LUMINESCENCE PROPERTIES OF ZINC OXIDE DOPED
WITH RARE EARTH IONS

A Thesis Presented to
The Faculty of the
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Of the Requirement for the Degree
Master of Science

By
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# TABLE OF CONTENTS

ACRONYMS .................................................................................................................. vi
LIST OF TABLES .......................................................................................................... vii
LIST OF FIGURES ....................................................................................................... ix

Chapter 1 Introduction .................................................................................................. 1
  1.1 Review of study on zinc oxide ........................................................................... 2
  1.2 Characteristics of zinc oxide ........................................................................... 6
  1.3 4f-4f luminescence of rare earth centers ....................................................... 7
  1.4 Electronic states of rare earth centers .............................................................. 9
  1.5 Energy levels of rare earth centers .................................................................. 11

Chapter 2 Sample Preparation ..................................................................................... 13
  2.1 ZnO: RE $^{3+}$ single crystals ........................................................................... 13
  2.2 ZnO:RE $^{3+}$ thin films .................................................................................. 15

Chapter 3 Material Characterization Methods ............................................................ 17
  3.1 Cathodoluminescence ...................................................................................... 18
    3.1.1 Introduction .............................................................................................. 18
    3.1.2 Electron-beam interactions in solids ......................................................... 18
    3.1.3 Cathodoluminescence experiment setup ............................................... 20
  3.2 Photoluminescence ........................................................................................... 23
    3.2.1 Intrinsic luminescence ............................................................................ 23
    3.2.2 Extrinsic luminescence .......................................................................... 25
    3.2.3 Photoluminescence experiment setup .................................................... 27
  3.3 kinetics measurement for ZnO:RE $^{3+}$ ............................................................. 30

Chapter 4 PL and CL of the ZnO:RE $^{3+}$ .................................................................. 33
  4.1 ZnO:RE $^{3+}$ single crystal ............................................................................. 33
    4.1.1 CL of ZnO:Dy, Li single crystal ............................................................... 33
    4.1.2 PL of ZnO:Er, Li single crystal ............................................................... 38
    4.1.3 CL of ZnO:Er, Li single crystal ............................................................... 40
    4.1.4 CL of ZnO:Ho, Li single crystal ............................................................... 42
    4.1.5 CL of ZnO:Pr, Li single crystal ............................................................... 43
  4.2 ZnO:RE $^{3+}$ epi-layer ..................................................................................... 47
Chapter 5 Kinetics of ZnO:RE$^{3+}$ epi-layer
5.1 Introduction
5.1.1 Radiative recombination
5.1.2 Auger recombination
5.1.3 Hall-Shockley-Read (HSR) recombination
5.2 Curve fitting functions
5.3 Kinetics of three peaks of ZnO: Dy epi-layer
5.3.1 Kinetics of peak at 500 nm
5.3.2 Kinetics of peak at 550 nm
5.3.3 Kinetics of peak at 590 nm
5.4 Kinetics of ZnO:Er thin film
5.5 Kinetics of ZnO: Sm epi-layer
5.6 Summary

Chapter 6 Conclusions
6.1 Excitation mechanism
6.2 Energy transfer mechanism
6.3 Cathode-ray efficiency
6.4 Summary

REFERENCE
## ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>CL</td>
<td>cathodoluminescence</td>
</tr>
<tr>
<td>EL</td>
<td>electroluminescence</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>RE</td>
<td>rare earth</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 1.1 Electron configurations of rare earth atoms, rare earth ions, covalent radii, and electronegativity. ............................................................................................................. 7

Table 2.1 Sample information of bulk ZnO: RE$^{3+}$ single crystals................................. 14

Table 2.2. Sample information of ZnO:RE$^{3+}$ epi-layer ............................................. 16

Table 3.1 The experimental parameters for kinetics measurements ......................... 31

Table 4.1 The peak assignment for the CL of ZnO:Dy, Li single crystal .................. 36

Table 4.2 The peak assignment for CL of ZnO:Dy, Li single crystal annealed 150°C ................................................................................................................................. 37

Table 4.3 peak assignment for the CL of ZnO:Er, Li single crystal ............................ 41

Table 4.4 The peak assignment for CL of ZnO:Ho, Li single crystal annealed at 150°C ................................................................................................................................. 43

Table 4.5 peak assignment for CL of ZnO:Pr, :Li single crystal annealed at 150°C . 45

Table 4.6 The peak assignment for the CL of ZnO:Sm epi-layer annealed at 150°C .. 49

Table 4.7 peak assignment for the CL of ZnO:Er epi-layer annealed at 150°C .... 51

Table 5.1 The transitions corresponding to the peaks of ZnO:Dy epi-layer ............... 58

Table 5.2 The parameters in fitting ZnO:Dy epi-layer transition $^4F_{9/2} - H_{15/2}$ at 9K .... 59

Table 5.3 The parameters in fitting ZnO:Dy epi-layer transition $^4F_{9/2} - H_{15/2}$ at 300K ...... ................................................................................................................................. 60

Table 5.4 The parameters in fitting ZnO:Dy epi-layer of transition $^4F_{9/2} - H_{13/2}$ at 9K .... ................................................................................................................................. 62
Table 5.5 The parameters in fitting ZnO:Dy epi-layer of transition $^4F_{9/2} - ^6H_{13/2}$ at 300K .......................................................... 63

Table 5.6 parameters in fitting ZnO:Dy epi-layer peak at 590 nm at 9K......................65

Table 5.7 The parameters in fitting ZnO:Dy epi-layer transition $^4F_{9/2} - ^6H_{13/2}$ at 100K.66

Table 5.8 The parameters in fitting ZnO:Dy epi-layer transition $^4F_{9/2} - ^6H_{13/2}$ at 200K.67

Table 5.9 The parameters in fitting ZnO:Dy epi-layer transition $^4F_{9/2} - ^6H_{13/2}$ at 300K.... .......................................................... 68

Table 5.10 parameters in fitting ZnO:Er epi-layer transition $^4F_{9/2} - ^6H_{13/2}$ at 9K...........71

Table 5.11 parameters in fitting ZnO:Er epi-layer of transition $^2S_{3/2} - ^4I_{15/2}$ at 100K ...72

Table 5.12 parameters in fitting of transition $^2S_{3/2} - ^4I_{15/2}$ at 200K ZnO:Er epi-layer .... 73

Table 5.13 The parameters in fitting ZnO:Er epi-layer of transition $^2S_{3/2} - ^4I_{15/2}$ at 300K .................................................................. 74

Table 5.14 The parameters in fitting ZnO:Sm epi-layer transition $^4G_{7/2} - ^6H_{15/2}$ at 9K .. 76

Table 5.15 parameters in fitting ZnO:Sm epi-layer transition $^4G_{7/2} - ^6H_{15/2}$ at 50K ........77

Table 5.16 parameters in fitting ZnO:Sm epi-layer $^4G_{7/2} - ^6H_{15/2}$ at 100K...................78

Table 5.17 parameters in fitting ZnO:Sm epi-layer $^4G_{7/2} - ^6H_{15/2}$ at 150K...................79

Table 5.18 parameters in fitting ZnO:Sm epi-layer $^4G_{7/2} - ^6H_{15/2}$ at 200K ..................80

Table 5.19 parameters in fitting ZnO:Sm epi-layer $^4G_{7/2} - ^6H_{15/2}$ at 250K .................81

Table 5.20 parameters in fitting ZnO:Sm epi-layer $^4G_{7/2} - ^6H_{15/2}$ at 300K .................82
LIST OF FIGURES

Figure 1.1 The energy levels of rare earth ions ................................................................. 8

Figure 3.1 Cathodoluminescence experiment set up ......................................................... 22

Figure 3.2 Photoluminescence experiment set up ............................................................ 29

Figure 3.3 Kinetics experiment set up ............................................................................. 32

Figure 4.1 CL spectrum of ZnO:Dy, Li single crystal under different annealing conditions measured at 9K ......................................................................................... 34

Figure 4.2 CL spectrum of ZnO:Dy, Li single crystal annealed in the air for 0.5hr. at 150°C measured at 9K, 50K, 223K and 300K .............................................................................. 37

Figure 4.3 Photoluminescence spectrum of the ZnO:Er, Li single crystal annealed in the air for 4.5hr at 1000°C ................................................................................................. 39

Figure 4.4 Cathodoluminescence of the ZnO: Er, Li single crystal ................................. 41

Figure 4.5 Cathodoluminescence spectrum of ZnO:Ho, Li single crystal .......................... 42

Figure 4.6. CL spectrum of ZnO:Pr, Li single crystal samples: unannealed, annealed in the air for 0.5 hr. at 170°C, 230°C, 270°C respectively measured at 9K ................. 44

Figure 4.7. Cathodoluminescence spectrum of ZnO:Pr, Li single crystal measured at 50K, 128K and 300K .............................................................................................................. 46

Figure 4.8. cathodoluminescence spectrum of ZnO:Sm epi-layer samples: unannealed, annealed in the air for 0.5 hr. at 150°C, 230°C, 270°C, 300°C ................................. 48

Figure 4.9. Cathodoluminescence spectrum of ZnO:Sm epi-layer measured at 9K 49

Figure 4.10. CL spectrum of ZnO:Er epi-layer samples: annealed in the air for 0.5 hr at 150°C, 230°C, 270°C, 300°C respectively ................................................................. 50

Figure 4.11. Cathodoluminescence spectrum of the ZnO:Er epi-layer sample annealed in the air for 0.5 hr at 150°C measured at 9K ................................................................. 51
Figure 5.1 Rise and decay profiles of transition $^{4}F_{9/2} - ^{6}H_{15/2}$ cathodoluminescence spectrum of ZnO: Dy epi-layer measured at 9K, 300K

Figure 5.2 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} - ^{6}H_{15/2}$ in cathodoluminescence measured at 9K with TableCurve fitting analysis results

Figure 5.3 Rise and decay profiles of transition $^{4}F_{9/2} - ^{6}H_{15/2}$ at 300K together with TableCurve fitting results of ZnO: Dy epi-layer

Figure 5.4 Rise and decay profiles of transition $^{4}F_{9/2} - ^{6}H_{13/2}$ in cathodoluminescence of ZnO:Dy epi-layer

Figure 5.5 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} - ^{6}H_{13/2}$ at 9K with parameters from the one exponential function fitting analysis

Figure 5.6 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} - ^{6}H_{13/2}$ at 300K with table curve fitting using the one exponential function

Figure 5.7 Rise and decay profiles of ZnO:Dy epi-layer Cathodoluminescence transition $^{4}F_{9/2} - ^{6}H_{13/2}$ measured at 9K, 100K, 200K, 300K respectively

Figure 5.8 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} - ^{6}H_{13/2}$ at 9K with parameters from the one exponential function fitting analysis

Figure 5.9 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} - ^{6}H_{13/2}$ at 100K with parameters from the one exponential function fitting analysis

Figure 5.10 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} - ^{6}H_{13/2}$ at 200K with parameters from the one exponential function fitting analysis

Figure 5.11 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} - ^{6}H_{13/2}$ at 300K with parameters from the one exponential function fitting analysis

Figure 5.12 Temperature dependence of the time constant for the rise of transition $^{4}F_{9/2} - ^{6}H_{13/2}$ in cathodoluminescence spectrum of ZnO:Dy epi-layer sample

Figure 5.13 Temperature dependence of the time constant for the decay of transition $^{4}F_{9/2} - ^{6}H_{13/2}$ in cathodoluminescence spectrum of ZnO:Dy epi-layer sample
Figure 5.14 Rise and decay profiles of transition $^3S_{3/2} \rightarrow ^1I_{15/2}$ in cathodoluminescence spectrum of ZnO: Er epi-layer measured at 9K, 100K, 200K, 300K

Figure 5.15 Rise and decay profiles of ZnO: Er epi-layer transition $^3S_{3/2} \rightarrow ^1I_{15/2}$ at 9K with parameters from the one exponential function fitting analysis

Figure 5.16 Rise and decay profiles of transition $^3S_{3/2} \rightarrow ^1I_{15/2}$ at 100K with parameters from the one exponential function fitting analysis of ZnO: Er epi-layer sample

Figure 5.17 Rise and decay profiles of transition $^3S_{3/2} \rightarrow ^1I_{15/2}$ at 200K with parameters from the one exponential function fitting analysis of ZnO: Er epi-layer sample

Figure 5.18 Rise and decay profiles of ZnO: Er epi-layer transition $^3S_{3/2} \rightarrow ^1I_{15/2}$ at 300K with parameters from the one exponential function fitting analysis

Figure 5.19 Rise and decay profiles of transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ in cathodoluminescence of ZnO:Sm epi-layer measured at 9K, 50K, 100K, 150K, 200K, 250K, 300K

Figure 5.20 Rise and decay profiles of ZnO: Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 9K with parameters from the one exponential function fitting analysis

Figure 5.21 Rise and decay profiles of transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ measured at 50K with parameters from the one exponential function fitting analysis of ZnO: Sm epi-layer

Figure 5.22 Rise and decay profiles transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 100K with parameters from the one exponential function fitting analysis of ZnO: Sm epi-layer

Figure 5.23 Rise and decay profiles of ZnO: Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 150K with parameters from the one exponential function fitting analysis

Figure 5.24 Rise and decay profiles of ZnO: Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 200K with parameters from the one exponential function fitting analysis

Figure 5.25 Rise and decay profiles of ZnO: Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 250K with parameters from the one exponential function fitting analysis

Figure 5.26 Rise and decay profiles of ZnO: Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 300K with parameters from the one exponential function fitting analysis

Figure 5.27 Temperature dependence of the time constant for the rise of transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ in cathodoluminescence spectrum of ZnO:Sm epi-layer sample
Figure 5.28 Temperature dependence of the time constant for the rise of transition $^4G_{7/2} - ^6H_{7/2}$ in cathodoluminescence spectrum of ZnO:Sm epi-layer sample ............... 84

Figure 6.1 The processes occurred when ZnO:RE$^{3+}$ is excited by an electron beam. . 87

Figure 6.2 Schematic diagram of trapping electron on rare earth related state, the recombination energy of trapped electrons and the free hole excites the rare earth ions. ........................................................................................................... 88

Figure 6.3 Schematic diagram of trapping hole on rare earth related state, the recombination energy of free electron and the trapped hole excites the rare earth ions. ........................................................................................................... 89

Figure 6.4 Schematic diagram of trapping electron and holes on rare earth related state, the recombination energy of trapped electron and hole excites the rare earth ions. .... 89

Figure 6.5 Schematic diagram of excitation of electron hole pair, the recombination energy of free electron and hole excites the rare earth ions. ................................................. 90
Chapter 1
Introduction

Wide band-gap semiconductors have attracted great interest for some time. In particular, there is strong commercial desire to produce efficient lasing blue light emitting diodes (LED) and short wavelength laser diodes.

Zinc oxide (ZnO) is n-type semiconductor with a wide band gap, with a room-temperature band gap of 3.37 eV [1] and it has so many promising properties.

ZnO possesses high piezoelectricity as well as high optical transmittance in the visible range; it has a variety of potential applications. ZnO films find applications in surface acoustic wave devices [2,3], low loss optical wave guides [4], electrostatic modulators [5], and hydrogen gas sensors [6]. The high optical transmittance and electrical conductivity of ZnO films compared with indium tin oxide and tin oxide have been used as top contact window layer in a-Si: H [7], CdTe [8], and CuInSe₂ based solar cells [9].

ZnO now has gained more concentrations for being considered as a suitable substrate for GaN growth because of its stacking order match and close lattice match. More recently ZnO has been used as compliant buffer layer in the growth of high quality GaN [10] by various growing methods.
1.1 Review of study on zinc oxide

Rare-earth doped semiconductors have attracted the attention of several research groups, as they constitute materials for optical-electronic devices such as light-emitting diodes (LED).

II-VI compounds containing rare earth activators have been of interest for many years, such materials have a discrete ion as the principal source of luminescence emission, the $f-f$ transitions yielding narrow emission bands or lines. In the fifties and sixties research on rare earth doped II-VI compounds was mainly stimulated by efforts towards developing efficient phosphor materials (particularly for CRT application) and, during some time, laser materials, a new impetus came, in the middle of seventies, from the activities aiming at multicolor electro-luminescence displays, and these have initiated the extensive work performed in this field up to the present time.

Since the pioneering studies of Destriau [11] on the behavior of ZnO and ZnS-type phosphors, knowledge concerning the luminescence of II-VI materials has been considerably enlarged.

While at first the alkaline earth sulfide have received greater attention than oxides in view of their applications as phosphor materials in display screens and active research work has been developed with ZnS, ZnSe and CdS. Insertion of rare-earth ions into ZnO also has been investigated but not so actively as the sulfur derivatives, probably because of the weaker light emission of ZnO as compared to that of ZnS.
While the emission of a number of II-VI solids like ZnS, ZnSe activated with ions of lanthanides manifest lines characteristic of inner-center f-f electron transition, ZnO was an exception.

In the early studies carried out during the late seventies and early eighties: only broad bands (around 550 nm) were observed [12, 13, 14, 15] in the photoluminescence spectra, on the other hand, the electroluminescence of these materials is somewhat similar from one doped sample to the other, and consists of three distinct bands in the 400-640 nm range [16]. The electroluminescence of ZnO: Ln (lanthanide), were ascribed to electron transitions between donor levels of the activators and acceptor levels.

Quang and his colleagues [17] observed slightly expressed lines superposed on the predominant broad emission band in ZnO activated by firing with Eu in N2. This behavior can be explained by the assumption that the photons of the exciting UV light are absorbed to a very low degree by the lanthanide ions themselves and that the excitation energy introduced is consumed exclusively for radiative or non-radiative transitions outside the lanthanide ions.

K. Kynev and V. K. Kuk [18] got hints from early studies that the rise in the concentration of the incorporated Ln$^{3+}$ and the decrease in the concentration of the centers determining self-activated (SA) luminescence and/or acting as acceptors should be favorable to the growth of the relative intensity of the emission due to the transitions within the 4f level. With the appropriate choice of conditions of activation
corresponding to the above requirements they obtained ZnO: Ln phosphors whose emission spectra showed lines characteristic of $f$–$f$ transitions.

Cathodoluminescence [19] brought a new extension of the luminescent behavior of rare earths. This emission is believed to originate from thermally populated excited states of the rare earths contained in mixed oxides. It appears in the form of narrow bands and it is found at positions slightly higher in wavelength than the absorption of the same species in aqueous solution. Such an emission was found only with rare earths (Nd, Ho, Er and Tm) showing relatively strong absorption bands, while Eu, Sm and Dy which absorb only weakly in the visible, seem to produce almost no signal typical of the rare earth but rather a broad and continuous spectrum.

Recently, Y. -K. Park and his colleagues sintered ZnO: EuCl$_3$ phosphors in vacuum [20], in which Eu exists in the host lattice as EuOCI and effectively quenches the broad-band emission of the ZnO host, consequently isolating the red emission due to Eu$^{3+}$ ion.

J. Kossanyi and his coworkers made extensive investigation of the rare earth centers in zinc oxide. They studied the electroluminescence of the Sm$^{3+}$, Ho$^{3+}$ ions in ZnO varistor-type structure [21, 22], and observed the characteristic luminescence of Ho$^{3+}$ ions. This luminescence evidences the presence of hot electrons as responsible for the excitation of the trivalent rare earth ions and the possibility to use zinc oxide varistors as electroluminescent devices. In their early studies of photoluminescence of zinc oxide sintered at 1100°C and doped with rare earths(Tm, Ho, Nd and Er) under excitation conditions (around 390 nm), they couldn’t see the emission from the rare
earth and only the luminescence of the semiconducting substrate in which the rare earth put the fingerprint of its absorption. Only holmium presents an emission when excited in its absorption band at 450 nm[23].

J. Kossanyi and his coworkers also studied the photoluminescence of the polycrystalline sintered ZnO co-doped with Li⁺ and trivalent rare-earth (RE³⁺) ions (Dy³⁺, Er³⁺, Eu³⁺, Ho³⁺, Nd³⁺, Sm³⁺ and Tm³⁺)[24]. They observed that the UV excitation of the Eu³⁺, Dy³⁺, Sm³⁺ and Tm³⁺ doped samples induces the characteristic lines of the 4f of the rare earth ions in addition to the broad ZnO pattern. While the UV excitation of the Er³⁺, Ho³⁺ and Nd³⁺ doped samples induces only the luminescence of ZnO with a partial reabsorption of the light by the RE³⁺ ions, no emission from the RE³⁺ ions being observed. J. Kossanyi and his coworkers also concluded that the presence of Li⁺ ions increases the absorbance of the RE³⁺ ions and enables the observation of their luminescence under direct 4f-4f photo excitation. And the RE³⁺ ions are mainly located outside the ZnO micro-crystals in the grain boundaries of the polycrystalline matrix where they are closely associated with Li⁺ ions.

Now it is well known that trivalent rare-earth ions in II-VI compound materials show luminescence spectrum which is characterized by a broad-band emission and a narrow line emission as well. The first one is assumed to be due to radiative transitions in rare earth (RE) ion-vacancy complex centers [25], whereas the narrow line emissions is a result of f-f inner-shell transitions in the rare earth (RE) centers themselves [26]. The 4f orbits of rare-earth ions are so deeply buried within the electronic shell that the energy levels of the (4f)ⁿ configuration are only slightly perturbed when the ion is
placed within a crystal. Generally the spin-orbit splitting of the levels is around
$10^3\text{cm}^{-1}$ while the crystalline Stark splitting of a level of given $J$ is about $100\text{cm}^{-1}$. As
a result of the relatively weak interaction with the environment, the picture of an
isolated ion slightly perturbed by the surrounding crystal has been extremely fruitful.
Further, it has been possible to use the rare-earth ions as probe to observe solid state
phenomena such as phonons and magnetic interactions.

1.2 Characteristics of zinc oxide

Zinc oxide, ZnO, has the molecular weight of 81.37, average atomic weight of
40.69(a.m.u.), average atomic number of 19, and enthalpy of formation (298.15K) of−
350.5KJ/mol [27].
Under normal conditions, ZnO crystallizes into the wurtzite structure (space group
P6$_3$mc). Natural zincite has lattice parameters $a=0.32495 \pm 0.00005$ nm and
$c=0.52069 \pm 0.00005$ nm at 298 ± 5K. ZnO has the melting point of 2248K; the room
temperature X-ray density of ZnO is 5.6750± 0.0018g/cm$^3$. ZnO is a direct band gap
semiconductor material. Its minimum energy gap is 3.2 eV at room temperature and
3.44 eV at 4K. The optical band gap measured on thin films is close to 3.2 eV (300K).
The carrier effective mass in ZnO is virtually scalar and equal to 0.24$m_o$ and 0.59$m_o$
for electrons and holes, respectively.
1.3 4f-4f luminescence of rare earth centers

Table 1.1 shows the electron configuration of rare-earth elements and ions, the covalent radius and electronegativity. Figure 1.1 is the energy levels of RE$^{3+}$ ions [28].

Table 1.1 Electron configurations of rare earth atoms, rare earth ions, covalent radii, and electronegativity.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration of RE atoms</th>
<th>Electron Configuration of RE$^{3+}$ ions</th>
<th>Covalent radius (Å)</th>
<th>Electronegativity (Pauling's)</th>
</tr>
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<tr>
<td>Cerium</td>
<td>4f$^2$5s$^2$5p$^6$6s$^2$</td>
<td>4f$^2$5s$^2$5p$^6$</td>
<td>1.65</td>
<td>1.12</td>
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<tr>
<td>Praseodymium</td>
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<td>4f$^3$5s$^2$5p$^6$</td>
<td>1.65</td>
<td>1.13</td>
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<td>Neodymium</td>
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<td>1.14</td>
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<td>Promethium</td>
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<td>4f$^5$5s$^2$5p$^6$</td>
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<td>1.13</td>
</tr>
<tr>
<td>Samarium</td>
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<td>4f$^6$5s$^2$5p$^6$</td>
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<td>1.17</td>
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<td>1.22</td>
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</tr>
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<td>1.24</td>
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<tr>
<td>Ytterbium</td>
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<td>4f$^{14}$5s$^2$5p$^6$</td>
<td>1.74</td>
<td>1.10</td>
</tr>
</tbody>
</table>
Figure 1.1 The energy levels of rare earth ions [28]
RE dopants are found to be incorporated mostly as 3+ ions, but the doubly positive charge state is also observed in some cases. For the RE$^{3+}$ ions having a partly filled 4f shell the electron configuration is $4f^65s^25p^6$, where $n$ varies from 1 to 13 when going from Ce ($Z=58$) to Yb ($Z=70$).

### 1.4 Electronic states of rare earth centers

Because we are concerned with optical transitions within the partly occupied 4f shell, so we shall first deal with the electronic states of RE centers originating from the 4f free-ion states.

The electronic states of RE centers are usually discussed on the basis of the crystal-field model [29]. Thus the Hamiltonian for the 4f electrons is written as

$$H = H_0 + H_{ee} + H_{so} + H_{cf}$$

(1.1)

($H_0$ Hartree-Fock part of the Hamiltonian, $H_{ee}$ Coulomb interaction between the electrons (part not contained in), $H_{so}$ spin-orbit coupling, $H_{cf}$ crystal-field potential). The free-ion levels results from the splitting of the 4f configuration due to $H_{ee} + H_{so}$ and are, as usual, denoted in the form $2S+1L_J$th S, L, spin orbital parts of angular momentum, J total angular momentum). Generally speaking, $H_{ee}$ and $H_{so}$ have comparable effects, so one is concerned with “intermediate” spin-orbit coupling (intermediate between LS and jj coupling). Therefore J is generally the only “good” quantum number characterizing the n-electron states which (particularly at the end of the lanthanide series) frequently contain comparable contributions of different $L$ and $S$. 
Under the action of $H_{cf}$ the free-ion levels $(2J+1)$-fold degenerate are generally split into several components. The set of splitting components ("Stark components") originating from a given free-ion levels is usually referred to as a Stark multiplet or Stark manifold. Since due to the shielding by the $5s^25p^6$ shell), $H_{cf}$ is considerably smaller than $H_{ee}$ and $H_{so}$, this splitting (typically $< 200 \text{cm}^{-1}$ (about 25 meV)) is often much less than the separation of those levels. Therefore, $H_{cf}$ is mostly (including all work on II-VI: RE systems) treated as a first-order perturbation ("weak-field limit" of crystal-field theory), i.e. ignoring the mixing of states that belong to different free-ion levels ("J-mixing").

$H_{cf}$ is usually introduced by an expansion into spherical harmonies,

$$H_{cf}(r) = \sum_{l,m} \gamma_l^m r^{-l} Y_l^m(\theta, \phi)$$

(1.2)

($\gamma_l^m$). Of this expansion only terms with $l = 2, 4$ and 6 contribute to matrix elements between $4f$ states. Further, in many cases center symmetry leads to relations between some of the $\gamma_l^m$ makes some of them vanish. In particular, for centers of cubic symmetry (which have been predominantly dealt with in the work on RE-doped II-VI compounds) one is left with only two independent $\gamma$-coefficients.

The crystal-field splitting of RE$^{3+}$ levels is frequently analyzed by means of the "operator equivalents method"[30]. This method involves replacing the expansion terms in (2) by certain combinations of components of the total angular momentum operator, the relevant matrix elements of which are tabulated. For systems of cubic
symmetry one can make use of the results of Lea et al [31] who have calculated on this basis energy splits and eigen states for all types of free-ion levels as functions of two parameters.

The extensive literature on RE$^{3+}$ ions in crystalline solids shows that the experimental 4f-4f spectra due to a given center can be satisfactorily reproduced by means of fitted values of crystal-field coefficients. Frequently a set of fitting parameters denoted by $A_i^m \langle r^l \rangle$ is employed. The $A_i^m$ which is simply related to the $\gamma_i^m$ describes the effect of the crystal-field, while the “radial integrals” $\langle r^l \rangle$ are averages of the factors in (2) over the 4f states. Within this framework, the two parameters used in the case of cubic symmetry are $A_i^0 \langle r^4 \rangle$ and $A_i^0 \langle r^6 \rangle$. On the other hand, the crystal-field parameters calculated on the basis of the electrostatic field due to the charges of the surrounding crystal usually are in rather poor agreement with experiment, even for very sophisticated models (e.g. [32]). The reasons for this discrepancy which is due, roughly speaking, to covalence effects and generalization of the crystal-field concept have been discussed, e.g., by Newman [33].

1.5 Energy levels of rare earth centers

There is little doubt that for II-VI: RE systems the positions of the 4f levels relative to each other (in particular the Stark splitting) can be described by the crystal-field approach in the same sense as for RE’s in other groups of materials studied more thoroughly. This is essentially confirmed by the available investigations of optical
spectra. Unfortunately, such data are rather scarce, particularly because for most of
the centers separated only one or two Stark multiplets have been analyzed.

An interesting problem is the position of the 4f levels relative to the energy bands of
the host crystals. Apart from the cases of ZnS: Eu and ZnS: Yb to be discussed later,
there seems to be (just as for RE ions in other groups of materials) no detailed data on
this question. Some general information comes from the fact that with a few
exceptions (Eu in several hosts), ZnS: Yb and CdTe: Tm only the 3+ charge state has
been detected in optical and EPR work. This shows that usually the 3+ ground level
lies rather deep, most probably within the valence bands, while the 2+ ground level
should normally be located about the conduction band range.
Chapter 2
Sample Preparation

To better understand the rare earth doped ZnO systems, we prepared two groups of samples. They are: ZnO single crystals and ZnO thin films.

2.1 ZnO: RE$^{3+}$ single crystals

ZnO single crystals are grown by hydrothermal process. The rare earth ions are implanted into the samples after growth. The implantation condition is shown in Table 2.1, which also provide the thickness of the ZnO samples and electron concentrations. The implantation ion beam was inclined at 10° to the normal of the ZnO surfaces to prevent the channeling. The simulated depth profiles, the projected ranges and peak concentration were calculated using the Pearson distribution (see Table 2.1). The rare earth ions was implanted among three different energies and the doses of the implanted ion is varying in the range of $1 \times 10^{14}$ ions/cm$^2$ to $1.6 \times 10^{16}$ ions/cm$^2$ at fluencies chosen to give an approximation of a square implant profile in the ZnO epi-layer.
### Table 2.1 Sample information of bulk ZnO: RE$^{3+}$ single crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>Ion energy [KeV]</th>
<th>Doses of ions $[^{[cm^2]}]$</th>
<th>Projected range [nm]</th>
<th>Ions concentr. $[^{[cm^{-3}]}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO: Pr</td>
<td>0.5</td>
<td>150</td>
<td>$1 \times 10^{14}$</td>
<td>~35</td>
<td>$3.1 \times 10^{19}$</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>50</td>
<td>$2.8 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
<td>$1.4 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO: Dy</td>
<td>0.5</td>
<td>150</td>
<td>$1 \times 10^{14}$</td>
<td>~30</td>
<td>$3.7 \times 10^{19}$</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>50</td>
<td>$3.2 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>$1.6 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO: Ho</td>
<td>0.5</td>
<td>150</td>
<td>$1 \times 10^{14}$</td>
<td>~30</td>
<td>$4.1 \times 10^{19}$</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>50</td>
<td>$3.2 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
<td>$1.6 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO: Er</td>
<td>0.5 mm</td>
<td>150</td>
<td>$1 \times 10^{14}$</td>
<td>~25</td>
<td>$4 \times 10^{19}$</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>48</td>
<td>$2.8 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
<td>$1.7 \times 10^{13}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2 ZnO:RE$^{3+}$ thin films

ZnO:RE$^{3+}$ thin films are grown by metal organic chemical vapor deposition (MOCVD), on the basal plane of 2 inch diameter sapphire substrates. The ZnO are high-quality n-type undoped and the rare earth doped epi-layers implanted at room temperature under the conditions shown in Table 2.2, which also provide the thickness of the ZnO layers and electron concentrations. The implantation ion beam was inclined at 10° to the normal of the ZnO epi-layers to prevent the channeling. The simulated depth profiles, the projected ranges and peak concentration were calculated using the Pearson distribution (see Table 2.2). The rare earth ions was implanted at three energies at fluencies chosen to give an approximation of a square implant profile in the ZnO epi-layer. The implanted wafer was cut into a sample with dimensions 2x2 mm before annealing. This sample was given isochronal thermal annealing treatments (duration 30 min) at temperatures from 650°C to 1150°C. The ions are implanted into the films using same methods as that for single crystals.
Table 2.2. Sample information of ZnO:RE$^{3+}$ epi-layer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (µm)</th>
<th>Ion energy [keV]</th>
<th>Doses of ions [cm$^2$]</th>
<th>Projected range [nm]</th>
<th>Ions concentr. [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:Sm</td>
<td>0.5</td>
<td>150</td>
<td>1×10$^{14}$</td>
<td>~31</td>
<td>3.5×10$^{19}$</td>
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<tr>
<td></td>
<td></td>
<td>50</td>
<td>3×10$^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
<td>1.4×10$^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO: Er</td>
<td>0.5</td>
<td>150</td>
<td>1×10$^{14}$</td>
<td>~30</td>
<td>4.1×10$^{19}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>3.2×10$^{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
<td>1.6×10$^{13}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 3
Material Characterization Methods

It is interesting to study rare earth ions in ZnO because of the possible application in light emitting devices and for their unique optical and electrical properties. The rare earth luminescence depends very little on the nature of the host and the ambient temperature. The $4f$ orbits of rare earth ions incorporated into semiconductors are so deeply buried within the electronic shell that the energy level of the $4f^6$ configuration are only slightly perturbed as compared to free-ion energy levels. The electronic structure of the rare earth luminescence centers and their electrical activities, as well as their indirect photoluminescence (PL) and electroluminescence (EL) excitation mechanisms, are still not well understood.

We have undertaken an extended study of the luminescent properties under well-defined experiment conditions of rare earth doped semiconducting zinc oxide. Photoluminescence (PL) and cathodoluminescence (CL) has been taken to investigate the lattice structure and optical properties of our samples. To better understand the experimental results, some introduction to these experimental techniques is necessary.
3.1 Cathodoluminescence

3.1.1 Introduction

The term cathodoluminescence (CL) derives from the use of high-energy electrons (cathode rays) as the means of excitation. The earliest use of cathodoluminescence (CL) was probably by William Crookes in the 1880s, which applied the technique to the characterization of lead glasses. However, it was the development of the analytical (x-ray) electron microprobe in the late 1950s that promoted the current interest in CL. Early investigations were in mineralogy and petrology. Structural and compositional variations in quartzes, dolomites, and feldspars were visible with CL imaging, as well as residual skeletal structures of fossils. During the 1960s, the commercial availability of scanning electron microscopes (SEM), along with advances in emerging technologies, such as space exploration and microelectronics, brought about a further increase in CL applications. For example, CL was useful in the development of optical electronic materials and devices. Today, there are CL systems commercially available, such as those marketed by Oxford Instruments for SEMs and Nuclide Corporation for optical microscopes.

3.1.2 Electron-beam interactions in solids

An appreciation of how energetic electrons interact with solids is important to an understanding of CL. The dielectric response of the solids is fundamental to physical
interpretation. One can view the incoming fast electrons as an impulse of applied electric field (charge) to the solid. When electrons enter a solid:

(1) the host charge can redistribute to oppose the sudden change in electric field;

(2) interactions with the crystal lattice can result in well-defined energy losses of the incident electrons;

(3) such characteristic energy losses can involve single-particle and collective (plasmons) excitations of the host electrons.

It is the subsequent relaxation to the ground state, between characteristic energy levels of the solid, that produces the photons that are detected as CL. These transitions may involve discrete atomic levels (rare-earth metal d- and f- states), extended band (conduction band to hydrogen-like shallow impurity states), and F-centers. Transitions between tightly bound inner core states result in x-ray photon emissions of very high energies (>1 keV). Excitation of bulk (volume) plasmons in inorganic crystals such as SiC, GaAs gives rise to energy losses in the range 10-30 eV. Characteristic CL photons fall in the visible part of the electromagnetic spectrum (0.5-6.0 eV). Other electron-solid interactions can also produce light. When a fast electron is slowed down by Coulombic interaction with the host atoms, the deceleration (energy loss) results in braking radiation. This background light is characterized by a continuous spectrum from zero energy to the incident-electron energy. Another source of light is Cerenkov radiation, which occurs when the velocity of the electron in the solid exceeds the speed of light in the solid (dependent on the refractive index). Radiative decay of surface plasmons in metals can also produce visible photons.
The retardation of electrons of given energy is characterized by a depth-dependent energy loss function and the range (the ultimate penetration depth into the solid). The incoming electrons undergo either elastic (large-angle) or inelastic (small-angle) scattering on sensing the lattice potential. These interactions result in zigzag trajectories within the solid. The deviations from the projected primary trajectory broaden the original probe diameter, determined by the initial electron subsequent diffusion produces a pear-shaped excitation volume in a typical solid. This interaction volume defines the source for CL. In semiconductors, the CL generation volume is typically larger than the initial interaction volume (of radius, $r_g$) because of minority carrier transport (determined by the carrier diffusion length $L$). In bulk solids, one expects the effective CL probe diameter to be proportional to $(L^2 + r_g^2)^{1/2}$.

3.1.3 Cathodoluminescence experiment setup

In our system, the cathodoluminescence was excited by an electron beam incident upon the sample at a $45^\circ$ angle from an electron gun (Electronscan EG5 VSW), which was a common vacuum (of $\sim 5 \times 10^{-7}$ Torr) with cryostat. The emitted light was collected by a quartz lens on the entrance slit of the spectrograph monochromator (ISA model HR-320) operated in Czerny-Turner configurations with different holographic gratings. The optical signal was detected by a Princeton Instruments back-illuminated charged-coupled device (CCD). The CCD system used for the experiments is TE/CCD-512SF (Princeton Instruments Inc.) with a UV/AR coating and controlled by
a computer. Our CCD system is back illuminated system, the advantage of back illuminated system over the front illuminated version is super quantum efficiency, typically for our system we have the average QE (quantum efficiency) of > 60% over the range 500 to 900 nm as opposed to 5-10% in the front illuminated case. The CCD system is controlled by a computer via a controller which also controls the step motor of the monochromator. The experimental data is saved in ASCII format.

Since we are interested with the temperature dependence of the cathodoluminescence of the ZnO:RE$^{3+}$ single crystals and epi-layers, we need to have thermo control system in our experiments. Our thermo controlling system consists of a compressor, modular cooling system and temperature controller. The compressor will compress the liquid helium, so the lowest temperature that the cryostat can reach is 9K. We made extensive investigation of the temperature effect on the cathodoluminescence spectrum of the ZnO:RE$^{3+}$ single crystals and epi-layers samples by controlling the temperature of the cryostat. One thing need to notice here is that when we increase the temperature of the cryostat, the vacuum is turning worse, so we monitor the vacuum with the vacuum gauge and when we found the vacuum is worse than $10^{-6}$ torr, we would turn on the vacuum system during the high temperature measurement. The experiment set up is show in Figure 3.1.
Figure 3.1 Cathodoluminescence experiment set up
3.2 Photoluminescence

Luminescence in solids is the phenomenon in which electronic states of solids are excited by some energy from an external source and the excitation energy is released as light. When the energy comes from short-wavelength light, usually ultraviolet light, the phenomenon is called photoluminescence. Photoluminescence (PL) in solids is classified from the point of view of the nature of the electronic transitions producing photoluminescence.

Photoluminescence is divided into two major types, namely intrinsic and extrinsic luminescence. In the former there are three kinds, band-to-band luminescence, exciton luminescence, and cross-luminescence. The latter is divided into unlocalized and localized types, depending on whether excited electrons and holes of excitatin and emission processes are confined to localized centers. Luminescence materials and phenomena that have been studied by a large number of scientists as early as the late 19th century belong to this category.

3.2.1 Intrinsic luminescence

There are three kinds of intrinsic luminescence: band-to-band luminescence, exciton luminescence, and cross luminescence.
3.2.1.1 Band-to-band luminescence

Luminescence owing to the band-to-band transition, i.e. to the recombination of an electron in the conduction band with a hole in the valence band, can be observed in very pure crystals at relatively high temperatures. This has been observed in Si, Ge and some III-V compounds such as GaAs. At low temperatures, this luminescence is transformed into exciton luminescence. Light emission from very bright type light-emitting diodes and semiconductor lasers is due to the band-to-band transition.

3.2.1.2 Exciton luminescence

An exciton is a composite particle of an excited electron and a hole interacting with one another. It moves in a crystal conveying energy and produces luminescence owing to the recombination of the electron and the hole. There are two kinds of excitons: the Wannier (or Wannier-Mott) exciton and the Frenkel exciton.

The Wannier exciton model expresses an exciton as composed of an electron in the conduction band and a hole in the valence band bound together by the coulomb interaction. Thus a Wannier exciton is analogous to a hydrogen atom. This model works well for inorganic semiconductors such as III-V and II-VI compounds. The Wannier exciton moves in a crystal but does not contribute to electric conduction. It emits luminescence by the recombination of the electron and hole composing it. The
expanse of the wavefunctions of the electron and hole in a Wannier exciton is usually much larger than the lattice constant.

Wannier exciton are stable only at relatively low temperatures, where the binding energies of excitons are higher than the thermal energy. Luminescence of Wannier excitons is observed only at such temperatures. At higher temperatures, where the thermal energy is higher, the excitons are no longer stable and band-to-band luminescence appears instead.

The Frenkel exciton model is used in cases where the expanse of the electron and hole wavefunctions is smaller than the lattice constant. Typical examples are organic molecular crystals such as anthracene and tetracene and inorganic complex salts.

3.2.1.3 Cross-luminescence

So called cross luminescence is produced by the recombination of an electron in the valence band with a hole created in the outermost core band. This luminescence was first observed in BaF$_2$ under x-ray pulse excitation in 1982. It has now been observed in a number of alkali an dalkaline-earth halides and double halides.

3.2.2 Extrinsic luminescence

Luminescence caused by intentionally incorporated impurities, in most cases metallic impurities, or defects is classified a extrinsic luminescence as opposed to intrinsic luminescence. Most of the observed types of luminescence that have practical
applications belong to this category. Intentionally incorporated impurities are called activators and materials made luminescence in this way are usually called phosphors.

Extrinsic luminescence in ionic crystals and semiconductors is classified into two types: unlocalized and localized. In the unlocalized type, the electrons and holes of the host lattice, i.e., free electrons in the conduction band and free holes in the valence band, participate in the luminescence process, while in the case of the localized type the luminescence excitation and emission processes are confined in a localized luminescence centers.

3.2.2.1 Unlocalized type

In semiconductors, most important impurities are donors and acceptors that dominate semiconductive properties, and these act as luminescence activators. There are two types of luminescence transitions, i.e., the transition of a free carrier to a bound carrier, and the transition of a bound electron at a donor to a bound hole at an acceptor (which is also called donor-acceptor pair transition). These kinds of luminescence lines and bands are usually observed in typical compound semiconductors such as III-V and II-VI compounds.

Donor-acceptor pair luminescence is caused in two ways: The first is that after the band-to-band excitation an electron is trapped at an ionized donor, and a hole at a compensated acceptor, and they recombine. The second is the direct excitation of an electron in a compensated acceptor to an ionized donor level. Therefore, the donor-acceptor pair luminescence is an intermediate type between localized and unlocalized
luminescences. The emission energy if this luminescence depends on the spatial
separation between the donor and the acceptor in a pair. This luminescence is very
important in terms of practical applications.

In addition to those mentioned above, there are also the luminescence of Wannier
excitons bound to impurities and the luminescence owing to isoelectronic traps.

### 3.2.2.2 Localized type

Various kinds of metallic impurities intentionally incorporated in ionic crystals and
semiconductors often create efficient localized luminescence centers. Some kinds of
lattice defects also act as localized luminescence centers.

### 3.2.3 Photoluminescence experiment setup

We use the He-Cd (Helium Cadmium) laser emits 325 nm(UV) light as the excitation
light. The beam is then directed via mirrors and focused by a quartz lens onto the
sample surface mounted on the cold finger in the optical cryostat. The luminescence
emitted from the sample is collected by a quartz lens and fed to the monochromator.
The optical cryostat is pumped to below 10-6 torr with the vacuum system(Pfeiffer
Vacuum TCP 015) and then cooled down to 9K. The cooling system is a closed circuit
liquid Helium system by CTI Cryogenics(Model 22C), the cooling temperature is
controlled by the Palm Beach model 4075 thermo controller. The monochromator
separates polychromatic light it receives into monochromatic light of individual
wavelength Monochromatic light thus obtained is used to illuminate the sample. The wavelengths scanned across the exit slit opening are detected using a Hamamatsu R928 photo multiplier tube (PMT) and measured for intensity at individual wavelengths. Individual wavelengths focused at different horizontal positions along the exit port of the spectrograph are detected simultaneously by the CCD system. The CCS system used for the experiments is TE/CCD-512SF (Princeton Instruments Inc.). It is back illuminated system, the advantage of back illuminated system over the front illuminated version is super quantum efficiency, typically for our system we have the average QE (quantum efficiency) of > 60% over the range 500 to 900 nm as opposed to 5-10% in the front illuminated case.

The signal from CCD is sent to a computer via a controller to be recorded as ASCII data. The computer also controls the stepper motor that moves the grating of the spectrograph. Our Photoluminescence experiment set up is show in Figure 3.2.
Figure 3.2 Photoluminescence experiment set up
3.3 kinetics measurement for ZnO:RE$^{3+}$

To better understand the process occurring with the ZnO: RE systems, we made the kinetics measurements. It is realized by excite the sample with a square pulse of a laser light and then measure the emitting response from the sample. The rise and decay of the PL emitted is analyzed to investigate the energy transfer process inside the sample.

The typical duration of the pulse generated by our pulse generator is 2.5 ms, and the rise and decay time are less than 2 ns. This laser light is modulated by a acousto-optic modulator and then directed onto the sample mounted on the cold finger in the cryostat. The emission from the sample is collected and filtered to remove the source laser light and then fed into the monochromator. The interested wavelength light is then delivered to the photomultiplier (PMT). PMT preamplify the signal and the outgoing signal is directed to a Multi Channel Scaler (EG&G Ortec MCS T 914). The start pulse generated by the MCS is synchronous with the pulse generated by the pulse generator. The signal output from the MCS is stored in a computer as ASCII file. This file is then analyzed by curve fitting softwares (Table Curve2, Origin 5). Table 3.1 is the parameters of cathode-excitation for kinetics measurement. Our kinetics experiment set up is shown in Figure 3.3.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filament current (A)</td>
<td>1.4</td>
</tr>
<tr>
<td>Beam current (mA)</td>
<td>0.8 ~ 0.9</td>
</tr>
<tr>
<td>Electron voltage (KV)</td>
<td>12</td>
</tr>
<tr>
<td>Slit (mm)</td>
<td>0.6</td>
</tr>
<tr>
<td>Excitation pulse width (ms)</td>
<td>3.9</td>
</tr>
<tr>
<td>Dwell time (ns)</td>
<td>1000</td>
</tr>
</tbody>
</table>
Figure 3.3 Kinetics experiment set up
Chapter 4
PL and CL of the ZnO:RE$^{3+}$

4.1 ZnO:RE$^{3+}$ single crystal

The sample preparation has been described in chapter 2. Believing that high annealing temperature is better for the crystallinity, at first we annealed the sample at pretty high temperature, like around 1000°C for a long period about 4-5 hours in the air, but from our results of photoluminescence experiment only a small trace of the luminescence from the rare earth has been seen. And then we decrease the annealing temperature and the annealing period step by step, at around 150°C, we found the strongest emission from the rare earth ions.

4.1.1 CL of ZnO:Dy, Li single crystal

We investigate the effect of annealing condition by comparing the cathodoluminescence of three different annealed samples: one is unannealed, one annealed at 150°C in the air for 30 minutes, and another sample annealed at 270°C in the air for 20 minutes. From Figure 4.1, we found that, the unannealed sample shows the sharp peaks from emissions of Dy$^{3+}$ is overlapping with the broad band luminescence of ZnO. Comparing with the other two samples, this unannealed sample shows the strongest and most rich emissions from Dy$^{3+}$. From the sample annealed at
Figure 4.1 CL spectrum of ZnO:Dy, Li single crystal under different annealing conditions measured at 9K

150°C, the emission of Dy$^{3+}$ is not as strong as those seen in the unannealed sample. In case of the sample annealed at the temperature of 270°C, only a small trace of the Dy$^{3+}$ emission from transition: $^4F_{9/2} - ^6H_{13/2}$ is seen. Various mechanisms have been proposed for the green and orange luminescence of ZnO. Early work ascribed the green luminescence to Cu impurities, and the orange luminescence was attributed to Li
acceptors substituting regular Zn lattice sites.[35]. Recent electron paramagnetic resonance measurements of commercial ZnO powders indicate a relation between singly ionized oxygen vacancies and the green luminescence[36]. The orange emission was observed in ZnO doped with lithium and other impurities[37]. More recently, Cocivera etc. found that orange luminescence of ZnO can be obtained without doping with lithium. They concluded that both green and orange luminescence were related to the amount of oxygen in the sample and not due to trace amounts of dopants. The green and orange luminescence bands resulted from the oxygen-poor and oxygen-rich states, respectively, in ZnO. In the case of the green luminescence samples the vacancies do not appear to penetrate deeply into the crystalline[38]. The two cathodoluminescence peaks locating at 579 nm, 667 nm are indentified as the transition of $^4F_{9/2} - ^6H_{13/2}$ and $^4F_{9/2} - ^6H_{11/2}$ respectively. The peak assignment is show in the table 4.1.
Table 4.1 The peak assignment for the CL of ZnO:Dy, Li single crystal

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>579 nm</td>
<td>$^4F_{9/2} - ^6H_{13/2}$</td>
</tr>
<tr>
<td>667 nm</td>
<td>$^4F_{9/2} - ^6H_{11/2}$</td>
</tr>
</tbody>
</table>

Figure 4.2 shows the relationship between the cathodoluminescence intensity and the measurement temperature. The ZnO:Dy, Li single crystal sample has been annealed in the air for half an hour at 150°C. We found that the intensity is decreased with the increasing of the temperature. At the measurement temperature of 9K, we see the strongest intensity for all the peaks, the Dy$^{3+}$ emission is overlapping with the broad band luminescence of ZnO material. Both the intensity of luminescence from the Dy$^{3+}$ and that from the ZnO is decreasing with the increasing of the measurement temperature from 9K to 50K, 223K to 300K. The inset of this figure shows the intensity dependency with measurement temperature for transition $^4F_{9/2} - ^6H_{13/2}$. We found that the peak intensity decreased drastically with the increasing of the temperature. Here we assigned that the peak intensity measured at 9K as unit 1. The peak assignment is shown in the table 4.2.
Figure 4.2 CL spectrum of ZnO:Dy, Li single crystal annealed in the air for 0.5hr. at 150°C measured at 9K, 50K, 223K and 300K

Table 4.2 The peak assignment for CL of ZnO:Dy, Li single crystal annealed 150°C

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>490 nm</td>
<td>(^{4}F_{9/2} - ^{6}H_{15/2})</td>
</tr>
<tr>
<td>579 nm</td>
<td>(^{4}F_{9/2} - ^{6}H_{13/2})</td>
</tr>
<tr>
<td>667 nm</td>
<td>(^{4}F_{9/2} - ^{6}H_{11/2})</td>
</tr>
<tr>
<td>750 nm</td>
<td>(^{4}F_{9/2} - ^{6}H_{9/2})</td>
</tr>
<tr>
<td>830 nm</td>
<td>(^{4}F_{9/2} - ^{6}H_{7/2})</td>
</tr>
<tr>
<td>900 nm</td>
<td>(^{4}F_{9/2} - ^{6}H_{9/2})</td>
</tr>
</tbody>
</table>
4.1.2 PL of ZnO:Er, Li single crystal

In our study of the annealing effects on the photoluminescence spectrum of ZnO: Er, Li single crystal, we started to anneal it with several different compounds in the air at high temperature range and for a long annealing period. But we found that at high annealing temperature, the luminescence from the rare earth ions would disappear, so we decrease our annealing temperature to a low temperature range and shorten the annealing period. The optimal annealing temperature that we found is pretty low, it is around 150° C, and the optimal annealing period is around half an hour.

Figure 4.3 is a three dimensional figure of Photoluminescence of ZnO single crystal sample implanted with Er, Li sample excited at 325 nm measured at 9K. The single crystal ZnO implanted with Er, Li is annealed with four different compounds: CuCl₂, Er(NO₃)₃, ErCl₃, Li₂CO₃ respectively, at 1000°C for 4.5 hour in the air in a open ampular. The photoluminescence intensity is in arbitrary units. The sharp peak around 350 nm is coming from the free exciton. The bump at around 500 nm is from ZnO. It turns out that only from the sample co-annealed with Li₂CO₃ can we find a small trace of Er³⁺ emission, and this emission is assigned to transition: ⁴I₁₅/₂⁻→ ⁵D₁. 
PL of ZnO:Er:Li (single crystal) annealed 4.5 hrs at 1000°C, exc. at 325 nm, 9 K

Figure 4.3 Photoluminescence spectrum of the ZnO:Er, Li single crystal annealed in the air for 4.5 hr at 1000°C

Then we lowered the annealing temperature and decreased the annealing period step by step, we found that when the annealing temperature is higher than 300°C the luminescence from the rare earth ions is very weak, only at the temperature lower than that the emission from the rare earth ions become stronger. With lowering the annealing temperature we got the optimal annealing temperature at around 150°C for most of our
samples. Apparently, comparing with other semiconductor materials, this annealing
temperature is pretty low.

4.1.3 CL of ZnO:Er, Li single crystal

The single crystal sample has been annealed in the air at 150°C for half an hour.
Figure 4.4 shows the relationship between the cathodoluminescence intensity and the
measurement temperature. It is found that the cathodoluminescence intensity is
decreased with the increasing of the temperature. At 9K we can see the strongest
emission from the Er$^{3+}$ ions. With the increasing of the measurement temperature from
9K to 50K, 223K, 300K the cathodoluminescence intensity of all the peaks is
decreasing. The inset of this figure shows the intensity dependence of the
measurement temperature for the peak centered at 555 nm which is from the
transition: $^2S_{3/2}$ - $^4I_{15/2}$. The peaks locate at 536 nm, 555 nm, 665 nm, 984 nm correspond
to the transition from excited states ($^4H_{11/2}$, $^2S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$) to the ground state($^1I_{15/2}$) of
the Er$^{3+}$ ions. The peak at 856 nm corresponds to the transition from $^4I_{13/2}$ to $^4S_{3/2}$. The
assignment for all the peaks is shown in table 4.3
Table 4.3 peak assignment for the CL of ZnO: Er, Li single crystal

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Er&lt;sup&gt;3+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>536 nm</td>
<td>&lt;sup&gt;4&lt;/sup&gt;H&lt;sub&gt;11/2&lt;/sub&gt; - &lt;sup&gt;4&lt;/sup&gt;I&lt;sub&gt;15/2&lt;/sub&gt;</td>
</tr>
<tr>
<td>555 nm</td>
<td>&lt;sup&gt;2&lt;/sup&gt;S&lt;sub&gt;3/2&lt;/sub&gt; - &lt;sup&gt;4&lt;/sup&gt;I&lt;sub&gt;15/2&lt;/sub&gt;</td>
</tr>
<tr>
<td>665 nm</td>
<td>&lt;sup&gt;4&lt;/sup&gt;F&lt;sub&gt;9/2&lt;/sub&gt; - &lt;sup&gt;4&lt;/sup&gt;I&lt;sub&gt;15/2&lt;/sub&gt;</td>
</tr>
<tr>
<td>856 nm</td>
<td>&lt;sup&gt;4&lt;/sup&gt;S&lt;sub&gt;3/2&lt;/sub&gt; - &lt;sup&gt;4&lt;/sup&gt;I&lt;sub&gt;13/2&lt;/sub&gt;</td>
</tr>
<tr>
<td>984 nm</td>
<td>&lt;sup&gt;4&lt;/sup&gt;I&lt;sub&gt;11/2&lt;/sub&gt; - &lt;sup&gt;4&lt;/sup&gt;I&lt;sub&gt;15/2&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

Figure 4.4 Cathodoluminescence of the ZnO: Er, Li single crystal
4.1.4 CL of ZnO:Ho, Li single crystal

The single crystal ZnO sample implanted with Ho, Li has been annealed in the air at the temperature of 150°C for half an hour. Figure 4.5. is the cathodoluminescence of ZnO:Ho, Li single crystal measured at 50 K, 223 K, 300 K respectively. From this figure we found that with the increasing of the measurement temperature the cathodoluminescence intensity is decreasing. The two peaks located at 553 nm, 764 nm correspond to the transition from the ground state $^5\text{I}_8$ to the excited state of $^5\text{F}_3$, $^5\text{I}_4$ respectively. The peak assignment is shown in table 4.4

![CL of ZnO: Ho: Li, annealed 0.5 hr at 150°C](image)

Figure 4.5 Cathodoluminescence spectrum of ZnO:Ho, Li single crystal
Table 4.4 The peak assignment for CL of ZnO:Ho,Li single crystal annealed at 150°C

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Ho&lt;sup&gt;3+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>553 nm</td>
<td>$^5F_3 - ^3I_8$</td>
</tr>
<tr>
<td>764 nm</td>
<td>$^5I_4 - ^3I_8$</td>
</tr>
</tbody>
</table>

4.1.5 CL of ZnO:Pr, Li single crystal

Figure 4.6 shows the effect of the annealing condition on the cathodoluminescence of ZnO: Pr, Li. There are four samples, one is unannealed, and the other three are annealed in the air for half an hour at 170, 230, and 270°C respectively. The peak located at 630 nm, 880 nm correspond to the transition of $^3P_0 - ^3H_6$, $^1D_2 - ^3F_2$ respectively.
Figure 4.6. CL spectrum of ZnO:Pr, Li single crystal samples: unannealed, annealed in
the air for 0.5 hr. at 170°C, 230°C, 270°C respectively measured at 9K

The assignment of the transitions for the cathodoluminescence of ZnO:Pr, Li single
crystal sample are shown in table 4.5. Figure 4.7. shows the Cathodoluminescence is
of ZnO:Pr, Li single crystal which has been annealed in the air at 150°C for half an
hour measured at temperature of: 50K, 128K, 300K respectively. From this figure we
found that with the increasing of the measurement temperature from 50K, 128K to
300K, the cathodoluminescence intensity is decreasing. The four cathodoluminescence
peaks located at 629, 653, 728, 878 nm are identified as transition $^{3}P_{0} - ^{3}H_{6}, ^{3}P_{0} - ^{3}F_{6}, ^{3}P_{0} - ^{3}F_{4}$, $^{1}D_{2} - ^{3}F_{2}$ respectively. The inset is the temperature dependence of the transition $^{3}P_{0} - ^{3}H_{6}$.

Table 4.5 peak assignment for CL of ZnO:Pr, :Li single crystal annealed at 150°C

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Pr$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>629 nm</td>
<td>$^{3}P_{0} - ^{3}H_{6}$</td>
</tr>
<tr>
<td>653 nm</td>
<td>$^{3}P_{0} - ^{3}F_{6}$</td>
</tr>
<tr>
<td>728 nm</td>
<td>$^{3}P_{0} - ^{3}F_{4}$</td>
</tr>
<tr>
<td>878 nm</td>
<td>$^{1}D_{2} - ^{3}F_{2}$</td>
</tr>
</tbody>
</table>
CL of ZnO:Pr:Li, annealed 0.5 hr at 150°C
(same crystal)

Figure 4.7. Cathodoluminescence spectrum of ZnO:Pr, Li single crystal measured at 50K, 128K and 300K
4.2 ZnO:RE$^{3+}$ epi-layer

4.2.1. CL of ZnO:Sm epi-layer

ZnO:RE$^{3+}$ epi-layer samples have been annealed under different conditions to investigate the effect of annealing on the luminescence of rare earth ions. At first, we annealed the samples in the air for half an hour at higher temperature in the range of 400-1000°C, but we failed to see any emission from the rare earth ions. Then we lowered our annealing temperatures to 150°C, 230°C, 270°C, 300°C, while keeping the annealing period the same (half an hour). Figure 4.8. shows the annealing temperature effect onto the cathodoluminescence of ZnO:Sm epi-layer sample. The four samples are: unannealed, annealed at 150, 230, 270, 300°C respectively. We found that with the increasing of the annealing temperature from 150, 230, 270°C, the relative peak intensity from the transition of Sm$^{3+}$ is decreasing. When the annealing temperature reaches 300°C, the fine structure of the rare earth emission are totally lost.
Figure 4.8. cathodoluminescence spectrum of ZnO:Sm epi-layer samples: unannealed, annealed in the air for 0.5 hr. at 150°C, 230°C, 270°C, 300°C

Figure 4.9. is the cathodoluminescence of ZnO:Sm epi-layer sample which has been annealed in the air for half an hour at 150°C, measured at 9K. The four cathodoluminescence peaks located at 573 nm, 615 nm, 660 nm, 967 nm correspond to the transitions: \( ^4G_{5/2} \rightarrow ^6H_{5/2} \), \( ^4G_{5/2} \rightarrow ^6H_{7/2} \), \( ^4G_{5/2} \rightarrow ^6H_{9/2} \), \( ^4F_{11/2} \rightarrow ^6H_{5/2} \). The assignment of the transitions is shown in table 4.6.
Figure 4.9. Cathodoluminescence spectrum of ZnO:Sm epi-layer measured at 9K

Table 4.6 The peak assignment for the CL of ZnO:Sm epi-layer annealed at 150°C

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Sm$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>573 nm</td>
<td>$^4G_{5/2} - ^6H_{5/2}$</td>
</tr>
<tr>
<td>615 nm</td>
<td>$^4G_{5/2} - ^6H_{7/2}$</td>
</tr>
<tr>
<td>660 nm</td>
<td>$^4G_{5/2} - ^6H_{9/2}$</td>
</tr>
<tr>
<td>967 nm</td>
<td>$^4F_{11/2} - ^6H_{5/2}$</td>
</tr>
</tbody>
</table>
4.2.2. CL of ZnO:Er epi-layer

Figure 4.10. CL spectrum of ZnO:Er epi-layer samples: annealed in the air for 0.5 hr at 150°C, 230°C, 270°C, 300°C respectively

Figure 4.10 shows the annealing effects of cathodoluminescence spectrum of ZnO:Er epi-layer samples. Figure 4.11. shows the cathodoluminescence of ZnO:Er epi-layer sample which has been annealed in the air for half an hour at 150°C, measured at 9K. We see the emission of Er ions, and we assigned the transition as in the figure. The five cathodoluminescence peaks located at 556 nm, 665 nm, 758 nm, 908 nm, 984 nm correspond to the transitions of $^2S_{3/2} - ^4I_{15/2}$, $^4F_{9/2} - ^4I_{15/2}$, $^2P_{3/2} - ^4S_{3/2}$, $^4I_{9/2} - ^4I_{15/2}$, $^4I_{11/2} - ^4I_{15/2}$ respectively. The assignment of the peaks is shown in table 4.7.
Figure 4.11. Cathodoluminescence spectrum of the ZnO:Er epi-layer sample annealed in the air for 0.5 hr at 150°C measured at 9K.

Table 4.7 peak assignment for the CL of ZnO:Er epi-layer annealed at at 150 °C

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Er$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>556 nm</td>
<td>$^2S_{3/2}$-$^4I_{15/2}$</td>
</tr>
<tr>
<td>665 nm</td>
<td>$^4F_{9/2}$-$^4I_{15/2}$</td>
</tr>
<tr>
<td>758 nm</td>
<td>$^2P_{3/2}$-$^4S_{3/2}$</td>
</tr>
<tr>
<td>908 nm</td>
<td>$^4I_{9/2}$-$^4I_{15/2}$</td>
</tr>
<tr>
<td>984 nm</td>
<td>$^4I_{11/2}$-$^4I_{15/2}$</td>
</tr>
</tbody>
</table>
Chapter 5
Kinetics of ZnO:RE$^{3+}$ epi-layer

5.1. Introduction

The measurement of excited state lifetimes has become a pervasive and invaluable tool in the realms of experimental and theoretical spectroscopy, solution kinetics, solid state physics, energy transfer, laser and solar energy technology, analytical chemistry, and biology. Lifetimes are regularly used to make state assignments, to obtain quenching constants for slow and diffusion-limited bimolecular solution processes, and to evaluate solid state energy transfer parameters. They also find application in static and dynamic conformational information about macromolecules, membranes, and monolayers. The results of lifetime measurement are reported in journals of biology, physics, chemistry, spectroscopy, and analysis. In short, luminescence lifetime measurements have become an indispensable tool in the physical and biological sciences.

The most common methods of measuring excited state lifetimes involve monitoring the time dependence of the sample emission while exciting it with pulsed or modulated excitation. From the sample response relative to the excitation pulse, information about the rise and decay kinetics can be obtained. [39].
It is known that when electrons and holes are injected into the conduction and valence bands of a semiconductor, they will recombine with each other. In the case of the absence of any photon density in the cavity (i.e., $n_{ph} = 0$), the emission rate is the spontaneous emission rate, which is up to several nanoseconds, provided an electron, is present in the state $K$ and a hole is present in the same state $K$ in the valence band. In reality, however, the rate depends upon the occupation probabilities of the electron and hole with the same $K$-value. Therefore, we have to include the distribution functions for electrons and holes and integrate over all possible electronic states.

5.1.1 Radiative recombination

Radiative recombination occurring from band to band is just the inverse of intrinsic optical absorption. This is a very weak process for an indirect gap solid, since optical absorption is weak in these solids. However, radiative recombination can be very efficient process for a direct gap semiconductor, and the luminescence for some direct gap semiconductors can be fairly efficient. When $n$ and $p$ are made very large as a result of some externally produced influence, the spontaneous radiative recombination is significantly augmented by stimulated radiative recombination. Under suitable conditions, the stimulated recombination can become sufficiently dominant to produce lasering conditions.

Radiative recombination can be a two-step process, the first step being formation of an electron-hole exciton, with subsequent radiative annihilation of exciton. It was predicted by Keldysh (1968) and verified experimentally by Pokrovsky et al. that a
large exciton population accumulated in a semiconductor as a result of massive pair creation can under appropriate conditions condense into discrete spherical droplets of degenerate electron-hole plasma a few um in diameter. The radiative lifetime of such droplets is long enough in an indirect gap semiconductor (such as Ge or Si) at low temperatures so that the droplets can be observed by optical techniques such as Rayleigh scattering.

5.1.2 Auger recombination

A direct gap semiconductor (in which it is possible for radiative recombination to be a very efficient process) is also likely to have some recombination of the Auger or three-body type. This process is the inverse of impact ionization, a hole and an electron recombine and dominate the annihilation energy to a third particle, either an electron or a hole. Such an event must occur in a manner, which conserves both energy and momentum, and the probability for such processes is enhanced if the ratio \( \frac{m_e}{m_h} \) is considerably smaller than or larger than unity.

For a direct gap semiconductor, the excess carrier lifetime permitted by the combination of radiative and Auger recombination is likely to be quite small (in the range \( 10^{-10} \) to \( 10^{-7} \) sec depending on the equilibrium hole and electron densities). However, the mutual satisfaction of energy and momentum conservation required for Auger recombination is much more difficult to accomplish in an indirect gap solid, since the radiative process is the inverse of the rather inefficient indirect absorption
process. Thus the calculated excess carrier lifetime for an indirect gap semiconductor might range from $10^{-2}$ to $10^{-6}$ sec if we had to depend on band-to-band recombination process only.

### 5.1.3 Hall-Shockley-Read (HSR) recombination

Despite the above forecasts of a very large band-to-band lifetime for an indirect gap semiconductor, carrier lifetimes in the range of $10^{-7}$ to $10^{-3}$ seconds are far more typically measured in crystals of well-known indirect gap solids. The recombination in these materials is completely dominated by two-step processes involving accidental (and sometimes deliberate) localized flaw centers. Presumably, any crystal of a direct gap solid also has some contribution to the recombination from these flaw-aided processes, but they have less chance to be dominant because the direct processes are so efficient.

It was realized separately by Hall and by Shockley and Read that a flaw could act as a capture agent in promoting electron-hole recombination, and the so-called HSR model has proved to be valid under a variety of conditions. When a flaw captures first an electron and then a hole, it has returned to its original state of charge and can start the process all over again. The HSR model can become quite complicated even when recombination occurs via a single set of flaws at one energy within the gap. Consideration of flaws which can capture several holes (or electrons) one after another before having to start the capture of the opposite carrier species leads to much greater complexities in the analysis.
The flaw states, which facilitate electron-hole recombination, are usually not the ones that are major contributors to the carrier density at equilibrium. Flaw states are most efficient at recombination when they are nearer to the middle of the gap. Even though flaw states at a variety of energies may play some minor role in the recombination process, a single type of flaw often is much more important than all other types combined.

5.2 Curve fitting functions

To understand the mechanism of energy transfer in the cathodoluminescence of ZnO:RE$^{3+}$ epi-layer materials, we need to analyze our experimental results with the theoretical model. We fit the experimental data with the following four sets of functions first. It turns out that the first set of function which is the one exponential function for both the decay and rise could fit the experimental data very well which support the conclusion that there is one dominant process inside the energy transfer process.

1. One exponential for rise and one exponential for decay.

Rising function: \[ I = I_{R0} \left[ 1 - e^{-\frac{t}{\tau_{R0}}} \right] \] (5.1)

Decay function: \[ I = I_{D0} \cdot e^{-\frac{t}{\tau_{D0}}} \] (5.2)

2. Two exponential for rise and one exponential for decay.
Rising function: \[ I = I_{R0} \left[ 1 - e^{\frac{-t}{\tau_{R0}}} \right] + I_{R1} \left[ 1 - e^{\frac{-t}{\tau_{R1}}} \right] \] (5.3)

Decay function: \[ I = I_{D0} \cdot e^{\frac{-(t-T)}{\tau_{D0}}} \] (5.4)

3. One exponential for rise and two exponential for decay.

Rising function: \[ I = I_{R0} \cdot \left[ 1 - e^{\frac{-t}{\tau_{R0}}} \right] \] (5.5)

Decay function: \[ I = I_{D0} \cdot e^{\frac{-(t-T)}{\tau_{D0}}} + I_{D1} \cdot e^{\frac{-(t-T)}{\tau_{D1}}} \] (5.6)

4. Two exponential for rise and two exponential for decay.

Rising function: \[ I = I_{R0} \cdot \left[ 1 - e^{\frac{-t}{\tau_{R0}}} \right] + I_{R1} \cdot \left[ 1 - e^{\frac{-t}{\tau_{R1}}} \right] \] (5.7)

Decay function: \[ I = I_{D0} \cdot e^{\frac{-(t-T)}{\tau_{D0}}} + I_{D1} \cdot e^{\frac{-(t-T)}{\tau_{D1}}} \] (5.8)

5.3 Kinetics of three peaks of ZnO: Dy epi-layer

Kinetics of three peaks of ZnO:Dy epi-layer, which is annealed at 250°C for 20 min was monitored, they are 500 nm, 550 nm, and 590 nm respectively.

Table 5.1 is the summary of the transitions for the peaks that we monitored for ZnO:Dy epi-layer kinetics measurement.
Table 5.1 The transitions corresponding to the peaks of ZnO:Dy epi-layer

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Transition of Dy $^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>504 nm</td>
<td>$^{4}F_{9/2} - ^{6}H_{15/2}$</td>
</tr>
<tr>
<td>550 nm</td>
<td>$^{4}F_{9/2} - ^{6}H_{13/2}$</td>
</tr>
<tr>
<td>590 nm</td>
<td>$^{4}F_{9/2} - ^{6}H_{13/2}$</td>
</tr>
</tbody>
</table>

5.3.1 Kinetics of peak at 500 nm

Kinetics of cathodoluminescence peak at 500 nm (corresponding to the transition of $^{4}F_{9/2} - ^{6}H_{13/2}$ of ZnO:Dy epi-layer (annealed at 250°C for 20 min) was measured at 9K, and 300K respectively (Figure 5.1).

![Graph](image)

Figure 5.1 Rise and decay profiles of transition $^{4}F_{9/2} - ^{6}H_{15/2}$ cathodoluminescence spectrum of ZnO: Dy epi-layer measured at 9K, 300K
The experimental data was fitted with software called Table Curve. It was fitted with function set 1 and function set 4 respectively. Since the single exponential parameter fitting is good enough, the double exponential fitting result is not shown here. Figure 5.2 is the single exponential fitting (the fitting function is function set 1) of the experimental data measured at 9K. The parameters that resulted from the fitting is summarized in table 5.2.

Figure 5.2 Rise and decay profiles of ZnO: Dy epi-layer transition \(^{4}F_{9/2} \rightarrow ^{6}H_{15/2}\) in cathodoluminescence measured at 9K with TableCurve fitting analysis results.

Table 5.2 The parameters in fitting ZnO:Dy epi-layer transition \(^{4}F_{9/2} \rightarrow ^{6}H_{15/2}\) at 9K

<table>
<thead>
<tr>
<th>(I_{R0})</th>
<th>(I_{D0})</th>
<th>(\tau_{R0}) (ms)</th>
<th>(\tau_{D0}) (ms)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.998</td>
<td>0.169</td>
<td>0.372</td>
<td>0.406</td>
<td>0.993</td>
</tr>
</tbody>
</table>
Figure 5.3 Rise and decay profiles of transition $^{4}F_{9/2} \rightarrow ^{6}H_{15/2}$ at 300K together with

TableCurve fitting results of ZnO: Dy epi-layer

Figure 5.3 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^{4}F_{9/2} \rightarrow ^{6}H_{15/2}$ measured at 300K. The parameters that resulted from the fitting is summarized in table 5.3.

Table 5.3 The parameters in fitting ZnO: Dy epi-layer transition $^{4}F_{9/2} \rightarrow ^{6}H_{15/2}$ at 300K

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}\text{(ms)}$</th>
<th>$\tau_{D0}\text{(ms)}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.030</td>
<td>0.764</td>
<td>0.660</td>
<td>0.519</td>
<td>0.995</td>
</tr>
</tbody>
</table>
Comparing with the two fitted parameters derived from the figure 5.2 and figure 5.3, it is found that with the increasing of temperature both the time constant for the decay and that for the rise are increasing, the rise time $\tau_{R0}$ changes from 0.372 ms to 0.660 ms, while the decay time changing from 0.407 ms to 0.519 ms.

### 5.3.2 kinetics of peak at 550 nm

Kinetics of cathodoluminescence monitored at 550 nm of ZnO:Dy epi-layer (annealed at 250°C for 20 min) was measured at 9K and 300K respectively. This peak position is corresponding to the ZnO host materials. Figure 5.4 shows kinetics for the four measurement temperature.

![Graph showing rise and decay profiles](image)

Figure 5.4 Rise and decay profiles of transition $^{4}F_{9/2}$-$^{6}H_{13/2}$ in cathodoluminescence of ZnO:Dy epi-layer
CL kinetics of ZnO:Dy epi-layer peak 550nm at 9K

\[ F_1 = A(1 - \exp(-X/B)), \quad F_2 = C\exp(-(X-T)/D) \quad Y = \text{IF}(X>T, F_2, F_1) \]

\[ r^2 = 0.99622038 \]

\[ a = 0.9799934 \quad b = 0.3453879 \]

\[ c = 0.34100335 \quad d = 0.13582844 \]

Figure 5.5 Rise and decay profiles of ZnO: Dy epi-layer transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ at 9K

with parameters from the one exponential function fitting analysis

Figure 5.5 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ measured at 9K. The parameters that resulted from the fitting is summarized in table 5.4.

Table 5.4 The parameters in fitting ZnO:Dy epi-layer of transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ at 9K

<table>
<thead>
<tr>
<th>I₀ (a.u.)</th>
<th>I₀ (a.u.)</th>
<th>τ₀ (ms)</th>
<th>τ₀ (ms)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.980</td>
<td>0.341</td>
<td>0.345</td>
<td>0.136</td>
<td>0.996</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Dy epi-layer peak 550nm at 300K

F1=#A*(1-EXP(-X/#B)), F2=#C*EXP(-(X-T)/#D) Y=IF(X>T,F2,F1)

r^2=0.98233273

a=0.70152693 b=0.64981315
c=0.28373201 d=0.82522693

Figure 5.6 Rise and decay profiles of ZnO: Dy epi-layer transition ^4F_{9/2} -> ^5H_{13/2} at 300K with table curve fitting using the one exponential function

Figure 5.6 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition ^4F_{9/2} -> ^5H_{13/2} measured at 300K. The parameters that resulted from the fitting are summarized in table 5.5.

Table 5.5 The parameters in fitting ZnO:Dy epi-layer of transition ^4F_{9/2} -> ^5H_{13/2} at 300K

<table>
<thead>
<tr>
<th>I_{R0}</th>
<th>I_{D0}</th>
<th>\tau_{R0}(ms)</th>
<th>\tau_{D0}(ms)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.702</td>
<td>0.284</td>
<td>0.650</td>
<td>0.825</td>
<td>0.982</td>
</tr>
</tbody>
</table>
Comparing with the two fitted parameters derived from figure 5.5 and figure 5.6, it is found that with the increasing of temperature both the time constant for the decay and that for the rise are increasing, the rise time $\tau_{R0}$ changes from 0.345 ms to 0.650 ms, while the decay time changing from 0.136 ms to 0.825 ms.

**5.3.3 Kinetics of peak at 590 nm**

Kinetics of cathodoluminescence peak at 590nm (corresponding to $^{4}F_{9/2}$-$^{6}H_{13/2}$ transition) of ZnO:Dy epi-layer (annealed at 250°C for 20 min) was measured at 9K, 100K, 200K and 300K respectively. Figure 5.7 shows kinetics at the four different measurement temperature.

Figure 5.7 Rise and decay profiles of ZnO:Dy epi-layer Cathodoluminescence transition $^{4}F_{9/2}$-$^{6}H_{13/2}$ measured at 9K, 100K, 200K, 300K respectively.
Figure 5.8 Rise and decay profiles of ZnO: Dy epi-layer transition $^4F_{9/2}$-$^6H_{13/2}$ at 9K with parameters from the one exponential function fitting analysis.

Figure 5.8 is the rise and decay profiles of the luminescence intensity as a function of time, comparing with the one exponential function fitting results from the table curve analysis.

Table 5.6 Parameters in fitting ZnO:Dy epi-layer peak at 590 nm at 9K

<table>
<thead>
<tr>
<th>$I_R^0$</th>
<th>$I_D^0$</th>
<th>$\tau_R^0$ (ms)</th>
<th>$\tau_D^0$ (ms)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.985</td>
<td>0.340</td>
<td>0.402</td>
<td>0.265</td>
<td>0.996</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Dy epi-layer peak 590nm at 100K
F1=\#A*(1-\text{EXP}(-X/\#B)), \quad F2=\#C*\text{EXP}(-(X-T)/\#D) \quad Y=\text{IF}(X>T,F2,F1)
\[ r^2=0.99658061 \]
\[ a=0.99659356 \quad b=0.37902332 \]
\[ c=0.35745064 \quad d=0.22994113 \]

Figure 5.9 Rise and decay profiles of ZnO: Dy epi-layer transition ^4F_{9/2} \rightarrow \ ^6H_{13/2} \quad \text{at} \quad 100K

with parameters from the one exponential function fitting analysis

Figure 5.9 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition ^4F_{9/2} \rightarrow \ ^6H_{13/2} \quad \text{measured at} \quad 100K. \quad \text{The parameters that resulted from the fitting is summarized in table 5.7.}

Table 5.7 The parameters in fitting ZnO:Dy epi-layer transition ^4F_{9/2} \rightarrow \ ^6H_{13/2} \quad \text{at} \quad 100K

<table>
<thead>
<tr>
<th>( I_{R0} )</th>
<th>( I_{D0} )</th>
<th>( \tau_{R0}(\text{ms}) )</th>
<th>( \tau_{D0}(\text{ms}) )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.997</td>
<td>0.357</td>
<td>0.379</td>
<td>0.230</td>
<td>0.997</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Dy epi-layer peak 590nm at 200K

\[ F_1 = A \cdot (1 - \exp(-X/B)), \quad F_2 = C \cdot \exp(-(X-T)/D) \]
\[ Y = \text{IF}(X>T,F_2,F_1) \]
\[ r^2 = 0.99636612 \]
\[ a = 0.98079507 \quad b = 0.65088881 \]
\[ c = 0.58511811 \quad d = 0.57398922 \]

Figure 5.10 Rise and decay profiles of ZnO: Dy epi-layer transition $^{4}F_{9/2} \rightarrow ^{6}H_{13/2}$ at 200K with parameters from the one exponential function fitting analysis.

Figure 5.10 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^{4}F_{9/2} \rightarrow ^{6}H_{13/2}$ measured at 200K. The parameters that resulted from the fitting is summarized in table 5.8.

Table 5.8 The parameters in fitting ZnO:Dy epi-layer transition $^{4}F_{9/2} \rightarrow ^{6}H_{13/2}$ at 200K

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}$ (ms)</th>
<th>$\tau_{D0}$ (ms)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.981</td>
<td>0.585</td>
<td>0.651</td>
<td>0.574</td>
<td>0.996</td>
</tr>
</tbody>
</table>
Figure 5.11 Rise and decay profiles of ZnO: Dy epi-layer transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ at 300K with parameters from the one exponential function fitting analysis.

Figure 5.11 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ measured at 300K. The parameters that resulted from the fitting is summarized in table 5.9.

Table 5.9 The parameters in fitting ZnO:Dy epi-layer transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ at 300K

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}$ (ms)</th>
<th>$\tau_{D0}$ (ms)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.011</td>
<td>0.756</td>
<td>0.873</td>
<td>0.654</td>
<td>0.997</td>
</tr>
</tbody>
</table>
Figure 5.12 Temperature dependence of the time constant for the rise of transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ in cathodoluminescence spectrum of ZnO:Dy epi-layer sample

Figure 5.13 Temperature dependence of the time constant for the decay of transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ in cathodoluminescence spectrum of ZnO:Dy epi-layer sample
5.4 Kinetics of ZnO:Er thin film

Kinetics of three peaks of ZnO:Er thin film (annealed at 250°C for 20 min) was monitored, they are 560 nm which correspond to the transition $^2S_{3/2} \rightarrow ^4I_{15/2}$.

![Graph showing rise and decay profiles of transition $^2S_{3/2} \rightarrow ^4I_{15/2}$ in cathodoluminescence spectrum of ZnO: Er epi-layer measured at 9K, 100K, 200K, 300K]

Figure 5.14 Rise and decay profiles of transition $^2S_{3/2} \rightarrow ^4I_{15/2}$ in cathodoluminescence spectrum of ZnO: Er epi-layer measured at 9K, 100K, 200K, 300K.
Figure 5.15 Rise and decay profiles of ZnO: Er epi-layer transition $^2_{3/2}S_{3/2} - ^4_{15/2}I_{15/2}$ at 9K with parameters from the one exponential function fitting analysis.

Figure 5.15 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^2_{3/2}S_{3/2} - ^4_{15/2}I_{15/2}$ measured at 9K. The parameters that resulted from the fitting is summarized in table 5.10.

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}(\text{ms})$</th>
<th>$\tau_{D0}(\text{ms})$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.022</td>
<td>0.833</td>
<td>0.352</td>
<td>0.054</td>
<td>0.991</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Er epi-layer peak 560nm at 100K

\[ F_1 = A \cdot (1 - \exp(-X/B)), \quad F_2 = C \cdot \exp(-(X-T)/D) \]

\[ r^2 = 0.99507013 \]

\[ a = 1.0114846, \quad b = 0.33108236 \]

\[ c = 1.0439862, \quad d = 0.041360331 \]

Figure 5.16 Rise and decay profiles of transition \( \frac{1}{2}S_{3/2} \rightarrow \frac{1}{2}I_{15/2} \) at 100K with parameters from the one exponential function fitting analysis of ZnO: Er epi-layer sample.

Figure 5.16 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition \( \frac{1}{2}S_{3/2} \rightarrow \frac{1}{2}I_{15/2} \) measured at 100K. The parameters that resulted from the fitting is summarized in table 5.11.

<table>
<thead>
<tr>
<th>( I_{R0} )</th>
<th>( I_{D0} )</th>
<th>( \tau_{R0}(\text{ms}) )</th>
<th>( \tau_{D0}(\text{ms}) )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.011</td>
<td>1.044</td>
<td>0.331</td>
<td>0.041</td>
<td>0.995</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Er thin film monitored at peak 560nm

\[ F_1 = \#A \times (1 - \text{EXP}(-X/\#B)) \]
\[ F_2 = \#C \times \text{EXP}(-(X-T)/\#D) \]
\[ Y = \text{IF}(X>T,F_2,F_1) \]

\[ r^2 = 0.99372755 \]
\[ a = 1.0079247 \]
\[ b = 0.34418722 \]
\[ c = 0.74965915 \]
\[ d = 0.057967032 \]

Figure 5.17 Rise and decay profiles of transition \( ^2S_{3/2} \rightarrow ^4I_{15/2} \) at 200K with parameters from the one exponential function fitting analysis of ZnO: Er epi-layer sample.

Figure 5.17 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition \( ^2S_{3/2} \rightarrow ^4I_{15/2} \) measured at 200K. The parameters that resulted from the fitting is summarized in table 5.12.

Table 5.12 Parameters in fitting of transition \( ^2S_{3/2} \rightarrow ^4I_{15/2} \) at 200K ZnO:Er epi-layer

<table>
<thead>
<tr>
<th>( I_{R0} )</th>
<th>( I_{D0} )</th>
<th>( \tau_{R0}(\text{ms}) )</th>
<th>( \tau_{D0}(\text{ms}) )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.008</td>
<td>0.750</td>
<td>0.344</td>
<td>0.058</td>
<td>0.994</td>
</tr>
</tbody>
</table>
Figure 5.18 Rise and decay profiles of ZnO: Er epi-layer transition $^2S_{3/2} - ^4I_{15/2}$ at 300K with parameters from the one exponential function fitting analysis.

Figure 5.18 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^2S_{3/2} - ^4I_{15/2}$ measured at 300K. The parameters that resulted from the fitting is summarized in table 5.13.

Table 5.13 The parameters in fitting ZnO:Er epi-layer of transition $^2S_{3/2} - ^4I_{15/2}$ at 300K

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}$ (ms)</th>
<th>$\tau_{D0}$ (ms)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.016</td>
<td>0.866</td>
<td>0.315</td>
<td>0.050</td>
<td>0.982</td>
</tr>
</tbody>
</table>
5.5 Kinetics of ZnO: Sm epi-layer

Kinetics measurement of three peaks of ZnO: Sm epi-layer (annealed at 150°C for 30 min) was monitored, they are 534 nm, which correspond to the transition $^4G_{7/2} \rightarrow ^6H_{7/2}$.

Figure 5.19 Rise and decay profiles of transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ in cathodoluminescence of ZnO:Sm epi-layer measured at 9K, 50K, 100K, 150K, 200K, 250K, 300K.
Figure 5.20 Rise and decay profiles of ZnO:Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 9K with parameters from the one exponential function fitting analysis.

Figure 5.20 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ measured at 9K. The parameters that resulted from the fitting is summarized in table 5.14.

Table 5.14 The parameters in fitting ZnO:Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 9K

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}(\text{ms})$</th>
<th>$\tau_{D0}(\text{ms})$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.043</td>
<td>0.510</td>
<td>0.831</td>
<td>1.037</td>
<td>0.996</td>
</tr>
</tbody>
</table>
Figure 5.21 Rise and decay profiles of transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ measured at 50K with parameters from the one exponential function fitting analysis of ZnO: Sm epi-layer.

Figure 5.21 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ measured at 50K. The parameters that resulted from the fitting is summarized in table 5.14.

Table 5.15 parameters in fitting ZnO:Sm epi-layer transition $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 50K

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}(ms)$</th>
<th>$\tau_{D0}(ms)$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.010</td>
<td>0.524</td>
<td>0.821</td>
<td>1.007</td>
<td>0.996</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Sm thin film monitored at peak 530nm

\[ F1 = A'(1-\exp(-X/B)), \quad F2 = C\exp(-(X-T)/D) \]

\[ r^2 = 0.99662743 \]

\[ a = 0.94732903, \quad b = 0.96235267, \quad c = 0.63186251, \quad d = 1.0307151 \]

Figure 5.22 Rise and decay profiles transition \( ^4G_{7/2} \rightarrow ^5H_{7/2} \) at 100K with parameters from the one exponential function fitting analysis of ZnO: Sm epi-layer.

Figure 5.22 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition \( ^4G_{7/2} \rightarrow ^5H_{7/2} \) measured at 100K. The parameters that resulted from the fitting is summarized in table 5.16.

Table 5.16 parameters in fitting ZnO:Sm epi-layer \( ^4G_{7/2} \rightarrow ^5H_{7/2} \) at 100K

<table>
<thead>
<tr>
<th>( I_{R0} )</th>
<th>( I_{D0} )</th>
<th>( \tau_{R0} ) (ms)</th>
<th>( \tau_{D0} ) (ms)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.947</td>
<td>0.632</td>
<td>0.962</td>
<td>1.031</td>
<td>0.997</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Sm thin film monitored at peak 530nm
\[ F_1 = A(1 - \exp(-X/B)), \quad F_2 = C \exp(-C(X-T)/D) \]
\[ r^2 = 0.99633828 \]
\[ a = 0.99297726, \quad b = 1.176474, \quad c = 0.75633472, \quad d = 1.1202123 \]

Figure 5.23 Rise and decay profiles of ZnO: Sm epi-layer transition \(^4G_{7/2} \rightarrow ^6H_{7/2}\) at 150K

with parameters from the one exponential function fitting analysis

Figure 5.23 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition \(^4G_{7/2} \rightarrow ^6H_{7/2}\) measured at 150K. The parameters that resulted from the fitting is summarized in table 5.17.

Table 5.17 parameters in fitting ZnO:Sm epi-layer \(^4G_{7/2} \rightarrow ^6H_{7/2}\) at 150K

<table>
<thead>
<tr>
<th>(I_{R0})</th>
<th>(I_{D0})</th>
<th>(\tau_{R0})(ms)</th>
<th>(\tau_{D0})(ms)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.993</td>
<td>0.756</td>
<td>1.176</td>
<td>1.120</td>
<td>0.996</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Sm thin film monitored at peak 530nm

\[ F1=A(1-\exp(-X/B)), \quad F2=C\exp(-(X-T)/D) \]

\[ r^2=0.99639396 \]

\[ a=1.0961546, \quad b=1.2816378, \quad c=0.87842936, \quad d=1.1938563 \]

Figure 5.24 Rise and decay profiles of ZnO: Sm epi-layer transition $^4G_{7/2} \rightarrow {}^6H_{5/2}$ at 200K with parameters from the one exponential function fitting analysis

Figure 5.24 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^4G_{7/2} \rightarrow {}^6H_{5/2}$ measured at 200K. The parameters that resulted from the fitting is summarized in table 5.18.

Table 5.18 parameters in fitting ZnO:Sm epi-layer $^4G_{7/2} \rightarrow {}^6H_{5/2}$ at 200K

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}$ (ms)</th>
<th>$\tau_{D0}$ (ms)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.096</td>
<td>0.878</td>
<td>1.282</td>
<td>1.194</td>
<td>0.996</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Sm thin film monitored at peak 530nm

\[ F_1 = A(1 - \exp(-X/B)), \quad F_2 = C\exp(-(X-T)/D) \]

\[ r^2 = 0.99717874 \]
\[ a = 1.0792118 \quad b = 1.4670198 \]
\[ c = 0.86909839 \quad d = 1.2313104 \]

Figure 5.25 Rise and decay profiles of ZnO: Sm epi-layer transition \(^4\Gamma_{3/2} \rightarrow ^6\Delta H_{3/2}\) at 250K with parameters from the one exponential function fitting analysis.

Figure 5.25 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition \(^4\Gamma_{3/2} \rightarrow ^6\Delta H_{3/2}\) measured at 250K. The parameters that resulted from the fitting is summarized in table 5.19.

<table>
<thead>
<tr>
<th>(I_{R0})</th>
<th>(I_{D0})</th>
<th>(\tau_{R0}(\text{ms}))</th>
<th>(\tau_{D0}(\text{ms}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.079</td>
<td>0.869</td>
<td>1.467</td>
<td>1.231</td>
<td>0.997</td>
</tr>
</tbody>
</table>
CL kinetics of ZnO:Sm thin film monitored at peak 530nm
F1=A*(1-EXP(-X/#B)), F2=CEXP(-(X-T)/#D)

$\chi^2=0.99677567$
a=1.084921 b=1.4588598
c=0.8987574 d=1.2648488

Figure 5.26 Rise and decay profiles of ZnO: Sm epi-layer transition $^4G_{7/2} - ^6H_{7/2}$ at 300K with parameters from the one exponential function fitting analysis

Figure 5.26 also shows the single exponential fitting (the fitting function is function set 1) of the experimental data of the transition $^4G_{7/2} - ^6H_{7/2}$ measured at 300K. The parameters that resulted from the fitting is summarized in table 5.20.

<table>
<thead>
<tr>
<th>$I_{R0}$</th>
<th>$I_{D0}$</th>
<th>$\tau_{R0}$ (ms)</th>
<th>$\tau_{D0}$ (ms)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.084</td>
<td>0.898</td>
<td>1.458</td>
<td>1.268</td>
<td>0.996</td>
</tr>
</tbody>
</table>
From the above analysis, we found that with the increasing of the temperature, the time constant for both the rise and decay is increasing. Figure 5.27 is the temperature dependency of the time constant of rise and Figure 5.28 shows the temperature dependence of time constant of decay of ZnO:Sm epi-layer sample.

Figure 5.27 Temperature dependence of the time constant for the rise of transition $^4G_{5/2} \rightarrow ^6H_{7/2}$ in cathodoluminescence spectrum of ZnO:Sm epi-layer sample
Temperature dependence of decay time for ZnO:Sm epilayer

Figure 5.28 Temperature dependence of the time constant for the rise of transition $^4G_{7/2} - ^6H_{7/2}$ in cathodoluminescence spectrum of ZnO:Sm epi-layer sample

5.6 Summery

In ZnO:RE$^{3+}$ epi-layer samples, the recombination process could be divided into several sub-processes. From out fitting result of the experimental data, we found that in the temperature range from 9K to 300K, both the rise and decay period can be fitted with the one exponential expression. This means there is a dominated recombination process in the ZnO: RE$^{3+}$ epi-layer systems. In case of ZnO: Dy and ZnO: Sm epi-layer with the increasing of the measurement temperature the time constant for rise and decay are all decreasing. This phenomenon deserves more deeply investigation.
Chapter 6
Conclusions

The electronic structure of the rare earth luminescence centers and their electrical activities as well as their indirect photoluminescence and cathodoluminescence excitation mechanisms, are still not well understood[40]. The research undertaken is up to date with the currently ongoing effort by scientists all over the world to better understand the microscopic processes involved in the ZnO doped with rare earth ions. This thesis attempts to further the knowledge of intricate processes with ZnO when doped with rare earth elements.

Cathodoluminescence temperature dependence, annealing effects on the photoluminescence and cathodoluminescence, kinetics of the cathodoluminescence for the ZnO doped with rare earth ions single crystals and epi-layers has been taken.

The optimized annealing conditions for both the ZnO:RE$^{3+}$ single crystals and epi-layers are found for the first time. Since many groups have tried the high annealing temperature, under which condition the luminescence of ZnO:RE$^{3+}$ is characterised by the broad band luminescence from ZnO, no characteristic lines from the rare earth ions is observed.

Our extensive study on the kinetics of the ZnO: RE$^{3+}$ epi-layer samples give us better understanding of the energy transfer process inside the materials. The temperature dependence of the time constant for decay and rise is found for the first time.
6.1 Excitation mechanism

Several physical processes occur when ZnO:RE$^{3+}$ materials is excited by an electron beam. Primary electrons penetrate the ZnO host and produce electron-hole pairs (e-h pairs) which then diffuse through the ZnO host and either transfer their energy to rare earth ions that subsequently emit light, or recombine at killer centers nonradiatively[41].

We would discuss two of these processes here. One is the collision between the host electrons and the host will create the electron hole pairs and the recombination energy of these pairs will be transferred from the hosts to the luminescence center via the different energy transfer processes. The other process is: the hot electrons can directly collide the rare earth impurities to excite the ions. Consequently, one more channel is available to excite the rare earth ions in cathodoluminescence due to the collision between the core electrons of the structured impurities and hot electrons. Since the ions can populate on all the possible excited states due to the hot electrons can provide most of the necessary energy. So the depth of the impurities doped inside the host will affect the quantum efficiency of the sample for the cathodoluminescence. The penetration depth of electrons in solids is dependent on the beam energy. The higher the beam energy the deeper the electrons penetrate, which means the shallower impurities layer will have better quantum efficiency in cathodoluminescence. Figure 6.1 shows the processes occurring when ZnO:RE$^{3+}$ sample is excited by electron beam.
Figure 6.1 The processes occurred when ZnO:RE$^{3+}$ is excited by an electron beam. Electron beam (a) will directly produce electron hole pair, electron beam (b) will bombard the rare earth luminescent center.

6.2 Energy transfer mechanism

The kinetics model is fairly complicated due to the energy transfer between the localized states in the forbidden gap and the localized core states of the rare earth impurities. The trivalent rare earth ions inside the ZnO crystal field can be in several different conditions.

Four mechanisms for the energy transfer in ZnO doped rare earth materials could be possible [40]. The first mechanism is: the excitation electrons excite the electron and hole pair, the generated electron could be trapped by some impurity state which is related to the rare earth ions and inside the forbidden gap (Figure 6.2). Or the hole in
the valence band is trapped by the impurity state that is related to the rare earth ions (Figure 6.3). Then by Auger energy transfer process, the recombination energy of the bound electron and the free hole (or the recombination energy of the free electron and the bound hole) is transferred to the rare earth luminescence center. The third mechanism is the transfer energy of the bound exciton to the localized core electrons (Figure 6.4). Here both the electron and the hole are trapped by the impurity states inside the forbidden gap. While it is also possible for the recombination energy of the free exciton to the localized rare earth ions 4f states (Figure 6.5), where the electron is in the conduction band and the hole is in the valence band.

Figure 6.2 Schematic diagram of trapping electron on rare earth related state, the recombination energy of trapped electrons and the free hole excites the rare earth ions.
Figure 6.3 Schematic diagram of trapping hole on rare earth related state, the recombination energy of free electron and the trapped hole excites the rare earth ions.

Figure 6.4 Schematic diagram of trapping electron and holes on rare earth related state, the recombination energy of trapped electron and hole excites the rare earth ions.
Figure 6.5 Schematic diagram of excitation of electron hole pair, the recombination energy of free electron and hole excites the rare earth ions.

6.3 Cathode-ray efficiency

The excitation of luminescence by energetic electrons can be described by the following sequence of steps[42]:

1. The primary electrons loose energy predominantly by exciting electrons from inner shells of ions, thereby leaving a trail of fast secondaries and excited ions.
2. The excited ions decay, principally by Auger transitions, producing additional secondary electrons and excited ions. A small fraction (about 1%) of the excitation is lost through x-ray emission.
3. The process 1 and 2 continue, each successive step reducing the average energy of the secondaries and excited ions.
4. The excitations initially formed may consist of a mixture of free electrons and holes, plasmons, and excitons. It is as though the electron hole pairs were excited directly by the energetic primary and secondary electrons.

5. The total excitation energy of a typical electron-hole pair is 20-30 eV. This energy consists of the band gap energy plus the energy of the energetic electron relative to the conduction band minimum and that of the energetic hole relative to the valence band maximum. An energetic electron (or hole) can excite an additional electron-hole pair if its energy exceeds a threshold energy. It can also excite phonons. Theoretical calculation[43] show that a very energetic charge carrier loses much more energy to pair creation than it does to phonon excitation. However, as its energy decreases, the cross-section for pair creation decreases, while the phonon cross-section remains essentially constant. Obviously, a carrier with a kinetic energy less than the threshold energy can excite phonons but not pairs. It may also excite defects or impurities, including activators. Carries having insufficient energy to excite additional electron hole pairs eventually thermalize by phonon emission.

6.4 Summary

The rare earth ions replacing the Zn$^{2+}$ or O$^{2-}$ require association with other near distant charge compensating lattice defects or impurities. The conclusion is supported by the fact that the atomic covalent radii for all rare earths are bigger than atomic radii of Zn and O that they are replacing. Since rare earth ions in ZnO can occupy different sites
(not only substitution) and they are very active chemically, they can create a more complex center involving other impurities or native defects.

In this work we have developed a kinetics model of energy transfer from the host lattice to the localized core excited states of rare earth ions. The outer electron configurations of RE$^{3+}$ ions are the same $5s^25p^6$. The rare earth ions possess the unfilled $4f^n$ core shell. The structured luminescence arises from intra-configuration $f-f$ transitions in the core.

Clearly we need more theoretical and experimental investigations devoted to rare earth impurities to gain knowledge about the electrical activities of RE ions in semiconductors. Therefore, more experimental and theoretical work are necessary for better understanding the rare earth mechanisms in high quality ZnO single crystal and epi-layer. For the future work, kinetics measurement can be taken at smaller temperature steps and the relationship between the rise decay time constant and the temperature could be further analyzed together with the underlying mechanisms.
REFERENCE


