant damages in both lithography process and etching process always exist, which should be noted and solved.

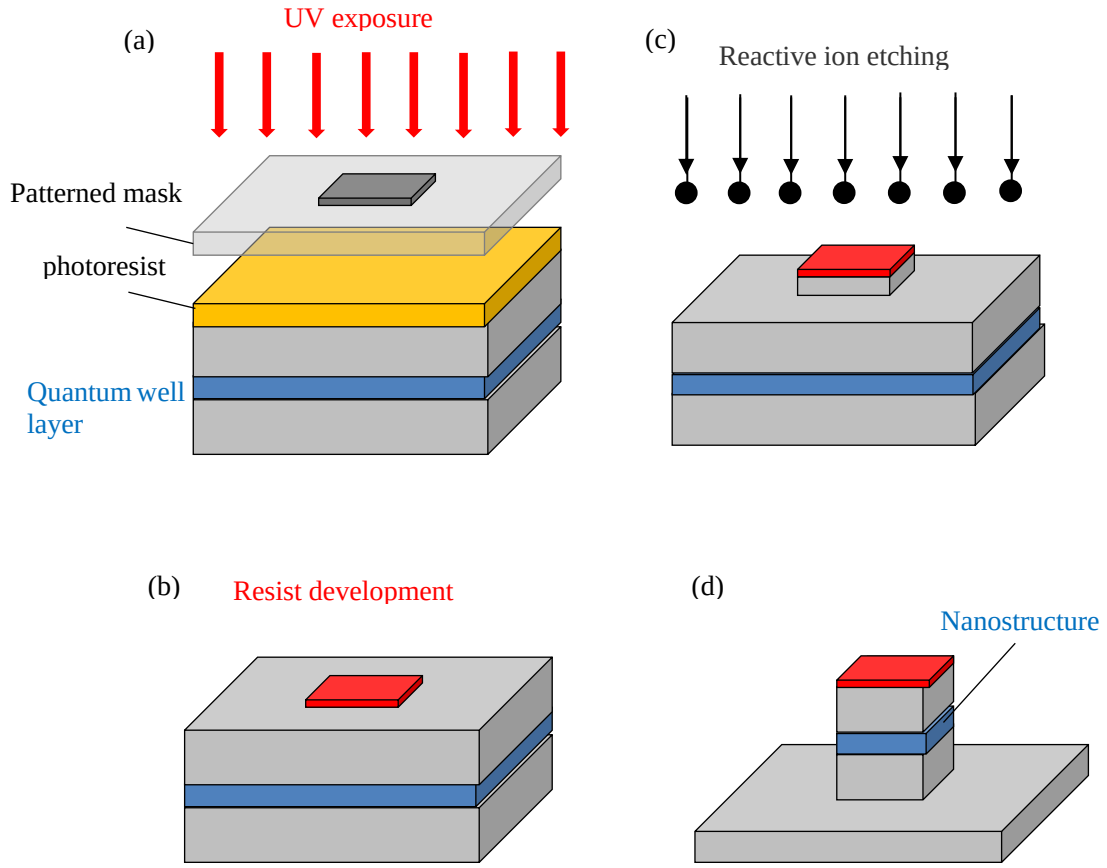


Figure 1.3| A basic photolithography process to fabricate a microstructure with (a) spin coating of photoresist and UV irradiation on a surface of sample, (b) development and stripping of photoresist, and (c) reactive ion etching. Finally, (d) a square-shaped microstructure is fabricated.

1.3 Nanostructure fabrication in III-V group material

1.3.1 Introduction

Compound semiconductors are usually formed from Group III and V or Group II and VI elements. These can control the band gap energy by controlling the composition of the three-component and four-component materials. In addition, since carrier mobility can be improved, there are advantages in the production and performance improvement of electronic and optical devices. Device characteristics basically depend on the material composition. As a result, nanostructures with various new functionalities can be fabricated by using heterostructure layers with different compositions, such as nanotubes [28], nanowires [29], and self-assembled QDs [30]. In addition, the development of III-V group nanostructure technology has greatly contributed to improving the characteristics of

heterojunction transistors, laser elements and light-emitting diodes (LEDs), and photovoltaic devices. Our research is related to nanostructures consisting of III-V group semiconductor materials primarily, particularly focuses on InGaN and InGaAs nanostructures. According to their various lattice structure and fabrication methods, the current situations of InGaN and InGaAs nanostructures are different. Section 1.3.2 and 1.3.3 would introduce the various InGaN and InGaAs nanostructures with three different nanostructure fabrication methods in section 1.2, respectively.

1.3.2 InGaN nanostructures

1.3.2.1 InGaN material properties

Indium gallium nitride (InGaN), as a new generation of compound semiconductor material, is mainly used in various optoelectronic devices as well as high temperature, high frequency and high-power electron devices [31]. Because of the intrinsic band-gap energy of 0.7 eV of InN and that of 3.4 eV of GaN, the band-gap energy of InGaN can be adjusted corresponding to a broad wavelength region of mainly visible light and potentially from UV (365 nm) to infrared (1770 nm) by tuning the In composition. This is the reason why this material of $\text{In}_{1-x}\text{Ga}_x\text{N}$ becomes a hot topic of research. In addition, InGaN has also other advantages, such as high thermal stability, non-toxic, strong resistance to chemical corrosion. The direct bandgap nature can realize high a light conversion efficiency based on an efficient electron-hole recombination rate. All of these properties are desirable for current and future optoelectric devices.

Although InGaN materials have so many advantages, it is still difficult to prepare InGaN quantum wells (QWs) with high optical quality, especially using high In-concentrations. This limits optical applications of the InGaN materials. First, there is a lack of suitable substrate that lattice structure matches well to the InGaN material for epitaxial processes. Usually a GaN substrate can be used, which lattice constant is the closest to that of InGaN. However, with higher In compositions, the lattice mismatch between the InGaN and GaN becomes larger, where that between InN and GaN can be as high as 11% [32]. When growing the hetero-epitaxial InGaN on a GaN substrate even other material substrates, lattice mismatch results in formation of large misfit dislocations, high-density defects, and roughness of the surface. Second, an equilibrium vapor pressure of InN is very high [33], leading to a lower decomposition temperature of InN. Therefore, InGaN with high In

compositions must be grown at low temperatures. Generally, lower growth temperatures inhibit sufficient migration of surface atoms [34], making it difficult to grow flat and high-quality InGaN QWs. Third, it is well known that the actual InGaN material becomes a mixture such as $\text{In}_x\text{Ga}_{1-x}\text{N}$ containing various In components due to marked phase separation, originating from the relatively large miscibility gap between the InN and GaN [35]. Finally, an intrinsic carrier concentration of the InGaN QWs can be limited up to $10^{17}\sim 10^{18} \text{ cm}^{-3}$ due to influences of nitrogen vacancies or other defects [36]. Therefore, it is difficult to fabricate a p-type layer with high hole concentrations, as well as low resistances.

1.3.2.2 InGaN nanostructure

Semiconductor QD-like nanostructures have nano-scale sizes less than several tens nanometers, which result in strong quantum confinement effects than other one-dimensional quantum wires or two-dimensional QWs. This enhanced quantum confinement is observed when the size of the nanostructure is enough small comparable to a wavelength of electron [37]. Furthermore, nanostructures with sufficiently small sizes may exhibit a wealth of unexpected properties: a quantum size effect, quantum tunneling, quantum interference effect, coulomb blockade, quantum confined stark effect, nonlinear optical effect and so on.

In this section, I focus on the suppression of defect formation as well as the quantum confinement effect relating to the quantum-confined Stark effect (QCSE) in InGaN nanostructures, compared with conventional QWs. In section 1.3.2.1, I have mentioned that the large lattice mismatch and the low miscibility lead to the interface roughness, composition fluctuations and defect formation between the GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ with high In compositions [38-40]. Combined with these influence factors, I can specifically explain the interface roughness and composition fluctuations leading to modified potential fluctuations in the InGaN QWs, as shown in figure 1.4. The amount of defects in an InGaN nanostructure active layer can be much less than those in the QW active layer because of significant strain relaxation in addition to the areal restriction. In the QW, electrons in a conduction band can be easily captured by defects which exist for example in the energy levels within the bandgap, which significantly degrade optical qualities such as an emission efficiency.

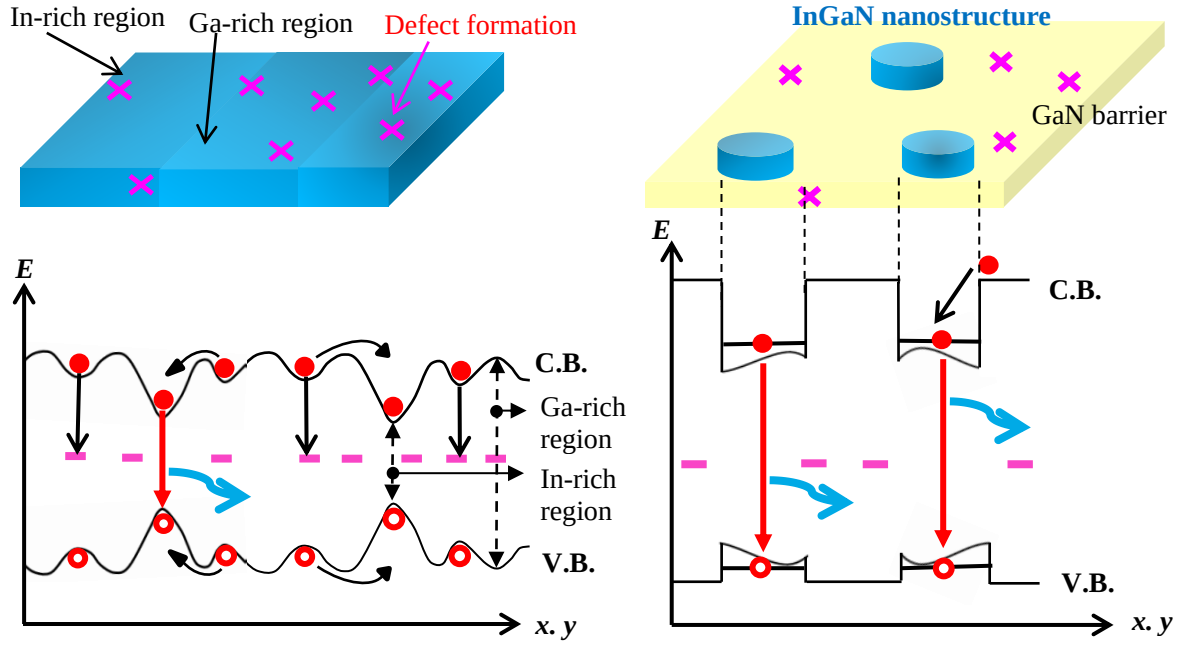


Figure 1.4| Sketch of the situation of the electron trapping due to a modified energy band diagram for a single QW (left) and nanostructures (right) taking defects and In concentration fluctuations into account.

In contrast, InGaN nanostructures result in higher internal quantum efficiencies (IQEs) due to strong quantum confinements and less defects, as well as suppressed piezo-electric fields than those in the QW. In a GaN bulk structure without strain, equivalent plus and minus charges can overlap completely leading to electric neutrality. As well known, if there is the large lattice mismatch between the QW and barriers, a strong strain will exist in the QW structure. Lattice constants of GaN ($a = 3.190 \text{ \AA}$, $c = 5.189 \text{ \AA}$) are quite different from those of InN ($a = 3.544 \text{ \AA}$, $c = 5.718 \text{ \AA}$) [41-45]. Hence, when the strain acts on the InGaN QW structure, equivalent plus and minus charges cannot overlap. This results in a built-in electric field called as a piezoelectric field, as shown in figure 1.5. In the ideal GaN crystal structure as shown in figure 1.5 (a), there is no strain and this situation makes overlapping of an equivalent plus charge (Ga^{3+}) and minus charge (N^{3-}). However, when the InGaN QW layer was grown on GaN barrier layers, there is transverse compressive stress and vertical tensile stress at the interface between the InGaN and GaN, because the lateral lattice constant of InGaN is larger than that of GaN. Hence, the equivalent plus charge of Ga^{3+} and minus charge of N^{3-} cannot overlap, which induces electric non-neutrality in the InGaN QW and the built-in electric field can be generated, as shown in figure 1.5 (b).

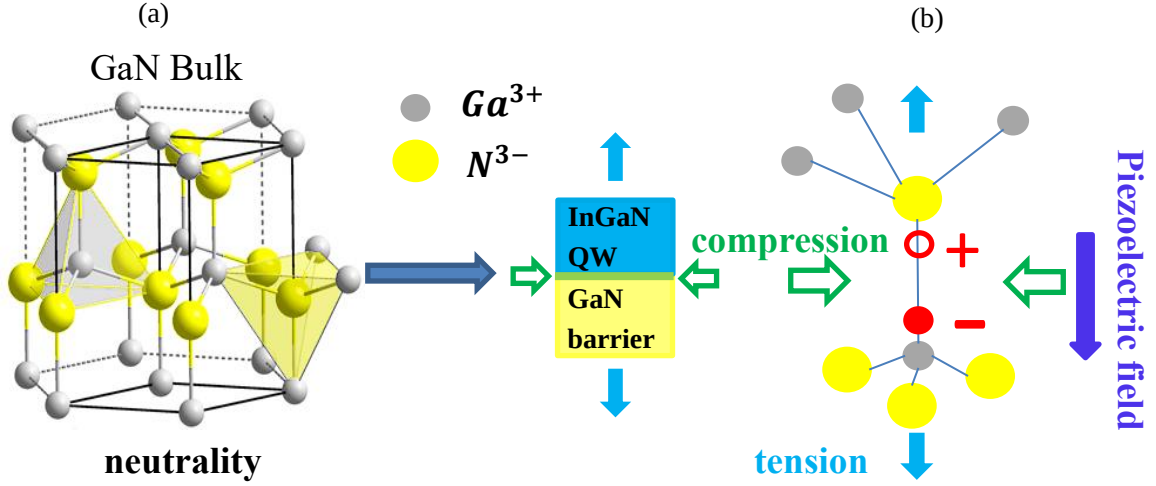


Figure 1.5| Illustration of generation mechanism of a piezoelectric field in the InGaN QW: (a) The ideal GaN crystal structure with no strain; (b) The crystal structure between the InGaN QW and GaN barriers with strain due to the lattice mismatch.

Then this strain-induced piezoelectric fields can significantly affect the band lineup across the well layer, which leads to the spatial displacement of carrier wave functions in the InGaN/GaN QWs, as schematically shown in figure 1.6 (a). A red shift of the emission spectrum and a significant reduction of the recombination efficiency will be induced. However, this interface strain can be relaxed by introducing free surfaces because of the large surface-to-volume ratios in the nanostructures. There can be almost no piezoelectric field which if the nanostructure is sufficiently small, which can lead to much higher overlapping of the carrier wave functions in the conduction band (an electron) and valence band (a hole), as shown in figure 1.6 (b). Moreover, QCSE inducing the red-shift of recombination energy and displacements of wave functions [46], can be suppressed when the strain is relaxed through the nanostructure formation or shielding the piezoelectric fields through carrier screening [47, 48]. In a smaller nanodisk, strain relaxation can be more efficient. As a result, the InGaN nanostructures become more applicable for miniaturized opto-electric devices including green LEDs than QWs.

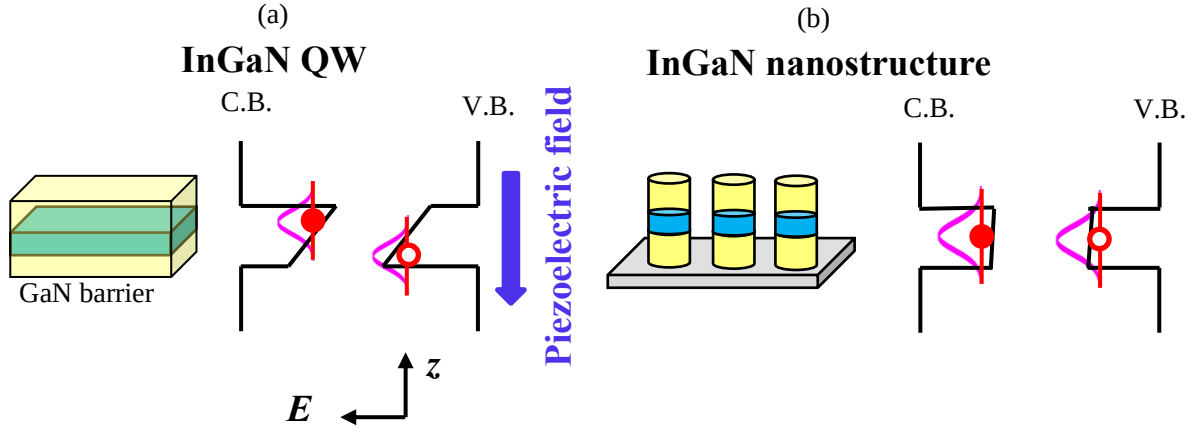


Figure 1.6 The potential modifications and the resultant wave-function displacements in (a) the InGaN QW and (b) the improvements of these problems in the InGaN nanostructure. The pink lines indicate schematic confined carrier wave functions.

1.3.2.3 Fabrication of InGaN nanostructure

At present, three main methods for making InGaN nanostructures are known: the SAG growth, self-assembled growth, and micro/nano lithography, which have been mentioned in section 1.2. Guangyu Liu et al. have fabricated a QD-like InGaN nanostructure with a density up to $8 \times 10^{10} \text{ cm}^{-2}$ and QD diameter of approximately 22-25 nm, applying a similar method indicated as figure 1.1 in section 1.2.1 [49]. Koichi Tachibana et al. also used the SAG method consisting of MOCVD and the photolithography to obtain InGaN QD at the tip of the pyramid-like structure [50]. In the literature [51] using a lithography method, Lei Zhang group prepared an InGaN/GaN QW structure and then fabricated an InGaN nanostructure with a diameter of 17 nm by using a pattern mask and reactive ion etching. For self-assembled growth, one usually utilized a GaN or Sapphire substrate and try to grow high-quality InGaN QDs. Satoru Tanaka et al. and Yang et al. developed a method inserting AlGaIn/AlIn layers to achieve the S-K growth of InGaN QDs on the m-plane GaN substrate [52, 53]. L.W.Ji et al. used an interrupted growth mode in MOCVD to fabricate self-assembled QDs with a typical lateral size of 25 nm, average height of 4.1 nm, and QD density of about $2 \times 10^{10} \text{ cm}^{-2}$ [54]. Saniya Deshpande et al. fabricated InGaN nanodisks in GaN nanowire hetero-structures on a silicon substrate by plasma-assisted MBE with the smallest diameter of about 20 nm but rather inhomogeneous [55].

In these literatures, InGaN nanostructures with relatively uniform size can be fabricated

by SAG and lithography methods, but those sizes of nanostructure are still not small enough. In addition, using self-assembled growth in MOCVD or MBE, it is still difficult to grow uniform nanostructures with high densities.

1.3.3 InGaAs nanostructures

1.3.3.1 InGaAs material properties

Compared with the InGaN material, Indium gallium arsenide (InGaAs) ternary alloys have already widely applied. They can be formed with rather flexible alloy compositions of InAs and GaAs with a sphalerite cubic crystal structure. When the In composition changes, its lattice constant varies from 5.6533 Å of GaAs to 6.0583 Å of InAs and its band-gap energy also changes from 1.43 eV to 0.35 eV [56], corresponding to the wavelength from 0.87 μm to 3.5 μm. In addition, In_{1-x}Ga_xAs materials have high mobilities and good anti-irradiation properties. Extremely high values of the electron mobility have been observed in a literature [57-59]. With these properties, InGaAs materials can be applied to miniature and highly reliable electronic and optical/photonic devices, such as a photodetector, laser diode, photovoltaics, a high-electron mobility transistor and so on.

The material fabrication technology of InGaAs has been sufficiently mature, including vapor phase epitaxy (VPE), liquid phase epitaxy (LPE), MOCVD, MBE, etc. to grow high-quality InGaAs epitaxial materials. Recently, high-quality InGaAs epitaxial structures, including QWs and self-assembled QDs, have been easily grown by MOCVD or MBE.

1.3.3.2 InGaAs nanostructure

In addition to all advantages of InGaN nanostructures, which have mentioned in the previous section 1.3.2.3, InGaAs nanostructures have some other important properties particularly on the research area of semiconductor spintronics: a study of the spin states of carriers and its associated magnetic moments. In InGaAs QD-based devices, the spintronics technology consists of the following three steps; generation and injection of spin-polarized carriers, storage of the spin state in QDs, and reading out of the spin states, as shown in figure 1.7. Inside the QD, the carrier momentum can be frozen by the strong three-

dimensional quantum confinements, resulting in suppression of carrier-spin relaxation [60-62]. Many phenomena relating to the spin dynamics, including the spin injection, spin-state filling (spin blocking due to Pauli's exclusive law), spin flip and spin relaxation, and so on, have been extensively observed using InGaAs QDs. In addition, the following three electron-spin relaxation mechanisms are well known: D'yakonov-Perel '(DP) mechanism [63, 64], Elliot-Yafet (EY) mechanism [65], and Bir-Aronov-Pikus (BAP) mechanism [66,67].

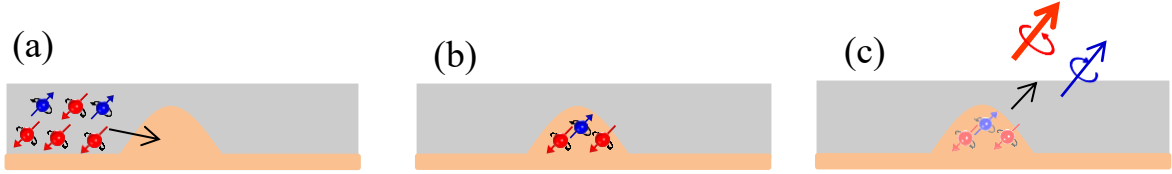


Figure 1.7 Sketch of an QD-based optical device using semiconductor spintronics, consisting of (a) generation and injection of spin-polarized electrons, (b) temporal conversion of the spin states in QDs, and (c) read-out of the spin states through spin-polarized recombination, which emits circularly polarized lights.

1.3.3.3 Fabrication of InGaAs nanostructure

According to the last section, I have tried to improve these spin-functional optical properties by means of varying the size, density, multiple layers, and integrating nano-scale lithography with the self-assembled QD growth. Position-controlled InGaAs nanowires (NWs) have been achieved by various SAG techniques [68-73]. InGaAs QDs also have been fabricated by selective area MOCVD growth early [74]. In addition, similar InGaAs nanostructure devices have been formed by lithography.

In recent years, many research groups focus to grow InGaAs QDs with an ultra-small size, ultra-high density, and sufficient uniformity by the self-assembled SK mode using MBE or MOCVD [75-80]. Novel lithography with nanospheres or bio-templates [81-83] have been proposed. Using the abovementioned InGaAs nanostructures with high controllability in size, shape, density, and multilayer stacking, one can expect to create high quality optical devices with spin functionalities.

1.4 Outline of this thesis

This thesis contains the following 6 chapters.

Chapter 1 explains mainly how to grow and fabricate semiconductor nanostructures, the defect formation that occurs during fabrication, and the advantages and disadvantages of these nanostructure properties. In addition, this Chapter 1 highlights the fabrication method of InGaN and InGaAs nanostructures, which is the subject of this research. Furthermore, the optical properties and electron spin properties of these nanostructures are explained.

Chapter 2 describes the purpose of this study, such as the importance of new optical and electron-spin properties which will be achieved by means of studying the fabrication and growth methods of the InGaN and InGaAs nanostructures.

Chapter 3 describes a process for creating a designable InGaN nanodisk using biotemplates suitable for fabrication of quantum-dot based optical active layers and neutral-beam etching that can sufficiently suppress in-process damages. Then, I will explain how to create a nano-pillar structure for a self-assembled InGaAs quantum-dot layer by lithography and dry etching using a nanosphere (polystyrene bead) mask. In addition, a brief overview of experimental techniques for structural characterizations and optical characterizations consisting of time-resolved photoluminescence (TRPL) measurements with and without circular polarizations.

Chapter 4 describes the carrier dynamics and related optical properties in designable $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ nanodisk structures, fabricated toward the final purpose of developing green LEDs. The time-resolved PL measurement results were quantitatively analyzed considering the non-uniformity in the emission decay characteristics. As a result, the carrier dynamics in the nanodisks are clarified, and the electron-hole recombination probability is significantly increased by sufficiently suppressing the piezoelectric fields generated in the mother InGaN QW layer. Furthermore, the thermal escape of the carrier from the nanodisks was clarified from the temperature-dependent PL characteristics. It is also revealed that the nanodisk fabrication process used in this study has sufficiently suppressed the defect formation that degrades optical properties.

In Chapter 5, I conclude the carrier dynamics and their spin states in InGaAs QDs embedded with GaAs nano-pillars. The circular polarization characteristics of the emission from the QDs directly reflect the electron-spin polarization contributing to luminescence recombination in the QDs. In conventional QDs, as a temperature rises, the degree of the

circular polarization of PL reduces due to relaxation of electron spin. However, the InGaAs QDs in this nano-pillar structures can show relatively high circular polarization degrees even at high temperatures. This mechanism will be explained based on the carrier and spin dynamics by TRPL measured.

Final Chapter 6 summarizes the results obtained in this study and introduces the prospects for the fabrication of designable nanostructures.

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Chapter 2 Research purpose

2.1 Final research target to study a designable nanofabrication process

In this research, I will try to develop nanostructure fabrication methods for III-V compound semiconductors, which can be designed by combining so-called bottom-up and top-down nanofabrication processes. By utilizing the designable nanostructure fabrication processes, InGaN nanodisks with a high In concentration and high controllability of uniform size and density were prepared in addition to excellent optical characteristics, which will be expected as a green-light-source material. Furthermore, hybrid nanostructures integrating self-assembled InGaAs quantum dots and nanofabrication processes demonstrated to maintain circularly polarized light emission characteristics reflecting electron spin polarizations at high temperatures. Therefore, I can expect that these nanostructures will be applied to future spin functional high efficiency optical devices.

2.2 Research purpose of InGaN nanostructures

To achieve high-performance green light-emitting LEDs, it is necessary to develop InGaN/GaN nanostructures with high optical qualities. By using bio-nano templates and neutral beam etching, $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ nanodisks with the size less than 10 nanometers were prepared. I clarify the optical characteristics by means of time-resolved PL. From the obtained optical properties, I study the carrier dynamics characteristic in this InGaN nanodisk. Specifically, radiative and non-radiative relaxation time constants, and the thermal activation energy obtained from the temperature dependence of the PL intensity and the decay time have been elucidated. From these carrier dynamics, I will discuss and clarify the useful optical performance of this InGaN nanodisk.

2.3 Research purpose of InGaAs QD-based nanostructures

In order to realize a nano-optical resonator aiming at coupling of light and electron spin states, hybrid nanostructures designed in the submicron region integrated with self-assembled InGaAs quantum dot layers are necessary. GaAs nano-pillar structures with embedded InGaAs QDs were fabricated by nanolithography using polystyrene beads of 300 nm down to 70 nm in size. I study the circularly polarized PL reflecting the electron-spin state and its temperature dependence, in these QDs embedded in the nano-pillars. I will discuss the spin dynamics from the obtained results and show their usefulness for future spin-functional optical devices.

Chapter 3 Experimental procedures

3.1 Fabrication of III-V group material nanostructure

3.1.1 Intruduction

In the section 1.2, I explain about semiconductor nanostructure growth methods. In addition, the current situation of nanostructure fabrication of III-V group compound semiconductor materials such as InGaN and InGaAs is also introduced in the section 1.3.2 and 1.3.3, respectively. Here, I describe in detail specific methods for the growth and fabrication of InGaN and InGaAs semiconductor nanostructures.

As previously mentioned, uniform InGaN nanostructures with the size less than 10 nm and high sheet densities cannot be achieved by the conventional SAG or self-assembled growth. Therefore, integration of bio-nano templates as bottom-up technology with neutral-beam etching was applied to fabricate uniform QD-like nanostructures called as nano-disks (NDs). Next, the well-established self-assembly growth of high-density InGaAs QDs was applied to form sub-micron or nano scale optical confinement, which can potentially enhance the optical coupling of electron spin states with light. A designable nanofabrication process with nanosphere lithography technique was used to such nano-pillar structures with optical active layers of the self-assembled InGaAs QDs.

3.1.2 Fabrication of $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ nano-disks structure

I have fabricated four types of sample, as follows; 2 nm- and 3 nm-thick single $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ ND layers, as well as the mother single $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ QW layers with the same 2 nm and 3 nm thicknesses as reference samples. First, $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ single QWs were grown on c-plane sapphire substrates by MOVPE, in which NH_3 , TEGa and TMIIn

were used as the precursors. Figure 3.1 shows a schematic drawing of the ND structure, compared with the initially grown mother QW structure. The QW structure was grown with a 1 μm -thick GaN buffer layer, followed by the growth of 2 nm- or 3 nm-thick $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ QW and a 10 nm-thick GaN capping layer, as shown in the figure 3.1.

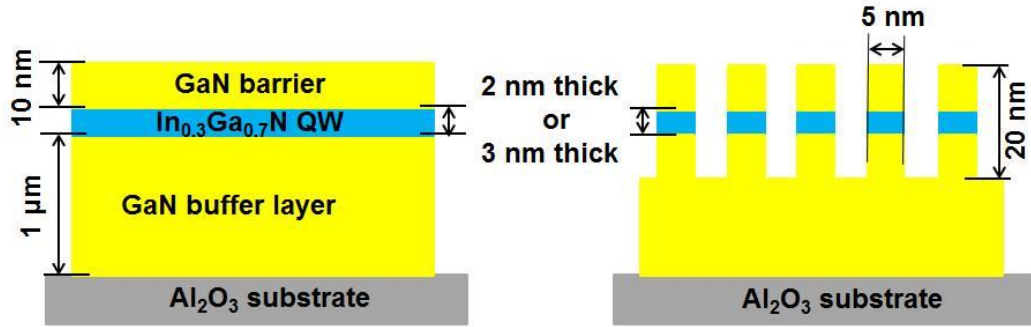


Figure 3.1 | Illustration of the cross-sectional sample structures of the mother $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ QW (left) and the NDs fabricated from the QW (right).

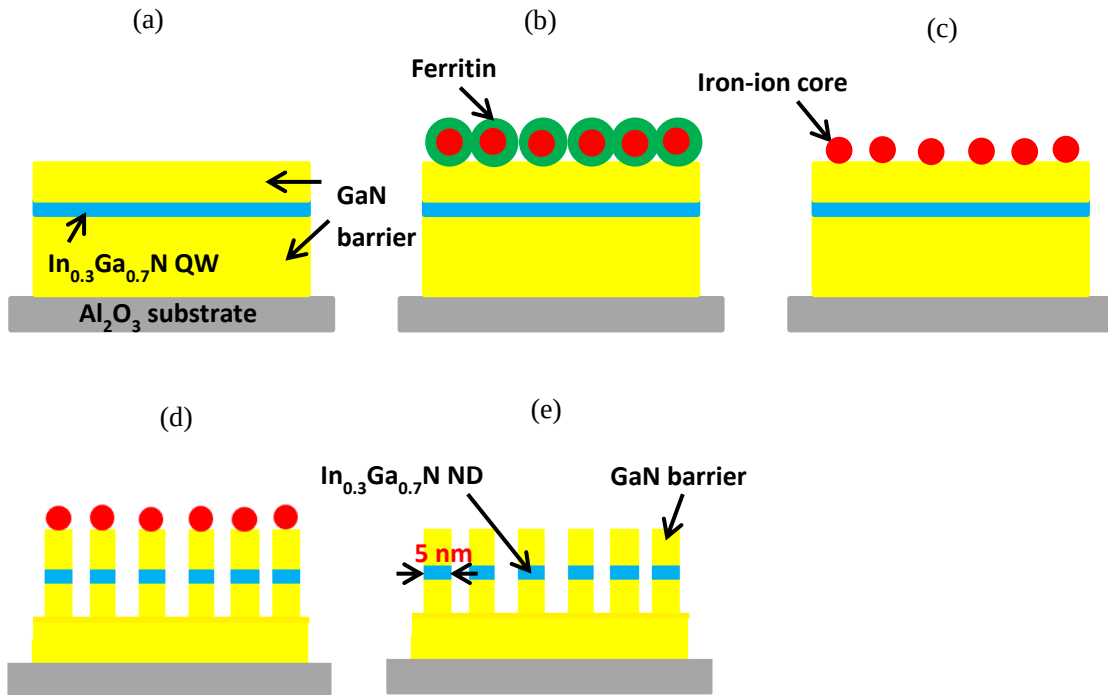


Figure 3.2 | Fabrication process of the InGaN NDs. (a) Starting sample of the mother QW, (b) Ferritin supramolecular arrangement as a bio-nano template containing Fe cores on the surface of GaN capping layer, (c) ashing treatment using oxygen and hydrogen radical cleaning to prepare the Fe cores as an etching mask, (d) ND formation processed by NBE, and (e) final Fe-core removal by wet etching.

At first, the InGaN QW sample was cleaned using organic treatment, followed by

deionized water in an ultrasonic bath to make the surface hydrophilic. The PEG-ferritin solution was dropped on the surface of the sample. Ferritin proteins (PEG-ferritins, as shown in figure 3.3) were amended with poly-ethylene glycol (PEG 2000, molecular weight: 2000 g/mol), where iron oxide cores were contained inside them [1]. After an incubation time of 4min, the solution was spin coated at 500 rpm for 2 s and at 3000 rpm for 30 s [2]. The 13 nm-diameter PEG ferritin was used to prepare the following etching mask. Oxygen annealing in vacuum was performed at 100 °C, with an oxygen flow rate of 100 sccm, and a chamber pressure of 35 Pa [2]. Then, 7 nm-diameter iron cores, as shown in Figure 2.2, were prepared on the surface and used as the etching mask, which can assure its molecule-level uniformity in both shape and size. And then, hydrogen radical treatment was performed to remove surface oxides at a chamber pressure of 55 Pa under 80 °C for 30 min [2]. After the H-radical treatment, the same flow condition was kept and the substrate temperature was reduced down to room temperature for 30 min to passivate the surface. Subsequently, the QW was etched completely to form NDs using 40 sccm Cl₂ at a chamber pressure of 0.1 Pa under 100 °C by means of neutral-beam etching using an inductive coupled plasma power of 500 W and a bias power of 10 W for 3 min [2]. As a result, InGaN NDs with around 5 nm diameter and 20 nm height could be etched. At last, hydrochloric acid solution was used to remove Fe cores before measuring the photoluminescence (PL).

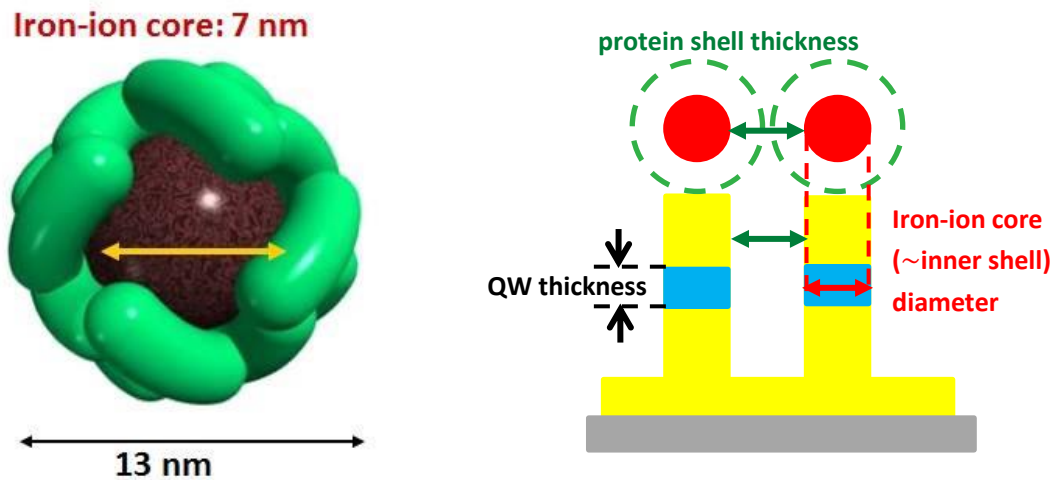


Figure 3.3| Illustration of the ferritin supra-molecule containing an Fe core, and possible design of the ND structure using the bio-nano template (right).

3.1.3 Fabrication of In_{0.5}Ga_{0.5}As quantum dots embedded in GaAs nanopillars

First, the In_{0.5}Ga_{0.5}As/GaAs single QD layer sample was grown by molecular beam epitaxy (MBE). A 400-nm-thick GaAs buffer layer was grown on a (100) GaAs structure at 580 °C. Then, the substrate temperature was decreased to 500 °C for the self-assembled growth of the In_{0.5}Ga_{0.5}As-QD layer with a nominal thickness of 2.3 nm. Finally, the QD-layer was capped by a 40-nm-thick GaAs layer at an elevated temperature to 580 °C. An image of atomic force microscopy (AFM) reveals a QD areal density of $9 \times 10^{10} \text{ cm}^{-2}$. This as-grown InGaAs QD sample was subsequently used to fabricate the columnar GaAs array nano-pillar structures as well as a reference sample.

The nanofabrication process for the nano-pillar structure, as shown in figure 3.4, was employed using polystyrene beads with specific sizes followed by reactive ion etching (RIE). After cleaning the sample surface, a two-dimensional monolayer polystyrene (PSt) beads of 350 nm or 200 nm in diameter (from Polysciences Inc.) were spread on the sample surface, which were used as a nanosphere lithography mask. The detail of the nanosphere lithography is described in the previous reports [3,4]. The polystyrene beads were subsequently etched by ICP-RIE (ELIONIX, EIS-700) to tailor the size of the beads with 30 sccm of oxygen at a radio frequency (RF) power of 100 W with diverse etching times of 7 min for the 350 nm PSt and 4, 6 min for the 200 nm PSt, respectively. The diameters of polystyrene beads decreased as 300, 165, and 130 nm after this etching using oxygen, as shown in figure 3.5(a), (b), and (c). And then ICP-RIE with BCl₃ was applied to fabricate the nanopillar array samples, and the etching time was set at 30 sec for the 300 nm PSt and 13 sec for the 165, 130 nm PSt. At last, the substrates were soaked ultrasonically in Tetrahydrofuran to completely remove the residual beads. A set of three samples with different average GaAs nanopillar diameters were prepared, i.e., $d_{\text{nanopillar}} = 300, 165, \text{ and } 70 \text{ nm}$, as shown in figure 3.5(d), (e), and (f). The sample morphologies were studied by utilizing field emission scanning electron microscopy (FE-SEM; Hitachi S-4800).

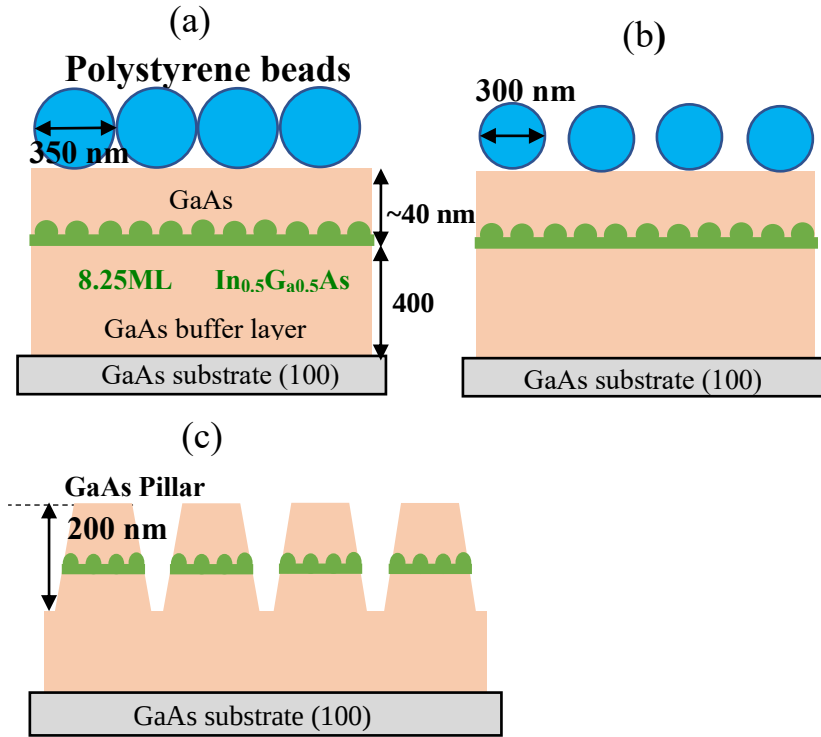


Figure 3.4| Fabrication process of the GaAs nano-pillar containing the single self-assembled QD layer; (a) Polystyrene-beads arrangement on the surface of GaAs, (b) Reactive ion etching using O_2 , (c) Reactive ion etching using BCl_3 and a final form after removing the polystyrene beads.

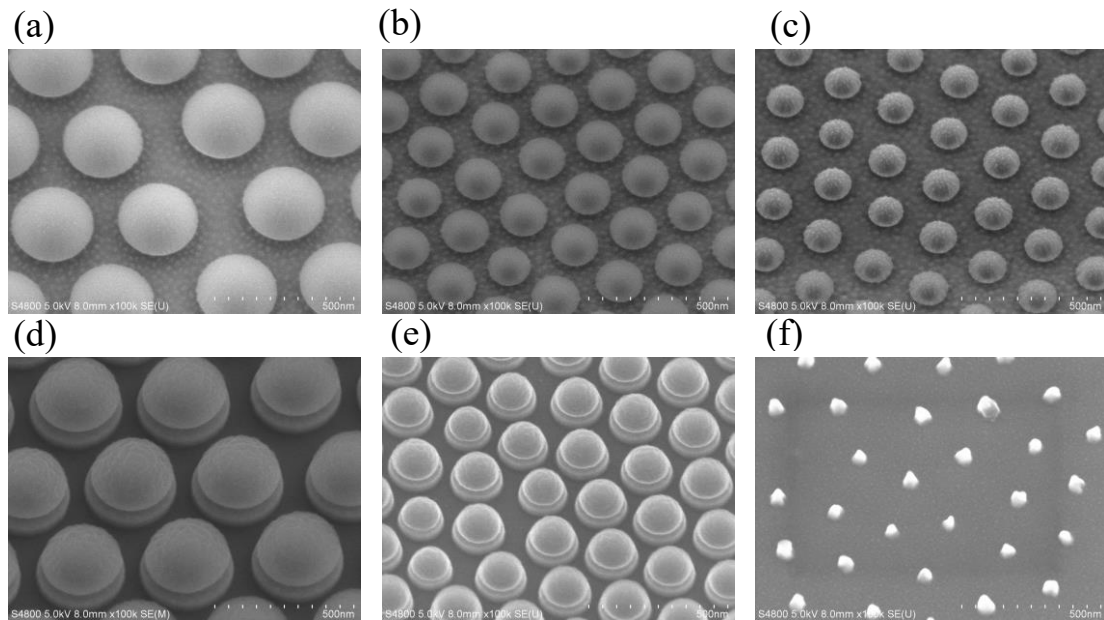


Figure 3.5| (a) Tilted-view SEM images for three samples after reactive ion etching using O_2 with polystyrene (PSt) beads of (a) 300, (b) 165, and (c) 130 nm diameters, which can form different diameters of (d) 300, (e) 165, and (f) 70 nm GaAs nano-pillars after reactive ion etching using BCl_3 .

As is seen in figure 3.5(c), the surface roughness of PSt beads increased with increasing etching time. After that, BCl_3 RIE continues to etch PSt beads and GaAs barriers at the same time, resulting in a non-ideal cylindrical GaAs nano-pillar shape with a smaller diameter, as shown in Figure 3.5 (f). Therefore, the optical and electron-spin related performances of the 70 nm-diameter nano-pillar sample are not good as other two 300 nm and 165 nm nano-pillar samples.

3.2 Measurement technique

3.2.1 Intruduction

After the fabrication of $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ NDs and $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ QDs embedded in GaAs nano-pillars in the chapter 3, this chapter gives a brief overview of experimental techniques for structural and optical characterizations. For structural characterization, the sample morphologies were observed by a scanning electron microscope (SEM), atomic force microscope (AFM), and transmission electron microscope (TEM). In this thesis, I just show SEM images in section 3.2.2.1 and AFM ones in section 3.2.2.2 to confirm the nanostructures after the fabrication processes. For optical characterization, I used time-resolved photoluminescence (TRPL), circularly polarized TRPL, and micro PL, depending on purposes of the measurement such as optical quality evaluation, the carrier dynamics, and the spin dynamics.

3.2.2 Structural characterization

3.2.2.1 Scanning electron microscopy (SEM)

SEM is commonly used to characterize from micro- down to nano-scale structures. The spatial resolution of SEM is significantly high as compared to a state-of-the-art

optical microscope [5]. The high vacuum inside the SEM equipment is important to reduce unwanted collisions between electrons and air molecules, extend the life of the electron source, and prevent discharge during observation. Depending on the acceleration voltage and the atomic density of the sample, the electron beam penetrates from the sample surface to different depths. For example, a high voltage (low density) increases the penetration depth. The excited electron beam interacts elastically and inelastically with the sample atoms, generating primary electrons (such as backscattering) and secondary electrons (such as secondary and Auger electrons), respectively. These electrons are backscattered (backscattered electrons) toward the electron source direction and detected by a detector placed above the sample surface. The electron scattering probability increases with the atomic number. Therefore, information about the composition of the sample (atomic number contrast) is also included. Secondary electrons usually contain information emitted from a depth of tens of nanometers. In this research, a Hitachi S-4800 system was used, providing a spatial resolution on the order of ~ 1 nm at 15 kV of acceleration voltage. The objective lens is semi-in-lens type and the electron gun is field emission type.

3.2.2.2 Atomic force microscopy (AFM)

One kind of scanning probe microscopes; AFM can observe the 3-dimensional surface topography by means of detecting the attractive and repulsive forces between the probe and sample surface. The lateral resolution of AFM is not so high, but the vertical resolution is very high and can reach to a scale of sub-angstrom. In order to acquire a structural image, the vertical and lateral deflection of the cantilever is optically detected. The beam is reflected from the back of the cantilever, which applied to drive the cantilever along a z-axis normal to a sample surface using a piezo device. As a result, the system can read quite small displacements in the z direction. In AFM, we often use two operation modes: “contact mode” and “tapping mode”, originating from Bruker Nano Surfaces. “Contact mode” has a raster-scanning probe while

monitoring a change in the cantilever deflection with a split photodiode detector. A constant cantilever deflection and a constant photodetector difference signal can be maintained by a feedback loop. The computer stores the distance that the scanner moves vertically at each x-y data point, forming a topographic image of the sample surface. This feedback loop maintains a constant force during imaging. "Tapping mode" uses a resonant cantilever at its resonant frequency and taps the tip of the surface during scanning. The root mean square (RMS) amplitude of the cantilever oscillation is detected by the laser. The feedback loop moves the scanner vertically at every x-y data point to maintain a constant vibration amplitude. Terrain images can be obtained by recording this movement of the scanner. Tapping mode eliminates the transverse shear forces present in contact mode. This is why the tapping mode is superior to the contact mode. This makes the tapping mode image soft, fragile, and bonded without damaging it. In this thesis, I used SEIKO SPI-3800 AFM to obtain topological images of the area of interest in the QD structure.

3.2.3 Optical characterization

3.2.3.1 Time Resolved Photoluminescence measurement

TRPL is a direct method for observing emission spectra from a sample and its time dependences. First, the sample is irradiated with a femtosecond laser pulse to generate electron-hole pairs. These photo-generated electron-hole pairs recombine and emit light with a wavelength corresponding to the transition energy. Therefore, TRPL measurement provides a way to measure the transition energy and a time constant of the recombination in a semiconductor sample. The resulting emission decay time reflects the recombination probability dynamics. The decay time is typically on the order of picoseconds or nanoseconds, and a streak camera can be used to observe weak emissions from the nanostructure. A schematic of the experimental set-up is shown in Fig. 3.6. The streak camera (Hamamatsu photonics, time resolution of ~ 15 ps)

combined with a monochromator (Hamamatsu photonics imaging spectrograph C5094) were used. The streak camera is an ultra-high-speed detector which captures light emission phenomena occurring in extremely short time periods [6]. To perform TRPL experiments, a sample under investigation is mounted on a cold finger in a vacuum cell of a closed cycle helium cryostat, which can cool the sample down to 6 K. Laser light excitation was made by a Ti:Sapphire pump laser with a wavelength of 800 nm. A pulse width of 0.2 ps with a repetition rate of 80 MHz was achieved by the mode-locked pulsed laser. During 3rd-harmonic frequency multiplier processing, our required laser light was generated, which wavelength of 266 nm was sufficiently above the band-gap energy of GaN barrier. Using a beam splitter and a photodiode, a small fraction of the laser light pulse is detected to high frequency. The electrical output of the photodiode triggers the streak camera. After proper neutral-density filters, PL was then collected by lens and sent to an entrance slit of the imaging spectrograph, directly connected with the input optics of the streak camera. At last, photon cloud picture image indicating the time response of the PL spectra was shown on a computer, as shown in figure 3.7. The horizontal axis means the PL wavelength. The vertical axis is as a function of PL response time after pulsed excitation on the order of picosecond or nanosecond.

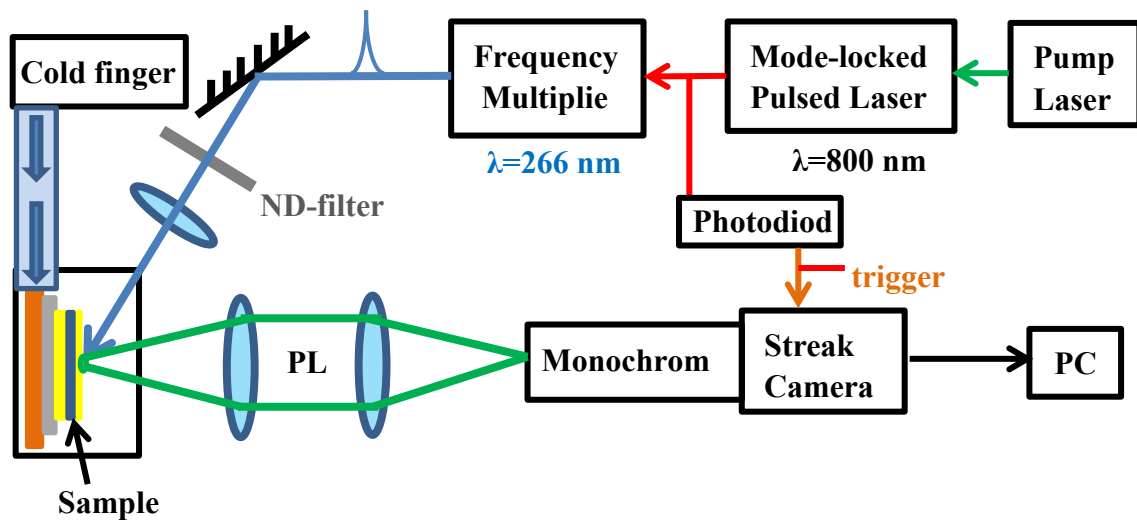


Figure 3.6| Schematic block diagram of the TRPL measurement system.

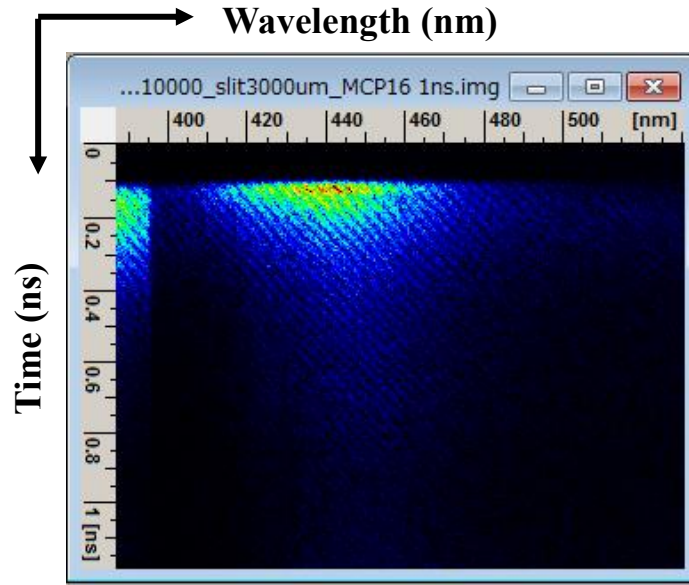


Figure 3.7 | A typical streak image of the TRPL observation.

I commonly need optical properties from the following two aspects; the excitation power dependence and temperature dependence to analyze the dynamics of photo-excited carriers in nanostructural samples. ND-filters can adjust a power of excitation laser light, for example, from 0.14 mW $\sim$ 2 mW for InGaN ND samples and 0.1 mW $\sim$ 10 mW for InGaAs QD samples at 6 K. The sample temperature was varied from 6 K to 300 K.

3.2.3.2 Circularly polarized Time Resolved Photoluminescence measurement

Circularly polarized TRPL was observed to measure time-dependent circular polarization properties of PL, which gave information about the electron-spin states depending on time after photo-excitation [7]. Based on the previous TRPL set up, some facilities were added to observe this circularly polarized TRPL: a linear polarizer and $\lambda/4$ plate to generate and detect the circularly polarized excitation light and PL with right-handed (σ^+) and left-handed (σ^-) polarizations, as shown in figure 3.8.

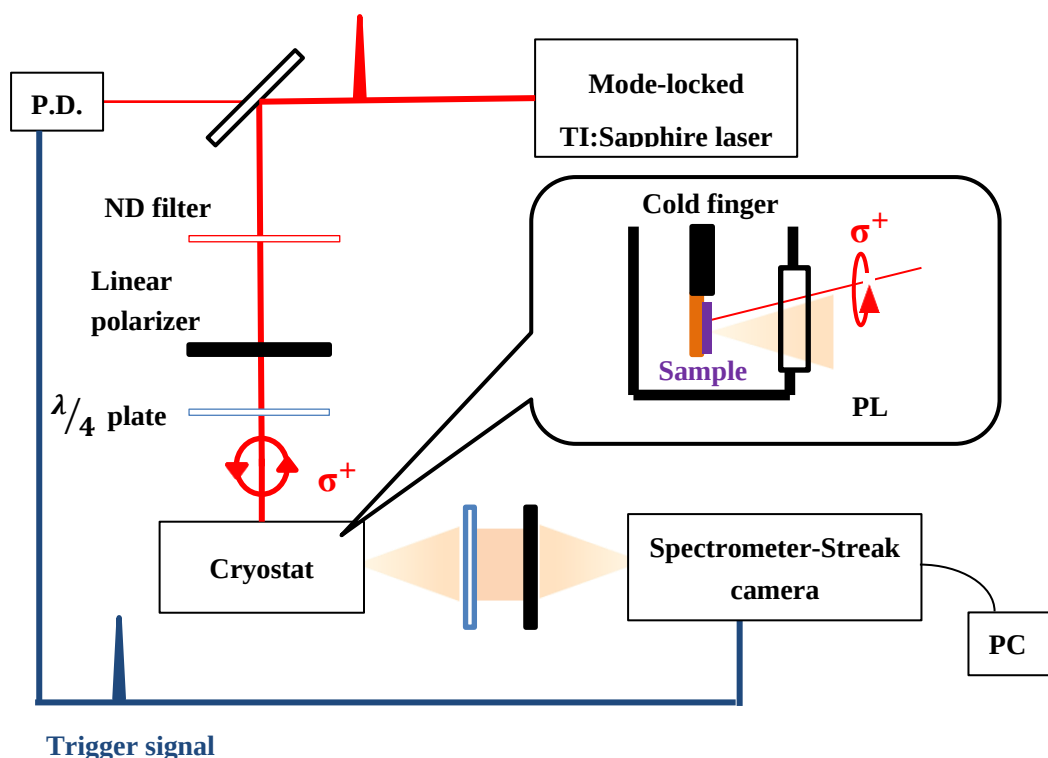


Figure 3.8 | Schematic of the circularly polarized TRPL measurement system.

The $\lambda/4$ plate is a birefringent crystal that can convert linearly polarized light into circularly polarized light or vice versa. Normally, a light can be divided into x and y component plane waves that are orthogonal to each other, but the refractive index and speed of the light differ depending on the vibration direction of the x and y components when the laser beam passes through birefringence. As a result, there is a

phase difference between the x and y component waves that are orthogonal to each other. The $\lambda/4$ plate is made so that the phase difference of $\lambda/2$ can be obtained by adjusting the crystal thickness. In the case of linearly polarized light, there is no phase difference when the light is split into x and y component waves, but the phase difference of circularly polarized light is $\lambda/2$. Therefore, conversion between linear and circular polarization can be performed by passing through a $\lambda/4$ plate. In this measurement, the combination of linear polarizer and $\lambda/4$ plate determines the circular polarization, as shown in figure 3.9.

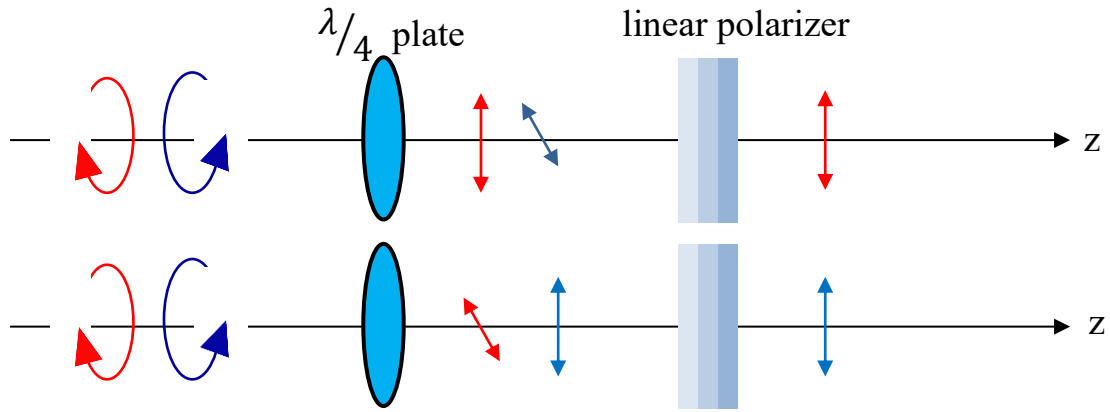


Figure 3.9| Schematic of the selective transmission of σ^+ and σ^- polarized lights by using the combination of a linear polarizer and $\lambda/4$ plate with different operation angles.

Subsequently, the circularly polarized light converted by the $\lambda/4$ plate excites the sample to generate spin-polarized carriers, in which spins, containing up spin and down spin components, are angular momenta equivalent to the rotation of a sphere electron, established in 1928 by Paul Adrian Maurice Dirac. When this σ^+ circularly polarized light excitation was performed on GaAs. Spin-polarized carriers can be generated with a ratio of down spin: up spin= 3:1, following the optical selection rules [8] as shown in figure 3.10. $\text{HH} \downarrow$ and $\text{LH} \downarrow$ are a heavy hole and light hole with down spin (angular momentum) in the valence band, respectively. m_j is the projection of the total angular momentum: J onto the $+z$ -axis. When the angular momentum is 1 and circularly polarized light excitation is σ^+ , carriers are generated as the angular momentum conservation law from $\text{HH} \downarrow$ to $\text{CB} \downarrow$ and from $\text{LH} \downarrow$ to $\text{CB} \uparrow$, which

generates the number ratio of the up : down spins = 1/3: 1 = 1: 3.

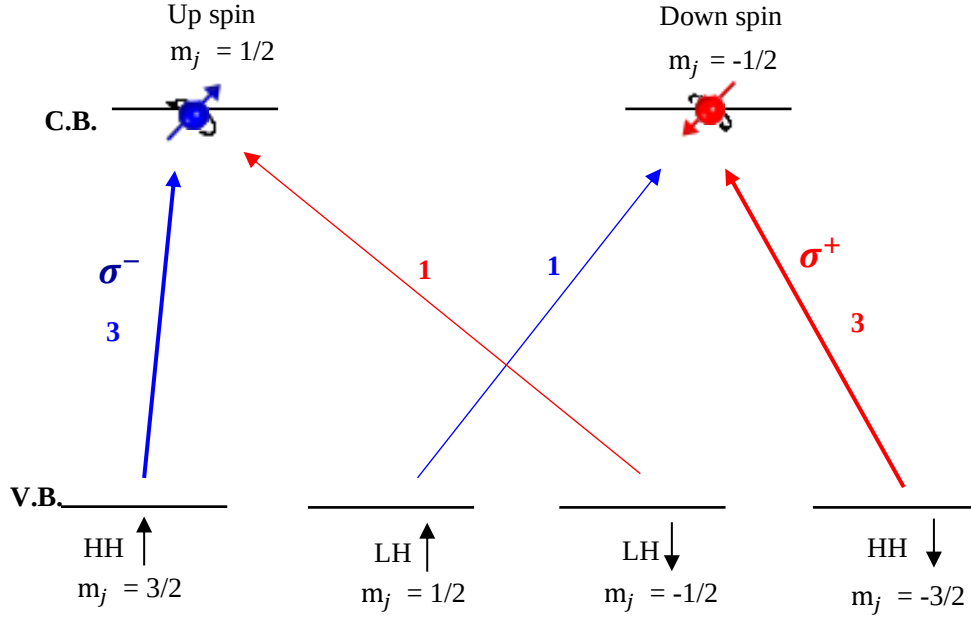


Figure 3.10 Schematic diagram of the optical selection rules in circularly polarized light excitation.

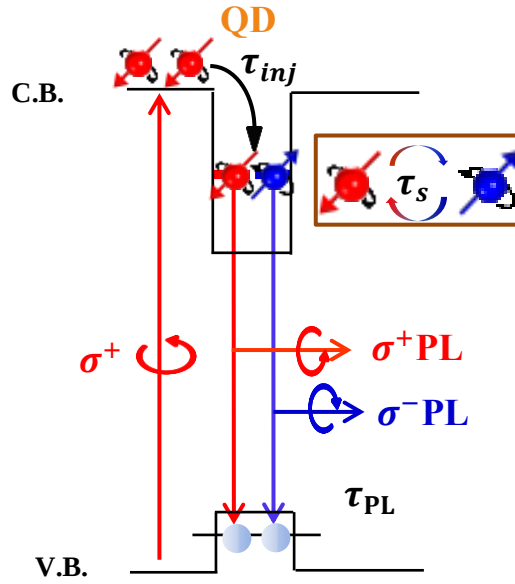


Figure 3.11 Diagram of the rate equation model in a InGaAs/GaAs QD structure with the spin dynamics.

After generation of the spin-polarized carriers in a GaAs barrier, these carriers are injected into InGaAs QDs and then the recombination of electron and hole with up/down spins emit circularly polarized light, following a rate equation as shown in figure 3.11. The rate equation is a differential equation that expresses how many number

density at a level generally increases or decreases per unit time, decided by time constant of spin injection (τ_{inj}), decay time of PL (τ_{PL}), time constant of spin relaxation mechanism (τ_s) and so on. In this study, this rate equation is used to analyze the temporal change of observed carrier emission with spin information.

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Chapter 4 Carrier dynamics of In_{0.3}Ga_{0.7}N nano-disks structure

4.1 Introduction

As introduced in the section 1.3.2, the quantum confinement and piezoelectric effect can influence optical qualities in semiconductor nanostructures. After the sample preparations, time-resolved photoluminescence (TRPL) measurements described in the section 3.2.2 have been performed; excitation-power and temperature dependences, which indicates situations of radiative and non-radiative processes in the carrier dynamics as well as thermal PL quenching mechanism. To take full advantage of the high optical performance of future LEDs and lasers, it is necessary to analyze the transient PL as a function of temperature and understand the dynamics of photo-excited carriers in the InGaN nano-disks (NDs) compared to the mother quantum well (QW). In the ND samples, a lateral averaged diameter of the ND was controlled to be down to 5 nm with an extremely high sheet-density up to $2 \times 10^{11} \text{ cm}^{-2}$. Figure 4.1 shows an SEM images of the nano-pillar structure containing InGaN/GaN NDs (embedded in the nano-pillars). The calculated density is $2.1 \times 10^{11} \text{ cm}^{-2}$. This shows good etching selectivity between the core and the substrate because the density value does not change. The size distribution curve of the nano-pillar diameter based on the SEM image conforms to the Gaussian distribution. This diameter is centered around $10.5 \pm 1.4 \text{ nm}$, demonstrating good process suitability.

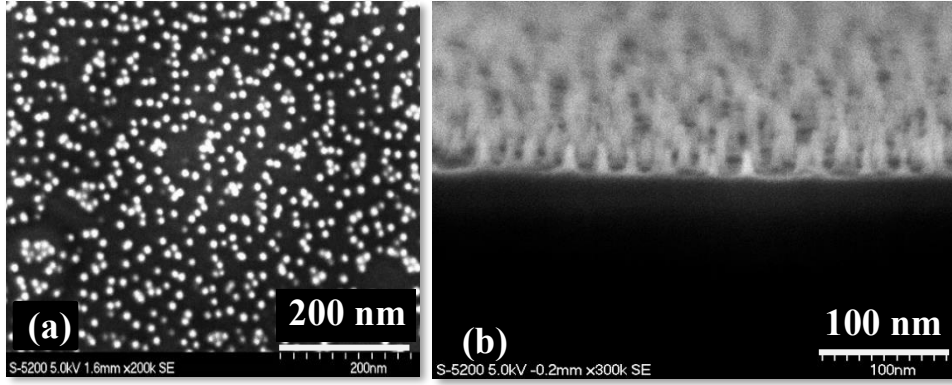


Figure 4.1 | SEM images of as-etched InGaN/GaN nano-pillars. (a) Top view after etching, and the (b) tilted view. [1]

4.2 Excitation-power dependence

During TRPL measurements, clear and bright PL emissions were maintained on these samples at 6 K. The PL peak position from the mother QW sample and NDs were obtained at 2.51 and 2.90 eV, respectively, as shown in figure 4.2. The peak of the ND PL signal blue-shifts about 0.4 eV with respect to the reference QW. I explain that this apparent blue shift of the ND PL peak energy is owing to strong suppression of quantum stark effect (QCSE) in addition to strong lateral confinement.

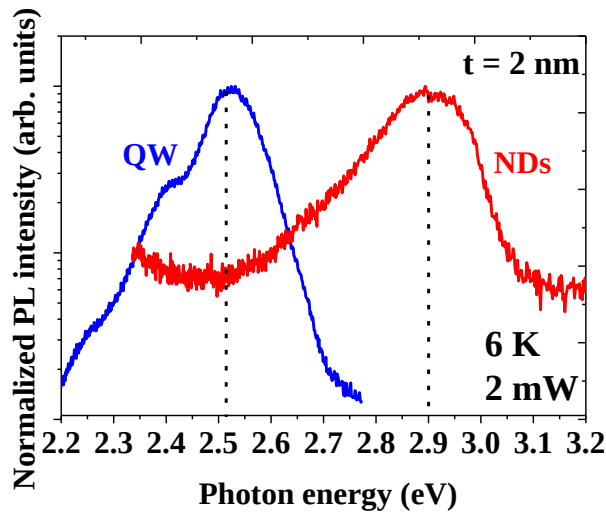


Figure 4.2 | PL spectra of the fabricated InGaN/GaN NDs (red line) and the mother QW (blue line) at 6 K.

Moreover, Yi-Chun Lai et al. solved the corresponding 3D Schrödinger equation with the finite difference method [1]. The estimated values of the transition energy, E_{SQW} e1-hh1 between the ground states of the electron e1 and heavy hole hh1 in the fully strained $In_{0.3}Ga_{0.7}N$ single layer QW was 2.47 eV at 6 K [2,3]. This indicates that the quantum energy level for the hh1 in the QW fields with high-Indium-content InGaN fields are localized at the tip of the band edge of the valence band, as shown in figure 4.3 (a). This is due to strong internal electrical fields caused by their piezoelectricity. On the other hand, the transition energy E_{ND} e1-hh1 in the strained InGaN ND was 2.93 eV. These values are in good agreement with the experimental results. In the InGaN ND conduction band, as shown in figure 4.3 (b), a large quantum energy shift for hh1 in the valence band of the InGaN ND occurs due to strain relaxation and significant reduction of the QCSE within the ND structure. Moreover, it is considered that the measured blueshift of the ND PL comes mainly from strain relaxation rather than quantum confinement, because the slope of the InGaN ND became flatter in the conduction and valence bands. This kind of PL blueshift as the signature of the reduction of the QCSE has been reported in the literature [4], although its degree of blueshift and confinement are different since the diameter of these reported InGaN NDs is much larger than that in the present study.

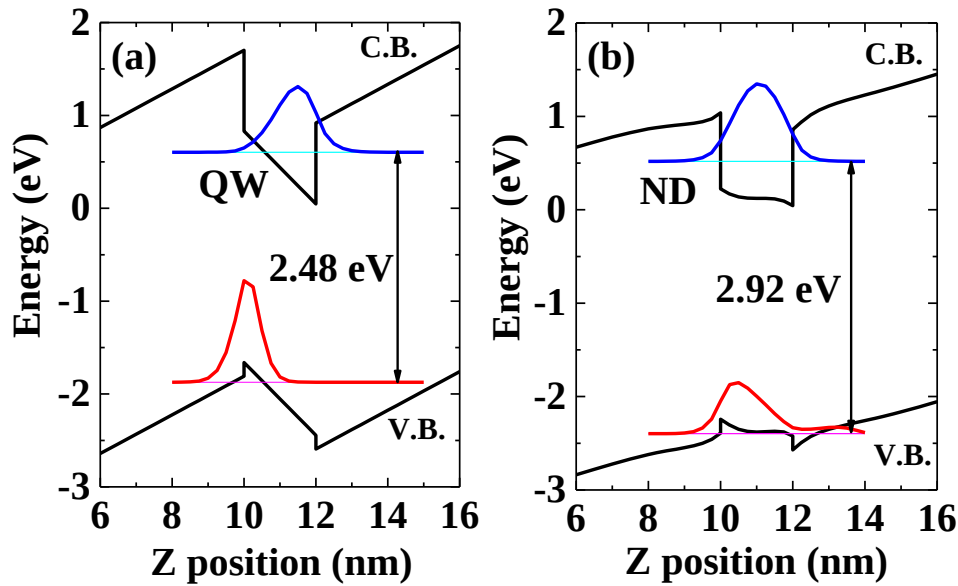


Figure 4.3 Simulated band line-ups (black lines) and the resultant carrier wave functions (electron: blue line and hole: red line) of the strained QW (a) and ND (b) [1] taking the realistic structural parameters obtained by SEM images.

In the excitation power dependence, figure 4.4 shows PL spectra of $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ for four samples with various excitation powers of Laser. The PL peak position from 3-nm-thick QW, 3-nm-thick NDs, 2-nm-thick QW and 2-nm-thick NDs samples were obtained at 520 nm, 435 nm, 490 nm and 427 nm, respectively. And PL intensities of QW samples are about one order larger than that of NDs samples, where the total QD volumes are much smaller than those of the 2-dimensional QWs. The PL intensity as a function of excitation power is plotted in figure 4.5. The PL intensity of 2 nm-thick QW is larger than that of 3 nm QW because of weakened piezo-electric field due to quantum effect. However, the PL intensity of 2 nm-thick ND is less than that of 3 nm ND because of almost no piezo-electric field affecting on the ND and the smaller active emission volume with the same diameter but different thickness.

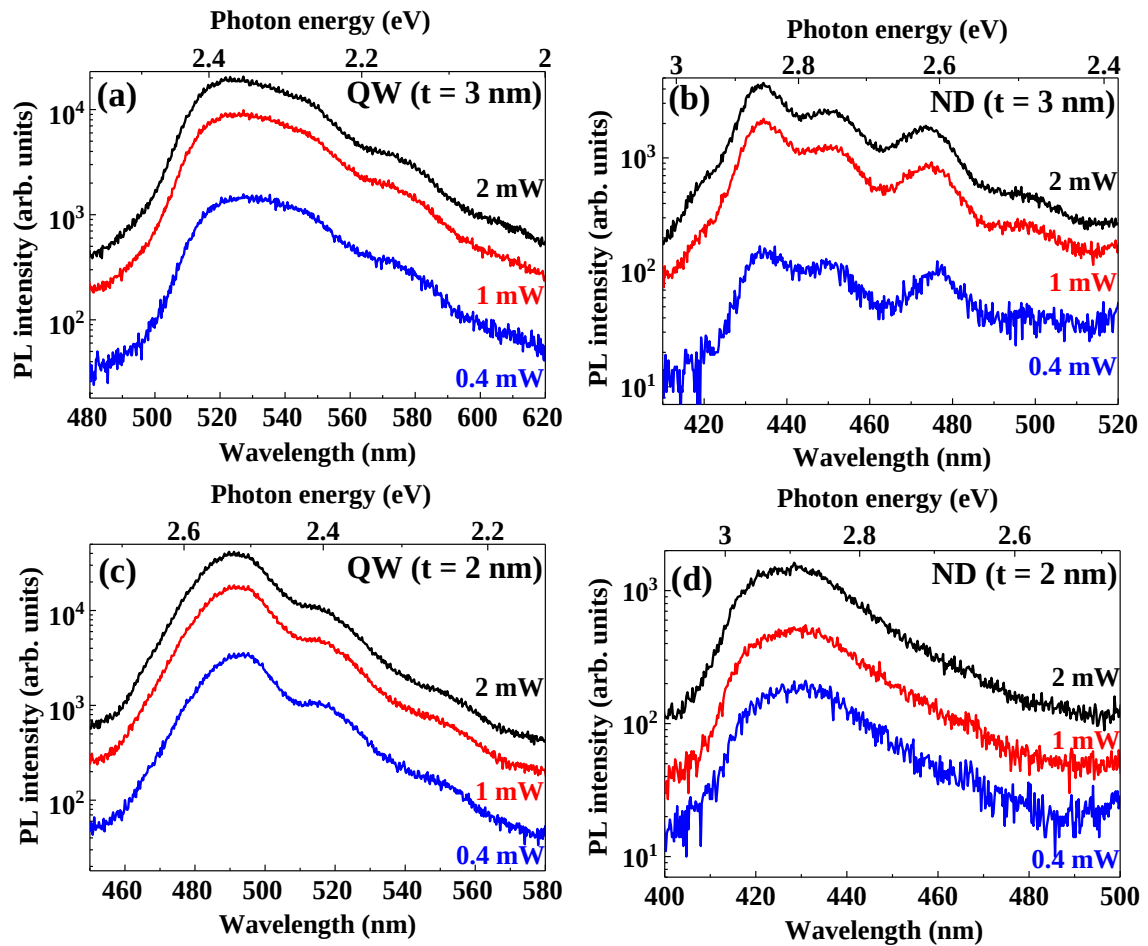


Figure 4.4| PL spectra of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ (a) 3-nm-thick QW, (b) 3-nm-thick NDs, (c) 2-nm-thick QW, and (d) 2-nm-thick NDs with various excitation powers.

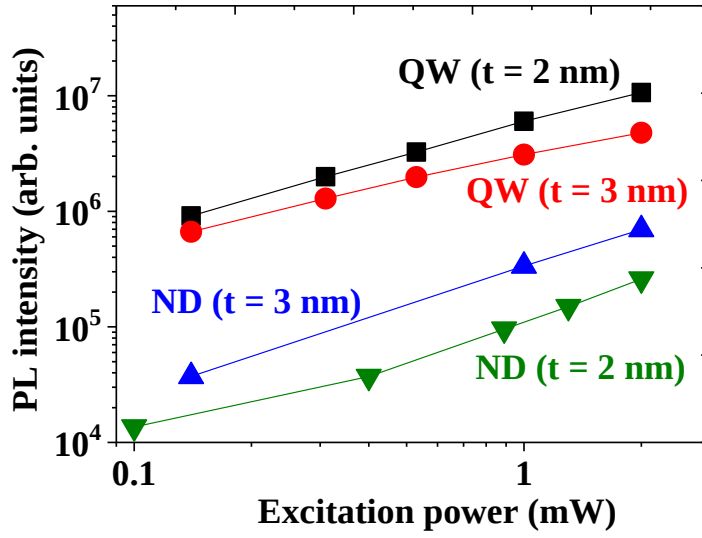


Figure 4.5| PL intensities as a function of excitation power for the 4 types of $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ sample.

4.3 Temperature dependence

4.3.1 Radiative and nonradiative processes

Figure 4.6 shows PL spectra of four types of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ samples with various temperatures. Typical TRPL time profiles for these samples are shown in figure 4.7. The PL decay times in the NDs are shorter than those of the mother QWs. This phenomenon can be understood that the ND-PL decay times reflect an oscillator strength depending on spatial overlapping of the electron and hole wave functions, in addition to PL quenching by non-radiative recombination centers. The PL kinetics are non-exponential and clearly dependent on temperature. This non-exponential PL time response curve is known to be described by a stretched exponential,

$$I(t) = I_0 \exp \left[- \left(\frac{t}{\tau_{PL}} \right)^\beta \right] \quad (4.1)$$

where β is a stretching parameter between 0 and 1. $I(t)$ is a PL intensity as a function of time and I_0 is the peak intensity. τ_{PL} is a decay time (exciton lifetime). This

stretched exponential function has been frequently used to describe the dynamics of heavily disordered time-response systems for over 100 years [5, 6]. The first observation of stretched exponential PL decay in a disordered semiconductor was made by X. Chen et al [7]. The TRPL from porous silicon has been also well known to be described by this stretched exponential. The underlying physical mechanism of the PL time responses of the porous silicon are known to be a combination of topological disorder and distribution of traps with different energies [8, 9]. Nano-scale composition fluctuations of the indium concentration can produce formation of the disorder time-responses as well as re-combination energies in InGaN. It is interesting to note that simulations for the porous silicon demonstrated that PL from excitons and un-correlated electrons or holes yield the characteristic stretched exponential decays [10].

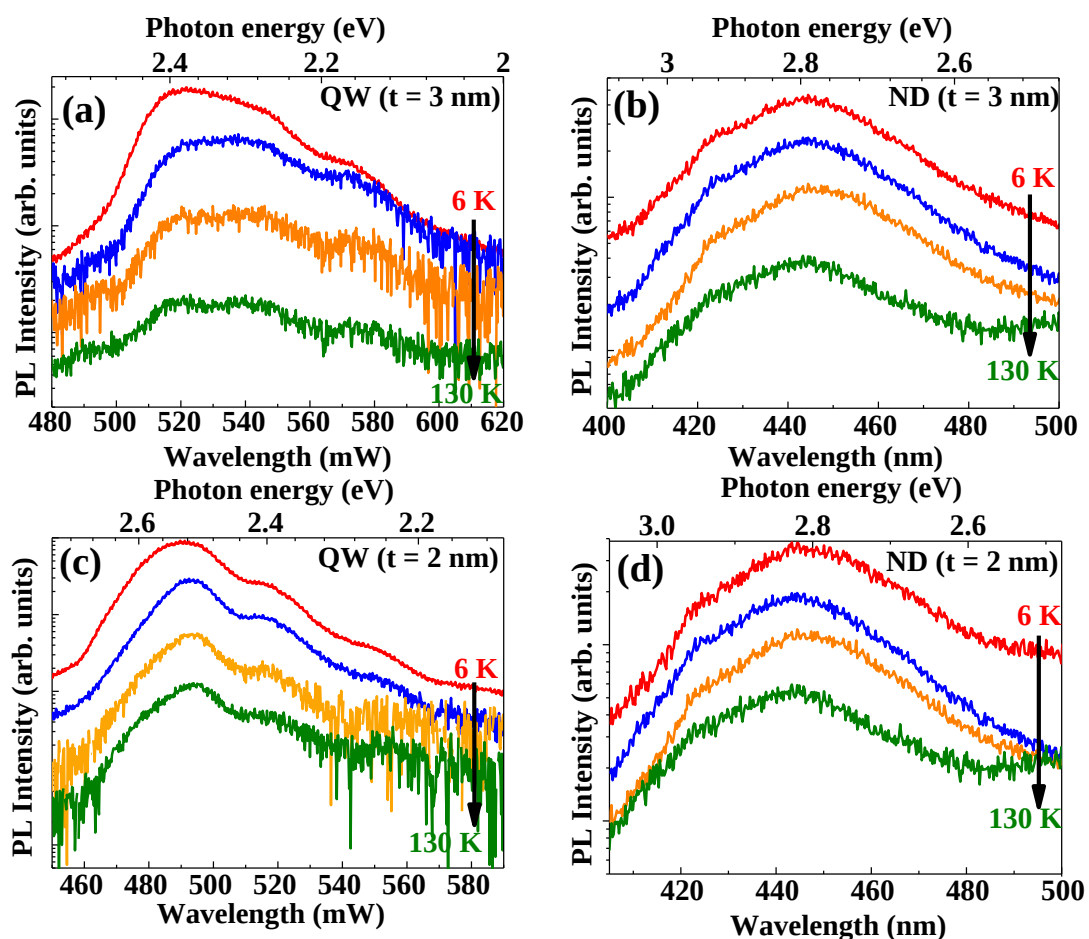


Figure 4.6 PL spectra of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ (a) 3-nm-thick QW, (b) 3-nm-thick NDs, (c) 2-nm-thick QW, and (d) 2-nm-thick NDs with various temperatures: 6 K (red line), 50 K (blue line), 90 K (orange line), and 130 K (green line).

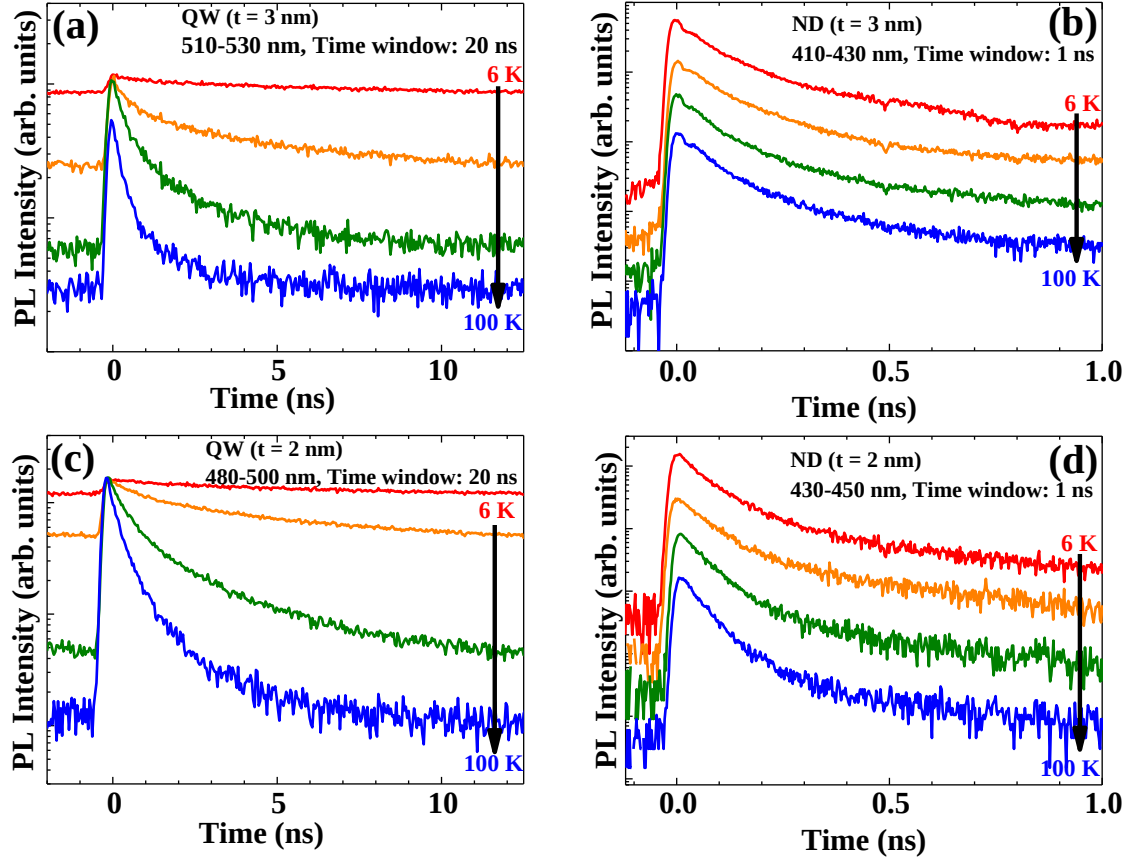


Figure 4.7 | PL time profiles of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ (a) 3-nm-thick QW, (b) 3-nm-thick NDs, (c) 2-nm-thick QW, and (d) 2-nm-thick NDs, as a function of temperature (6, 40, 70, and 100 K).

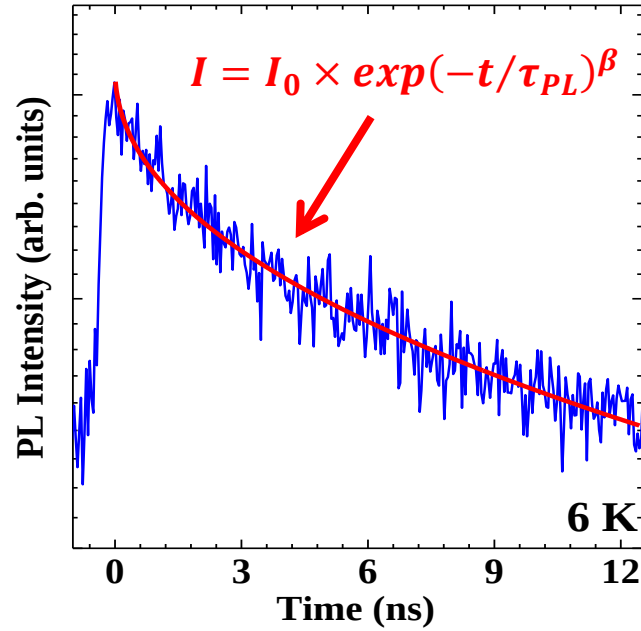


Figure 4.8 | Typical fitting result of the PL decay curve using a stretched exponential function.

The measured temperature dependences of TRPL data in figure 4.7 can be fitted by the stretched exponential function, as shown in figure 4.8. A radiative (τ_r) and non-radiative (τ_{nr}) decay times can be derived from the measured total recombination decay time and the internal quantum efficiency (IQE) η_{IQE} using the following relations;

$$1/\tau_{PL} = 1/\tau_r + 1/\tau_{nr} \quad (4.2)$$

and
$$\eta_{IQE} = \frac{1/\tau_r}{1/\tau_r + 1/\tau_{nr}} . \quad (4.3)$$

The value of η_{IQE} as a function of temperature (T) can be estimated from the temperature dependent PL intensities in figure 4.6, as a ratio of PL intensities at T and 6 K, assuming that the PL intensity at 6 K indicates 100 % IQE such as $\eta_{IQE} = 1$. At this low temperature (6 K), a capture rate by potential defects is assumed to be negligible for the emissive sites. It also means non-radiative recombination centers are frozen and the overall recombination can be attributed only to radiative recombination. However, at higher temperatures, the defects are thermally activated, capturing photo-excited and thermally migrated excitons. As a result, the overall PL intensity from sample $I_{PL}(T)$ is weaker than $I_{PL}(6\text{ K})$. By taking the ratio of them,

$$\eta_{IQE}(T) = I_{PL}(T)/I_{PL}(6K) , \quad (4.4)$$

the IQE at T can be derived. Using the equation 4.4, I have obtained temperature dependent IQE for all samples, as shown in figure 4.8. According to equations 4.2, 4.3 and 4.4, one can get $\tau_r = \frac{\tau_{PL}}{\eta_{IQE}}$ and $\tau_{nr} = \frac{\tau_{PL}}{1-\eta_{IQE}}$. Finally, one can derive the following four parameters: η_{IQE} , τ_{PL} , τ_r and τ_{nr} .

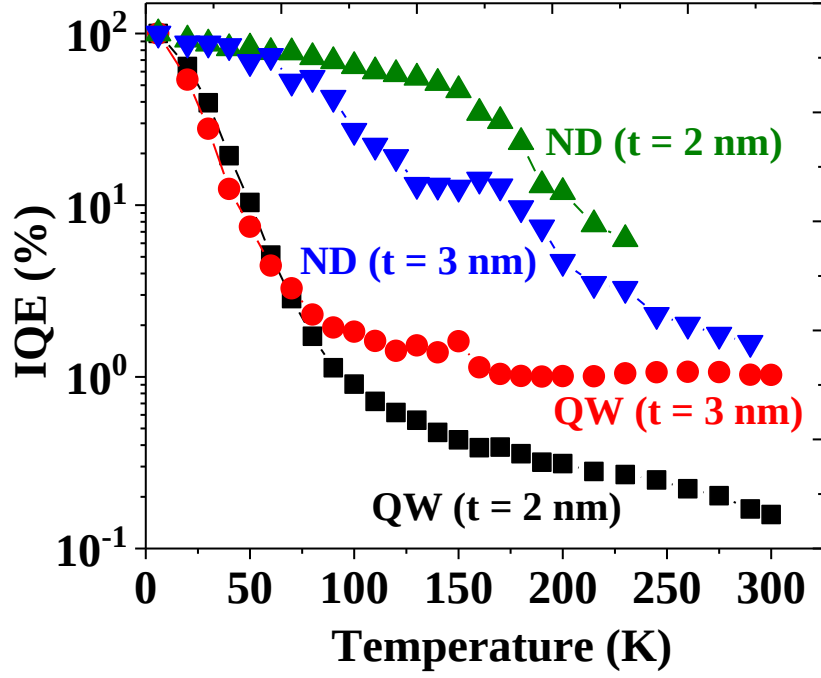


Figure 4.9] Internal quantum efficiency (IQE) as a function of temperature for the 4 types of $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ sample.

As can be seen in figure 4.9, the IQE decreases with increasing temperature. Thermal quenching of the PL intensity tends to be suppressed in the NDs, while the PL intensity in the QWs rapidly decreases with increasing temperature, originating from non-radiative recombination because of the potential defect formation at the lattice-mismatched QW interface as well as inhomogeneous In compositional distribution. I attribute this thermally stable PL intensity of the NDs compared with the QW to efficient carrier confinements due to the ND formation with small volumes and much less existence of defects inside the ND.

Time constants responsible for the transient PL are shown in figure 4.10, as a function of temperature. As can be seen, the PL decay times (τ_{PL}) in NDs are relatively fast around 0.1 ns or less and decreases with increasing temperature. Moreover, τ_{PL} in the NDs is approximately one-order shorter than that in the QW for the whole temperature range. This significant shortening of τ_{PL} compared to the mother QW can be concluded to be an essentially characteristic of the NDs.

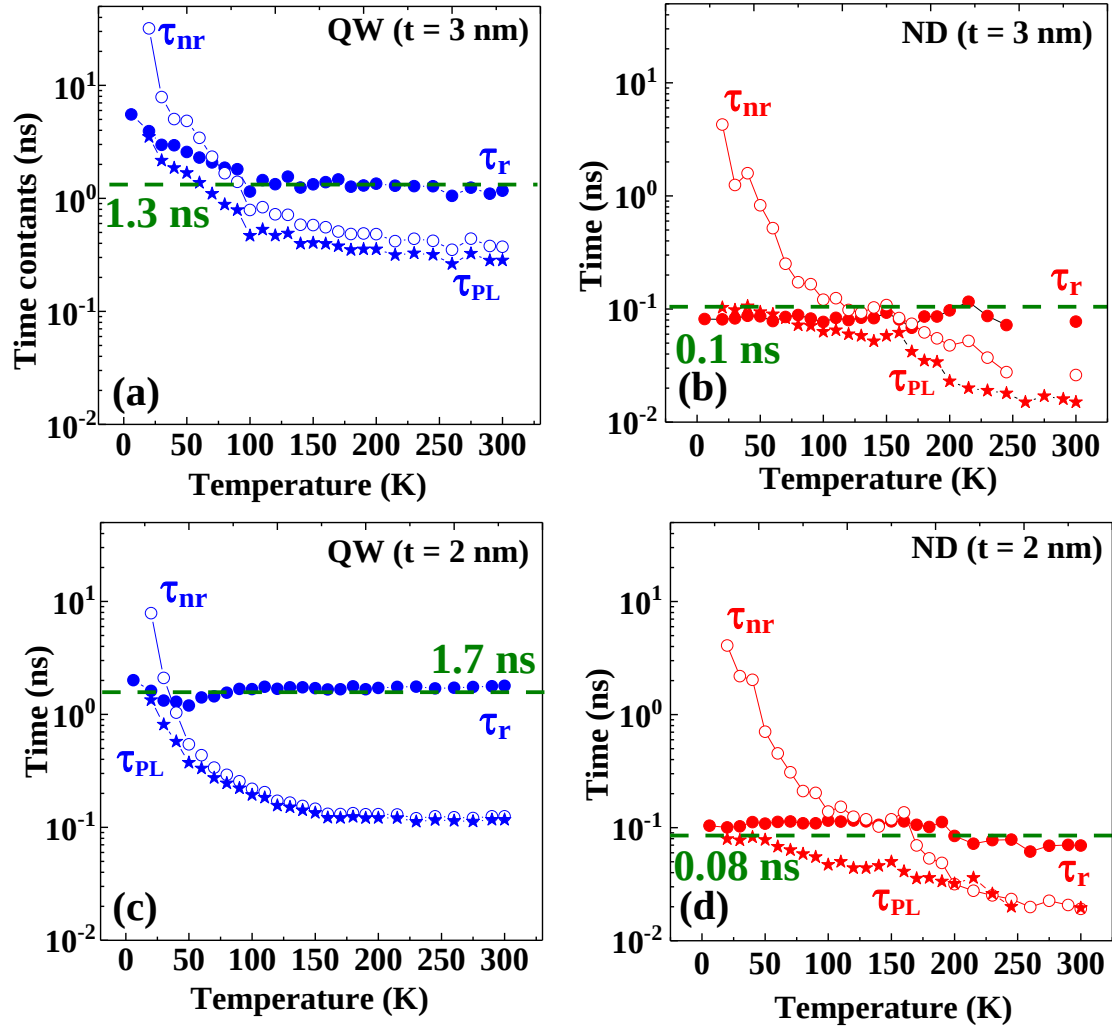


Figure 4.10 Time constants obtained from the TRPL measurements: a PL decay time (closed star), non-radiative decay time (open circle), and radiative decay time (closed circle), as a function of temperature in the $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ (a) 3-nm-thick QW, (b) 3-nm-thick NDs, (c) 2-nm-thick QW, and (d) 2-nm-thick NDs.

From τ_{PL} and the PL intensity, I have deduced time constants of radiative recombination decay time (τ_r) as well as of non-radiative one (τ_{nr}) as a function of temperature. τ_r in the NDs is found to be significantly shorter than that of the QW and about 0.1 ns which value is almost constant for temperature. τ_{nr} in the NDs is also shorter and decreases with increasing temperature. As a result, at the high-temperature region above 170 K, the non-radiative process becomes dominant in the PL decaying property of the ND, corresponding to the equation 4.2. The remarkable shortening of τ_r as described above can be attributed to the significantly weakened piezo-electric field effect masked by a strong lateral quantum confinement, in addition to strain relaxation. τ_r can directly reflect the oscillator strength originating from overlapping of wave functions of an electron and a hole. Therefore, the strong quantum confinement can enhance the spatial overlapping of the wave functions. Thermal escape of carriers from the ND beyond the potential barrier is responsible for the non-radiative decay process at the higher-temperature region as described above. The confined electron and hole states are significantly lifted up from the potential bottom in the ND because of strong quantum confinement induced by prominently small size of our NDs. Therefore, this thermal quenching in the NDs may greatly be improved by an intentional potential design of the ND since we can design and control compositions of the barrier material as well as of the QW and the thickness or lateral size of the ND.

4.3.2 Distribution of lifetime and the average radiative and nonradiative decay times in InGaN nano-disks structure

The stretched-exponential function was widely used in analyses of time-dependent decay-curve fittings in this InGaN/GaN system and the other inhomogeneous decaying systems such as Si nano-particles. However, the PL decay times obtained by this stretched-exponential function are not well-defined and rather weighted average values with unclear weight. In section 4.3.1, the stretched exponential parameter β of equation

4.1 is an indicator of the distribution of PL decay time. The low value of β reflects the broad distribution of the decay time. And τ_{PL} is a decay time when β is 1. However, the fitting result; β of the PL decay curve in the NDs shows the markedly lower value than 1 and the broad distribution of the decay time at high temperatures, which reflects that τ_{PL} by obtained equation 4.1 in NDs cannot represent the true decay time. The temperature dependent β of 3 nm-thick QW and NDs have shown in the figure 4.11.

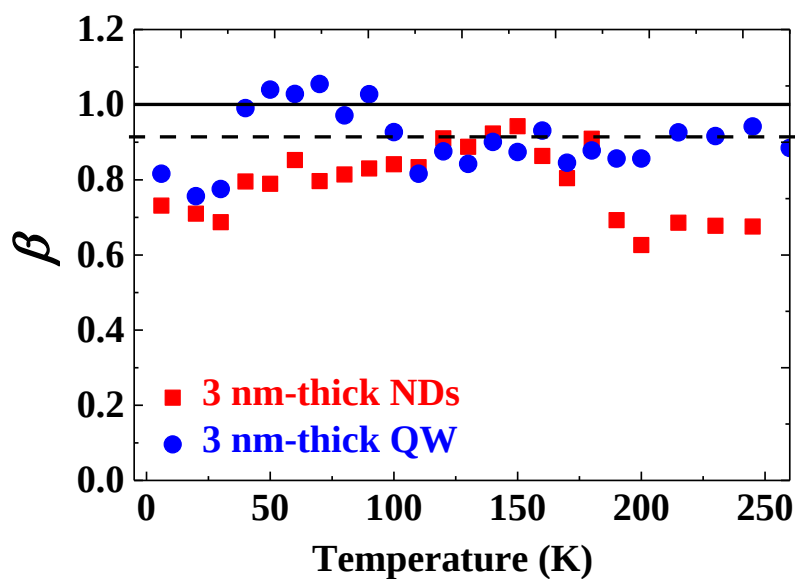


Figure 4.11 | Stretched exponential parameter β as a function of temperature in the 3 nm-thick NDs (red square) and 3 nm-thick QW (blue circle). A black solid line is the visual guide at $\beta = 1$.

To overcome this problem, I have analyzed the data by employing more rigorous approach [11, 12]. The stretched exponential function can be also expressed by the following function;

$$I(t) \propto \exp\left\{-\left(\frac{t}{\tau}\right)^\beta\right\} \propto \int_0^\infty f(\tau_0) \exp\left(-\frac{t}{\tau_0}\right) d\tau_0, \quad (4.5)$$

where $f(\tau_0)$ is an intrinsic distribution function of PL decay time τ . The essential distribution of lifetime $f(\tau_0)$ can be obtained from the Inverse Laplace transform of the stretched exponential function. This formula was expressed in Appendix A of the above reference [12], as follows;

$$H(K) = \frac{1}{\pi} \int_0^{\infty} \exp \left\{ -u^{\beta} \cos \left(\frac{\beta\pi}{2} \right) \right\} \cos \left\{ u^{\beta} \sin \left(\frac{\beta\pi}{2} \right) - Ku \right\} du, \quad (4.6)$$

where $K = 1/T$ and $T = t/\tau$.

I used the above function to analyze the previous data obtained by the stretched exponential fitting, and the results are summarized below. The distribution of τ is broadened at low temperatures. The distribution of τ in the 3 nm-thick NDs is broadened similarly at high temperatures.

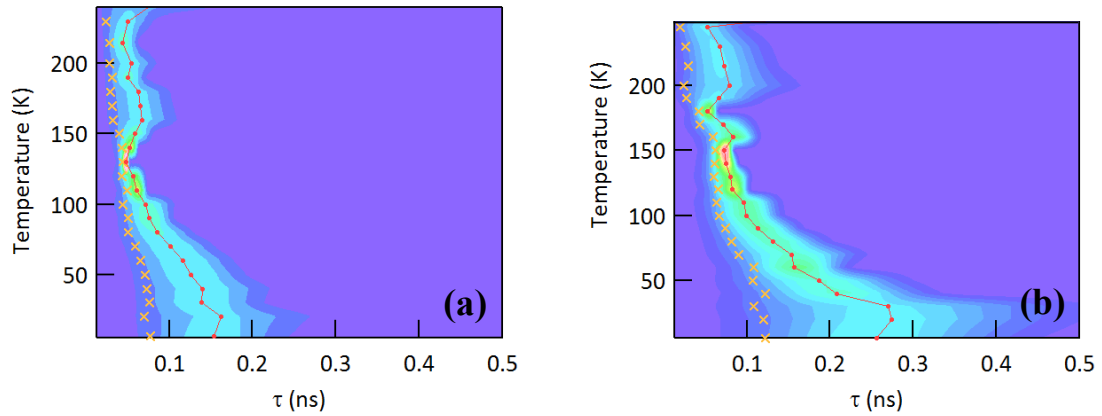


Figure 4.12 | Distribution function $f(\tau)$ of the PL-decay time as a colour-scale plot together with the PL decay time; τ_{PL} (orange cross) obtained from the stretched exponential fitting and the average PL decay time; τ_{PL}^a (red dot) for the (a) 2 nm-thick NDs and (b) 3-nm-thick NDs.

The average PL decay time: τ_{PL}^a of the InGaN ND samples is obtained as a function of temperature in the figure 4.12. According to equation 4.2, 4.3 and 4.4, I can deduce the average decay times of radiative recombination (τ_r^a) as well as of non-radiative process (τ_{nr}^a) as a function of temperature, as shown in figure 4.13.

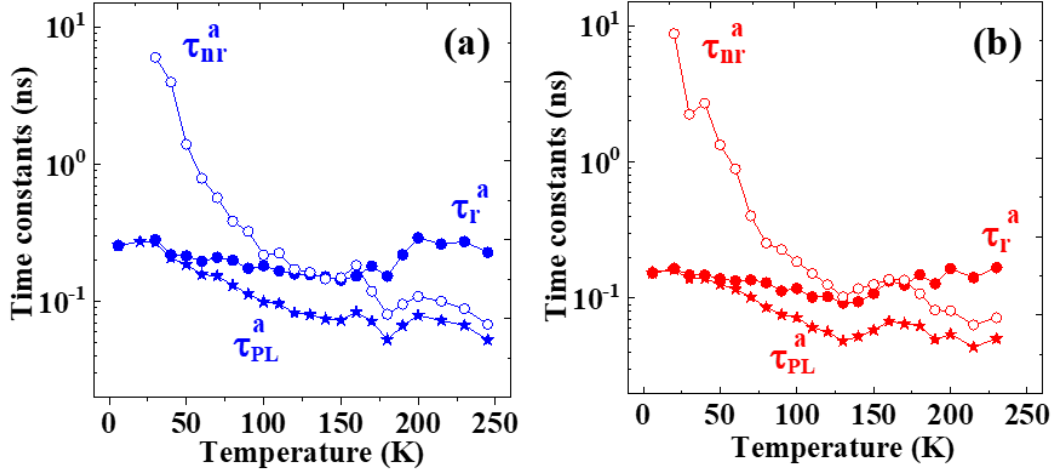


Figure 4.13 Time constants of average PL decay (closed star), non-radiative decay (open circle), and radiative decay (closed circle) as a function of temperature in the (a) 3 nm-thick NDs and (b) 2 nm-thick NDs.

The stretched exponential parameter β in NDs then can be re-considered, as shown in Fig. 4.14, which was initially obtained as a function of temperature from the stretched-exponential function in combination with Fig. 4.12. At low temperatures (less than about 130 K for 2 nm-thick NDs and 150 K for 3 nm-thick NDs), β increases with temperature below 100 K because of the suppression of weak localization of excitons, as previously reported [13]. The relatively low β values at low temperature also correspond with the broaden distribution of τ in the figure 4.12. Here, $\beta = 1$ corresponds to a single exponential decay curve with a constant τ_{PL} , which indicates the most concentrated distribution of τ at 150 K. In contrast, at temperatures higher than 150 K, the value of β obviously decreases from 1 with a rise in temperature, which means that the developed broad distribution of τ_{PL} with increasing temperature. I assume first that non-radiative recombination centers do not exist inside the NDs emitting the PL. From the band-diagram calculations and thermal activation energies of PL quenching, I conclude that holes inside the ND thermally escape beyond potential barriers on the valence band in the ND structure [13]. The starting temperature of 150 K for reduction in the value of β coincides well with this temperature that τ_{nr} starts to become dominant in τ_{PL} , as shown in Fig. 4.10 and 4.13. From these facts, I consider

that the reduction in β can be attributed to variations in hole-escape rates in NDs with various potential heights possibly due to significant fluctuations of the indium composition. The temperature dependence of β in the 3 nm-thick NDs is almost similar to that in the 2 nm-thick NDs, but a slight difference exists between the two NDs in the maximum β values and the temperatures corresponding to the largest β . Below 250 K, the PL decay time distribution $f(\tau_0)$ in eq.4.5 obeys the temperature dependence of the decay time τ of PL time profile obtained by the simple stretched exponential function fitting, while the average value τ_{PL}^a of the PL decay time distribution $f(\tau_0)$ is meaningfully larger.

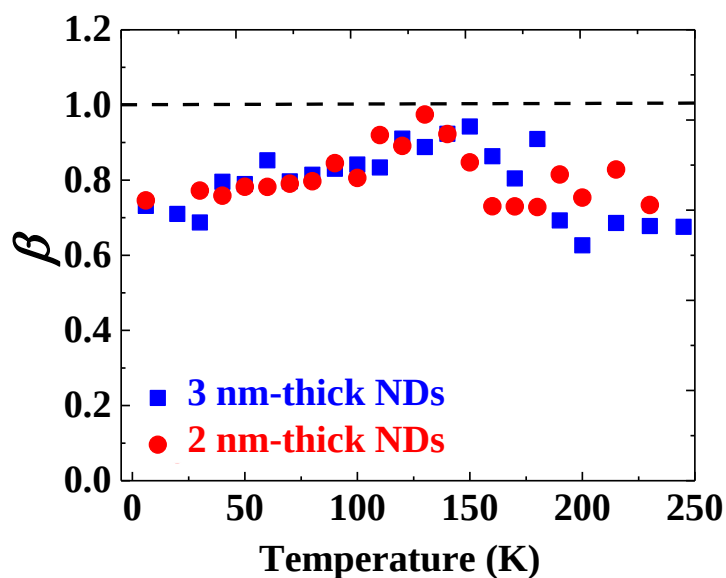


Figure 4.14 | Stretched exponential parameter β as a function of temperature in the 3 nm-thick (blue square) and 2 nm-thick (red circle) NDs. A black broken line is the visual guide at $\beta = 1$.

4.3.3 Thermal activation energy

In general, the temperature dependence of the PL quenching behavior can be analyzed by an Arrhenius-type equation, which is usually used to determine an activation energy in a thermally activated process, as follows [14];

$$I(T) = \frac{I_0}{1 + \sum_i C_i \exp\left(-\frac{E_{ai}}{kT}\right)} \quad , \quad (4.7)$$

where I_0 is a PL intensity at 0 K, E_{ai} represents the activation energies responsible for non-radiative relaxation, C_i represents process-rate parameters relating to the probability of the processes, and k is Boltzmann's constant.

I fitted the normalized PL intensities I_{PL} , normalized τ_{PL} and normalized τ_{nr} of four samples as a function of inverse temperature by the Arrhenius-type equation with two temperature-dependent terms;

$$I(T) = \frac{I_0}{1 + C_1 \exp\left(-\frac{E_{a1}}{kT}\right) + C_2 \exp\left(-\frac{E_{a2}}{kT}\right)} \quad , \quad (4.8)$$

where I_0 is the PL decay time at 6 K. E_{a1} is the thermal activation energy in the low temperature regime and E_{a2} is that in the relatively high temperature region [15]. $C_{1,2}$ are coefficients relating to the number of non-radiative centers [16–18].

I_{PL} , τ_{PL} and τ_{nr} always saturate with decreasing temperature. Above 6 K the PL intensity decreases exponentially with thermal activation energy E_{a2} . Exact evaluation shows that two thermal activation energies E_{a1} and E_{a2} are necessary for a satisfactory fit of figure 4.15. The best fit results for I_{PL} , τ_{PL} as well as τ_{nr} are summarized in Table 4.1. E_{a1} and E_{a2} are deduced from the best-fit calculations for the temperature dependence of PL intensity; such as 12 meV and 104 meV for the 3 nm-thick NDs, and 12 meV and 117 meV for the 2 nm-thick NDs, respectively.

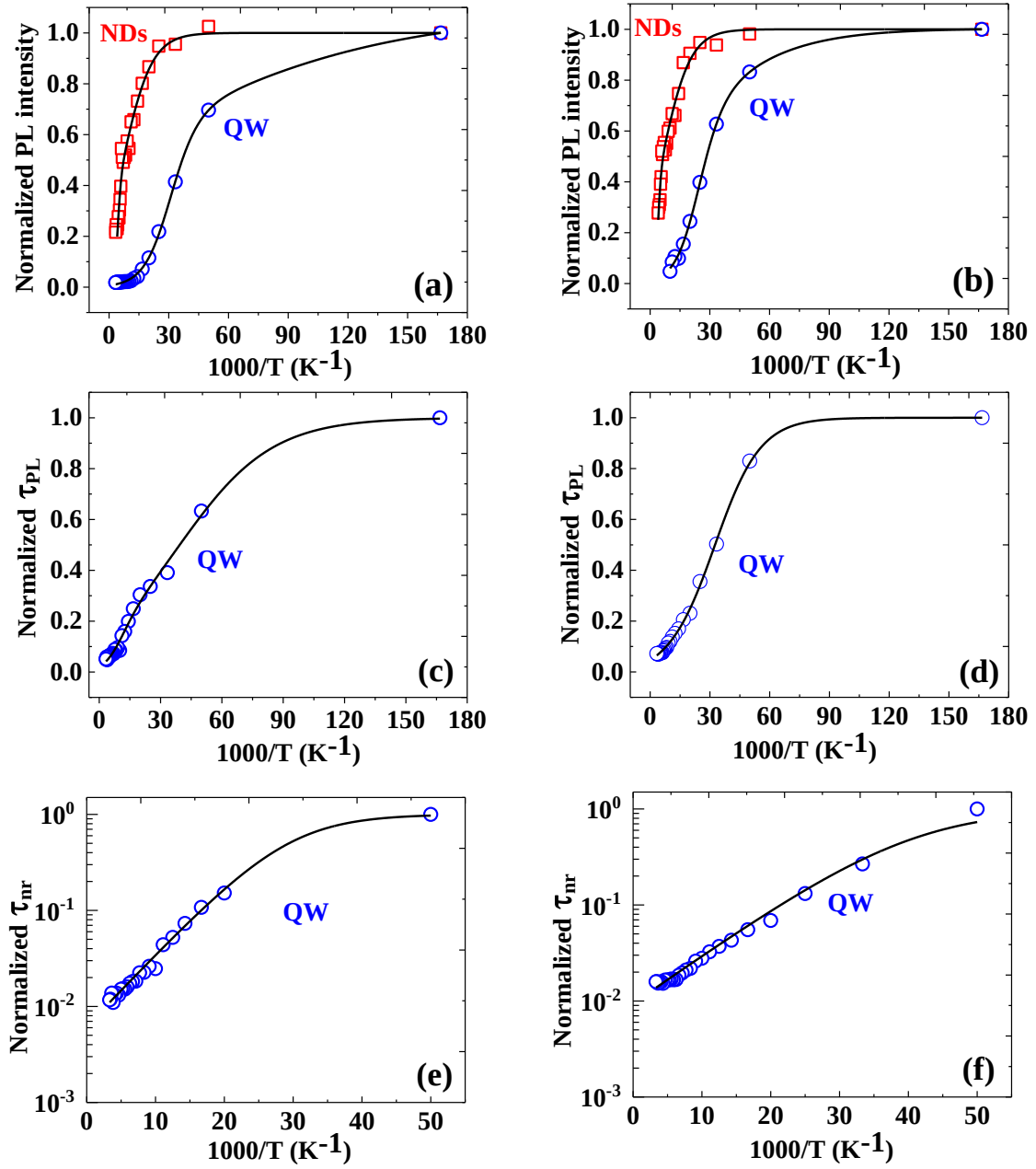


Figure 4.15 Integrated normalized PL intensities, τ_{PL} and τ_{nr} of the In_{0.3}Ga_{0.7}N/GaN (a), (c), (e) 3-nm-thick QW and NDs, (b), (d), (f) 2 nm-thick QW and NDs as a function of inverse temperature. The black lines are fitting results obtained using the Arrhenius-type equation.

	3 nm-thick ND	2 nm-thick ND	3 nm-thick QW			2 nm-thick QW		
	I_{PL}	I_{PL}	I_{PL}	τ_{PL}	τ_{nr}	I_{PL}	τ_{PL}	τ_{nr}
C_1	3	2						
E_{a1} (meV)	12	12	13	23	13	15	12	16
C_2	345	422						
E_{a2} (meV)	104	117						
C_1/C_2 (%)	0.75	0.57						

Table 4.1| Best-fitted parameters deduced from the Arrhenius-type equations for I_{PL} in the 3 nm- and 2 nm-thick NDs, as well as I_{PL} , τ_{PL} , and τ_{nr} of the reference QWs, respectively.

To support the above activation values in the ND samples, I evaluated the experimental data of temperature-dependent τ_{PL}^a by using the following Arrhenius-type equation with one temperature-dependent term;

$$\tau_{PL}(T) = \frac{\tau_{6K}}{1 + C_1 \exp\left(-\frac{E_{a1}}{kT}\right)} . \quad (4.9)$$

E_{a1} of 3 nm-thick and 2 nm-thick NDs are 13 meV and 12 meV, respectively, which values are similar with E_{a1} of I_{PL} . As can be seen in the figure 4.16, at high temperatures above 250 K, the significantly broadened distribution of the PL decay time discussed above disturbs the reasonable Arrhenius analysis using the average PL decay time τ_{PL}^a . Therefore, I combined with the Arrhenius values of I_{PL} , which is widely used to determine the activation energy of PL intensity quenching thus of non-radiative decaying process, with the latter Arrhenius plots of the average PL decay time only at lower temperatures less than 250 K.

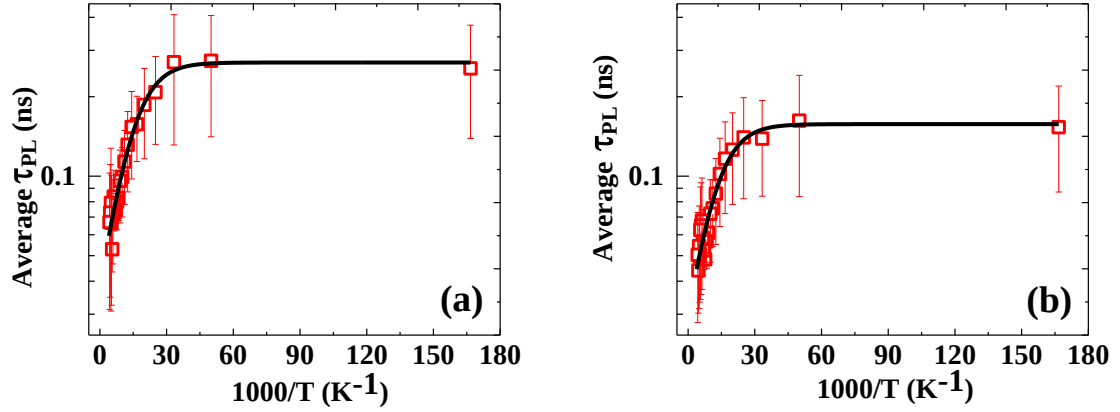


Figure 4.16 | The average τ_{PL} of the (a) 3 nm-thick NDs and (b) 2 nm-thick NDs as an inverse function of temperature. The black line shows the best fitted calculation using a 2-component Arrhenius-type equation.

According to the calculated values of the quantum energy level and valence band potential in the QW and ND structures, as shown in figure 4.3, the experimental values of thermal activation energy E_{a1} both in the QWs and NDs are not sufficient to overcome the potential barriers for electrons and holes. Those excitons just can overcome the small potential fluctuations due to the In composition fluctuation or interface roughness, and diffuse in the lateral direction of QW plane schematically, as shown in figure 4.17. It should be noted that this E_{a1} contribution to the PL quenching at low temperatures can be negligible in the NDs, which is indicated by extremely lower values of C_1 in the above fitting results. The formation of nan-scale lateral potential barriers in the NDs can sufficiently suppress the above low-temperature PL quenching process markedly in the QW.

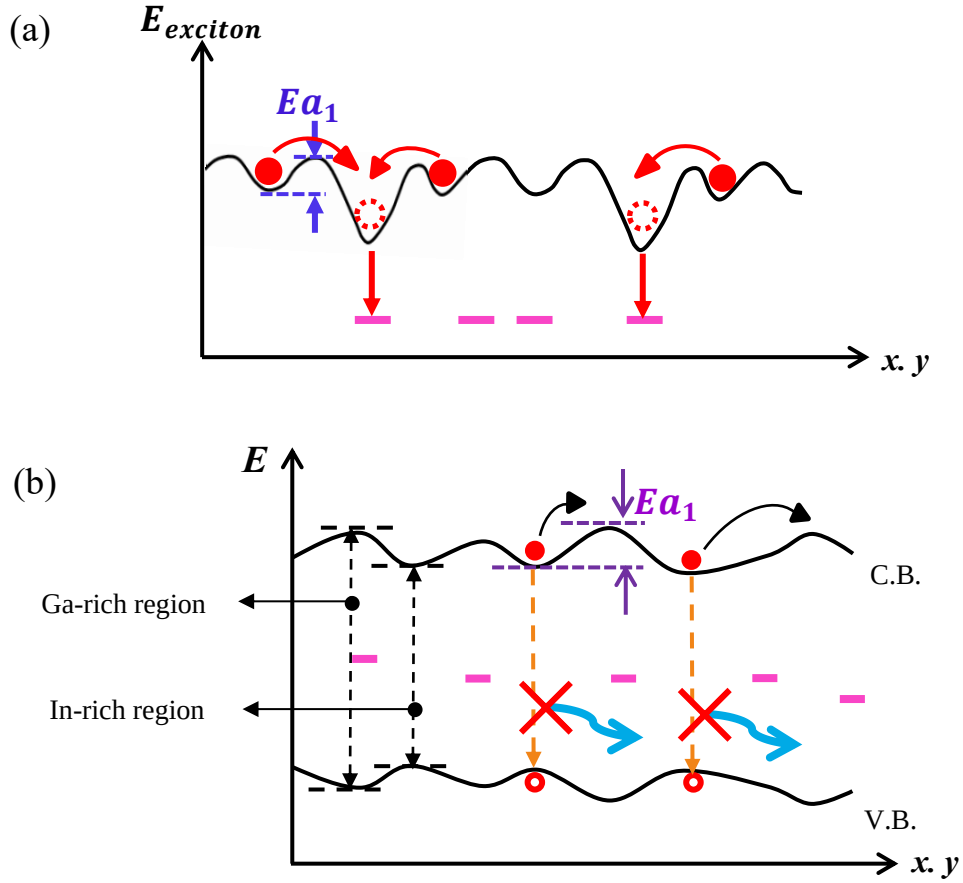


Figure 4.17 Schematic illustration of the fluctuated band diagram in the heavily In doped QW and the possible carrier dynamics at low temperatures, thermal migration of excitons can enhance non-radiative trapping by defects (a) and separate migration of electrons with the lighter effective mass from the exciton states with heavy holes (b).

The experimentally obtained E_{a2} values about 110 meV in the NDs agree reasonably with the potential barrier height on the valence band, which height is sufficiently lower than that on the conduction band. Exciton diffusion or separation of electron and hole in lateral direction can be almost eliminated in the NDs because of the lateral quantum confinement formed by the ND formation. Therefore, the hole escape and the resultant spatial separation of an electron from the hole is responsible for this PL quenching at high temperatures. Holes escaped from the NDs may be finally trapped by surface defects of the nano-pillars of GaN barriers. In connection with this discussion, LO-phonon energy in GaN is about 90 meV [19, 20]. This LO-phonon energy is also close to the above thermal activation energy responsible for the PL intensity quenching at high temperatures. One possible contribution of LO-phonon

scattering to the thermal escape of hole from the ND is LO-phonon-assisted tunneling at thermally excited states of the valence band in the ND, where the excited hole by the LO-phonon scattering can tunnel across the thin valence-band barrier.

The contribution of E_{a1} is not visible in the I_{PL} curves, where the ratio of C_1/C_2 is less than 1 %. Therefore, I suggest only that quenching due to non-radiative centers such as defects originally formed in the QW samples still exists in a very small number of NDs. This suggestion is also supported by the existence of thermal activation energy for the average τ_{PL} at low temperatures as shown in Fig. 4.16 and TABLE 4.1. This suggestion also leads to the insight that additional defects are not significantly formed during our process of ND fabrication using neutral beam etching, because the influence of the non-radiative center initially formed in the QW is not apparently masked in the NDs by other newly formable defects.

4.4 Summary

Transient PL intensity decay curves in the NDs were studied as a function of temperature and compared to those of the mother QWs. Thermal quenching of the PL intensity is significantly suppressed in the NDs due to efficient carrier confinement and much fewer defects due to the ND structure compared to the QW. More importantly, the radiation decay time of the NDs is almost constant at around 0.1 ns with respect to temperature, which is significantly shorter than the radiation decay time of the QW by an order of magnitude or more. This high-speed radiation process in the NDs can be attributed that the piezoelectric electric fields have been eliminated due to a strong confinement effect in addition to strain relaxation by fabrication of ND structure.

The thermal activation energy was deduced from the temperature dependence of the PL intensity and its decaying characteristics in the ND and QW. In addition, I calculated the wave functions of an electron and a hole in the potentials of the QW and ND structures. The thermal activation energy of 110 meV in the high temperature

region obtained in the ND matches the barrier height of the valence band in the ND and is due to thermal escape of the holes.

The thermal activation energy that causes PL quenching at low temperatures is dominant in the mother QW. This quenching was also observed in the ND. However, the contribution of this low-temperature quenching process in the ND can be negligible compared to a significant PL quenching at high temperatures. This indicates that the quenching processes caused by defects and potential fluctuations formed in the original QW are sufficiently suppressed in the ND. In this context, the expanded exponential parameter β was derived from the transient PL fitting. The value of β decreases when the temperature exceeds 150 K and reflects the variation in the hole escape rate. This may be due to variations in the ND valence barrier height, possibly due to variations in the indium content of the mother QW.

In summary, the non-radiative trap process dominant in the original QW exists only in about 1% of ND, but other new defect formation do not appear significantly. Therefore, I can conclude that almost no additional defects were formed during the ND fabrication process by neutral beam etching assisted by the bio-nano-template. Therefore, this extremely small and high-density $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ ND is expected to be applied to green LEDs and lasers due to its excellent carrier dynamics.

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Chapter 5. Carrier and spin dynamics of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ quantum dots embedded in GaAs nanopillars

5.1 Introduction

According to introduction in the section 1.3.2.2, I understand the 3-dimensional strong quantum confinements can suppress the electron or exciton spin relaxation significantly in self-assembled InGaAs QDs. After the sample preparation, circularly polarized time-resolved PL (TRPL) was measured in the InGaAs QDs embedded in the GaAs nano-pillars as described in the section 3.2.3; excitation-power and temperature dependences indicating the spin dynamics including spin relaxation, spin injection, and the related carrier dynamics. To fully exploit high optical performances with spin functionalities in future optical devices, it is necessary to analyze the carrier and spin dynamics as a function of excitation power and temperature in various types semiconductor QDs.

In the reference QD sample, a high sheet-density of the single self-assembled QD layer was controlled up to $9 \times 10^{10} \text{ cm}^{-2}$. Figure 5.1(a) shows the surface AFM image of the reference InGaAs QD sample. The upper diameter of the single GaAs nano-pillar after dry etching is 300 nm with the average bottom diameter of 350 nm and the height of 200 nm, as shown in figure 5.1(b). The inhomogeneous distribution of polystyrene beads on the surface results in the inhomogeneous bottom diameter (340-400 nm) of the nano-pillars. However, the upper diameter of nano-pillar appears relatively uniform.

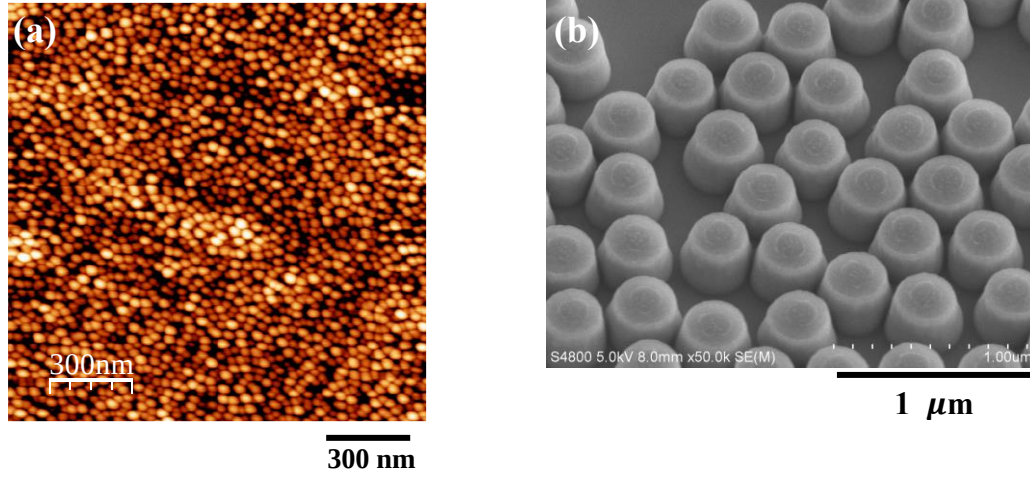


Figure 5.1| (a) Top-view image of AFM for the reference InGaAs QD layer. (b) Tilted-view image of SEM for the as-etched nano-pillars.

5.2 Excitation-power dependence

Figure 5.2 shows circularly polarized PL spectra for the reference InGaAs QD sample and the same InGaAs QD-in-pillar samples at 6 K. Excitation light powers were varied from 1 mW to 10 mW. The red and blue line indicate the PL with σ^+ and σ^- polarizations, respectively. Here, the degree of the circular polarization (CPD) is defined as $(I_{\sigma^+} - I_{\sigma^-}) / (I_{\sigma^+} + I_{\sigma^-})$ with the circularly polarized PL intensities $I_{\sigma^\pm}$. This CPD is indicated as a function of emission energy by the green line, which value is plotted according the right vertical axis. The peak PL intensity locates at 1.28 eV, which indicates the ground state of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ QD. In addition, the peak value of CPD locates around 1.35-1.45 eV for the reference QDs and 1.35-1.40 eV for the QD-in-pillar sample, which corresponds to the QD excited states. The peak intensity of the CPD value decreases with increasing excitation power due to a spin-state filling effect. This spin filling effect on the OD-in-pillar appears slightly weakened than that on the reference QD.

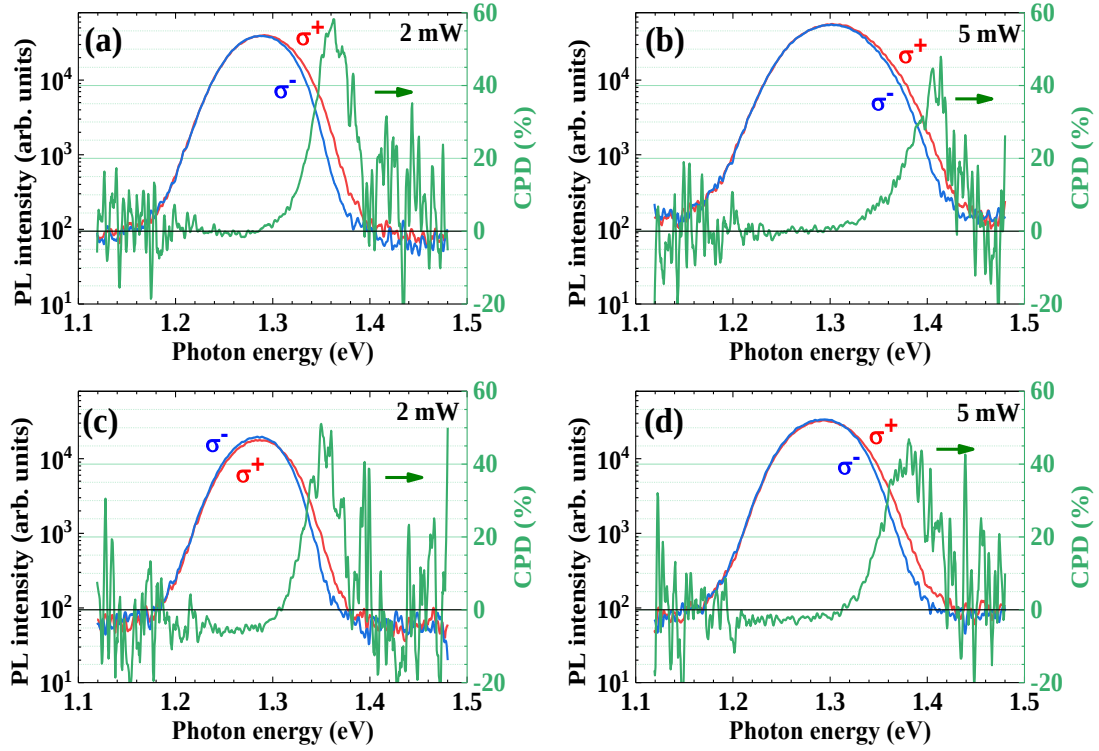


Figure 5.2| Circularly polarized PL and the corresponding CPD at 6 K as a function of emission energy, for the reference InGaAs QD sample measured with the excitation power of 2 mW (a) and 5 mW (b) and the QD-in- pillar sample at 2 mW (c) and 5 mW (d).

Circularly polarized TRPL was detected at the excited states with the detection window of 1.35 - 1.37 eV in the figure 5.2, as shown as figure 5.3. The CPD decay time indicates a half of time constant of spin relaxation. The spin filling effect on the reference QD at 5 mW is more visible than that at 2 mW, which is shown by the faster CPD decay time. In addition, the CPD decay times of the QD-in-pillar appear slower than those of the reference QD, especially at 5 mW.

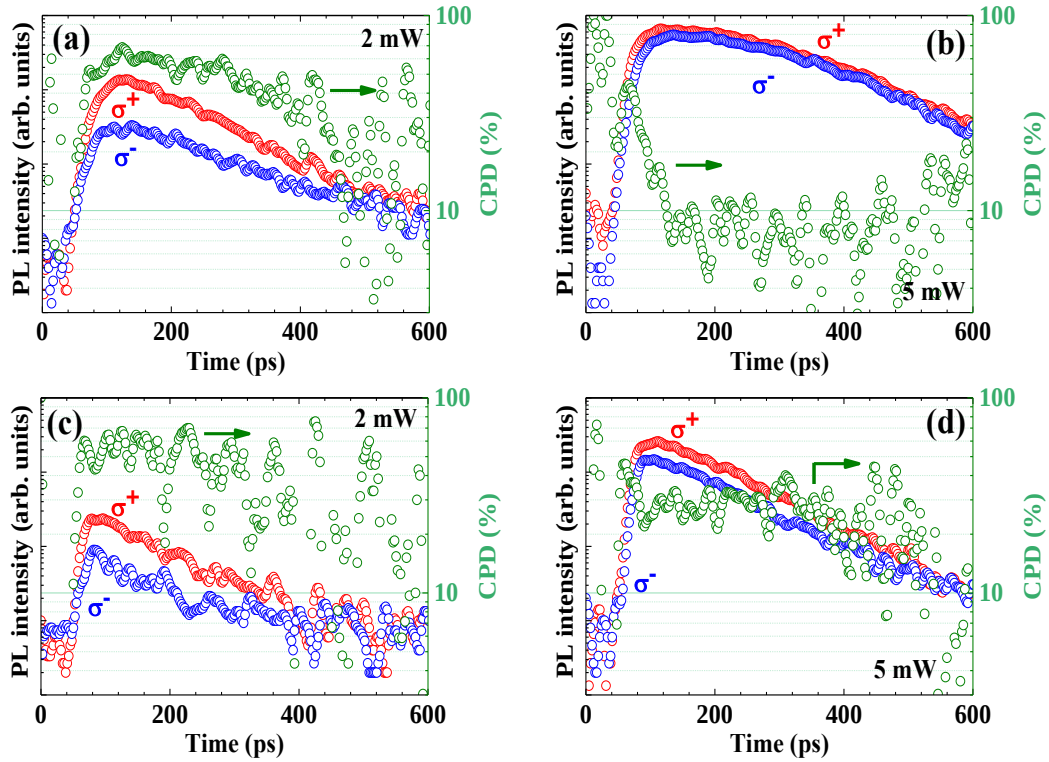


Figure 5.3| Circularly polarized TRPL and the corresponding CPD responses for the reference InGaAs QD sample measured at 2 mW (a) and 5 mW (b) as well as those in the QD-in-pillar sample at 2 mW (c) and 5 mW (d), detected at an optical window with 1.35 - 1.37 eV corresponding to the QD excited states.

The initial CPD values on the CPD decay curves just after the pulse excitation in figure 5.3 indicate the initial spin polarization degree of exciton immediately after the injection from the GaAs barrier to the InGaAs QDs. Excitation power dependences of the initial CPD for the reference QD and QD-in-pillar samples are shown in figure 5.4. With increasing excitation power, the initial CPD values decreases originating from the Bir-Aronov-Pikus (BAP) spin relaxation mechanism at low temperatures, which can be induced by enhanced effective hole density (or hole exchange field) against for the electron spin in the GaAs barrier prior to the spin injection into the QDs. As can be seen, the initial CPD of the QD-in-pillar sample was lower than that of the reference QD sample at the whole excitation power range. At low temperatures, the exciton states can be maintained in the GaAs barriers and optical electric-field confinement due to the QD-in-pillar structure can enhance the hole exchange field, which can affect more strongly to the electron spin relaxation. Therefore, the BAP spin relaxation mechanism

can act stronger in the nano-pillar structure of the GaAs barrier than in the reference QD.

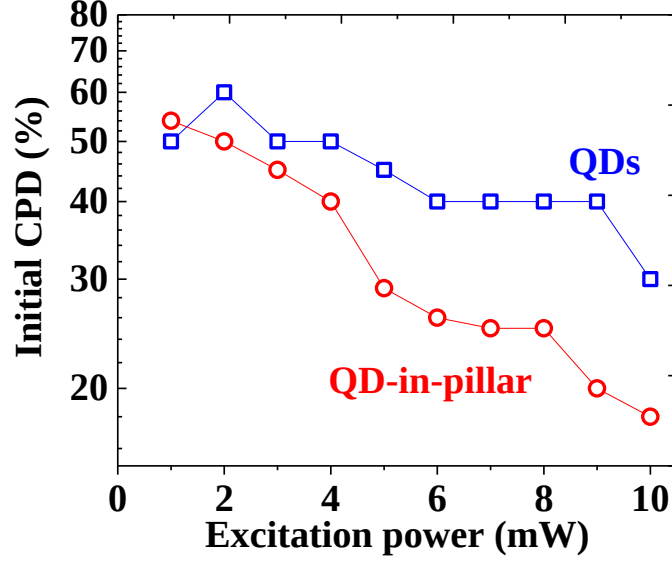


Figure 5.4| Initial spin polarization degree:CPD as a function of excitation power for the reference InGaAs QD and the InGaAs QD-in-pillar samples at 6 K.

5.3 Temperature dependence

5.3.1 Carrier and spin dynamics of InGaAs QDs in $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ quantum dots embedded in GaAs nanopillars

5.3.1.1 Carrier and spin dynamics of InGaAs QDs

Figure 5.5 shows circularly polarized PL spectra of the InGaAs QD reference sample at 2 mW and the QD-in-pillar sample at 5 mW with various temperatures from 6 K to 297 K. According to spin-dependent pauli blocking, the excited state shows the essential spin polarization degree, which is not marked by the state filling effect if the excitation-power condition is properly tuned. Therefore, in this research, the excited state (1.35 eV - 1.37 eV), in which the highest CPD is visible in 6 K, was chosen to

observe the spin dynamics in QDs. The different excitation powers of two samples were operated to make a situation with identical state filling at the same excited state, which can largely affect the spin relaxation dynamics.

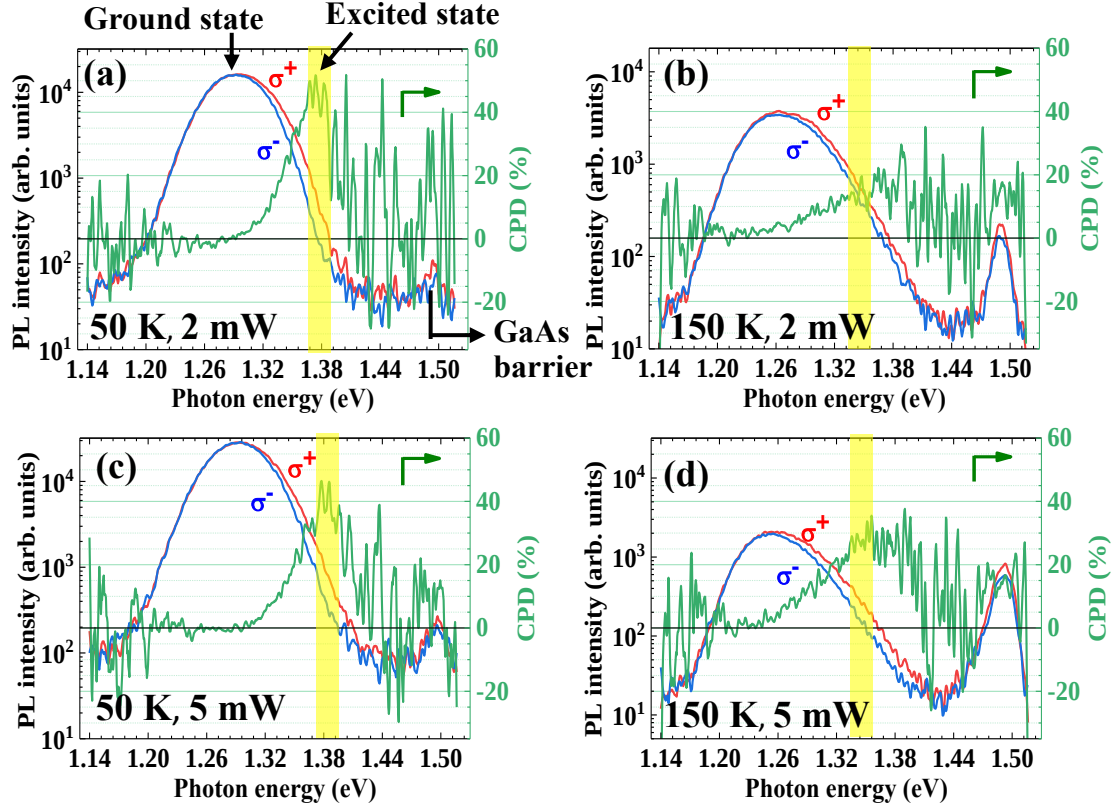


Figure 5.5 Circularly polarized PL spectra and the corresponding CPD values as a function of temperature for the reference InGaAs QD sample measured at 50 K (a) and 150 K (b) with the excitation power of 2 mW as well as the QD-in-pillar sample at 50 K (c) and 150 K (d) with the excitation power of 5 mW.

As is seen in figure 5.5, the CPD values of the excited states (1.35 eV - 1.37 eV) in the reference QDs are higher at low temperatures than those in the QD-in-pillar due to the higher initial CPD values. However, the CPD of the QD-in-pillar becomes higher at high temperatures. According to figure 5.5, the average CPD value of the excited states in both samples are plotted in figure 5.6. The CPD of the QD-in-pillar is lower than that of the reference QD at low temperatures, originating from the lower initial CPDs at 5 mW as shown in the previous figure 5.4. However, the higher CPD of the QD-in-pillar than the reference QD can be visible at high temperatures, in addition to

the almost constant CPD values in the QD-in-pillar for the whole temperature range.

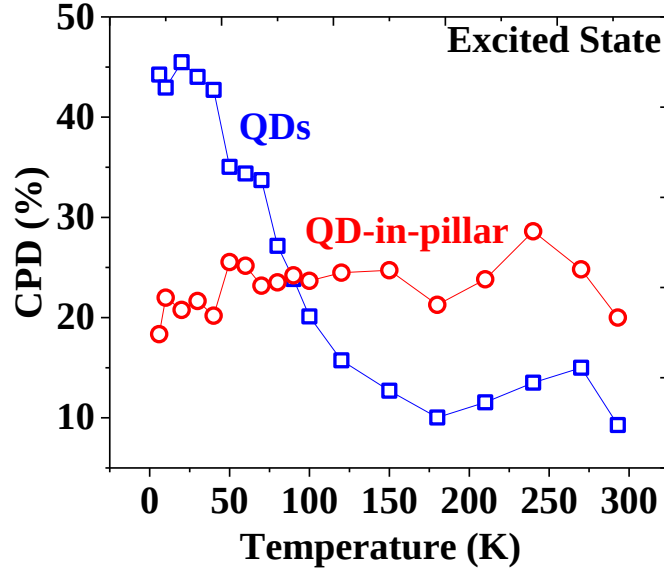


Figure 5.6 Time-integrated CPD at excited states in the reference QD and the QD-in-pillar sample as a function of temperature.

Circularly polarized TRPL at the excited states (1.35 eV-1.37 eV) are shown in figure 5.7. Significantly faster PL decay characteristics; $\tau_{PL}(\sigma^+)$ in the QD-in-pillar is observed at high temperatures. The PL decay time was derived using a single exponential function, as shown in figure 5.8.

In the reference QD sample, τ_{PL} increases from 6 K to 150 K, but decreases from 150 K to 297 K, which trend of τ_{PL} is different from the other normal InGaAs QDs [1-6]. This unexpected phenomenon at low temperatures results potentially from a relatively low recombination probability of exciton due to marked electron transfer and the resultant electron-hole separation among QDs, originating from this ultra-high density ($9 \times 10^{10} \text{ cm}^{-2}$) QD structure in the single QD layer. At high temperatures, the decrease in τ_{PL} is common and caused by usual thermal escape of carriers from the QD to the barrier. The QD-in-pillar sample shows the monotonic decrease in τ_{PL} with increasing temperatures, indicating the above thermal escape. In this QDs in the pillar, the electron transfer among QDs dominantly at low temperatures can be sufficiently suppressed by limitation of lateral QD coupling owing to the nano-pillar formation.

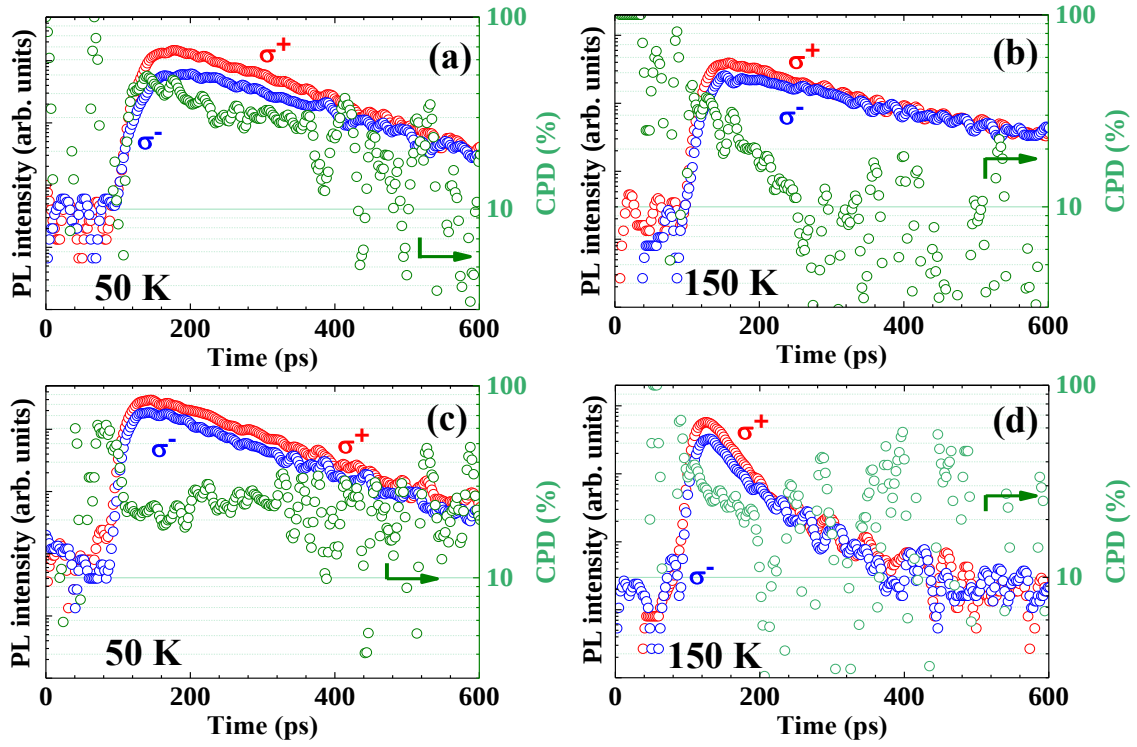


Figure 5.7 Circularly polarized TRPL and the corresponding CPD responses for the reference InGaAs QD sample at 50 K (a) and 150 K (b), as well as the QD-in-pillar sample at 50 K (c) and 150 K (d), detected at an optical window with 1.35 - 1.37 eV corresponding to the excited states.

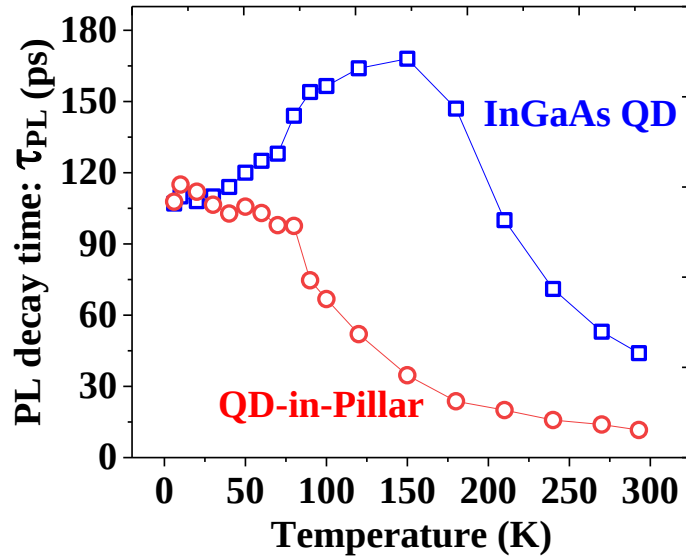


Figure 5.8 PL decay times of PL intensity in the InGaAs QD (blue open squares) and the QD-in-pillar (red open circles) samples, as a function of temperature.

Circularly polarized TRPL typically shown in figure 5.7 was fitted by a single exponential function to derive the CPD decay time; τ_{CPD} , which reflects spin relaxation speed in QD, as shown in figure 5.9. In the reference QD sample, τ_{CPD} decreases with increasing temperature because of the dominant spin relaxation: the BAP spin relaxation mechanism due to the smaller distance of electron and hole in the QD, which results from thermal excitation effect. In addition, τ_{CPD} of the QD-in-pillar is almost identical to that of the reference QD at high temperature from 180 K, originating from the same composition and size of the individual QD in the reference QD and QD-in-pillar. The decay of CPD in the QD-in-pillar was difficult to be clearly identified at low temperatures below 90 K, as shown in fig. 5.7 (c).

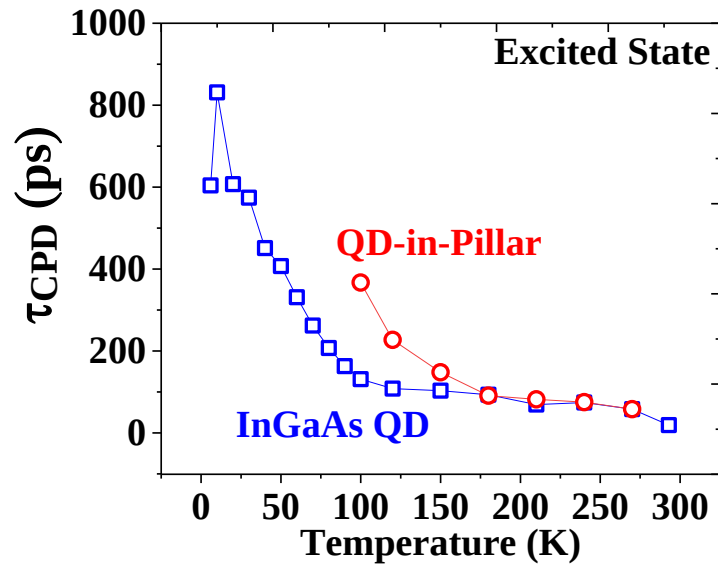


Figure 5.9 | CPD decay time; τ_{CPD} of the reference InGaAs QD (blue open squares) and the QD-in-pillar (red open circles) samples, as a function of temperature.

5.3.1.2 Spin dynamics of GaAs nanopillars before spin injection

In the section 5.3.1.1, I have discussed the carrier and spin dynamics in the InGaAs QDs. Nevertheless, those dynamics in the QD-in-pillars should be researched because of the potential interplay between the QD and GaAs barrier layers. The initial CPD values of both samples were plotted as shown in figure 5.10, as a function of temperature.

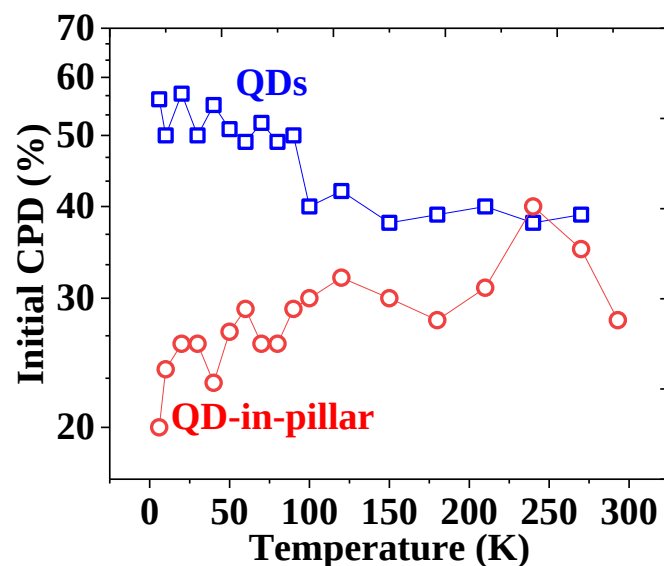


Figure 5.10| Initial CPD values of the reference InGaAs QD (blue open squares) and the QD-in-pillar (red open circles) samples, as a function of temperature.

As can be seen, the initial CPD, indicating the degree of spin polarization just after the injection into the QDs from the GaAs barriers, is lower in the QD-in-pillar than that of the reference QD sample. Optical electric-field confinement becomes important on the QD-in-pillar structure with the scale of several hundred nanometers. This enhanced optical field condensation can enhance the hole exchange field for the electron spin in the barrier. Therefore, the BAP spin relaxation mechanism can act stronger at low temperatures in the nano-pillar structure of the GaAs barrier and degrades the spin polarization. In addition, the initial CPD of the GaAs barrier in the QD-in-pillar

increases with increasing temperature, indicating significant suppression of spin relaxation in the nano-pillar structure of the GaAs barrier. The dominant spin relaxation is known to be induced by the D'yakonov-Perel' mechanism, where the scattering of electron spin can enhance the spin relaxation through a spin-orbit interaction. Therefore, spatial limitation by the nano-pillar formation can suppress this D'yakonov-Perel' spin relaxation mechanism at high temperatures in the GaAs barriers.

5.3.2 Mechanism of the high CPD in In_{0.5}Ga_{0.5}As quantum dots at high temperature

In section 5.3.1.1, the significant advantage of the QD-in-pillar sample is a higher CPD than the CPD of the InGaAs QD sample at room temperature in Figure 5.6. According to a relation of the CPD value to the PL and CPD decay times [7, 8]:

$$CPD \sim \frac{P_{initial}}{1 + \frac{\tau_{PL}}{\tau_{CPD}}}, \quad (5.1)$$

where $P_{initial}$ is the initial CPD, the CPD value is inversely proportion to τ_{PL}/τ_{CPD} . The initial CPD values at high temperatures have been shown in figure 5.10, in which the CPDs between both samples are almost similar. Therefore, one can ignore the difference of $P_{initial}$. The temperature dependent τ_{CPD} has been shown in figure 5.9. Combined with the τ_{PL} in figure 5.8, τ_{PL}/τ_{CPD} at high temperatures can be observed in figure 5.11. The τ_{PL}/τ_{CPD} of the reference QDs is one order larger than that of the QD-in-Pillar. Therefore, the fast τ_{PL} of the QD-in-pillar contributes dominantly to the higher CPD values at high temperatures.

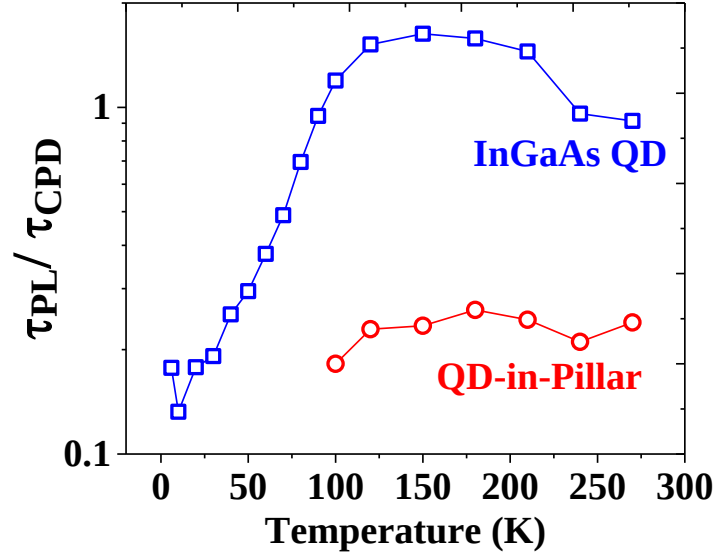


Figure 5.11| Values of τ_{PL}/τ_{CPD} of the reference InGaAs QD (blue open squares) and the QD-in-pillar (red open circles) samples, as a function of temperature.

5.3.3 Mechanism of the fast PL decay time in $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ quantum dots at high temperature

In section 5.3.2, it has reflected that the higher CPD of the QD-in-pillar at high temperatures is owing to the faster PL decay time; τ_{PL} in figure 5.8. The mechanism of the faster τ_{PL} in the QD-in-pillars should be researched from both the QD and GaAs barrier layers. First, according to circularly polarized PL spectra in figure 5.5, the temperature dependent peak PL intensities of InGaAs QD at 1.28 eV and GaAs barrier at 1.5 eV for the reference QD sample and QD-in-pillar sample were plotted, as shown in figure 5.12. The PL intensity in both samples decreases with increasing temperature due to usual PL quenching originating from thermal escape of carriers from the QDs to the barriers. Nevertheless, the PL intensity of GaAs barrier at 1.5 eV in the QD-in-pillar is almost one order of magnitude larger than that of the reference QD in the whole temperature range, and even the PL intensity from the GaAs barrier is stronger than that of the QDs in the QD-in-pillar sample at high temperatures, which reflects that an

electron-hole recombination efficiency in the GaAs barrier of the QD-in-pillar is higher than that in the barrier of the reference QD.

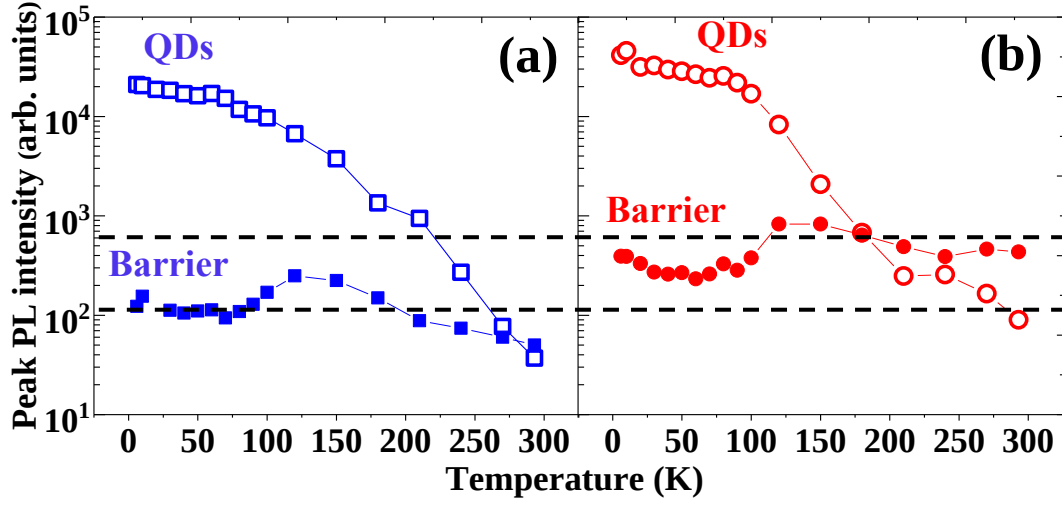


Figure 5.12 | Spectral-peak PL intensity of the InGaAs QD active layer and the GaAs barrier in the reference QD (a) and QD-in-pillar (b) samples, as a function of temperature.

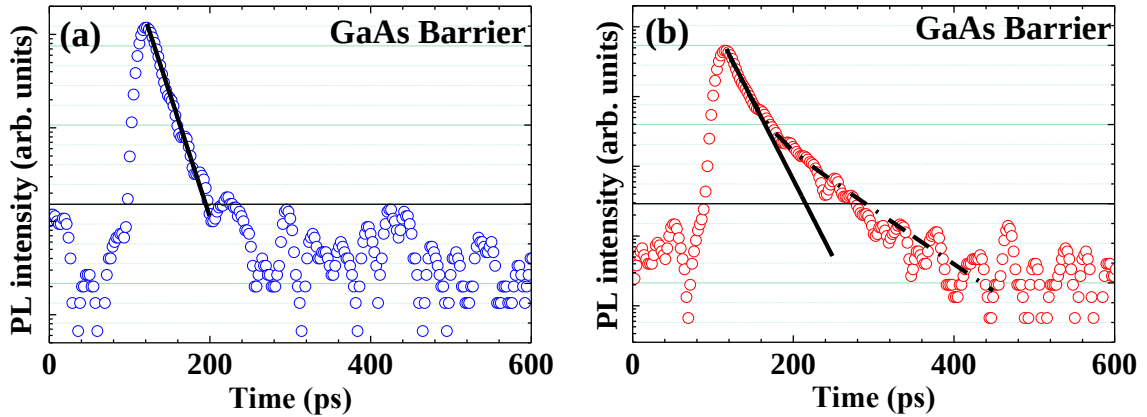


Figure 5.13 | TRPL of σ^+ -polarized PL components for (a) the reference QD and (b) QD-in-pillar samples at 210 K at an optical window with 1.46 - 1.48 eV, corresponding to the GaAs barrier in nano-pillar. The black line is the best fitted calculation using the equation 5.1.

To confirm the carrier dynamics in the GaAs barriers, TRPL was observed at 210 K in figure 5.13. The first component of PL decay curve: the decay time $\tau_{PL1}(\sigma^+)$ in both samples is almost the same [$\tau_{PL1}(\sigma^+)$ -QD = 16 ps, $\tau_{PL1}(\sigma^+)$ -QD-in-pillar = 15 ps]. The QD sample shows only this $\tau_{PL1}(\sigma^+)$ component, but the second components can be observed in the QD-in-pillar. This second component $\tau_{PL2}(\sigma^+)$ is 55 ps in the QD-

in-pillar, which indicates the recombination between the thermally escaped electrons and holes from QDs to barriers. Spatial restriction of the electron diffusion owing to the pillar formation in the nano-pillar GaAs structure can contribute higher recombination rates of the electron and hole in the barrier before re-injection from the barrier into the QDs. However, the recombination between the thermally escaped carriers can hardly be visible in the GaAs barrier of the other QD sample. Instead, the diffusion of electron with lighter effective mass in the GaAs barrier with much longer diffusion length rather than the nano-pillar sample would be more significant after thermal escape from the QDs. Therefore, the thermally escaped electrons can be efficiently re-injected into the QDs prior to recombination with holes in the plane GaAs barriers. This situation can explain why the stronger PL was observed in the GaAs barrier in the QD-in-pillar than that in the reference QDs in figure 5.12, which results in the faster τ_{PL} in the QDs in the QD-in-pillar in figure 5.8. The electron migration in the barriers can cause the spin relaxation and thus re-injection of the spin-relaxed electrons into the QDs can enhance the spin relaxation in the QDs. Therefore, more efficient recombination of the electron with holes in the barrier of the QD-in-pillar sample can prevent this thermally induced spin relaxation. The more visualized explanation is given in figure 5.14.

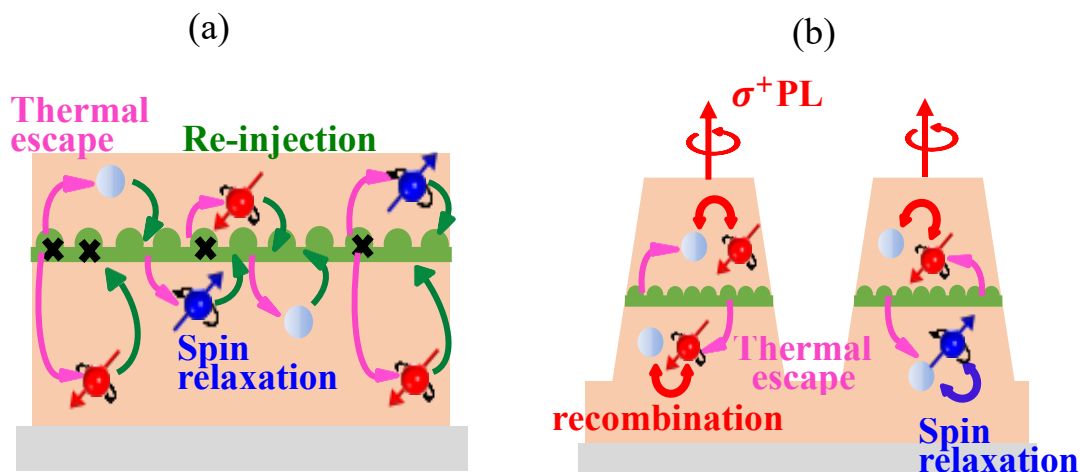


Figure 5.14 | Schematic illustration of the carrier and spin dynamics thermally activated in the GaAs barriers from the QDs at high temperatures in the conventional QD sample (a) and the QD-in-pillar sample (b).

5.4 Summary

$\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ QDs embedded in GaAs nano-pillars with a diameter of 300 nm and a height of 200 nm were fabricated from a high density self-assembled QDs with $9 \times 10^{10} \text{ cm}^{-2}$ by plasma reactive ion etching using bottom-up technology using nanosphere lithography. I measured the excitation power and temperature dependences of circularly polarized TRPL, and investigated the carrier and its spin dynamics. At temperatures above 90 K, the QPD-in-pillar sample shows meaningfully higher electron-spin polarization CPD (CPD $\sim 25\%$) than that of the reference QD sample (CPD $\sim 12\%$). In this high temperature range, the QD-in-pillar sample also showed faster PL decay characteristics. This fast PL decay time in the QD-in-pillar sample is due to the high radiative recombination probability in the nano-pillar GaAs barrier after thermal escape of carriers from the InGaAs QDs. The nano-pillar structure promotes this radiative recombination because the migration of electrons in the barrier is spatially limited. On the other hand, in the conventional QD sample, the spin state of the electron thermally excited in the barrier remarkably relaxes as the temperature increases, and the spin-relaxed electrons can be reinjected into the QD. In other words, high circular polarization characteristics were obtained by suppressing re-injection of spin-relaxed electrons from the nano-pillar structure barrier to the QD. This is considered to be useful for future development of spin-functional optical devices.

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Chapter 6. Conclusion

The purpose of this study is to create optically functional III-V compound semiconductor nanostructures using designable nanofabrication processes combined with bottom-up technology. These optical properties were also revealed mainly by means of TRPL. In this paper, I have focused on specific nanostructures of InGaN and InGaAs compound semiconductor materials.

Using a unique bio-nano-template, nanodisks (NDs) with a lateral diameter of 5 nm was formed from $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ QWs by neutral beam etching without inducing etching damage. The excellent properties of InGaN NDs relating to the carrier dynamics are described in Chapter 4, which will be promising and useful for applications to green LEDs and lasers.

The reduction of the electron-hole recombination probability due to the built-in piezo electric field, which is a main subject of the InGaN QW with high In concentration, is shown to be significantly eliminated by the ND formation. Due to the temperature dependence of the TRPL characteristics, the quenching phenomenon in the high temperature region of the ND can be attributed to thermal escape of holes. A detailed TRPL analysis was performed, taking into account the non-uniform distribution of the hole escape rate from the NDs to barriers due to variations in the In composition introduced in the original InGaN QW. It was also confirmed that the generation of defects in the ND fabrication process was sufficiently suppressed.

In addition, GaAs-based nano-pillars with various uniform diameters and the high controllability were fabricated containing self-assembled InGaAs QD layers by nanolithography using polystyrene beads and dry etching. Chapter 5 shows the improvement in the circular polarization characteristics of the PL emitted from the QD layers at high temperatures by suppressing the electron spin relaxation in the GaAs nano-pillars. In conventional QDs, the spin relaxation of electrons thermally escaped from the QDs to the barriers can be accelerated at high temperatures, and the circularly polarized emission property is degraded by the effect of reinjection of the electrons after

spin relaxation in the barriers into the QDs. The nano-pillar structure significantly suppresses this reinjection of thermally escaped and spin-relaxed electrons into the QDs. This will contribute to improve spin functionalities of future semiconductor spintronic optical devices.

Based on the above, a designable nanofabrication process with high structural controllability can be effectively applied to many III-V compound semiconductor materials. In addition, these designable nanofabrication processes can help miniaturize microscale to nanoscale optical devices.

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