Fabrication and Optical Properties of ZnO Nanocrystal/GaN Quantum Well Based Hybrid Structures

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Abstract

Optical properties of hybrid structures based on zinc oxide nanocrystals (NCs) and Gallium Nitride quantum well (QW) has been studied. The ZnO NCs thin films on the top of GaN QW structures were fabricated using spin coating. The surface morphology was characterized by scanning electron microscopy (SEM). We have performed temperature dependent time-resolved photoluminescence (TRPL) measurements of the bare AlGaN/GaN QW structures and hybrids, containing ZnO NCs. It was found that at some temperatures the QW PL decay has shorter decay time in the presence of ZnO NCs thin film compared to the bare QW. The effect was stronger for the samples with thinner cap layers. The results are discussed in terms of three models such as exciton nonradiative energy transfer (NRET), tunneling effect, and piezoelectric field influence on the QW exciton energy.
Preface

This master thesis is the result of half year’s work during my master studies in Thin Film Physics group.

I would like to thank my supervisor and also examiner very much, Docent Galia Pozina. In the beginning of the project, I did not have any research experience. She has taught me a lot of things such as how to operate the experimental instruments, the motivation of the project, the importance of our research, and how to do a presentation of the results. During the lab, a lot of measurements have been done together with Galia Pozina, and she also gave me many advices when I encountered a problem.

My gratitude also goes to the people who supported and helped me during my thesis work. Sergey Khromov, a Ph. D. student in Thin Film Physics group, he helped me to operate Scanning Electron Microscope and gave me some useful suggestions. Tang Zheng, a Ph. D. student in Biomolecular and Organic electronics, he taught me how to use spin coating setup, and helped me to search for the proper materials we may use in our research. Mathias Forsberg, a Ph. D. student in Thin Film Physics group with the same supervisor as me, helped me to correct my thesis, and we frequently discussed the research. Docent Fredrik Karlsson was very helpful to find a master project for me, and he introduced me to Galia, where I started my diploma work. In the end, I would like to thank my friends and my family companying me.
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1. Introduction

There have been numerous efforts to increase the efficiency of optoelectronic and photovoltaic (PV) devices, e.g. light-emitting diodes (LEDs), laser diodes (LD) and solar cells during the last decades. For applications in light-emitting diodes, efficient multicolor as well as white emissions are desirable but difficult to achieve from a single epitaxially grown device [1]. However, a blend of appropriate polymers, or quantum dots, gives rise to multiple emission bands in the visible and a proper mixture of them can produce a white light. Conventional inorganic semiconductors exhibit good electronic transport. On the other hand, colloidal nanocrystals (NCs) offer the possibility for flexible, simply processed, low-cost synthesis and a widely tunable absorption and emission spectral range by either changing their size or chemical composition [2]. There have been several attempts to integrate colloidal semiconductor NCs into photovoltaic and optoelectronic devices.

Despite of the outstanding properties of colloidal NCs, their performance is limited by low mobility of charge carriers [3]. Besides, they might be unstable, for example, the interface can be affected by thermal heating, or injection of high energy electrons. One method for overcoming the limitations associated with low carrier transport is to design a hybrid structure, composed of different materials such as colloidal NCs and epitaxially grown inorganic semiconductors. In such hybrid configurations depending on design, the photon-generated excitons in colloidal NCs and/or inorganic semiconductor can efficiently exchange energy by means of Förster coupling [4].

Förster coupling is nonradiative energy transfer (NRET) between excitons and is related to dipole-dipole coupling mechanism where the excitation energy of the donor material is transferred to the acceptor one [5]. It does not rely on carrier transport via electrical connectivity but on energy transfer of electron-hole pairs through dipolar coupling [1]. The efficiency of NRET can exceed that of traditional radiative energy transfer where a photon is emitted by a donor and subsequently absorbed by an acceptor [4].

In semiconductor field, one of the most desired applications is efficient white LEDs for general illumination. A majority of high-efficiency LEDs nowadays is manufactured for colors between red and yellow, while the modern green LEDs have a relatively poor efficiency decreasing with increasing wavelength. Gallium Nitride (GaN) is one of the most important semiconductors used for fabrication of blue and UV LED. Allorying GaN with Indium (In) allows to decrease the band gap energy and,
thus, to cover a broad range between blue and green wavelength. However, the
efficiency of such LEDs depends on the wavelength. For example, InGaN LED emitting
in green region at $\sim 530$ nm has efficiency by a factor of $\sim 2$ less than for LEDs emitting at $\sim 440$ nm. Additionally, InGaN has a disadvantage such as expensive fabrication costs and, also, indium is a relatively rare metal. On the other hand, different cheaper alternatives, such as conjugated polymers or colloidal NCs having efficient fluorescence in the visible, can be used for down conversion of blue and/or UV light in green. Since the technology for fabricating GaN-based LEDs and for synthesizing semiconductor colloidal NCs is mature, hybrid NCs-GaN LEDs are becoming promising for highly efficient multicolor lighting [2]. Inexpensive and easily prepared Zinc Oxide (ZnO) NCs having a broad defect luminescence in the visible region might be a promising alternative in hybrids despite a current problem with p-type control. ZnO has been widely studied over the past two decades since has a great potential for optical, electrical, catalytic and piezoelectric applications. The main technological interest of the ZnO NCs thin films based devices lies on their very low cost and ease of synthesis.

In this diploma work, for fabrication of hybrid structures we have used AlGaN/GaN/AlGaN quantum well (QW) structures with emission spectrum in UV region and colloidal ZnO NCs for down converting of UV light. A fundamentally new approach is to use hybrids designed for utilization of Förster interaction effect. In this case we deposit using a spin-coating a film of ZnO colloidal NCs directly on the surface of AlGaN/GaN/AlGaN quantum well structures containing thin cap layers. Such hybrid structures were characterized by temperature dependent time-resolved photoluminescence (TRPL) measurements as well as cathodoluminescence combined with scanning electron microscope (SEM). Thus, the aim of this thesis was fabrication and studies of the hybrids to justify if structural and material design was consistent with requirements necessary for utilization of NRET effect.

Table 1.1 in next page shows some common abbreviations which will be used in this thesis.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Complete name</th>
</tr>
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<tbody>
<tr>
<td>GaN</td>
<td>Gallium Nitride</td>
</tr>
<tr>
<td>AlGaN</td>
<td>Aluminium Gallium Nitride</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc Oxide</td>
</tr>
<tr>
<td>NCs</td>
<td>Nanocrystals</td>
</tr>
<tr>
<td>QW</td>
<td>Quantum Well</td>
</tr>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>TRPL</td>
<td>Time Resolved Photoluminescence</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>NR</td>
<td>Nonradiative</td>
</tr>
<tr>
<td>NRET</td>
<td>Nonradiative Energy Transfer</td>
</tr>
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</table>
2. Properties of Materials

2.1 AlGaN/GaN/AlGaN Quantum Well

AlGaN/GaN/AlGaN quantum well (QW) is a type I potential well, when the minimum of the conduction band corresponds to the maximum of the valence band. GaN is a III-V group semiconductor with a relatively wide direct bandgap energy of 3.4 eV at room temperature. Alloying of GaN with Al allows increasing the band gap energy from 3.4 eV (GaN) to 6.2 eV (AlN). In the studied structures content of Al was about 14%, corresponding to the band gap energy of ~4.0 to 4.2 eV. QWs were formed in our samples by gallium nitride sandwiched between two layers of AlGaN with a wider bandgap, shown in Figure 2.1. These structures can be grown by molecular beam epitaxy or metal organic chemical vapor deposition with control of the layer thickness down to monolayers.

![Figure 2.1 Schematic drawing of the potential profile for the AlGaN/GaN/AlGaN quantum well.](image-url)
We have studied photoluminescence decay time for the AlGaN/GaN/AlGaN single quantum well of 2nm width with 3-9 nm cap layer. The QWs were grown on sapphire substrates by MOCVD, and the ZnO colloidal NCs thin film was deposited on the top of the cap layer, shown in Figure 2.2. We have investigated three different QW samples denoted as v3805s, v3806s, and v3807s with the cap layer of 3, 6 and 9 nm, respectively.

![Figure 2.2 Schematic of hybrid configuration.](image)

### 2.2 Zinc Oxide Nanocrystals

Zinc Oxide (ZnO) is a II-VI semiconductor with a direct wide band gap of $\sim 3.3$ eV at room temperature, and it can be tuned further to 3-4 eV by alloying with magnesium or cadmium oxide [6]. This semiconductor has several favorable properties, including good transparency, high electron mobility, wide band gap, and strong room-temperature luminescence.

ZnO colloidal NCs in the form of a white powder insoluble in water supplied by Prof. Qingxiang Zhao was synthesized by a chemical precipitation method from the water solution of ZnCl$_2$ and NH$_4$HCO$_3$ mixed with dodecyl sodium sulfate. We have processed these ZnO NCs with the solvent ethanol. In addition, two types of zinc oxide NCs samples from the company SIGMA-ALDRICH were also utilized in our experiments. One of them was ZnO nanoparticles dispersed in ethanol (40 wt %). The other one was 40 wt% dispersion of ZnO nanoparticles in butyl acetate. An average particle size for both type of samples was $< 130$ nm determined by dynamic light scattering (DLS), which is a technique in physics that can be used to determine the size distribution profile of small particles in suspensions or in polymers solutions [7]. Butyl acetate is an organic compound made from acetic acid and butanol in the presence of sulfuric acid.
3. Experimental Techniques

3.1 Fabrication of Zinc Oxide Nanocrystals

In our work, we have mainly used two types of material to make ZnO NCs films. One was 15 wt% ZnO NCs dispersed in ethanol, denoted as type A in this thesis. The other one was 10 wt% ZnO NCs ethanol suspension, in the following referred as type B.

To fabricate type A samples, the solution of 15 wt% ZnO NCs in ethanol was prepared by aqueous synthesis method. In fact, the solubility of ZnO is a drawback in processing, because zinc ions may interact with other ingredients in formulations. Moreover, zinc ions are a strong ligand for polyelectrolytes [8]. Thus, the ZnO NCs can likely aggregate in ethanol. To prevent them from aggregating, the solution was placed into the ultrasonic bath, which uses high frequency sound waves to agitate molecules in a liquid, to suspend and disperse ZnO particles. During the few-steps spin coating process the ultrasonic bath was used several times to keep the ZnO NCs well dispersed in the suspension.

To fabricate type B films, we have used a 10 wt% solution of ZnO NCs in ethanol. For that, we blend the original product of 40 wt% zinc oxide dispersion supplied by SIGMA-ALDRICH, with a proper amount of ethanol to reduce the concentration of NCs. Several attempts were made to optimize the NCs concentration for coating of thin films with a necessary thickness, which should be only of few tens of nm, i.e. transparent for the laser beam in our experiments. We have found that a 1:3 mixture of 40 wt% zinc oxide dispersion with ethanol (99.5 %) provides a ZnO NCs film thickness suitable for optical studies.

Except the materials mentioned above, we have also utilized ZnO NCs dispersion in butyl acetate from SIGMA-ALDRICH, denoted as type C samples. Despite good photoluminescence properties of this type ZnO NCs, it was very difficult to get a small film thickness. Thus, the NCs film was not transparent for the laser beam and the QW could not be excited from the surface side. Moreover, we have synthesized zinc oxide nanoparticles from zinc acetate, ethanol and ammonium hydroxide using method described in Ref. 9.
3.2 Spin Coating

Spin coating is a process used to deposit uniform thin films on flat substrates. In short, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the solvents by centrifugal force. An instrument used for spin coating consists of a spinner, connected to the speed controller, and of a foot switch (see Figure 3.1). In this work, spin coating was done using The Headway Research EC 101Dt-R790 instrument, which is a low cost resist spinner for multifunctional applications. The substrate size could be adjusted by using different vacuum chucks available in the diameter range from 0.75 to 4.5 inch. The machine was equipped with a timer, speed controller, and foot switch. However, there were no any programmable options. The spin coater was installed under the hood, so some volatile and aggressive solvents could be processed too.

![Image of spin coating setup](image)

**Figure 3.1** Spin coating setup at Linköping University.

Hybrids were fabricated as following. Starting with type A material, i.e. a 15 wt% ZnO NCs, thin films were deposited on the top of three quantum well samples, v3805s, v3806s, and v3807s with a cap layer thickness of 3, 6, and 9 nm, respectively, by spin coating method with the speed of 1000 rotations per minute (rpm) acting during 30 s. The spin coating deposition was performed several times (multiple-step spin coating process) using 1-12 cycles until the desired interface contact area was obtained. For the type B samples, 10 wt% ZnO NCs ethanol dispersion from SIGMA-ALDRICH was deposited in a one-step process on the top of the same three QW structures using a spin speed of 2000 rpm. Samples of type C were fabricated using a 40 wt% ZnO dispersion in butyl acetate deposited with the speed ranged from 1000 to 4000 rpm under a 30 s rotation time. The deposition was performed by a multi-step process (1-12 cycles). Details about material and spin coating process
parameters are summarized in Table 3.1.

**Table 3.1** Comparison of three materials in composition and spin coating process.

<table>
<thead>
<tr>
<th></th>
<th>Type A</th>
<th>Type B</th>
<th>Type C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>ZnO NCs 15 wt%</td>
<td>ZnO NCs 10%</td>
<td>ZnO NCs 40%</td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethanol</td>
<td>Ethanol</td>
<td>Butyl acetate</td>
</tr>
<tr>
<td>Speed (rpm)</td>
<td>1000</td>
<td>2000</td>
<td>1000-4000</td>
</tr>
<tr>
<td>Number of cycles</td>
<td>1-12</td>
<td>1</td>
<td>1-12</td>
</tr>
<tr>
<td>Rotation time (s)</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Origin</td>
<td>Internal</td>
<td>SIGMA-ALDRICH</td>
<td>SIGMA-ALDRICH</td>
</tr>
</tbody>
</table>

3.3 Scanning Electron Microscopy

SEM is mainly used for surface topographic studies where the surface of the sample is examined with high magnification and high resolution. The basic idea in the SEM is to scan a focused electron beam over the surface of the sample and at the same time detect the electrons emitting from every point of the surface. Furthermore, the most common contrast mode is secondary electron detection. The emitted low-energetic electrons, known as secondary electrons, are used in the SEM to create contrast and reproduce the surface [10].

Figure 3.2 shows a schematic draw of the SEM system. At the top of the column electrons are generated in an electron gun, then accelerated down through the column and focused on the specimen. The magnetic lenses focus the electron beam into a beam with a small diameter and high current. Scanning coils scan the electron beam over the surface area of the specimen in the vacuum chamber. Different detectors in the vacuum chamber are used to detect secondary electrons, backscattered electrons, X-rays, etc.
Surface morphology study was carried out using a standard high resolution SEM, type LEO 1550 GEMINI Field Emission Scanning Electron Microscope, shown in Figure 3.3. The GEMINI column’s electron source is a Schottky Field Emission type made of tungsten (W) and Zirconia (ZrO$_2$). The system has two types of secondary electrons detectors:

- **InLens**: installed inside the column (high resolution detector)
- **SE2**: installed out of the column axis (better topography visualization)

The chamber vacuum of few 10$^{-7}$ mbar is held by a couple of primary/turbomolecular pumps and the gun vacuum of few 10$^{-10}$ mbar is held by an ionic pump. The GEMINI column has two advantages: First of all, we can use a low electronic acceleration from 0.5 keV to several keV according to the sample, so the charge accumulation effects because of the insulators materials are limited. Secondly, both detectors are complementary and it is very easy to compare their performances.
SEM images were also performed using a tabletop SEM, which is a low voltage and high pressure SEM from FEI called the PHENOM, shown in Figure 3.4. This microscope is operated at an acceleration voltage of 5 keV and at a chamber pressure of approximately $3 \times 10^{-3}$ mbar. This SEM uses a cerium hexaboride ($\text{CeB}_6$) source, permanent magnets for electron focusing, and backscatter detectors arranged in four quadrants. The touch screen features allowing the users to navigate the entire sample, which makes characterization process easier and requires considerably less time [11].
3.4 Time Resolved Photoluminescence

Photoluminescence (PL) is a widely used characterization technique in semiconductor physics due to a number of reasons; it is usually non-destructive technique and requires no special sample preparation, it is a highly sensitive and rather simple method. In typical PL experiments we excite the sample with a photon energy above the bandgap, $E_{\text{exc}} > E_g$. This energy will excite electrons from the valence band to the conduction band, thus, creating electron-hole pairs. When the electrons recombine then with the holes, the energy can be emitted as light photons. Luminescence from the sample can be dispersed to produce a PL spectrum.

A basic semiconductor PL setup consists of three main parts: an excitation source, a monochromator, and a light sensitive detector. The excitation source is usually a laser, and in addition to room temperature PL measurements, a special cryostat is used to cool the samples to a lower temperature of about 5 K. The sample is placed in a sample chamber using a long sample holder, which is immersed into liquid helium inside the cryostat. A schematic drawing of the liquid helium bath cryostat is shown in Figure 3.5.

![Figure 3.5 Schematic drawing of a helium bath cryostat.](image)

The monochromator selects the detection wavelength. In this work, we have used a single monochromator, which contains one grating, shown as $R_1$ in Figure 3.6. This grating is the dispersive element in the monochromator, for instance by constructive or destructive interference. The reflected light from the grating are spatially separated into different wavelength components. Only a very small
wavelength region of the dispersed light will pass through the exit slits of the monochromator, shown as $F_s$ in Figure 3.6. The PL signal at chosen wavelength will reach the detector placed after the exit slit of the monochromator. If we make the slits narrower, we will get a higher wavelength (or spectral) resolution, but at the same time less light or intensity will reach the detector [12].

**Figure 3.6** Optical scheme of a single monochromator.

The detector converts the luminescence signal to a measurable electric signal. In this work a Hamamatsu streak camera and CCD (Charged-Coupled Device) were used. The streak camera is a device to measure ultra-fast light phenomena and delivers intensity vs. time and intensity vs. position (or wavelength) information. These cameras would “streak” reflected light onto the film. Furthermore, it can be used with proper optics, for example, in combination with a spectroscope. Thus, temporal variation of the incident light intensity with respect to wavelength can be measured, which is known as time-resolved photoluminescence spectroscopy.

Figure 3.7 shows the operating principle of streak camera. The light being measured passes through a slit and focused on the slit on the photocathode of the streak tube. Via photoelectric effect, the incident light is converted into a number of electrons proportional to intensity of incident light. Then electrons pass through a pair of electrodes, where they are deflected sideways and meanwhile accelerated to bombard the phosphor screen. When the electrons pass the micro-channel plate (MCP), they are multiplied several thousands of times, after that they impact against the phosphor screen, where they are converted into light again. On the phosphor screen, the earliest arrived light is placed on the uppermost position. The vertical direction serves as time axis and the horizontal direction serves as the location of incident light. Besides, the brightness of various images corresponds to the intensity of incident light [13]. Aside from streak camera, a linear detector, such as a CCD array is used to measure the streak pattern on the screen, and thus the temporal profile of
Another instrument commonly used as a detector in PL measurement is a photonmultiplier tube (PMT) with a GaAs cathode, which is sensitive in the wavelength range of 200 – 900 nm (we have not used PMT for TRPL measurements, but applied PMT in cathodoluminescence). A typical PMT consists of a photo-emissive cathode followed by focusing electrodes, an electron multiplier and an electron collector (anode) in a vacuum tube, as shown in Figure 3.8. When light hits the photocathode, photoelectrons are emitted into the vacuum, known as photoelectric effect. These photoelectrons are then directed by the focusing electrode voltages towards the electron multiplier where they are accelerated and multiplied by a secondary emission at the dynodes, due to impact ionization. The multiplied electrons are collected by the anode as an output signal [12].

A simplified overview of a PL setup is given in Figure 3.9. For the TRPL measurements in this thesis, the excitation light from a Titanium-sapphire laser, was modulated by an amplifier, which gave rise to the third harmonics (λ = 266nm), and
then focused on the samples placed in the cryostat. The sample temperature could be controlled in a broad range of $5 - 300$ K using a temperature variable liquid helium optical cryostat. The photoluminescence was collected with lens and focused onto the slit of monochromator. Then it is spectrally and temporally resolved by using a Hamamatsu C5680 streak camera (with a $\sim 20$ pico second time resolution) combined with a digital camera, C4742-95.

\[
\text{Helium cryostat (Temp $\leq 2.2$ K)}
\]

\[
\begin{array}{c}
\text{Sample} \\
\text{Lenses} \\
\text{Tunable Ti:Sapphire Laser} \\
\text{Amplifier} \\
\text{Solid-state laser} \\
\text{Computer} \\
\text{Detector} \\
\end{array}
\]

\textbf{Figure 3.9} Schematic drawing of photoluminescence set up.
4. SEM Experimental Results

4.1 Sample Specification

In this section we clarify the notations of the studied samples and experimental conditions. As semiconductor QW we have used three AlGaN/GaN/AlGaN quantum well structures with the thickness of GaN QW of 2 nm and with the cap layer of different thickness of 3, 6, and 9 nm, named v3805s, v3806s and v3807s, respectively. These samples were grown by MOCVD technique on sapphire substrates. To fabricate hybrid structures two types of zinc oxide (ZnO) nanocrystals (NCs) film were deposited on these three QW samples, Hybrids were named as, for instance, v3805sZnO, or v3805sZnO10%, where ZnO stands for the material type A, and ZnO 10% stands for the material type B, as explained in section 3.1. The last notation denotes the ambient temperature, for example, the complete notation looks like v3805sZnO50K or v3805sZnO10%RT. For additional conditions, description is added behind the notations. In general, the experimental data for each sample have the following identification:

Notation = QW + deposited film + temperature + special treatment

<table>
<thead>
<tr>
<th>Three QWs</th>
<th>Deposited NCs film</th>
<th>Temperature</th>
<th>Special condition: TRPL acquire</th>
</tr>
</thead>
<tbody>
<tr>
<td>v3805s</td>
<td>ZnO (Type A)</td>
<td>5K - 300K</td>
<td>after 5 minutes</td>
</tr>
<tr>
<td>v3806s</td>
<td>ZnO10% (Type B)</td>
<td>RT = 291K</td>
<td>after 10 minutes</td>
</tr>
<tr>
<td>v3807s</td>
<td></td>
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</table>

The following is a description of how we try to fabricate the optimized ZnO NCs thin film and hybrid structures. The optimal number of spin coating cycles was determined by the following characterizations. For type A, we have started with one cycle of spin coating and subsequent characterization of the surface morphology by SEM. After try and error, it was found that an optimized interface contact area can be achieved when spin coating has been consequently done more than 10 times. Based on this, we have also used a 10 step spin coating when deposited the ZnO NCs of type C. The SEM images have shown that a rather uniform film can be obtained on
the sample surface. Unfortunately, the results of optical characterization of the QWs covered by the type C film was not satisfied since no PL from QW could be detected. That was explained by a very thick ZnO NCs coating film with a thickness exceeding 100 nm, which was not transparent for the laser beam. Even with a reduced number of the spin coating cycles (experiments were done with 5, 3 or 1 cycles) and with an increased rotation speed of 4000 rpm, the problem of film thickness was not solved. Thus, we have concluded that the type C ZnO NCs material in its original form is not suitable for fabrication of the prototype hybrid structures.

Thus we backed to the original solvent which was ethanol, and selected a commercially available 40 wt% ZnO NCs dispersion in ethanol from SIGMA-ALDRICH for fabrication of NCs films. Based on the experience of type C material, we have deposited films using a one cycle spin coating. However, the results were unsatisfactory from the optical point of view. Therefore, new method was carried out to solve the problem. We have decided at lowering the concentration from 40 wt% down to 10%, 5%, and even 1%, and tried again with spin coating. Finally, after a number of tries and failures the type B samples were found to be a satisfactory for optical characterization.

### 4.2 Surface Morphology of the Material Type A

Surface morphology investigation was performed using scanning electron microscopy (SEM). This was done to get information about surface distribution of the ZnO NCs before PL measurements. Such parameters as planar density and the size of ZnO particles, as well as formation of clusters or agglomerations were controlled.

The material type A was deposited on the top of the QW structures as shown in Figure 4.1. The ZnO NCs thin film was deposited by spin coating at 1000 rpm under the rotation time of 30 seconds. This procedure was repeated 5 times (SEM image of the obtained NCs film for this case is shown in Figure 4.1 (a)) and 10 times (see Figure 4.2 (b)). It was experimentally established that numbers of spin coating played an important role in preparing high quality ZnO NCs thin film. It was found that more than 10 times of spin coating cycles permitted to obtain the optimized thin film with high density of ZnO particles. The SEM images taken with a higher magnification are shown in Figure 4.2, where we can observe that ZnO particles agglomerate forming bigger clusters. We have established that 10 cycles of spin coating result in the NCs film with a higher density of ZnO particles compared to 5 cycles, however no any apparent difference in the average size of the clusters has been observed.
In order to make the clusters smaller, we have fabricated the ZnO NCs thin film by a slightly modified way. The thin film was deposited by spin coating for 12 times at the 1000 rpm speed during rotation time of 30 seconds. In this case, every second time after spin coating we placed the ZnO suspension into the ultrasonic bath for 3 minutes to prevent agglomeration of NCs in ethanol. The overall procedure was built as 2 cycles of spin coating $\rightarrow$ ultrasonic bath under 3 minutes $\rightarrow$ 2 cycles of spin
coating → ultrasonic bath under 3 minutes and so went on, until 12 times of spin coating were finished. The result is shown in Figure 4.3, where one can see that the size of cluster did not change very much, however, the film became more uniform and the NCs density is slightly increased in comparison with the films deposited under fewer cycles of spin coating. Thus, the density of ZnO particles increases with increasing cycle number for a determined rotation speed.

Figure 4.3 Surface morphology of the ZnO NCs thin film deposited by spin coating in 12 steps process.

4.3 Surface Morphology of Material Type B

ZnO NCs thin film is also fabricated with the material of type B, i.e. 10 wt% ZnO NCs dispersed in ethanol. In the initial attempts, ZnO NCs were deposited by spin coating repeatedly (1-10 cycles) at the rotation speed of 1000 rpm and during rotation time of 30 s with 40 wt% ZnO dispersion. However, we could not observe any separated particles under SEM taken with low magnification. We made the amount of material for deposition even less, for example using one drop, and meanwhile increased the spinning speed up to 4000 rpm. By doing so, we were still unable to observe any separated particles by using a tabletop SEM.

To penetrate with the laser beam through the NCs films (for example, the polymer film was rather thin (~15 nm) in Ref.12), we needed to fabricate ZnO coating of only few nanometers thick. Hence the original 40 wt% dispersion was blended with additional amount of ethanol to make the concentration down to 10 wt%, namely the type B material. After that ZnO NCs were deposited by one step spin coating process at the speed of 2000 rpm during 30 seconds. The surface
morphology is shown in Figure 4.4 revealing a much higher density of NCs than for fabrications using the type A material. We have observed that ZnO NCs thin film was uniform, and there were practically no cluster or agglomeration formations. Figure 4.4 (a), (b) and (c) show the deposited thin film on different QW structures, v3805s, v3806s, and v3807s, respectively.

Figure 4.4 Surface morphology of ZnO NCs thin film with material type B.

a) Deposited on QW v3807s.

Figure 4.4 b) Deposited on QW v3805s.

Figure 4.4 c) Deposited on QW v3806s.
5. TRPL Experimental Results

5.1 TRPL of Hybrid Structures Based on Material Type A

In this thesis work, thermal evolution of dynamics of excitons confined in the quantum well (QW) was measured for the bare QW structures and for the hybrid configurations, i.e. samples with and without ZnO NCs have been studied by TRPL at different temperatures. The exciton lifetime was extracted from PL decay curves assuming single exponential decay law. Results described in this section were obtained for ZnO NCs of the type A. Some parameters regarding PL measurements are shown in Table 5.1. Ambient temperature was 18 °C, which corresponds to the constant clean room temperature. The power of the laser beam was adjusted by manual alignment, and measured by the power meter.

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<tr>
<td>Integration time and number of acquisitions.</td>
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</table>

In TRPL experiments, we measure PL decay time of the QW exciton in hybrids and in the bare QW structures. The different point between three hybrid structures is the thickness of cap layer which is sandwiched between GaN QW and ZnO NCs thin film. Figure 5.1 shows the comparison of PL decay between samples with (the red lines) and without (the black lines) ZnO NCs films. We measured the bare quantum well samples at temperature 290 K, and the hybrid structures at clean room temperature 291 K. The graphs on the left column are from direct measurements right after excitation by the laser, while the graphs on the right column are from measurements after 5 minutes of excitation. We can easily see that some of PL decays became faster in the presence of ZnO NCs films. Effect happened to be even stronger after 5 minutes excitation in the sample labeled as v3805s and v3806s. However, the v3807s hybrid structure does not show any obvious effect, judged from the result that the decay time is insignificantly shorter than that of the bare quantum well.
Figure 5.1 Normalized PL decay curves of the bare QWs (black lines) and of the hybrid structure (red lines). a) The uppermost two graphs are v3805sZnORT. b) In the middle is v3806sZnORT. c) Graphs at the bottom are v3807sZnORT.

Temperature dependent TRPL measurements have been also done. The hybrid structures were held at a temperature in the range of 5-300 K using a liquid helium bath optical cryostat. In this case, the laser beam was aligned to pass through the optical window into the cryostat. Temperature in the cryostat could be controlled. Measurements were done with the step of 20 K until 200 K, and with the step of 30 K between 200 K and room temperature.
Table 5.2 TRPL experiment parameters.

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<tr>
<td>Power of laser</td>
<td>17 – 18 mW</td>
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<tr>
<td>Exposure time and number of acquisitions.</td>
<td>10 seconds × 5</td>
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</table>

Temperature dependence of the decay time in the bare QW labeled v3805s with and without ZnO NCs films is shown in Figure 5.2. At some temperatures, the PL decay of the QW was observed to accelerate in the presence of ZnO NCs. The difference between PL decay times was particularly strong at the low temperatures, such as 5 K, 10 K, 20 K, 30 K, 50 K and temperatures close to room temperature. We have detected the strongest effect at 50 K. However, we have also observed that the effect suddenly disappeared when the samples was heated further above 50 K, which can be explained by mechanical degradation of the interface between AlGaN cap layer and ZnO NCs film due to difference in the thermal expansion coefficient. The accelerated PL decays measured at these specific temperatures are shown in Figure 5.3.

![Figure 5.2 Temperature dependence of decay time of the v3805s QW (black line) and v3805sZnO (red line).](image)
Figure 5.3 Accelerated PL decay of v3805sZnO at single temperature. a)5K b)10K c)20K d)30K e)50K f)240K g)270K h)290K

It can be easily observed in the experimental spectra when we have an apparent accelerated PL decay. For example, the accelerated decay for v3805s hybrid structure is shown in Figure 5.4. The decay time is much shorter in the hybrid structure (bottom figure) than that in the bare QW (top figure), while the peak emission practically have the same wavelength.

Figure 5.4
Experimental TRPL image of v3805s QW (top figure) and v3805sZnO (bottom figure).
Temperature dependence of decay time in v3806s as well as in v3807s is shown in Figure 5.5 and 5.6, respectively. For these structures, the PL decay of the QW was accelerated only insignificantly in the presence of the ZnO NCs.

**Figure 5.5** Temperature dependence of the decay time in v3806s QW (black line) and v3806sZnO (red line).

**Figure 5.6** Temperature dependence of the decay time in v3807s QW (black line) and v3807sZnO (red line)
Concluding the results of section 5.1, we have experimentally observed that for all three bare QWs and for hybrid structures, the decay time decreases with increasing temperature. Furthermore, it was found that the v3805s hybrid structure has the most evident acceleration effect in PL decay detected for certain temperatures. For v3806s and v3807s hybrid structures, we only insignificant effects could be detected both at low temperature (5K) and at room temperature (300 K). The decrease of the decay time is related to different thickness of cap layer. The thicker cap layer was, the less effect was observed. For thicknesses above 6 nm the effect was inhibited.

5.2 TRPL of Hybrid Structures Based on Material Type B

The PL decay of the QW excitons has been measured at different temperatures for the samples with and without ZnO NCs using the material type B, i.e. 10 wt% ZnO dispersion in ethanol. Judging from SEM analysis, the density of NCs in the film was high. Several PL measurements on samples with the type B material have been done before it was decided that the film obtained with the 10 wt% concentration of NCs was suitable for optical characterization.

In the beginning, we did PL measurements with an original product material, which was 40 wt% ZnO dispersion. However, the NCs film was very thick, so we could not detect any PL signal from the quantum well. The only signal was from ZnO NCs. When the ZnO NCs colloidal film is too thick, it absorbs all of energy from the laser. Therefore, we have either fabricated the material using the lower concentration of NCs in ethanol or increased the spin coating speed, which gives the thinner film. Finally, when the ZnO NCs concentration was reduced to 10 wt%, we have got an obvious PL signal from the quantum well. Some parameters regarding PL measurement is shown in Table 5.3

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<td>Power of laser</td>
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<td>Exposure time and number of exp.</td>
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</table>

Table 5.3 TRPL experimental parameters.

Figure 5.7 shows photoluminescence decay curves of three different QWs with (red lines) and without (black lines) ZnO NCs colloidal film. The graphs on the left
column are from direct measurements right after excitation by the laser, while the graphs on the right column are from the measurements after an exposition during 10 minutes to the laser excitation. We have observed that some PL decays measured for the QW excitons accelerated in some cases in the presence of ZnO NCs colloidal film, which means that the exciton recombination time became shorter in hybrid compared to the bare quantum well. The effect was rather strong in the v3805sZnO10%RT hybrid, less obvious in v3806sZnO10%RT, while in v3807sZnO10%RT there was almost no effect. After a 10 minutes excitation, the effect in the v3805s and v3806s hybrids becomes stronger, which means the decay time was getting shorter.

Figure 5.7 Normalized PL decay curves of the bare QWs (black lines) and hybrid
structure (red lines). a) The uppermost two graphs are the samples v3805sZnO10%RT. b) In the middle are v3806sZnO10%RT. c) At the bottom are v3807sZnO10%RT.

TRPL for this type of hybrids have also been performed for a range of temperatures between 100 K and 300 K. We have done the measurements with the step of 20 K between 100 K and 160 K. The data were also taken at 200 K, 240 K, and 300 K. Due to a temporary malfunction of the monochromator the experiment was interrupted, so no data were obtained for lower temperatures. Because of some instrumental problems with streak camera sensitivity at some pixels causing an intensity variation of the PL, fitting of the decay curve might be less accurate for these samples, and hence the real decay time in the hybrid structures might be slightly different than the calculated values.

Table 5.4 TRPL experiment parameters.

<table>
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<tr>
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<td>Power of laser</td>
<td>16 mW</td>
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<td>Exposure time and number of acquisitions.</td>
<td>10 seconds × 5</td>
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</tbody>
</table>

The difference between the PL decay time in the v3805s hybrid and in the bare configuration was especially strong for temperatures above 200 K, as shown in Figure 5.8. Three PL decay curves measured above 200 K for the hybrids and for the bare QW show such a difference as illustrated in Figure 5.9.
Figure 5.8 Temperature dependence of decay time in v3805s QW (black line) and v3805sZnO10% (red line).

Figure 5.9 PL decay curves of the v3805sZnO10% hybrid and bare QW taken at specific temperature. a) 200K b) 240K c) 300K
The temperature dependence of the decay time in the \text{v3806sZnO10\%} sample and \text{v3807sZnO10\%} is shown in Figure 5.10 and 5.11, respectively. For the \text{v3807sZnO10\%} sample, Figure 5.12 shows accelerated PL decay measured at 240 K and 300 K for hybrid configuration.

**Figure 5.10** Temperature dependence of the decay time in the bare \text{v3806s} QW (black line) and in the \text{v3806sZnO10\%} hybrid (red line).

**Figure 5.11** Temperature dependence of the decay time in the bare \text{v3807s} QW (black line) and \text{v3807sZnO10\%} (red line).
Figure 5.12 Accelerated PL decay of v3807sZnO10%240K on the left graph and in the v3807sZnO10% hybrid on the right graph.

To summarize the section 5.2, it was found that for three QWs and hybrid structures, decay time decreases with increasing temperature in spite of only a small trend in v3806s. Concerning the acceleration of the decay, we have found that again the v3805s hybrid structure demonstrates the most evident effect, while v3806s hybrid structure does not show any obvious effect. However, the v3807s hybrid structure unexpectedly shows acceleration of the PL decay above 240 K, which means that there might be different mechanisms besides NRET causing the phenomenon.

5.3 Time-Integrated PL Spectra

The study of the photoluminescence spectra was carried out for the bare configurations and hybrid structures.

The nominal thickness of the GaN QW in all structures L_w was fixed at 2 nm, producing photoluminescence peaks at 350 ± 1 nm, as shown in Figure 5.13. The second highest peak at 364 ± 1 nm observed in PL spectra was related to the GaN buffer layer, which has band gap 3.4 eV at room temperature. We note here, that for the bare QW structure (the black line) the GaN buffer related peak has lower relative intensity because of adjustment procedure so mainly the emission from the quantum well was focused on the entrance slit of the monochromator. Several peaks above 370 nm were originated likely from different donor bound excitons in ZnO NCs, which has band gap approximately at 3.3 eV.
Figure 5.13 Normalized photoluminescence spectra of the bare v3805s QW (black line) and hybrid structures (red line).

TRPL data are shown in Figure 5.14. Top image corresponds to the time-integrated PL spectrum shown by the black line in Figure 5.13, and the bottom spectrum corresponds to the PL spectrum shown by the red line. From TRPL images, we can directly observe that the light emission from ZnO above wavelength 370 nm is quite strong, and the emission wavelength from quantum well is the same as in the bare QW structure. The two images were taken at the different detection wavelength corresponding to the center wavelength.
Figure 5.14 TRPL images of the v3805s QW at 290K (top) and v3805szno10% hybrid structure at 300K (bottom).

We have studied temperature dependent PL spectra in the v3805s hybrid structure. The PL intensity of the QW exciton decreases rapidly with increasing temperature, while the PL intensity from the ZnO NCs is maximal at 300 K, as shown in Figure 5.15. The QW PL intensity changes reflect that the radiative recombination
dominating at low temperatures starts to compete with non-radiative (NR) recombination dominating at room temperature. The recombination for ZnO NCs is governed by non-radiative recombination mechanisms even at low temperatures. The PL spectra here are shown only for the v3805s hybrid structure, since results were similar for other two structures with thicker cap layer.

In Figure 5.16, the v3805s QW emission shows thermal broadening with increasing temperature, and the peak of emission wavelength shifts by 5 nm, equal to 50 meV. The variation of the photoluminescence wavelength is mostly dominated by the position of excitation on the samples [14].

![Figure 5.15 Time-integrated PL spectra measured at different temperatures for the v3805szno10% hybrid structure.](image)

![Figure 5.16 Normalized PL spectra of hybrid structure are shifted in vertical direction for clarity.](image)
6. Discussion

In this section, we discuss the possible processes which can occur in our hybrid structures, and we consider three models to explain the experimental results. The first model is connected to non-radiative resonant energy transfer (NRET), which explains energy transfer between excitons in QW and in ZnO NCs. The second model is related to tunneling effect, i.e. assuming electrons can tunnel through the cap layer, and recombines via the surface non-radiative recombination center. The third model regards polarization effect and in-build piezoelectric field, which may explains the influence of the surface potential on the QW potential profile.

6.1 Nonradiative Energy Transfer

6.1.1 Theoretical Calculations

In order to obtain information about exciton dynamics from TRPL spectra, we have to extract experimental decay time $\tau$ (or decay rate $\Gamma$), and then we can calculate the energy transfer efficiency $\eta$. Decay time here is the life time of the exciton confined in the GaN quantum well, and the decay rate, correspondently, is its recombination rate. Since the PL decay curve taken for the QW emission obeys the exponential decay law, we can extract the decay time by fitting using the equation:

$$I(t) = I_0 \exp(-t/\tau) \quad \text{(eq. 6.1)}$$

The fitting procedure of the experimental curves was done using equation 6.2, where $y_0$ represents the background signal, while $A$ and $t_0$ correspond to maximum intensity and the x-position of the peak, respectively. $I(t)$ denotes the intensity of the signal, which changes with time $t$, and the decay time we would like to extract is $\tau$.

$$I(t) = y_0 + A\exp\left(-\frac{(t-t_0)}{\tau}\right) \quad \text{(eq. 6.2)}$$

Figure 6.1 shows an example of exponential fitting performed in OriginPro 8 program. Fitting was done at the fixed background value $y_0$, peak intensity value $A$, and the position of the peak $t_0$. The table in figure 6.1 shows these three parameters.
The obtained decay time was around 134.44 ps for this case. The blue line in Figure 6.1 shows the fitting of the PL decay curve.

**Figure 6.1** Exponential decay fitting of the PL decay measured for the QW exciton (v3805sQW270K TRPL image).

The decay time was calculated for different temperatures. The decay (or recombination) rate $\Gamma$ is reciprocal decay time, equal to $1/\tau$. Total recombination rate of the QW exciton can be written as the sum of the radiative and non-radiative terms [1]:

$$
\Gamma_{\text{bare,QW}} = \Gamma_{\text{rad}} + \Gamma_{\text{nonrad}} = \frac{1}{\tau_{\text{QW}}} \quad \text{eq. (6.3)}
$$

For hybrid configuration, when we have an increased recombination rate we have to add an additional term due to energy transfer processes:

$$
\Gamma_{\text{tot,hybrid}} = \Gamma_{\text{rad}} + \Gamma_{\text{nonrad}} + \Gamma_{\text{ET}} = \frac{1}{\tau_{\text{tot,hybrid}}} \quad \text{eq. (6.4)}
$$

Therefore, the energy transfer rate can be quantified from the increased decay rate in the presence of ZnO NCs. The subscripts hybrid and bare denote the QW with and without ZnO NCs, respectively.
\[ \Gamma_{\text{ET}} = \Gamma_{\text{tot,hybrid}} - \Gamma_{\text{bare,QW}} \quad \text{eq. (6.5)} \]

Finally, the efficiency of the process is defined as,

\[ \eta_{\text{ET}} = \frac{\Gamma_{\text{ET}}}{\Gamma_{\text{tot,hybrid}}} \quad \text{eq. (6.6)} \]

### 6.1.2 Discussion of NRET process

NRET is a process when the energy is transferred from the exciton in QW to the exciton in ZnO NCs film, as schematically shown in Figure 6.2.

![Figure 6.2 Illustration of energy transfer from the QW excitons to the ZnO nanocrystal and the corresponding energy diagram.](image)

We have measured the energy transfer rate in the hybrid structures by comparing the PL decay rate of hybrid structure, \( \Gamma_{\text{tot,hybrid}} \), and the bare QW, \( \Gamma_{\text{bare,QW}} \). Whereas in the bare QW, \( \Gamma_{\text{bare,QW}} \) is dominated by the exciton radiative decay rate and any NR recombination channels intrinsic to the QW structures, in the hybrid structure, \( \Gamma_{\text{tot,hybrid}} = \Gamma_{\text{bare,QW}} + \Gamma_{\text{ET}} \), where the exciton transfer contributes to the QW photoluminescence decay rate as an extra NR channel. Therefore, it shortens the lifetime of the exciton in QW, and, thus, an accelerated PL decays were measured. Assuming NRET process, we can see an enhanced recombination rate in experimental data obtained for both materials type A and type B used for fabricating ZnO NCs thin film. As described in section 5.1 and 5.2, the accelerated PL decay was apparent at clean room temperature. Decay times as well as decay rates are shown in Table 6.1 and Table 6.2 for the hybrids with type A and B material, respectively. The calculated energy transfer (ET) rate and the ET efficiency are shown in Table 6.3. The crosses of bare QWs mean that we did not measure at that conditions, but the crosses of
From these three tables, we can easily see that in the hybrids an additional non-radiative recombination channel likely due to NRET has appeared since the v3807sZnO10% in Table 6.3 mean it that we have not observed any NRET process.

### Table 6.1 Decay time and decay rate for three QWs and hybrid structures at clean room temperature with material type A.

<table>
<thead>
<tr>
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<th>Decay time (ps)</th>
<th>Decay rate (ns(^{-1}))</th>
<th>Decay time after 5mins</th>
<th>Decay rate after 5mins</th>
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<td>8.44 ±1</td>
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<td>x</td>
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<td>v3805sZnO</td>
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<td>6.02</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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### Table 6.2 Decay time and decay rate for three QWs and hybrid structures at clean room temperature with material type B.

<table>
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<th>Decay rate after 10mins</th>
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### Table 6.3 ET rate and ET efficiency for material type A and type B.

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<td>5.96</td>
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</tr>
<tr>
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</tr>
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decay rates for the hybrid structures became bigger than for the bare QWs. The calculated energy transfer rate was even larger when the hybrid structures were excited after a five or ten minutes by the laser beam. The varying ET rate means some instability in the emission. One of the possible explanations of such metastable phenomenon can be related to the formation of the additional mechanism for the carrier escape from the QWs. Deep defect levels originated from the organic compound in ZnO NCs and surface defects might be involved.

It was found that the QW exciton lifetime in hybrids decreases with increasing thickness of the cap layer and effect was the strongest for the sample with 3 nm thick cap layer, while it was mostly inhibited in v3807s with a thicker cap layer of 9 nm.

Next we show the temperature dependence of the total decay rate in the bare QW and the hybrid structures, which simply is the reversed graph of the decay times in section 5.1 and 5.2.

![Figure 6.3](image)

**Figure 6.3** Temperature dependence of decay rate for three bare QWs and for hybrid structures fabricated with the type A material.
Figure 6.4 Temperature dependence of the decay rate for three bare QWs and for the hybrid structures made using the type B material.

The exciton recombination rate measured in the bare QW as well as in the hybrids increases with temperature due to thermal activation of the NR recombination channels in the QW. These channels include carrier trapping at defect states, such as dislocations or AlGaN/GaN interfaces and phonon scattering. With increasing temperature in the range between 5 and 50 K a localized exciton (i.e. 0D) becomes free in the QW plane (i.e. 2D) and acquires kinetic energy, which promotes NR recombination to be more efficient.

In Figure 6.3, we can see difference between recombination rates at several temperatures which may be explained by NRET especially apparent in v3805s hybrid structure, while v3806s and v3807s hybrid structures the effect was insignificant. The effect was small at low temperatures even for v3805s hybrid structure due to strong localization of excitons at the potential fluctuations. We have also observed a strong increase of the recombination rate at 50 K for the v3805s hybrid, after which the effect was suddenly gone. To be sure that the measurements at 50K were accurate we are going to repeat similar experiment again for the same type of ZnO NCs. As temperature elevating, the difference between recombination rate in the bare QW and in the hybrid appears again at 240K, and becomes stronger in the high temperature range. We assume that there is thermal expansion while heating our samples, which might somehow destroy the interface contact. In that case there will
be no interaction between excitons in the QW and in the ZnO NCs and the both material systems will behave independently of each other. It might be other possible mechanisms except NRET, which should be considered to explain experimental results.

In Figure 6.4, we can see some difference between the recombination rates in the v3805s type B hybrid structures above temperature 200 K, while there is no effect in the v3806s hybrid. However, in the v3807s hybrid of the same type B we have unexpectedly detected a clear difference between recombination rates above temperature 240 K, even if we mentioned previously that the thick cap layer of 9 nm might inhibit the energy transfer in hybrid structures. Therefore in the next section the following possible mechanisms except NRET will be discussed to explain the experimental results.

6.2 Tunneling Effect

The second explanation of the accelerated PL decay assumes that the carriers in QW will perform tunneling through the cap layer to the ZnO NCs film. Tunneling effect is a quantum mechanical phenomenon describing a particle, which has no energy to pass over a potential barrier, may still tunnel through it, as shown in Figure 6.5. When a particle of energy $E < U$ approaches a potential barrier, according to classical mechanics the particle must be reflected. In quantum mechanics, the wave function of a particle is partly transmitted in the barrier, which means that the particle has a finite probability of penetrating the barrier [15].

The schematic band diagram of the v3805s hybrid structure is shown in Figure 6.6. The excitons are confined in the QW surrounded by the potential barriers. However,
in the hybrids the probability that the carriers can tunnel through the AlGaN cap layer can be increased if the potential barrier between the QW and the surface decreases in the presence of ZnO NCs. This means increasing non-radiative recombination related to the surface defects, which can act as donors or acceptors, but since they are normally deep levels, they act as NR recombination centers [16].

Figure 6.6 Schematic model showing surface potential fluctuations, NR recombination center, and possible tunneling from the electrons confined in QW to the surface.

Thus, the shorter decay time in hybrids can be explained from the fact that photogenerated electrons tunnels more efficient through the cap layer from QW to the surface in the presence of the ZnO NCs. In this case, the QW recombination is dominated by NR recombination centers not related to the excitons in ZnO NCs. For the thicker cap layers over 6 nm, the tunneling effect becomes less.

6.3. Polarization Effect

Polarity of the film defines surface properties and direction of spontaneous polarization in the crystal [17]. Spontaneous polarization is an intrinsic property of the material. All heterostructures based on GaN show spontaneous polarization. We have used AlGaN/GaN QW with wurtize GaN and AlGaN. Wurtzite structure is a
hexagonal structure which features in planes of only one type of atoms in [0 0 0 1] direction. Electronegativity of gallium is 1.6 and that of nitrogen is 3. Therefore, in GaN crystal, free electrons are likely to gather around nitrogen atoms, which leads to negatively charged nitrogen atoms and positively charged gallium atoms; thus, an internal electric field is created. For example, the spontaneous polarization is shown in Figure 6.4. The complete electric field in the III-nitride heterostructures is a sum of spontaneous polarization and piezoelectric field and its direction depend on the material system and structure design.

Hence, total polarization is the sum of the two components:

$$\vec{P}_{tot} = \vec{P}_{spon} + \vec{P}_{piezo}$$

![Crystal structure and a unit cell of wurtzite GaN](image)

**Figure 6.7** Crystal structure and a unit cell of wurtzite GaN [18].

Piezoelectric field is present in the film due to the stress generated by lattice mismatch between film and substrate during growth process. It has been shown previously that piezoelectric effects can exert a substantial influence on the concentration and distribution of free carriers in strained group III-nitride heterostructures with the wurtzite crystal structure grown in [0001] direction [19].

Currently the most of the GaN optoelectronic devices are based on c-direction [0001] grown films, which is a polar growth direction. The built-in polarization field leads to band bending, which in its turn leads, despite the QW confinement, to a significant spatial separation of the charge carriers. The spatial separation dramatically decreases the probability of their radiative recombination (Figure 6.5).
Figure 6.8 a) Energy band bending in AlGaN/GaN QW structure in the presence of the in-built electric field. b) Normal band structure.

From quantum mechanics point of view, the overlapping of wave functions can determine the probability of radiative recombination, which means

$$|\varphi_a|^2 \propto \frac{1}{\tau_a}$$

Where $|\varphi_a|^2$ is related to the oscillator strength, corresponding to the probability density of finding a particle in a given place at a given time, and $\tau_a$ is decay time of exciton in QW. Figure 6.5a shows less overlapping of wave functions than that in b, indicating that lifetime of excitons in bending quantum well is longer than that in normal quantum well. On the other hand, because the separation between ground energy states in conduction band and valence band get shorter, the exciton transition energy becomes smaller, leading to red-shift of the peak emission.

We have studied the AlGaN/GaN QW structures grown in c-direction and, thus, having band bending due to in-built electric field effect. This bending could be different in three samples, and also it can be affected by temperatures and surface potential. When ZnO NCs film was deposited on the top of QWs, an additional surface potential might affect the QW potential. To explain the experimental results, we suggest that surface potential could change the potential bending so the QW become, to some extent, more normal rectangular quantum well. Consequently, the PL decay will be accelerated in such normal quantum well compared to that in the original bended quantum well.

However, for structures with thicker cap layers, surface potential is less important. As we can see from results discussed in section 5.1, samples v3806s and v3807s do not show any apparent accelerated PL decay.
7. Conclusion

We have fabricated ZnO NCs thin films and studied the QW exciton recombination in the bare QWs and in the hybrid structures. Among all of the experiments, hybrid structures based on v3805s with the cap layer of 3 nm has the most apparent accelerated PL decay. The results from the type A and type B materials are slightly different although they practically have the same composition. The type B material was supplied by SIGMA-ALDRICH and has had a higher density of the ZnO NCs in the dispersion. The resulting ZnO film in hybrids was thicker with more particls per area unit. The results from the type A material hybrids (section 5.1) seems more consistent with the NRET model than that for the type B material hybrids (section 5.2). The accelerated PL decay in the hybrid structures can be explained besides the NRET process by the contribution of other additional NR recombination mechanisms. However, there is still no consistent model which could completely explain all the observed data. Especially, we have found in the hybrid structure v3807sZnO10% an unexpected behavior of the decay time at temperatures above 240K. More experiments are needed, for example temperature dependence of the PL decay time in the whole range of 5-300 K for the hybrid structure fabricated with the type B ZnO NCs material.

Understanding the effects governing the QW exciton lifetime in ZnO NCs/QW hybrid structures provides an important feedback to the development of hybrid optoelectronic devices. For the hybrid structures fabricated in this study, the emitted light was centered mainly in UV range, because both GaN QW and zinc oxide has band gap from 3.3 eV to 3.4 eV. However, ZnO NCs have demonstrated a strong broad defect band with peak position in the green region. The origin of this emission is associated with different defect states, such as for example, Zn and/or oxygen vacancies and interstitials. Similar defect luminescence in ZnO nanoparticles was successfully used in hybrid diodes to obtain the white-light emission [21]. Thus, the studied ZnO NCs/ GaN QW structures have both a strong interest for optoelectronic applications and for fundamental understanding of the recombination processes and interaction between excitons in such hybrids.
References


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