Luminescence in ZnO

Jin Xu
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Luminescence in ZnO

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University.

By

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ABSTRACT

LUMINESCENCE IN ZNO

By Jin Xu, M.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University

Virginia Commonwealth University, 2004

Major Director: Hadis Morkoc

As a wide band semiconductor with a large binding energy (about 60meV), ZnO is a promising candidate semiconductor material for the next generation of optoelectronic, light emission or high power and high frequency devices.

In order to make electrical device from ZnO, it is necessary to investigate optical properties of ZnO. In this thesis, PL setup and the properties of ZnO are introduced briefly and the optical properties of ZnO are investigated in detail. Temperature dependence of PL spectra of ZnO are measured and analyzed. Sharp emission line of PL spectra of rare earth (RE) doped ZnO are also investigated.
Chapter 1  Introduction

Recently wide-band semiconductors have attracted great interest, because their future possible applications in many area, such as UV sensors, light-emitting diodes (LEDs), laser diodes (LDs), and other high-speed high-power electronic devices\textsuperscript{[1-7]}. ZnO is a promising candidate for the next generation electronic devices due to its good properties. ZnO is a direct wide band gap semiconductor ($E_g$\textasciitilde 3.3eV at 300K), which is suitable of production of light emitting devices in the visible range of green, blue, ultraviolet, or white light. It has some substantial advantage over currently developed wide-band-gap semiconductor devices (e.g. GaN-based). For example, the high quality bulk single crystals are available now and it has a large exciton binding energy ($\textasciitilde$60meV) with potential for emitters utilizing exciton emission at room temperature (RT).

Since ZnO films are most expected to be applied in optical area, it is important to investigate the optical properties of different ZnO films. Not only does it help us to analyze the structure and other properties of ZnO, but also it contributes to the optimization of the growth process of ZnO, or to the application of optical devices. In this work, the photoluminescence (PL) of different ZnO films is investigated, such as n-type ZnO, p-type ZnO, ZnO-based alloys, rare earth doped ZnO. Temperature
dependences and intensity dependences are measured to give us an ideal of what happens to ZnO at different temperatures and PL excitation powers. The defects in ZnO are analyzed in detail. However, there are a lot of unknown areas in research of ZnO.

This thesis is divided into five parts. The first part gives background of this topic and the purpose of this project. The second part introduces the basic theory of PL and typical PL setup, including the measurement process. The third part introduces basic properties of ZnO material, including related information. The fourth part introduces the PL characterization of different ZnO samples and analyzes the possible luminescence source and defects in ZnO. The last part gives a conclusion of the paper and future work to be done.
Chapter 2 Luminescence

2-1 Luminescence Introduction

The light emission from any process other than blackbody radiation is called luminescence. Luminescence is a nonequilibrium process for it needs excitation source, such as lamp or laser. Depending on the different excitation sources, we have photoluminescence (PL), which requires optical excitation, electroluminescence (EL), which needs excitation by electrical current, cathodoluminescence (CL), which results from electron bombardment, and the other kinds of luminescence. PL is one of the most widely used experimental methods for study of semiconductors, especially wide-band-gap materials [8-13]. PL is divided into two major types: intrinsic and extrinsic luminescence.

The intrinsic luminescence has three kinds of luminescence, which are band-to-band luminescence, exciton luminescence, and cross-luminescence, respectively.

The recombination of an electron in the conduction band with a hole in the valence band generates band-to-band transition luminescence, which is sometimes shown in high purity crystals, such as Si, Ge and GaAs. At low temperatures, this luminescence
is often replaced by the exciton luminescence. The light emission from bright light-emitting diodes and semiconductor lasers is also usually due to the band-to-band transition process.

Extrinsic luminescence is normally generated by the impurities which are intentionally or unintentionally incorporated. These kinds of impurities are normally called activators. There are two kinds of extrinsic luminescence in semiconductors. One is unlocalized type, the other is localized type.

Different luminescence studies are applied for semiconductor characterization. Defects in semiconductors are studied by the steady-state PL (SS-PL) spectra, time-resolved PL (TR-PL), or PL excitation (PLE) spectra. Optically detected magnetic resonance (ODMR), a modification of the PL technique, is also a very efficient method, especially in identification of the defects.

2-2 PL setup
A typical PL system includes the following parts (Fig. 2-1):

1. A source of light for excitation. In case of GaN, it is usually He-Cd laser for the SS-PL and nitrogen pulse laser for TR-PL. A lamp with a monochromator or a laser with tunable wavelength is used for PL excitation.

2. A sample holder, which is usually in an optical cryostat for achieving low temperature.

3. Filters and collecting optics. One filter, which is on the way of the laser beam, is required to select the main laser emission line and cut off undesirable lines. Another filter
on the way of PL is needed to cut off the scattered laser light. Neutral density filters are used to attenuate the laser light intensity.

4 A dispersive element for spectral analysis of PL, usually a grating monochromator.

5 An optical detector with appropriate electronics and readout. For ZnO, photomultiplier tubes (such as R955 from Hamamatsu Co.) provide good sensitivity in the visible range where ZnO mostly emits.

Photon counting systems allow increasing sensitivity by accumulation the signal. TR-PL may require additional advanced technique, such as streak camera for very fast transients, however a simple digital oscilloscope in combination with inexpensive pulse nitrogen laser may be more useful for measuring the defect-related PL decays in ZnO which typically cover the range from a few ns to ms.

2-3 Measurement of PL

First, the excitation laser should be turned on and the high voltage supply, for photomultiplier tube (PMT), should be also turned on. Then a standard control sample is installed on the sample holder to check whether the setup works correctly. If the signal is weaker than usual, the position of the excitation beam should be adjusted to find the right position when the sample, condenser, and monochromator slit are aligned. After adjusting the setup, the sample to be measured is installed on the sample holder. The monochromator slit can be increased to enhance the PL signal from the sample and
increase the signal-to-noise ratio (SNR). But the maximal signal should be lower than $3 \times 10^4$ counts; otherwise the PMT may be damaged for high current generated. When the scanning range is from 350 to 560 nm, the 350 nm cut-off filter should be placed in front of the monochromator slit to cut off the scattered laser light (325 nm). The 540 nm cut-off filter (yellow) is useful to scan the range from 540 nm to 800 nm, where strong second-order emission may interfere with weak PL signal in this range.

The resolution of the spectrum depends on the scanning steps. Roughly, 1 nm equals to 8-9 meV in the photon range between 350 nm and 400 nm, which cover the DAP and exciton peaks range of ZnO. After collecting the data, the spectrum should be normalized accounting for the set-up responsivity curve, which is obtained by calibration data. Finally, the PL spectra can be plotted with the help of Kaleidagraph or Origin graphic software for data analysis and plotting.

2-4 A Steady-state photoluminescence

Steady-state photoluminescence (SS-PL) spectroscopy is widely used to qualitatively characterization of GaN, ZnO, and their alloys. Usually the SS-PL is generated in ZnO by illuminating it with a HeCd laser (325 nm) beam running at powers of up to ~ 60 mW. A special care should be taken to provide low enough excitation density, since the defect-related PL often saturates at power densities of the order of $10^2 - 10^4$ W/cm² and the PL spectrum may be distorted in favor of ultraviolet (UV) emission at
higher excitation densities. Additional distortion of the PL spectrum can arise from focusing the laser beam and using small slit widths of a monochromator for entire PL spectrum. In such case, the chromatic dispersion of lenses used to collect the PL, as well as different effective sizes of the emission spots for the UV and visible emission, attributed in particular to photon-recycling process, may lead to a marked artificial enhancement of the UV over the visible part in the PL spectrum. A low-temperature PL spectrum of high-quality n-ZnO is shown in fig 2-2.
Qualitative terms such as “very intense PL that confirms high-quality of the material” are omnipresent in the literature on GaN. However there have been very few attempts to estimate the absolute value of PL intensity or its quantum efficiency (QE). Although the direct measurement of the QE is not straightforward, there were attempts to estimate this important characteristic performed the simultaneous detection of the calorimetric absorption (measure of nonradiative recombination), transmission, reflection,
and excitation power. An indirect method based on quantitative analysis of the competition of radiative and nonradiative recombination channels was suggested by Reshchikov and Korotkov\textsuperscript{[13]}.

Quantitative studies of point defects in ZnO by PL were rarely undertaken. A qualitative estimation of the acceptor concentration in $n$-type ZnO was made by comparing the ratios between the defect and near-band-edge emission intensities. However, this ratio is shown to depend not only on the defect concentration but also on experimental conditions, in particular on excitation intensity, as was mentioned above. Temperature dependence of the defect-related PL intensity in ZnO was often used to determine the nature of an optical transition. However, the temperature behavior of PL may be complicated by a competition between several recombination channels as will be shown below in a simple phenomenological approach. A typical temperature dependence PL spectrum is shown in fig 2-3.
By measuring the PL intensity at chosen photon energy as a function of time delay after an excitation pulse, information can be obtained about the recombination mechanisms. A full emission spectrum can be measured also at successive points of time. Spectral analysis helps to distinguish overlapped PL bands, investigate, for example, the evolution of the PL band shape and its shift with time.

The luminescence decay is often non-exponential, especially at low temperatures. There may be several reasons for such behavior. The most common case of nonexponential decay of PL is explained in terms of the DAP recombination. When an
electron on a donor recombines with a photogenerated hole bound to an acceptor, the radiative recombination rate $W$ is not constant but depends exponentially on separation between the donor and acceptor $^{14-15]}$.

When increasing time delay, PL bands originating from the DAP-type transitions, especially those involving deep donors, are expected to red-shift significantly with time delay. This results from the faster recombination in close pairs, which contribute to the high-energy side of the band due to stronger Coulomb interaction. The deeper the donor, the larger shift is possible, but it still remains below the value of ionization energy of the donor. The absence of a noticeable shift of a band with the time delay may indicate that shallow donors are involved.

When increasing temperature the electrons from the shallow donor thermalized to the conduction band, and the DAP transitions are gradually replaced by transitions from the conduction band to the same acceptor (e-A transitions). For the e-A transitions, the decay is exponential and the characteristic time (radiative lifetime, $\tau_R$) depends on the free electron concentration $n_0$ (in assumption that $n_0 \gg \delta n$) and the electron-capture coefficient for the acceptor $C_n$ as

$$\tau_R = \frac{1}{C_n n_0}.$$  \hfill (2-1)
Chapter 3  ZnO Overview

3-1  ZnO growth

ZnO films have a lot of promising application in high frequency surface devices, optical devices, such as UV detector, LDs, LEDs, due to its wide band gap with large exciton-binding energy (60meV), which attract more and more research groups\textsuperscript{[16-18]}. It also has very good piezoelectric properties. Recently, high quality ZnO films are reported by advanced thin films growth techniques, such as MBE\textsuperscript{[19]}, MOCVD\textsuperscript{[20]}, HVPE\textsuperscript{[21]} and RF sputtering\textsuperscript{[22]}. Most of ZnO films are grown on sapphire (Al\textsubscript{2}O\textsubscript{3}). But there is a large lattice mismatch (18\%) between the sapphire substrate and ZnO films. For this reason ZnO films are also grown on other substrates, such as GaN, Si. For example, the lattice mismatch between ZnO and GaN is only 1.8\%, which is much smaller than that between ZnO and sapphire. There are some lattice constants of several substrate materials and mismatch of ZnO to different substrates listed in Table 3-1.

p-type ZnO films are important for the application on electrical devices. Currently it is hard to find a highly efficient p-type dopant. There are some p-type ZnO by HVPE reported\textsuperscript{[23]}. If well controlled p-type ZnO can be grown by some techniques mentioned above. Production of reliable p-type ZnO would greatly accelerate the market time of ZnO optoelectronic devices.
3-2 Doping of ZnO

1 n-type doping

Usually, undoped ZnO films show to be n-type with a high electron densities, due to intrinsic defects. One explanation is that Zn$_{i}$ is the dominant native shallow donor, which energy is about 30~50 meV$^{[24]}$. There is another assumption that the dominant donor comes from the hydrogen with ionization energy 30meV$^{[25]}$. This suggestion is based on the fact that hydrogen is present in almost all growth technique relative to ZnO. So it is possible that hydrogen penetrates into ZnO films.
n-type ZnO doped with Al, Ga, and In metals can achieve high conductivity property\textsuperscript{[26-29]}. For example, the low resistivity in n-type ZnO is reported by MOCVD\textsuperscript{[30]}. These low-resistivity n-type ZnO films can be used as transparent ohmic contacts.

2 p-type doping

Due to the compensation of the low-energy native defects, it is difficult to grow p-type ZnO films. Lithium, Copper, Silver, Zinc are the possible candidates of acceptor in ZnO. But these elements normally generate deep acceptor level, which can’t give much contribution to the conduction\textsuperscript{[31]}. There are two possible methods to achieve p-type doping ZnO. One is to substitute group- I metal, such as Li, Na, K, into Zn sites, the other is to substitute group-V elements, such as N, P, As, into O sites. Group-I may be better to achieve the shallow acceptor level than group- V (table 3-2\textsuperscript{[32]} shows some bond lengths data). While for the large bond lengths are observed for the group-I metals, native defects such as vacancies are generated. These vacancies compensate dopants. So it is difficult to grow p-type ZnO with these metals. Most group-V elements except N are also not good for p-type doping for the similar reason. So, N may be the best candidate for p-type ZnO doping\textsuperscript{[33]}. 
Table 3-2  Calculated nearest neighbor bond lengths, the defect energy levels for negatively charged substitutional impurities, and the energy (E) required to form the positively charged AX center from the substitutional acceptors. Ref[32]

<table>
<thead>
<tr>
<th>Element</th>
<th>Bond-length (Å)</th>
<th>Ei(eV)</th>
<th>□E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2.03</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>Group I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>2.10</td>
<td>0.17</td>
<td>1.04</td>
</tr>
<tr>
<td>K</td>
<td>2.42</td>
<td>0.32</td>
<td>1.38</td>
</tr>
<tr>
<td>N</td>
<td>1.88</td>
<td>0.40</td>
<td>0.13</td>
</tr>
<tr>
<td>Group V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>2.18</td>
<td>0.93</td>
<td>-0.46</td>
</tr>
<tr>
<td>As</td>
<td>2.23</td>
<td>1.15</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

3-3  Properties of ZnO

1  crystal structure

![Crystal structures of ZnO. Ref[34]](image)

Most group II–VI binary compound semiconductors have either cubic, zinc-blende...
or hexagonal wurtzite structure. ZnO belongs to group II–VI compound semiconductors. Its ionicity is at the boundary is between the covalent and ionic semiconductors. The crystal structure of ZnO can be rocksalt, zincblende, and wurtzite, as shown in figure 3-1. From the calculations of the ground state total energy of ZnO for different crystal structures by using a first principle periodic Hartree-Fock linear combination of atomic orbitals theory by Jaffee and Hess\textsuperscript{[34]}, the wurtzite structure appears to be the most thermodynamically stable phase.

2 Lattice parameters

Lattice parameters are important to consider when one develops semiconductor devices. There are four main factors which determine the lattice parameters of the semiconductor. The first factor is free-electron concentration which affects the potential of the bottom of conduction band normally occupied by electrons. The second factor is the concentration of impurities and defects and the difference in ionic radii between these defects and impurities and the substituted matrix ions. The third factor is the external strains. The last factor is the temperature-dependent in the semiconductors. There are some lattice constants of wurtzite structure ZnO, shown in table 3-3\textsuperscript{[35-38]}

| Table 3-3 | Measured and calculated lattice constants and \( \mu \) parameter of ZnO. Ref\textsuperscript{[35-38]} |
3 Electronic band structure

In order to apply some semiconductor in electronic devices, the band structure of this semiconductor should be described in details, which helps us to analyze the performance of devices. Several theoretical models, which have different complexity degrees, are used to calculate the band structure of different crystal structure ZnO. Normally, X-ray, UV absorption and reflection and emission techniques are used to measure electronic core levels. There are also other techniques such as photoelectron spectroscopy (PES), angle-resolved photoelectron spectroscopy (ARPES) technique, which are commonly used in this research area.

The experimental data of the energy levels of core electron in ZnO was reported by Langer and Vesely\textsuperscript{[38]}. X-ray induced photoemission spectroscopy was used in their experiment. Two main conclusions follow from their research. The first one is that the location of the Zn 3d level in ZnO is determined clearly. The second one is that the discrepancy is also found to be angular momentum dependent. A lot of experiments have

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>u</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2496</td>
<td>5.2042</td>
<td>1.6018</td>
<td>0.3819</td>
</tr>
<tr>
<td>3.2501</td>
<td>5.2071</td>
<td>1.6021</td>
<td>0.3817</td>
</tr>
<tr>
<td>3.286</td>
<td>5.241</td>
<td>1.595</td>
<td>0.383</td>
</tr>
</tbody>
</table>
been done to investigate the Zn 3d level. There are also some kinds of level quantitative disagreements and the location of the Zn 3d state can’t be predicted accurately.

4 Mechanical properties

Mechanical properties are also very important in semiconductors, which are related to the following concepts: hardness, piezoelectric constants, bulk modulus and yield strength, etc. There are five independent elastic constants in hexagonal crystals, which are $C_{11}$, $C_{33}$, $C_{12}$, $C_{13}$, $C_{44}$. The constants $C_{44}$ and $C_{66}$, can be calculated by the sound velocity of transverse modes propagating along $[0001]$ and $[1000]$ directions of the semiconductors.

The wurtzite structure ZnO with low symmetry causes the presence of spontaneous polarization. But it is really hard to measure the absolute value of spontaneous polarization in a nonferroelectric material. There are some experiments conducted to get the value of the spontaneous polarization in ZnO material by using a conventional approach, which is to define the spontaneous polarization of a low symmetry crystal as the polarization difference compared to a high symmetry structure of the same material.

Typical hardness measurements use the conventional diamond tip with certain shape, such as spherical or triangular shape. The information of the hardness and pressure-induced phase transformation of the material to be measured can be obtained from the depth-sensing indentation measurements. There is a good agreement between
theoretical predictions and experimental data in ZnO bulk material. The quality of ZnO and the theoretical predict are two important parts to estimate the physical properties of ZnO. For example, the estimated data of the elastic constants from theory is quite consistent with the real parameters in wurzite ZnO.

5 Thermal property

(1) TEC(thermal expansion coefficient)

The variation of temperature affects the lattice parameters of semiconductors. The thermal expansion coefficients (TEC), which are defined as the ratio $\frac{\Delta \alpha}{\alpha}$ and $\frac{\Delta c}{c}$, are used to describe the quantitatively temperature dependence of lattice parameters $\alpha$ and $c$. The stoichiometry, extended defects and free-carry concentration also affect the TEC. The X-ray power diffraction method by Reeber$^{39}$ was used to measure the temperature dependence of the lattice parameters of ZnO (Results are shown in figure 3-2).
(2) Thermal conductivity

Thermal conductivity ($\kappa$) is determined by vibration, rotation, and electronic degrees of freedom. And it is a really important property of semiconductors when these materials are used in high-power, high-temperature or optoelectronic devices. With light carrier concentration, the electronic thermal conductivity is very small, which can be negligible. In high purity semiconductor materials, phonon-phonon scattering is ideally proportional to $T^{-1}$ at the temperatures higher than the Debye temperature. Note the point defects in a ZnO affect the thermal conductivity of ZnO material.

The thermal conductivity of a fully sintered ZnO at temperatures from room
temperature to 1000 °C is measured \cite{40}. The dominant scattering mechanism is the resistive phonon-phonon interactions.

![Graph](image)

**Figure 3-3** Thermal conductivity of fully sintered ZnO heated from room temperature to 1000°C. Ref[40]

6 Electrical properties

As a direct and wide band gap semiconductor with large binding energy (about 60meV), ZnO is considered as a good candidate for electronic and optoelectronic devices. For example, a device made by material with a larger band gap may have a high breakdown voltage, lower noise, and can operate at higher temperatures with higher power. The performance of electron transport in semiconductor is different at low and high electrical field.
At very low electrical fields, the energy distribution of electrons in ZnO doesn’t change much, because the electrons can’t get much energy from the applied electrical field, compared with their thermal energy. So the electron mobility will be constant because the scattering rate, which determines the electron mobility, doesn’t change much.

At a high electrical field, the energy of the electrons from the applied electrical field is comparable with their thermal energy. The electron distribution function then deviates far away from its equilibrium value. These electrons become hot electrons, whose temperature is higher than the lattice temperature. When the electron drift velocity is higher than its steady-state value, it is possible to make a higher frequency device.
Chapter 4 Optical property of ZnO

4-1 Introduction

In order to make high-performance optoelectronic devices on ZnO, it is necessary to investigate the optical properties and transitions processes in ZnO. There are a lot of experimental techniques for the study of the optical transitions processes in ZnO, such as optical absorption, transmission, reflection, photoreflection, spectroscopic, ellipsometry, photoluminescence, cathodoluminescence, calorimetric spectroscopy etc.[41-42].

4-2 Free excitons

The conduction band of ZnO with wurtzite crystal structure is constructed from s-like state (\( \Gamma_5^s \)), which has a symmetric shape. The valance band is a \( p \)-like state. It is split into three bands because of crystal field and spin-orbit interaction\(^{[43]}\), which dominate the near bandgap intrinsic absorption and emission spectra. The related free-exciton transitions involving an electron from the conduction band and a hole from these three valance bands are named as A (corresponding to the heavy hole), B (corresponding to the light hole), and C (corresponding to crystal field split band).

The transition energies of the intrinsic excitons were measured with the various techniques, such as the low temperature absorption, reflection, photoreflectance (PR) and PL spectroscopy techniques, etc. The optical properties of the ZnO excitonic
transition process are investigated in detail with the aid of these techniques.

Photoluminescence (PL) is one of the most powerful techniques to investigate the exciton structure. There are a lot of PL spectra research results reported by many research groups \(^{[44-47]}\). Figure 4-2 shows a typical PL spectrum in the range of fundamental excitonic region at 15K. The emission line at 3.378eV is considered as the A-free excitons and their first excited state transitions. The similar peak position is also reported by Teker \(^{[48]}\).

![Figure 4-1 Free exciton region of the 15 K PL spectrum for ZnO](image)

Other research groups \(^{[48-50]}\) also investigated the excitonic peak energies for high
quality ZnO single crystals by PL, photoreflectance, absorption measurements. There is a good agreement in these experimental results, although there is a little quantitative difference, which may be caused by different ZnO samples or various experimental conditions.

4-3 Bound excitons

The discrete electronic energy levels in bandgap in ZnO are generated by the dopants or defects in semiconductor material. It influences the optical absorption and emission processes. The type and band structure of the semiconductor material influences the electronic states of the bound exciton. Neutral or charged donors and acceptors can bind exciton, which results in bounded excitons.

The neutral shallow donor-bound exciton (DBE) normally dominates in the low-temperature PL spectrum of high-quality ZnO films, due to the presence of donor sources which come from unintentional impurities or other shallow-level defects. The acceptor-bound exciton (ABE) is also sometimes observed in some ZnO films which contain substantial concentration of acceptors. The sharp lines in PL spectra generated by the recombination of bound excitons are the signal, which is used to identify different defects or impurities source. Most sharp donor bound and acceptor-bound exciton lines are observed in the range from 3.34 to 3.38 eV in high quality ZnO films.

An example of a typical low-temperature PL spectrum of ZnO is shown in figure 4-3.
Several sharp emission peaks are observed at 3.357eV, 3.361eV, 3.365eV, 3.372eV, respectively. It can be shown that the binding energies, for different donors.

![Graph of PL intensity vs. photon energy](image)

**Figure 4-3** Bound exciton region of the 15 K PL spectrum for ZnO film

The highest ABE peak is at 3.357eV, which may come from the Na or Li acceptors.

There may exit more ABE peaks, which may be resolved and can’t be identified clearly.

4-4 Two-electron satellites in PL
Two electron satellite (TES) transition process in high quality ZnO occurs can be observed in low temperature PL spectra in the photon energy, range from 3.30 to 3.34 eV. This transition process is generated by the radiative recombination of an exciton bound to a neutral donor, leaving the donor in the excited state. The energy position of the excited state of shallow donor can be roughly estimated from the energy distance between the the ground-state neutral-donor bound excitons and TES lines. Then the donor binding energy can be calculated because the excited-to-ground levels distance equals to $3/4$ of the donor binding energy $E_D$.

![Figure 4-4](image)

**Figure 4-4** 15 K PL spectrum for ZnO in the TES region of the main bound exciton lines.

One TES region PL spectrum is shown in figure 4-4. There are four separate TES at 3.313eV, 3.323eV, 3.332eV, 3.336eV in this spectrum. Corresponding DBE lines are
at 3.357eV, 3.361eV, 3.365eV, 3.372eV. So the calculated donor bonding energies are about 45meV, 51meV, 44meV, 48meV separately, which may be related to four different donors.

Teke et al.\textsuperscript{[48]} also found the separations between A-free exciton and the ground-state neutral DBEs as 16.5meV, 15.3meV and 12.1meV. The binding energy of the DBEs should be proportional to the binding energy of the corresponding donor with a factor 0.3\textsuperscript{[51]}, according the empirical Haynes rule. So the calculated values of the binding energies of the donors in ZnO are 43, 52, and 55meV, which fit the experimental data quite well. There are also reports about the TES in high quality ZnO materials\textsuperscript{[52]}.

4-5 shallow DAP emission in ZnO

Shallow donor-acceptor-pair(DAP) emission exhibiting the main zero-phonon peak at about 3.22eV followed by at least two LO phonon replicas is important processes in the optical properties of ZnO.
An example of the PL spectrum of high-quality ZnO (at about 15 K) is shown in figure 4-5. There are several phonon replicas peaks in this spectrum. It is clear that the LO phonon energy in ZnO is about 72 meV, which is 91 meV in another kind of wide band semiconductor GaN—another important wide band semiconductor.

4-6 Temperature dependent PL measurements

Temperature dependent PL measurements are used to study the temperature evolution of the peaks in ZnO PL spectra. It can be also as the support and complement evident of other experimental results.
One temperature dependent PL spectrum is shown in figure 4-6. This spectrum shows the curve only up to 300K. At low temperature, A and B exciton peaks can be identified clearly, while at high temperature it is hard to identify the peak positions. Then these free exciton peaks start to quench with the increasing of the temperature. The ABE peaks also quench when increase the temperature, and can’t be identified when temperature is higher than 40K. The main DBE peaks can be traced at the whole temperature range. The main peaks and its TES with their LO-phonon replicas quench
when increasing temperature.

The intensities ratio between DBE and free exciton decrease along the increment of temperature. The reason is that at low temperature, the thermal energy is lower than the binding energy, then the bound exciton transition process dominates, while at high temperature, the free exciton transition process dominates.

Figure 2-7 Temperature dependent peak positions of the A-free exciton. Ref[48]

The variation of A-free exciton and its 1LO, 2LO peak energies temperature dependence spectrum is shown in figure 4-7[48].

4-7 Time-resolved PL on ZnO

Time-resolved PL (TRPL) is also a useful technique, which is applied to investigate the optical properties of semiconductors. The free carrier and exciton lifetime are
important parameters related to material quality and device performance, which can be measured by TRPL spectroscopy. Normally the higher quality crystal, the longer the exciton lifetime. The efficiency of the radiative recombination depends on the decay time of the particular transition.

TRPL at room temperature of two ZnO bulk samples was reported by Teke et al.\cite{48}, which is shown in figure 4-8. The excitation energy density in a pulse in these experiments was about 540 μJ/cm². The decaying part of TRPL data can be well fit by a bi-exponential function:

\[ A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  \hspace{1cm} (4-2)

The decay constants and the amplitude ratios are shown in table 4-1\cite{48}. The fast decay constant \( \tau_1 \) most probably comes from the effective non-radiative recombination, while the slowly decaying component is related to the radiative lifetime of the free exciton at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>540 μJ/cm²</th>
<th>54 μJ/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_1 ) (ps)</td>
<td>( \tau_2 ) (ps)</td>
</tr>
<tr>
<td><strong>300 K (FX)</strong></td>
<td>As-received:</td>
<td>170.4±1.8</td>
</tr>
<tr>
<td></td>
<td>FG-annealed:</td>
<td>358.7±8.8</td>
</tr>
<tr>
<td><strong>85 K (DBE)</strong></td>
<td>As-received:</td>
<td>310.2±2.5</td>
</tr>
<tr>
<td></td>
<td>FG-annealed:</td>
<td>286.8±2.9</td>
</tr>
</tbody>
</table>
Figure 4-8 Room temperature time resolved PL data for the as received and the forming gas treated samples. Ref[48]

4-8 Defects in ZnO

The formation energies and electronic structure of native point defects and hydrogen in ZnO were calculated by Van de Walle et al[56-57]. The relationship between the concentration of defects in a crystal and their formation energies is determined by the following equation 4-3.

\[ c = N_{\text{sites}} \exp\left( \frac{-E_f}{k_B T} \right) \]  \hspace{1cm} (4-3)

Here \( N_{\text{sites}} \) is the concentration of available sites in the crystal where the defect can occur. From the equation 4-3, it follows the defects can’t be formed with high
formation energy. The formation energy can be found from equation 4-4

\[
E_f(q) = E_{tot}(q) - n_{Zn}\mu_{Zn} - n_{O}\mu_{O} - qE_F,
\]

(4-4)

Here, \(E_{tot}(q)\) is the total energy of a system containing \(n_{Zn}\) and \(n_{O}\) zinc and oxygen atoms, and \(\mu_{Zn}\) and \(\mu_{O}\) are the chemical potentials for zinc and oxygen, \(q\) is the charge of the defect, and \(E_F\) is the Fermi energy. The chemical potentials depend on the growth conditions. \(\mu_{Zn} = \mu_{Zn(bulk)}\) for zinc-rich case, while \(\mu_{O} = \mu_{O2}\) for oxygen-rich case.

Under Zn-rich conditions, oxygen vacancies dominate since the oxygen vacancies have lower formation energy than the zinc interstitials. In contrast under O-rich conditions, the zinc vacancies dominate instead. The transition level for the -1/-2 charge states of \(V_{Zn}\) is about 0.8eV above the valence band. So the transitions from the conduction band or a shallow donor to \(V_{Zn}\) acceptor are expected at about 2.6eV in n-type ZnO, which is in green luminescence range \[^{[58]}\]. The yellow luminescence in GaN is caused by analogous point defect.

Hydrogen is also a common impurity to be investigated in ZnO. Normally hydrogen acts as donor and is typically bound to an oxygen atom in ZnO, which form an OH bond. The formation energy for hydrogen in n-type ZnO is about 1.56eV. Incorporation of hydrogen when growing p-type ZnO may increase acceptor solubility and suppress the formation of compensating defects. After growth process, the hydrogen can be removed easily by a post-growth annealing method.
N is considered to be a promising candidate for the shallow acceptor source in p-type ZnO growth process\[19\]. \(\text{N}_0\) is a shallow acceptor, while \((\text{N}_2)_0\) is a double shallow donor in ZnO. There is a competition between N and \(\text{N}_2\) during doping of ZnO with N, which controls the doping type. Since N-N bond is a strong bond, \(\text{N}_2\) or \(\text{N}_2\text{O}\) gas is not efficient dopant for \(p\)-type doping. NO or \(\text{NO}_2\) may be good doping sources, since the O atoms are host atoms.

PL measurement at low temperature is the most common technique to investigate the point defects in ZnO. The shallow donor-acceptor pair band is observed near the 3.22eV. The green luminescence from high-quality undoped ZnO dominate the defect-related part of the PL spectrum\[58\].

In PL spectrum of ZnO, there is normally a sharp peak near 3.22eV with at least 2 LO phonon replicas are commonly observed. The emission lines between 3.25 and 3.4eV comes from the exciton recombination processes. With increasing temperature, the DAP line quenches and gives way to e-A line when the temperatures are above 30 K, due to thermal ionization of the shallow donor, which is supposed to be \(\text{N}_0\)\[59-60\].

There is another report\[61\] on ZnO with N doped, whose concentration is up to \(10^{19}\) cm\(^{-3}\). The PL spectrum shows a broad line at 3.315eV, which is attributed to an acceptor-bound exciton, related with \(\text{N}_0\) acceptor. There is also a weaker line occurring at 3.238eV, which might be DAP emission, which is superimposed with the LO phonon
replica of ABE. The activation energy of $N_0$ is also estimated as about 0.18 eV.

PL spectrum of N-doped ZnO (shown in figure 4-9) was investigated in detail by Zeuner$^{[62]}$. There is a DAP emission line at 3.235 eV, which is confirmed by transient PL studies on this band.

Figure 4-9. Low temperature PL spectra of undoped (a) and nitrogen doped (b) ZnO films. Ref$^{[62]}$

The origin source of the green luminescence (at about 2.5 eV) in high quality ZnO has been argued for a long time. One group$^{[63]}$ concluded that the green luminescence is related to the copper impurities in ZnO. Recently, another group$^{[24]}$ attributed that the GL band is related to the oxygen vacancy ($V_O$). There may be another assignment of this band
is shown in next part. Generally, GL band with a fine structure is related to the copper impurities, while the structureless GL band may come from the native point defects such as \( V_O \) or \( V_{Zn} \). Figure 4-10 shows a high-quality ZnO low temperature PL spectrum, which also shows a recombination model for the GL band peaked at 2.5 eV.

![Figure 4-10. PL spectrum of undoped ZnO excited with the 325 nm line of an HeCd laser (15 K). The inset shows a recombination model for the GL band peaked at 2.5 eV.](image)

There is YL band in some undoped bulk ZnO, as shown in figure 4-11. And there is
also a similar report\cite{48} that after a long time irradiation with a He-Cd laser, the GL gives a way to the YL band. The excitation intensity with a power of $10^{-3}$ W/cm$^2$ saturates the YL band, which means low concentration of the related defects. The temperature dependence of YL intensity exhibits no quenching up to 200K.

![Figure 4-11 Yellow luminescence band of undoped bulk ZnO](image)

There is red luminescence (RL) in some ZnO, which is shown in figure 4-12. The possible explanation is that there is some competition for holes between the acceptors responsible for the GL and RL bands. When temperature is higher than 200K, the GL
starts to quench and gives way to the RL band.

![Graph](image)

**Figure 4-12 Red band of undoped bulk ZnO.**

### 4-9 Modulation of band gap in ZnO

The modulation of band gap in ZnO is also an important part for the application of UV optoelectronic application. Alloys Zn,Mn$_{1-x}$O and Cd$_{x}$Zn$_{1-x}$O are suitable candidates for modulation of band gap in ZnO, because the band gap of MnO is about 7.7eV and that of CdO is only 2.3eV. In a few reports\(^{[67-68]}\) a successful the modulation of the band gap from 3.0 to 4.0 has been achieved. Figure 4-13\(^{[67]}\) shows the band gap modulation function vs. the composition of Mn or Cd.
Figure 4-13 Optical and structural properties of Cd$_x$Zn$_{1-x}$O and Mg$_x$Zn$_{1-x}$O alloy films mapped out in a plane of $a$-axis length and room-temperature band gap energy. Ref[67]

4-10 Rare earth doped ZnO

Rare earth is used to describe a group of chemically similar elements in which there are incompletely filled 4\,f shell. Most of them are trivalent ions and their properties are very important.

All these trivalent ions have the similar shell structure. An example is xenon with 54 electrons. The number of electrons in 4\,f shell ranges from 0 (La$^{3+}$) to 14 (Lu$^{3+}$). These
trivalent ions give fluorescence spectra with sharp lines in the visible or neighboring spectral regions, which is an important property for optoelectronic application. The similar sharp lines sometimes also occur in divalent salts.

It is hard to get high purity rare earths before the ion exchange and other methods occur and estimate the purity of the rare earth samples. Normally they are just labeled as high than 99.99% or 99.999%. There is a summary of the properties of trivalent rare earths, which is shown in table 4-2[69].

Table 4-2 The properties of trivalent rare earths. Ref[69]

<table>
<thead>
<tr>
<th>Z</th>
<th>N</th>
<th>Mass number (%)</th>
<th>I</th>
<th>μ</th>
<th>Ground state</th>
<th>2Jg</th>
<th>R(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>La</td>
<td>139(99.9)</td>
<td>½</td>
<td>2.76</td>
<td>½S½</td>
<td>0</td>
<td>1.061</td>
</tr>
<tr>
<td>58</td>
<td>Ce</td>
<td>140(88.5)</td>
<td>½</td>
<td>3.9</td>
<td>½P½</td>
<td>4.28</td>
<td>1.034</td>
</tr>
<tr>
<td>59</td>
<td>Pr</td>
<td>141</td>
<td>½</td>
<td>1.03</td>
<td>½H½</td>
<td>6.40</td>
<td>1.013</td>
</tr>
<tr>
<td>60</td>
<td>Nd</td>
<td>142(27.1) 144(23.9)</td>
<td>½</td>
<td>2.76</td>
<td>½S½</td>
<td>6.54</td>
<td>0.995</td>
</tr>
<tr>
<td>61</td>
<td>Pm</td>
<td>146(17.2) 148(12.2)</td>
<td>½</td>
<td>1.03</td>
<td>½H½</td>
<td>4.80</td>
<td>0.979</td>
</tr>
<tr>
<td>62</td>
<td>Sm</td>
<td>152(26.6) 154(22.5)</td>
<td>½</td>
<td>2.76</td>
<td>½S½</td>
<td>1.43</td>
<td>0.964</td>
</tr>
<tr>
<td>63</td>
<td>Eu</td>
<td>149(13.8) 147(15.1) 148(11.3)</td>
<td>½, ½</td>
<td>-0.83, -0.69</td>
<td>½F½</td>
<td>0</td>
<td>0.950</td>
</tr>
<tr>
<td>64</td>
<td>Gd</td>
<td>158(24.8) 160(21.8) 156(20.6)</td>
<td>½, ½</td>
<td>1.06, 3.6</td>
<td>½P½</td>
<td>14.00</td>
<td>0.938</td>
</tr>
<tr>
<td>65</td>
<td>Tb</td>
<td>157(14.8) 159(14.8)</td>
<td>½</td>
<td>1.5</td>
<td>½F½</td>
<td>18.00</td>
<td>0.923</td>
</tr>
<tr>
<td>66</td>
<td>Dy</td>
<td>164(28.2) 162(25.5)</td>
<td>½</td>
<td>1.5</td>
<td>½F½</td>
<td>20.00</td>
<td>0.908</td>
</tr>
<tr>
<td>67</td>
<td>Ho</td>
<td>165</td>
<td>½</td>
<td>3.3</td>
<td>½F½</td>
<td>20.00</td>
<td>0.894</td>
</tr>
<tr>
<td>68</td>
<td>Er</td>
<td>166(33.4) 168(27.1)</td>
<td>½</td>
<td>3.3</td>
<td>½F½</td>
<td>18.00</td>
<td>0.881</td>
</tr>
<tr>
<td>69</td>
<td>Tm</td>
<td>169</td>
<td>½</td>
<td>0.42</td>
<td>½F½</td>
<td>14.00</td>
<td>0.859</td>
</tr>
<tr>
<td>70</td>
<td>Yb</td>
<td>172(21.8) 172(18.9)</td>
<td>½</td>
<td>0.43</td>
<td>½F½</td>
<td>8.00</td>
<td>0.858</td>
</tr>
<tr>
<td>71</td>
<td>Lu</td>
<td>175(27.5)</td>
<td>½</td>
<td>2.9</td>
<td>½S½</td>
<td>0</td>
<td>0.848</td>
</tr>
</tbody>
</table>

Since a large-scale, high quality bulk (or thin films) ZnO can be grown, it is a possible candidate host material for rare earth(RE) ions doping. Luminescence in the range from
UV to infrared is expected from the samples when the carriers are excited by some sources, such as a laser. But there is a large obstacle for ZnO applied in this area, which is the luminescence from RE centers is weaker than that from excitons and defects. There are some methods reported\(^{[70-73]}\) to increase the luminescence intensity from RE\(^{3+}\) ions and decrease the intrinsic luminescence from the host material by doping with coactivators, such as lithium ions, nitrogen, chlorine compounds.

(1) \textbf{ZnO : Er}

For ZnO:Er thin films, there are many reports on luminescence in the visible and infrared (IR) ranges\(^{[74-75]}\). In order to make Er ions in ZnO to absorb the emission energy of the deep level defects in ZnO films, the RE metal is introduced into ZnO samples by thermal evaporation. When the energy from the deep level defects is transferred to the the Er\(^{3+}\) ions in the ground state (\(^4I_{15/2}\)), the excited Er\(^{3+}\) ions may fill the \(^2H_{11/2}\) state, and non-radiative relaxation rate for other ions are reduced\(^{[76]}\). For example the multiphonon relaxation processes from \(^4F_{5/2}\) are suppressed when ZnO: Er is excited by strong light source. Figure 4-14 shows the energy diagram of Er-doped ZnO thin films\(^{[77]}\).
A PL spectrum in figure 4-15 shows the emission line due to $\text{Er}^{3+}$ $4f$ shell transition from $^4I_{13/2}$ to $^4I_{15/2}$ ground state. The PL peak is at $1.54 \ \mu\text{m}$ with a FWHM of 4.3 nm. Temperature dependence in the range from 20 to 300K near $1.54 \ \mu\text{m}$ peak is also measured, as shown in figure 4-16.
Figure 4-15  The PL spectrum from the ZnO:Er thin film excited by the 488.0 nm line of an Ar$^+$ laser. Ref[78]

Figure 4-16. PL spectrum of Er implanted ZnO around 1.54 $\mu$m at 20–300 K. Ref[78]
The peak intensity at 1.54 \( \mu m \) (FWHM 8nm) starts to quench along with the increasing of temperature. At room temperature, the peak intensity reduces to 30% and the FWHM becomes 34nm. The similar PL characteristics occur in Er doped ZnO by laser ablation \(^{(79)}\). But the energy level of Er in ZnO films is not so established yet. Figure 4-17\(^{(80)}\) shows the comparison of PL spectra of the different semiconductor materials doped with Er. X.Zhao et al\(^{(81)}\) also reported the sharp emission line PL result in ZnO:Er. There are four identified peaks, which are related to Er ion 4\( f \) shell.

![PL spectrum comparison](image)

**Figure 4-17** Comparison of PL spectrum of various Er-doped semiconductors. Sample 1 is Er-implanted ZnO Sample 2 is Er-doped PS Sample 3 is Er-doped ZnO formed only by a sol-gel method. Ref[80]

\[(2)\] ZnO: Eu
Eu is also an important candidate RE for ZnO doping, due to its possible application in optoelectronic field, which attracts research groups \[82-83\]. Y.K. Park et al\[84\] investigated ZnO:EuCl$_3$ with different grow conditions.

Figure 4-18 shows the PL spectra in the visible range of ZnO:Eu. There are a few close sharp peaks related to Eu ions, which are near 620nm. Fig 4-19 shows the temperature dependence PL spectra of ZnO. The intensity of the sharp peak related to the $^5D_j(j = 0,1) \rightarrow ^7F_j(j = 0,1,2..6)$ transition of Eu ions decrease along with the decreasing of temperature when temperature is below 90K, then increase when increasing temperature up to room temperature. Another sharp peak lines are observed near 710nm, which are also related to the $^5D_j(j = 0,1) \rightarrow ^7F_j(j = 0,1,2..6)$. The exciton peak of ZnO keep on decreasing with the increasing temperature. The sharp emission line related to Er ion in ZnO at the similar position is also reported by other research groups such as Hiroko et al\[85\].
Figure 4-18 PL emission spectra for ZnO:Eu at room temperature
Figure 19  PL emission spectra for ZnO:Eu at different temperatures. Assignments of the sharp peaks near 2 eV are given in the text on page 51.

(3) Other RE doped ZnO

<1> ZnO : Nd

Figure 4-20[85] shows the PL results of Nd and Li co-doped ZnO at 10K and 300K. The broad-band luminescence centered at 600 nm is related to ZnO host. The sharp line at 910nm comes from the transition $^4F_{3/2} \rightarrow ^4I_{9/2}$. There are also weak sharp peaks related to Nd ions, which are marked in the figure.
Figure 4-20 The spectra of Nd\(^{3+}\) and Li\(^{+}\)-doped ZnO pellet: (a) PL excited by He-Cd (325 nm) measured at 10 K and 300 K and (b) PLE monitored at 904 nm and measured at 10 K. Ref[85]

<2> ZnO : Dy

W.M.Jadwisienzak et al\(^{[85]}\) also reported the PL luminescence spectra of ZnO: Dy, Li, which is shown in figure 4-21. There are several sharp peaks related to Dy ions, shown in the figure marked with possible transition processes. For example the emission line at 580nm at 10K is related to the transition from \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\).
Figure 4-21 The spectra of Dy\textsubscript{3} and Li\textsubscript{1} -doped ZnO pellet: (a) PL excited by He-Cd (325 nm) measured at temperature from 10–300 K and (b) PLE monitored at 579 nm and measured at 10 K. Ref[85]

![Figure 4-21](image-url)
Chapter 5 Conclusion

As a wide band semiconductor (3.24eV at room temperature) with a large binding energy, ZnO is becoming a hopeful candidate semiconductor material for the next generation of optoelectronic devices and light emission devices or high power and frequency devices.

In this thesis, the properties of ZnO are introduced briefly and the optical properties of ZnO are investigated in detail. Photoluminescence (PL) is a strong tool to investigate the optical properties of ZnO. The PL of high-quality bulk ZnO at room temperature shows a broad peak (FWHM is about 100meV) at 3.2 eV. At low temperature, the DBE peaks dominate at 3.42eV. The intensity of the exciton peaks decrease with the increasing of the temperature. The ratio of DBE to the free exciton peak decreases with increasing temperature. The e-A and phonon replica (LO phonon energy is 71meV) also appear in the range of 3.2~3.4eV. The DAP band is observed at 3.2eV. It can be used to estimate the donor binding energy, which is related to certain elements or defects. The green PL band (at 2.5eV) in high quality ZnO is attributed to transition from conduction band or shallow donor band to a deep acceptor (ionization energy of 0.8eV), which is thought to be the energy level of vacancy of Zn or oxygen. The green band quenches above 130K. In some undoped ZnO samples, the YL band is
observed, which may be due to the impurity or defects in ZnO. The RL band can be also seen in some samples, which is related transition between deep level donor and acceptor.

The modulation of the band gap in ZnO is important for the UV optoelectronics applications. The band gap can be modulated from 3eV to 4eV by adding Mn or Cd in ZnO.

High-quality bulk ZnO is considered as a promising candidate to the host material for rare earth (RE) doping, which can be used to make next generation of UV or visible lasers. But there is a big problem to be solved to improve the emission efficiency of RE ions in ZnO. Some researchers conclude that RE and lithium codoped ZnO would increase the emission efficiency of RE ions and suppress the luminescence from host material ZnO.

Although there is a lot of progress in ZnO research area, it is a long way before ZnO can be widely used to make electronic devices in industry. There are still a lots of area need to be worked on, such as band modulation, LDs based on ZnO, heterostructure FET on GaN and ZnO.
List of References
List of References


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