Investigation of excitonic recombination and its influence on random lasing phenomenon in ZnO semiconductors

Abiyasa, Agus Putu

2008

Abiyasa, A. P. (2008). Investigation of excitonic recombination and its influence on random lasing phenomenon in ZnO semiconductors. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/13288>

<https://doi.org/10.32657/10356/13288>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**INVESTIGATION OF EXCITONIC
RECOMBINATION AND ITS INFLUENCE ON
RANDOM LASING PHENOMENON IN ZNO
SEMICONDUCTORS**

AGUS PUTU ABIYASA

**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

2008

Investigation of Excitonic Recombination and Its Influence on Random Lasing Phenomenon in ZnO Semiconductors

AGUS PUTU ABIYASA

School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2008

To my father and mother

Acknowledgements

The author would like to express his gratitude to his supervisor, Assoc. Prof. Yu Siu Fung for his constant support and guidance during the research period. Also, the author thanks him for his insight about the research topics.

The author would also like to acknowledge the help of Assoc. Prof. Fan Wei Jun for providing the original FORTRAN code and also his help for the electronics band and quantum well discussion. His insight has helped the author to appreciate the important of k,p theory to understand semiconductor material.

Acknowledgement is also given to Assoc. Prof. Lau Shu Ping for giving me the opportunity to use the fabrication equipment. This has given the author a first hand experience of doing experimental research.

Thanks to Dr Li Hongdong for his valuable advice about ZnO material properties and the fabrication of ZnO random lasers. Furthermore, I would like to give my appreciations to Dr Clement Yuen for his guidance about fabrication and characterization of ZnO, Dr Eunice Leong for her guidance with the ion beam source, photolithography, photoluminescence and discussion on random laser, Dr Ji Xiaohong for her help with FCVA system, Dr Yang Hui Ying for her help on TEM characterization, Mr Tan Swee Tiam for his insight and discussion on ZnO, Mr Yoga Divayana for his valuable insight on surface plasmon phenomenon and many other staffs and students in Nanoelectronics laboratory for their creation of such a good research environment.

Acknowledgements

The author would also thank for the help of the Nanoelectronics laboratory technicians, Ms. Neo, Mr. Hasman and Ms. Janet for their technical and administration help during the research.

The author also thanks Nanyang Technological University for granting the NTU Scholarship and the opportunity of doing research.

Last but not least, the author would like to thank his father, mother, sister and brother for their never ending encouragement.

Table of Contents

Table of Contents

Acknowledgements	i
Table of Contents	iii
Thesis Summary	vi
List of Figures.....	viii
List of Tables	xiv
 Chapter 1	 1
Introduction.....	1
1.1 Background and Motivation	1
<i>1.1.1 ZnO as UV light source.....</i>	<i>4</i>
<i>1.1.2 ZnO random laser</i>	<i>6</i>
1.2 Objectives.....	7
1.3 Major contributions of the Thesis	8
1.4 Organization of the Thesis	11
 Chapter 2.....	 12
Literature Review	12
2.1 Introduction.....	12
2.2 Excitonic process in semiconductors	13
<i>2.2.1 Free-exciton</i>	<i>14</i>
<i>2.2.2 Exciton-exciton scattering</i>	<i>16</i>
<i>2.2.3 Electron Hole Plasma</i>	<i>17</i>
2.3 Excitonic optical properties of ZnO	19
2.4 Stimulated emission in ZnO	21
2.5 Random lasing in ZnO polycrystalline films	26
2.6 Concluding Remarks	29

Table of Contents

Chapter 3	31
Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells	31
3.1 Introduction	31
3.2 Electronics Band structures of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells	33
3.2.1 Theory	33
3.2.2 Result and Discussion	39
3.3 Excitonic Optical Gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells	46
3.3.1 Theory	46
3.3.2 Result and Discussion	52
3.4 Summary	58
 Chapter 4	 59
Excitonic Recombination and Random Lasing in Highly Disordered ZnO Polycrystalline Films	59
4.1 Introduction	59
4.2 Strain Dependence Random Lasing Mechanisms in Highly Disordered ZnO Polycrystalline Films	62
4.2.1 Experimental Procedure	62
4.2.2 Result and Discussion	63
4.3 High Temperature Random Lasing in Highly Disordered ZnO Polycrystalline Films	70
4.3.1 Experimental Procedure	70
4.3.2 Result and Discussion	71
4.4 Closed Loop Formation of Random Lasing in Highly Disordered ZnO Polycrystalline Films	80
4.4.1 Experimental Procedure	80
4.4.2 Result and Discussion	80
4.5 Summary	88

Table of Contents

Chapter 5	90
Design of Random Lasers	90
5.1 Introduction	90
5.2 Influence of Surface Roughness on Lasing Performance in Highly	
Disordered ZnO Polycrystalline Films	92
5.2.1 <i>Experimental Procedure</i>	92
5.2.2 <i>Result and Discussion</i>	93
5.3 Enhancement of Ultraviolet Lasing from Ag-coated Highly Disordered ZnO	
Polycrystalline Films by Surface Plasmons Resonance	98
5.3.1 <i>Experimental Procedure</i>	98
5.3.2 <i>Result and Discussion</i>	100
5.4 Summary	106
 Chapter 6	108
Conclusion and Recommendations	108
6.1 Conclusion	108
6.2 Recommendation for further research	111
 Author's Publications	114
 Appendix A	116
 References	129

Thesis Summary

In this thesis, the electronics band structures of wurtzite ZnO bulk materials is studied theoretically based on Empirical Pseudopotential Method (EPM) and 6-band $k\cdot p$ Hamiltonian. Furthermore, confined exciton state in Quantum Wells (QWs) is studied theoretically. By using the $k\cdot p$ Hamiltonian and variational calculation with biaxial strain and exciton-phonon interactions taken into consideration, excitonic optical gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is deduced. From the available experimental data, the band offset and conduction band deformation constant of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs are calculated to be 60/40 and -6.8 eV, respectively.

On the other hand, the recombination process due to free exciton state that contributed to random lasing action in highly disordered ZnO polycrystalline films is investigated experimentally. The intrinsic ZnO recombination processes that contribute to random lasing are found to be free-exciton, exciton-exciton scattering or electron hole plasma (EHP) depending on the conditions of ZnO films. The influence of mechanical strain, temperature, and pumping profile on the random lasing mechanisms inside highly disordered ZnO polycrystalline films are then investigated. It is found that 1) the stimulated emission inside ZnO films can be related to free-exciton or EHP depending on the variation of Mott's density which can be controlled by the mechanical strain, 2) the sustainability of high temperature random lasing action inside ZnO films is due to the strong confinement of excitons inside the ZnO grains and 3) the formation of closed-loop random lasing inside the ZnO films is dependent on optical gain profile which is determined by the operating temperature and pump beam profile.

Thesis Summary

The possibilities to improve the lasing performance (i.e., reduces threshold pump and increases slope efficiency) of highly disordered ZnO polycrystalline films are also investigated. It is found that edge emission from the highly disordered ZnO polycrystalline films can be improved by reducing the surface roughness. This can be done by using ion-beam milling and followed by the deposition of MgO layer. On the other hand, surface emission from the rough surface of the highly disordered ZnO polycrystalline films can be improved by employing the phenomenon of surface plasmons resonance (SPR). This can be done by depositing an Ag layer on the rough surface of the ZnO films to excite SPR. It is found that the corresponding threshold can be reduced (up to two times) and the slope efficiency can be increased (up to five times) for Ag coated ZnO random lasers.

List of Figures

Figure 2.1: A pair excitation in the scheme of valence and conduction band and in the exciton picture for direct band gap semiconductor. (As illustrated in ref. 41)	15
Figure 2.2: Exciton-polariton dispersion curve showing the kinematics of interaction of two excitons at a and a' such that final state near b and b' result. Photon b is observed in the experiment.....	16
Figure 2.3: Energy band diagram of wurtzite ZnO under the influence of crystal field and spin-orbit interaction. Left, splitting induced only by the crystal field; right, splitting induced only by the spin-orbit interaction; middle, the combined case	21
Figure 2.4: Room temperature spectrally integrated PL for ZnO samples normalized to the spontaneous emission. The inset shows the spectrally resolved PL for 1000 ⁰ C sample for different excitation densities. The downward pointing arrow in the inset indicates the exciton-exciton scattering induced stimulated emission peak. (The image is taken from ref. 45).....	23
Figure 2.5: Normalized PL intensities spectra for various excitation intensity at 550 K. (The image is taken from ref. 46)	25
Figure 2.6: Spectra of emission from the ZnO powder when the excitation intensities are 400, 562, 763, 875, and 1387 kW/cm ² (from bottom to top). The inset is a schematic diagram showing the formation of a closed-loop path for light through recurring scattering in the powder. (The image is taken from ref. 54)	27
Figure 3.1: Schematic of a Mg _x Zn _{1-x} O/ZnO QW with the lowest energy subbands. Excitons transition energy, E_X (where $X = A, B, \text{ or } C$) and binding energy, $E_{X,bind}$ are also shown in the figure	38

List of Figures

Figure 3.2: Form factors of the atom pseudopotentials for Zn and O.....	41
Figure 3.3: Band structures of wurtzite ZnO including SO interaction.....	42
Figure 3.4: ZnO valence bands computed by EPM (solid squares) and 6 band $k.p$ Hamiltonian (dashed lines) calculation for the case without biaxial strain. The three hole-bands, which are A-state (Γ_7 symmetry), B-state (Γ_9 symmetry) and C-state (Γ_7 symmetry), are indicated from top to bottom	44
Figure 3.5: In-plane valence bands energy dispersion of 15Å well width and 100Å barrier width $Mg_xZn_{1-x}O$ / ZnO QWs with $x = 0.12$ and 0.27. Solid (dashed) lines are the calculation with (without) the influence of biaxial strain	45
Figure 3.6: In-plane valence bands energy dispersion of (a) 40, (b) 60 , and (c) 80 Å well width and 100Å barrier width of $Mg_xZn_{1-x}O$ /ZnO QWs with $x = 0.2$	46
Figure 3.7: Excitonic transition energy of $Mg_xZn_{1-x}O$ /ZnO QWs for (a) $x = 0.27$ and (b) $x = 0.12$ Mg mole fraction as a function of well width. Solid (dashed) lines are the calculation with (without) the influence of biaxial strain. It is noted that the computed results of excitonic transition energy given in ref. 61 are similar to our calculation without biaxial strain (i.e., dashed lines). Experimental data (solid squares) obtained from ref. 59 is also plotted in the figure. The inset shows the resulting peak position as a consequence of A1- and B1-excitons overlapping.....	53
Figure 3.8: Total oscillator strength of A1- and B1-excitons of $Mg_xZn_{1-x}O$ /ZnO QWs for $x = 0.12$ and 0.27 as a function of well width. The optimum value of $L_w = 15\text{Å}$ is observed for a wide range of Mg mole fraction.....	55

List of Figures

Figure 3.9: Peak excitonic gain versus surface carrier density of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs for x varies from 0.05 to 0.30 and $L_w = 15\text{\AA}$. Solid (dashed) lines are the calculation with (without) the influence of biaxial strain. The inset shows the gain spectra versus surface carrier density of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $x = 0.12$ and $L_w = 15\text{\AA}$	56
Figure 3.10: The dependence of differential gain constant, g_N and transparency surface carrier density, N_o , of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $L_w = 15\text{\AA}$ versus the mole fraction of Mg. Solid (dashed) lines are the calculation with (without) the influence of biaxial strain.....	57
Figure 4.1: Emission spectra of the ZnO films (a) without and (b) with the MgO-buffer. The insets are the light–light curves.....	63
Figure 4.2: Scanning electron microscope images of ZnO films (a) without and (b) with the MgO buffer layer. (c) Bird-eye view of (b)	65
Figure 4.3: The strain ε_{ZZ} dependence of (a) the effective hole mass, m_h , and (b) the Mott's density, n_{Mott} , of the A- and B-exciton in strained ZnO film. The estimated values of exciton density, n_{ex} , for different samples a , b , c , d , and e are also shown in (b).....	67
Figure 4.4: Lasing spectra for (a) sample A and (b) sample B at different temperatures, T taken under the excitation intensity of $2 \times I_{\text{th}}$, where I_{th} is the pump threshold intensity at T . 'LE' and 'SE' refer to lasing and spontaneous emissions, respectively	72
Figure 4.5: Energy positions of LE and SE as a function of T for samples A and B. The dashed lines represent the linear fit of the experimental data. The data from Bagnall <i>etal</i> is also plotted for comparison	73
Figure 4.6: Lasing spectra for (a) sample A and (b) sample B at temperatures of 500 and 540 K, respectively, versus different excitation intensities.....	74

List of Figures

Figure 4.7: (a) Plot of I_{th} versus T for sample A and B. The insets give the cross-sectional transmission electron microscopy (TEM) image of sample A (right) and the high-resolution TEM image of the ZnO grain (left). Circles show the location of the nanocrystals. (b) RT current-voltage (I - V) characteristics of sample A before and after annealing. The insets show the schematic diagram of sample A (top) and the enlargement of the I - V curve at low bias voltage for the annealed sample (bottom)	76
Figure 4.8: (a) Plot of L_c versus T for samples A and B. The inset shows the FT spectra of the LE spectra of sample B taken at RT and 475 K. (b) The formation of closed-loop random cavities inside the ZnO films at low and high T	79
Figure 4.9: Lasing spectra for the highly disordered ZnO films (a) without and (b) with a rib waveguide structure at pump intensities of ~ 0.4 and ~ 0.6 MW/cm ² , respectively, for different temperatures	81
Figure 4.10: Fundamental cavity length (obtained from Fourier transform to the lasing spectra) versus temperature under different pump intensities for highly disordered ZnO films (a) without and (b) with a rib waveguide structure.....	83
Figure 4.11: Normalized carrier concentrations versus distance across the pump stripe for different values of L_n for highly disordered ZnO films (a) without and (b) with a rib waveguide structure	85
Figure 4.12: Normalized average gains versus the radius of the circular closed-loop random cavities at distance c away from the middle of the pump stripe for the highly disordered ZnO films without a rib waveguide structure	87
Figure 5.1: AFM images of the highly disordered ZnO films (a) without and (b) with ion-beam milling. The schematic diagram shows the cross section view of the films without and with ion-beam milling.....	93

List of Figures

Figure 5.2: (a) Light-light characteristics and (b) emission spectra of ZnO films before (■) and after (▲, ●) ion-beam milling. The corresponding value of I_{th} is ~ 0.34 MW/cm ² (~ 0.23 MW/cm ²) before (after) ion-beam milling condition. The inset shows the Fourier transform spectra of the corresponding lasing emission	94
Figure 5.3: (a) Light-light characteristics and (b) emission spectra of ZnO films with MgO cladding layer before (■) and after (▲, ●) ion-beam milling. The corresponding value of I_{th} before (after) ion-beam milling is ~ 0.30 MW/cm ² (~ 0.21 MW/cm ²). The inset shows the Fourier transform spectra of the corresponding lasing emission.....	96
Figure 5.4: Plot of $I_{th}b_N$ against L^{-1} for different ZnO films. The slope of the fitted lines, χ , are found to be ~ 31	97
Figure 5.5: (a) TEM image of a Ag-coated (~ 40 nm) ZnO (~ 200 nm) film deposited on quartz substrate. (b) Schematic diagram of the optical measurement setup	99
Figure 5.6: (a) Spontaneous emission intensity of ~ 200 nm thickness Ag-coated ZnO films versus emission angle, θ . Inset: (left) Spontaneous emission spectra measured at $\theta \sim 60^\circ$ and (right) AFM image of a ~ 20 nm thick Ag layer deposited on a ~ 200 nm thick ZnO film. (b) Spontaneous emission intensity of ~ 120 nm thickness Ag-coated ZnO films versus emission angle, θ . Inset: (right) Spontaneous emission spectra measured at $\theta \sim 45^\circ$ and (left) AFM image of a ~ 20 nm thick Ag layer deposited on a ~ 120 nm thick ZnO film. Emission characteristics of bare ZnO films are also included for comparison	101
Figure 5.7: (a) Lasing emission intensity of ~ 200 nm thickness Ag-coated ZnO films versus angle, θ . Inset: Lasing emission spectra measured at $\theta \sim 60^\circ$. (b) Lasing emission intensity of ~ 120 nm thickness Ag-coated ZnO films versus angle, θ . Inset: (right) Lasing emission spectra measured at $\theta \sim 45^\circ$ and (left) rms roughness density of Ag-coated surface versus average ZnO grains size. Lasing characteristics of bare ZnO films are also included for comparison	103

List of Figures

Figure 5.8: Light-light characteristics of ~ 120 nm thickness Ag-coated ZnO films. Inset: The surface rms roughness of ~ 120 nm thickness Ag-coated ZnO films versus different thickness of Ag coating. Lasing characteristics of bare ZnO films are also included for comparison	105
--	-----

List of Tables

List of Tables

Table 1.1: Materials for semiconductor light sources.....	2
Table 3.1: Band-edge energies at Γ point, crystal field and spin-orbit splitting energies for wurtzite ZnO	40
Table 3.2: Parameters for calculation of the valence subbands in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs	43
Table 3.3: Hole effective masses of wurtzite ZnO	49

Chapter 1

Introduction

1.1 Background and Motivation

Light-matter interaction is a fundamental physics phenomenon and has been intensively studied since the development of quantum mechanics. The investigation has been further advanced by the invention of laser to serve as a high intensity single frequency light source. On the other hand, the fabrication of p - n junction, which forms the fundamental technology in microelectronic industries, from semiconductor materials has been invented for more than half-a-century. Furthermore, direct band-gap semiconductor materials, which served as the foundation of optoelectronics technology, have also been realized. Now, semiconductor optoelectronics devices have contributed enormously to the vast development in information technology.

Semiconductor laser diodes (LDs) are crucial components used in photonic integrated circuits and have a wide range of applications in the information technology. In comparison with other types of lasers, semiconductor lasers have many merits such as high efficiency, high modulation speed, compact size and low production cost. Therefore, semiconductor lasers offer better performances as well as larger bandwidth in digital data communication due to its higher frequency (i.e., infrared and visible light frequency). Table 1.1 lists the band-gap and emission wavelength of the available direct band-gap semiconductor materials which can be used to fabricate semiconductor

Chapter 1: Introduction

LDs. Therefore, we should be able to have semiconductor LDs emitting at the ranging from infra-red (IR) to ultraviolet (UV) emission.

Table 1.1: Materials for semiconductor light sources

System	Compound	Band Gap (eV)	Wavelength (μm)
III-V	InAs	0.35	3.54
	InP	1.35	0.92
	GaAs	1.43	0.88
	AlGaAs	1.95-1.40	0.63-0.88
	InGaAsP	1.35-0.75	0.92-1.65
	GaN	3.34	0.41
II-VI	ZnSe	2.58	0.52
	CdSe	1.74	0.71
	CdS	2.42	0.51
	ZnO	3.37	0.39

For the past four decades, LDs are fabricated based on narrow band gap semiconductor materials (e.g., GaAs, InP and their tertiary compounds) and the wavelength is limited to spectral range from infrared to visible wavelength (i.e., red). These materials have been used to fabricate LDs for the applications in optical communication and optical data storage. In fact, LDs with much shorter wavelength are needed. This is because shorter wavelength implies higher resolution; the use of wide band gap material could find applications in high density optical data storage, high resolution laser printer, and many more.

GaAs, InP and its compounds can only provide band gap as large as ~ 1.95 eV (i.e., red emission). Hence, search for new material with shorter wavelength (i.e., green to blue-ultraviolet emission) had started since the early 1980s. At the time, ZnSe

Chapter 1: Introduction

compound was considered to be the best candidate for green-blue emission. The first green-blue LD operating at 77 K was demonstrated by using ZnSe based single quantum wells in 1991.¹ This achievement was due to the successful development of *p*-type doping in ZnSe using Nitrogen as the acceptors.^{2,3} Furthermore, H. Jeon *etal* has observed optically pumped room temperature (RT) lasing action in ZnSe-based multiple quantum wells. This is the evidence of RT excitonic gain due to the enhancement of excitonic confinement by the multiple quantum wells.⁴ It is believed that excitonic induced light emission in ZnSe-based multiple quantum wells has higher optical gain as well as lower stimulated emission threshold. However, other reports have suggested that the origin of stimulated emission in ZnSe epilayers is attributed to radiative recombination of electron-hole pairs in electron hole plasma (EHP).^{5,6,7} Although theoretical calculations show that excitonic gain can exist in ZnSe epilayer at RT, there has been no clear experimental evidence of RT excitonic lasing.^{8,9,10} In spite of these controversies, rapid progress is made in the performance of ZnSe-based LDs. Researchers from SONY have reported that the production of ZnCdSe/ZnSSe/ZnMgSSe heterostructure LDs that can operate at RT with a lifetime of 100 hours.¹¹ This LD structure had a ZnCdSe single quantum well as an active layer and the lasing wavelength was at 515 nm.

In early 1990s, GaN, which is a wide band gap semiconductors ($E_g \sim 3.4$ eV at RT), have shown to be the best candidate for the realization of blue LDs. Optically pumped stimulated emission has been observed in GaN epilayer at RT by several groups.^{12, 13, 14, 15} S. Nakamura *etal* have made the first nitride-based LD at the beginning of 1996. The device used InGaN strained multi quantum well in GaN core with AlGaN cladding and was grown on sapphire substrate using metal-organic

Chapter 1: Introduction

chemical vapor deposition (MOCVD) method. In the following years, continuous-wave operation of InGaN-based LDs with over 10,000 hours of lifetime has been achieved.¹⁶

1.1.1 ZnO as UV light source

It is quite clear that the next challenge in the research of semiconductor lasers is to make the lasing emission wavelength even shorter (i.e., emission at UV or deep UV). It is noted that lasing mechanism in most of the semiconductor lasers used today is due to the induction of electron hole recombination in EHP state.¹⁷ However, the threshold of stimulated emission in EHP mechanism is higher than that of excitonic induced stimulated emission. Therefore, if excitonic lasing can be realized, low threshold LDs can be achieved. Recently, attention has been focused in using ZnO semiconductor materials to fabricate UV light source owing to its direct wide band-gap (~ 3.37 eV at 300 K). Furthermore, ZnO holds as a promising material to sustain excitonic induced stimulated emission at RT. With relatively high exciton binding energy of about 60 meV and small excitonic Bohr's radius a_B of 1.8 nm, it will result in excitonic lasing processes at RT with low lasing threshold.^{18,19,20,21,22}

ZnO is not a newly discovered material. Research on ZnO has continued for eight decades with interest following a roller coaster pattern. ZnO is the hottest research direction at the time my PhD study was started. The first report on ZnO in literature can be traced back as early as in 1935. As examples, investigation on lattice parameters,^{23, 24, 25, 26} optical properties and processes as well as its refractive index^{27,28,29,30} have been studied many decades ago. Vibrational properties which were studied by techniques such as Raman scattering were also reported early on.^{31,32,33}

ZnO has advantage over GaN in term of films growth method. MOCVD and molecular beam epitaxy (MBE) are the commonly used methods to grow GaN crystal. The growth of GaN using MOCVD technique involves the reaction between trimethyl gallium, which is a toxic gas and moisturizer sensitive, with ammonia. This will require special handling of the chemicals and proper safety monitoring procedure which will contribute to the additional cost for the fabrication process. Furthermore, sophisticated design is needed for high temperature growth ($>1000\text{ }^{\circ}\text{C}$) which will further increase the fabrication cost. As for MBE, although low temperature of GaN growth is possible, it requires high energy plasma to create nitrogen radical for reaction with gallium. However, this will result in higher nitrogen ion energy which hinder the reaction process and form defective films. Expensive equipment such as electron cyclotron resonance is used with MBE to solve the problem.³⁴ On the other hand, ZnO films can be easily grown at low temperature (below $700\text{ }^{\circ}\text{C}$) using MOCVD technique which requires non-toxic Zn precursor and oxygen gas for the chemical reaction. Furthermore, fairly high-quality ZnO bulk crystal is available in market which eliminates the need of expensive substrates (such as sapphire and SiC) for the growth of ZnO films. ZnO also has superior performance such as thermal stability, resistance to chemical attack and oxidation. Many works have been concentrated on the fabrication of high-crystal-quality (i.e., minimum defect states) ZnO films to realize high efficiency band-edge excitonic UV emission for the realization of RT UV LDs.

In order to make ZnO LDs, it is required to obtain relatively high conductivity *n*- and *p*-type ZnO for the realization of *p-n* junction. *n*-type ZnO can be easily obtained due to the intrinsic defects (i.e., Zn interstitial and O vacancies). However, *p*-

Chapter 1: Introduction

type ZnO is still a major challenge in ZnO research. Despite all the progress that has been made and the reports of *p*-type conductivity in ZnO films using various growth methods and various group-V dopant elements (N, P, As, and Sb), a reliable and reproducible high quality *p*-type conductivity has not yet been achieved for ZnO. To the best of our knowledge, only the Japanese group led by M. Kawasaki has reported repeatable *p*-type ZnO growth.³⁵ Despite of this difficulty, the advantages of ZnO are being explored and exploited by alternative methods such as heteroepitaxy in which *p-n* heterostructures can be obtained by depositing *n*-type ZnO films on other *p*-type materials while still utilizing ZnO as the active layer. Recently, latest breakthrough has been reported by Ryu *etal* for ZnO LDs fabrication. Using Hybrid Beam Deposition (HBD) method, very high doping concentration of Ga doped *n*-type and As doped *p*-type ZnO have been fabricated for realization of ZnO LDs.³⁶ Using ZnO/BeZnO quantum wells structure as the active region, the ZnO LDs has threshold current density of 420 A/cm².

1.1.2 ZnO random laser

Another challenge to realize ZnO LDs is the formation of mirrors for optical feedback (i.e., laser cavity) from the ZnO films. The available methods to obtain laser cavities in ZnO films are 1) cleaving ZnO films to obtain Fabry-Perot (FP) structures, and 2) using disordered ZnO films or nano-composite films to exhibit random lasing action. However, the realization of FP cavity using cleaved mirror proof to be an uneasy task as the wurtzite crystal does not have cleaving plane as in zinc-blende crystal.³⁷ Recent observation of random lasing action in ZnO polycrystalline films have opened up a new possibility to create laser cavities. ZnO random cavities offer

simplicity in fabrication because its formation is a self assembly process.³⁸ However, its performance still needed to be investigated in order to be realized as a reliable method to form laser cavities. Recently, the realization of the first ‘ZnO random laser’ diode has been reported using SiC as the *p*-type layer.³⁹

Nevertheless, the understanding of radiative recombination mechanisms in ZnO at elevated temperatures is still not well understood. By further study, a better understanding of excitonic recombination will be important for designing RT operation of optoelectronics devices. However, fabricating reliable and reproducible *p*-type ZnO is still the major obstacles for the realization of ZnO LDs. If the problem of attaining reproducible *p*-type ZnO can be overcome in the near future, the prospect to fabricate RT excitonic ZnO light emitters will produce more efficient light source than the current nitride-based light emitters. This will also pave a way to realize very efficient RT excitonic lasing with superior threshold performance.

1.2 Objectives

The objectives of the thesis can be summarized as follows:

1. To study the electronics band structures of wurtzite ZnO and calculate the ZnO parameters (e.g., band-edge energies, holes effective masses, deformation constant)
2. To study excitonic states theoretically and calculate the excitonic optical gain in MgZnO/ZnO Quantum Wells (QWs).
3. To investigate the excitonic induced stimulated emission in ZnO films experimentally.
4. To design and realize RT excitonic lasing in ZnO films

1.3 Major contributions of the Thesis

In this work, the optical properties of wurtzite ZnO are studied by using Empirical Pseudopotential Method (EPM) and $k.p$ Hamiltonian. On the other hand, the excitonic induced stimulated emission mechanisms in highly disordered ZnO polycrystalline films are investigated. These include the study of random lasing phenomenon and the design of ZnO random lasers with improved lasing performances (i.e., lower threshold and higher efficiency). Some major contributions that have been achieved in our research works are as follows:

1. The electronics band structures of wurtzite ZnO have been calculated using EPM. Effective mass parameters of 6-band $k.p$ Hamiltonian have also been obtained by fitting the EPM calculation result for wurtzite ZnO. We calculated for the first time the Zn and O Schluter's parameters for pseudopotential form factors.
2. The excitonic optical gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Strained QWs has been calculated by using 6-band $k.p$ Hamiltonian and plane wave expansion method with the consideration of exciton-phonon interaction and biaxial strain. Comparing the experimental data with our calculation, we can deduce the band offset and conduction band deformation of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ strained QWs.
3. Random lasing due to multiple scattering processes that form closed-loop path with phase correlation has been observed in highly disordered ZnO polycrystalline films. The observed phenomenon is affected by excitonic

induced stimulated emission processes in ZnO films. Mott's density inside the ZnO films can be controlled by the corresponding induced mechanical strain (i.e., due to different substrate and growth condition). Hence, random lasing in highly disordered ZnO polycrystalline films can be supported by either free-exciton or EHP radiative recombination.

4. Lasing characteristics of highly disordered ZnO polycrystalline films at high temperature on different substrates were studied. The random lasing at high temperature in highly disordered ZnO polycrystalline films is found sustainable up to 570 K with the corresponding characteristics temperature of 127 K. The high temperature lasing is due to strong excitons confinement inside the ZnO grains. Furthermore, the closed-loop path of light by random lasing action allows the size variation of random cavities which maintain the optical gain for lasing at high temperature.
5. Closed-loop formation of the random lasing in highly disordered ZnO polycrystalline films with and without rib waveguide structure was investigated. It is found that the size and location of the random cavities (i.e., closed-loop path of light) were influenced by the optical gain profile of the random media which is determined by the temperature and the pump beam profile. Furthermore, the optical gain profile of random media with rib waveguide structure can be altered by carriers with small diffusion length as the non-radiative recombination center increased at the side of the rib waveguide. This

shows that the formation characteristics of the closed-loop random cavities are not mainly due to the material properties of the random media.

6. 2-dimensional edge emitting random laser using highly disordered ZnO polycrystalline films with excitonic lasing mechanism have been fabricated. The surface roughness of the random cavities has been improved by ion beam milling. Furthermore, deposition of MgO cladding layer further reduce the surface scattering loss due to smooth MgO/ZnO interfaces. With lower scattering loss, it is found that the corresponding threshold can be lowered and the slope efficiency can be increased for edge emission random lasing. This experiment has shown the possibility of using disordered ZnO grains to sustain coherent optical feedback in wurtzite ZnO.
7. Surface emitting random laser using highly disordered ZnO polycrystalline films has been fabricated. It is found that the surface emission of the laser is direction dependent. The emission direction is determined by the surface corrugation of ZnO random grains which acts similar to that of a diffraction grating. Furthermore, efficient surface emission can be realized by depositing Ag layer on the surface to induce surface plasmons resonance. It is found that the surface emission of ZnO random laser with Ag coating have an improved lasing performance (i.e., the threshold reduced by two times and the slope efficiency increased by more than five times) compared to without Ag coating.

1.4 Organization of the Thesis

This thesis is organized as follows: In chapter 2, we outline the recent progress in ZnO research. Theoretical background of excitonic mechanisms is briefly discussed and the corresponding concept is used to explain the experimental observation of ZnO emission. In chapter 3, theoretical investigation on the electronics band structures of wurtzite ZnO and $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is presented. Excitonic optical gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is also deduced in chapter 3. We present the experimental study on the excitonic processes related to random lasing phenomena in highly disordered ZnO polycrystalline films in chapter 4. In chapter 5, we propose the design of excitonic random lasing to achieve better performances (i.e., lower threshold and higher slope efficiency) from highly disordered ZnO polycrystalline films. Chapter 6 outlines the conclusion of our research works and recommendation for continuing future works.

Chapter 2

Literature Review

2.1 Introduction

ZnO semiconductor material has attracted a lot of attention due to its prospects in optoelectronics applications such as its direct wide band gap (~ 3.37 eV) and large exciton binding energy (~ 60 meV) at room temperature (RT). Some optical properties of ZnO can be used to replace GaN to realize blue-ultraviolet and white light emitting devices. In fact, the advantages of ZnO over to that of GaN are the availability of fairly high-quality ZnO bulk single crystals and its large exciton binding energy. ZnO also has much simpler crystal growth technology resulting in a potentially lower cost in the fabrication of ZnO based devices.

In this chapter, we briefly review the recent progress in ZnO research. Special attention is concentrated towards its excitonic processes since its high exciton binding energy could realize excitonic radiative recombination of ZnO to achieve very efficient ultraviolet lasing at RT. In section 2.2, we briefly introduce the excitonic effect occurs in semiconductor materials. The discussion is followed by the study of optical properties of wurtzite ZnO in section 2.3. In section 2.4, the literature review on the excitonic induced stimulated emission in ZnO films fabricated by various growth methods is presented. Random lasing phenomenon in highly disordered ZnO polycrystalline films are then discussed in section 2.5. Section 2.6 gives a concluding remark of this chapter.

2.2 Excitonic process in semiconductors

Excitonic process is the recombination between conduction electron and valence hole under the influence of Coulomb attraction force.⁴⁰ Due to the large spatial separation between electron and hole pairs, exciton in semiconductors is called Wannier-Mott exciton.⁴¹ Wannier-Mott exciton is a delocalized exciton which can freely move around the crystal lattice. There is another type of exciton called Frenkel exciton. This type of exciton is localized in space and occurs in ionic compound (like NaCl) and organic crystal (like anthracene). In this review, only Wannier-Mott exciton will be discussed. Wannier-Mott exciton can be distinguished as intrinsic and extrinsic types. Again, only intrinsic exciton will be discussed in details as it is more related to our works.

Extrinsic exciton is exciton bound into external dopant, mostly donor or acceptor atoms and to defects site.⁴¹ Intrinsic exciton in semiconductors can be observed as free-exciton, biexciton, exciton-exciton collision and exciton-electron or exciton-hole collision. Another state of excitons is called electron hole plasma (EHP) where the excitons lose their quasi-particles state characteristics and behave as a sea of free particles screened by the Coulomb force. These different states are related to the exciton density which is determined by the excitation density (e.g., the intensity of optical pumping). In low density regime, only the free-exciton state is observed. With low density of excitons existed, the quasi-particles characteristics of the excitons are conserved. In the intermediate density regime, new quasi-particles called biexciton is formed. At the same time, interacting excitons in the form of exciton-exciton scattering (as well as exciton-free carrier scattering) states are also observed. Eventually at very

Chapter 2: Literature Review

high density regime, the excitons start to lose their quasi-particles state and transfer into EHP.

In the following paragraphs, brief explanation of excitonic process in different density regime is discussed. Simple parabolic bands of direct gap semiconductor will be used to illustrate the relationship between free-exciton wave vector and energy. The interacting excitons in term of exciton-exciton scattering process are then explained by using exciton-polariton dispersion. A simple equation can be deduced to calculate the generated photon due to the excitons collision. Finally, the EHP, which is a consequence of Pauli Exclusion Principle between the interacting fermions in the high density excitation, is also discussed.

2.2.1 Free-exciton

In effective mass approximation, the exciton can be described as electron-hole pair bound together under the Coulomb attractive force (i.e., in analogy to hydrogen atom). In a direct band gap semiconductor, the simple parabolic band used to explain the conduction electron and valence hole dispersion can be replaced by a single quasi-particle band of ‘exciton’. Based on this parabolic model, we can separate the relative motion between the electron and hole and the motion of the center of mass. This leads to the dispersion relation of exciton as shown in figure 2.1. In analogy to hydrogen atom, the exciton energy solution can be written as^{40,41}

$$E_{ex}(n, \mathbf{K}) = E_g - R_y^* \frac{1}{n^2} + \frac{\hbar^2 \mathbf{K}^2}{2M} \quad (2.1)$$

where E_g is the band gap energy, E_{ex} is the exciton energy, R_y^* is the effective Rydberg energy (or binding energy) defined as $R_y^* = 13.6 \frac{\mu}{m_0} \frac{1}{\epsilon^2}$ (in eV). $\mu = \frac{m_e m_h}{m_e + m_h}$, is the

Figure 2.1: A pair excitation in the scheme of valence and conduction band and in the exciton picture for direct band gap semiconductor. (As illustrated in ref. 41).

exciton effective reduced mass, m_e is the electron effective mass, m_h is the hole effective mass, m_0 is the electron mass and ϵ is the dielectric constant. n is the principal quantum number and $\hbar$ is the Planck's constant. The last term on the right hand side of (2.1) describes the total kinetic energy of the translational motion where the translational mass and total wavevector are defined as $M = m_e + m_h$ and $\mathbf{K} = \mathbf{k}_e + \mathbf{k}_h$, respectively. The physical length of exciton is given by the Bohr's radius, $a_B = 0.53 \times \frac{\epsilon}{\mu/m_0}$ (in Å). Using typical semiconductors parameters value, the range of the exciton Bohr's radius is approximately $\sim 50 \text{ nm} \geq a_B \geq 1 \text{ nm} > a_{\text{lattice}}$, where a_{lattice} is the lattice constant. This means that both electron and hole orbit their center of mass over many unit cells in the periodic lattice of the crystal. This is a very important property of Wannier-Mott excitons which justifies the use of effective mass approximation.

2.2.2 Exciton-exciton scattering

Exciton-exciton scattering is a mechanism involving two excitons with the same energy states. These excitons' collision result in one exciton scatter into a higher exciton state or into continuum state (i.e., gains energy) and the other exciton scatters from exciton-like state to a photon-like state (i.e., loses energy) while their total momentum and energy related are conserved. In the photon-like state, the 'exciton-polariton' is free to propagate through the crystal lattice to emerge as a luminescence photon. Exciton-exciton scattering process is schematically shown in figure 2.2.

Mathematically, the total momentum and energy conservation of exciton-exciton scattering process can be written as⁴⁰

$$\hbar k_{i,1} + \hbar k_{i,2} = \hbar k_{f,1} + \hbar q \quad (2.2a)$$

$$E_{i,1} + E_{i,2} = E_{f,1} + \hbar \omega \quad (2.2b)$$

Figure 2.2: Exciton-polariton dispersion curve showing the kinematics of interaction of two excitons at a and a' such that final state near b and b' result. Photon b is observed in the experiment.

Chapter 2: Literature Review

where the subscripts i, f refer to initial and final states, respectively. 1 and 2 refer to the corresponding excitons in collisions. $\hbar q$ is the photon momentum which is much smaller than the exciton momentum. Hence, we can write the equations of energy conservation as

$$E_{ex} + \frac{\hbar^2 k_{i,1}^2}{2M} + E_{ex} + \frac{\hbar^2 k_{i,2}^2}{2M} = E_{ex} + E_b^{ex} \left(1 - \frac{1}{n^2}\right) + \frac{\hbar^2 (k_{i,1} + k_{i,2})^2}{2M} + \hbar\omega \quad (2.3a)$$

$$\hbar\omega = E_{ex} - E_b^{ex} \left(1 - \frac{1}{n^2}\right) - \frac{\hbar^2 k_{i,1} \bullet k_{i,2}}{M} \quad (2.3b)$$

The last term on the right hand side of (2.3b), equivalent to $2E_k$, is the kinetic energy of the excitons. We can approximate the kinetic energy as, $E_k = (3/2)kT$. In the final state, one exciton will be excited into a higher state ($n = 2, 3, 4, \dots, \infty$), and the other exciton will emit a photon which energy can be expressed as⁴⁰

$$P_n = E_{ex} - E_b^{ex} \left(1 - \frac{1}{n^2}\right) - 3\delta kT \quad (n = 2, 3, 4, \dots, \infty) \quad (2.4)$$

where P_n is the photon energy, E_{ex} is the free-exciton energy, E_b^{ex} is the binding energy of the exciton, n is the quantum number of the envelope function and kT is the thermal energy. δ has a value ranging from 0 to 1.

2.2.3 Electron Hole Plasma

EHP is a high density excitation process where the excitons lose their identity as individual quasi-particles and a new collective phase is formed. The exciton's density at which the EHP starts to exist is called Mott's density transition. The Mott's density can be calculated as⁴¹

$$n_{Mott} = \frac{k_B T}{2a_B^3 R_y^*} \quad (2.5)$$

Chapter 2: Literature Review

where k_B is the Boltzmann constant, T is the absolute temperature in K, a_B is the Bohr's radius and R_y^* is the effective Rydberg energy of the exciton. If the exciton's density is larger than the Mott's density, the excitons will lose their quasi-particles state and transfer into EHP phase.

The consequences of this high density electron-hole pairs are the effective screening of Coulomb interaction in the excitons as well as band gap renormalization. The effective screening of Coulomb interaction removes the binding energy of the exciton at the Mott's density and the electron is no longer bind into a certain hole; instead we have the new collective EHP phase. The band gap renormalization is the reduction of the forbidden energy gap due to *exchange* and *correlation* effect of EHP.⁴¹ This is explained by the Pauli Exclusion Principle where the exchange interaction forbids two identical fermions (e.g., electron with the same spin) to stay at the same unit cell. It means that the distance between two identical fermions will be increased which in turn reduce it repulsive force. This subsequently reduces the total energy of the system. In semiconductor materials, it reduces the total energy of the electron system (as well as the hole system) and hence the band gap energy is reduced. The correlation energy is spin independent and describes the fact that the electron-hole pair system can lower its energy further if the distribution of electrons and holes relative to each other is not random (i.e., if in the vicinity of a hole, an electron is found with higher probability than the other hole and vice versa). The occurrence of this correlation is due to Coulomb interaction between electron and hole. Another effect that contributes to EHP formation at Mott's transition is called phase-space filling.⁴¹

2.3 Excitonic optical properties of ZnO

The band structures of a given semiconductor material are pivotal in determining its potential utility. Consequently, an accurate knowledge of the band structures is critical to study the electrical and optical properties of semiconductor materials. Several theoretical approaches of varying degrees of complexity have been employed to calculate the band structures of ZnO. The first theoretical work on band structures calculation of ZnO was proposed by Rössler using Green's function in 1969.⁴² However, several experimental works have proved that Rössler's prediction on the electronic structures of ZnO is far from satisfactory. Langer and Vesely⁴³ have reported experimental data related to the energy levels of core electrons in ZnO using x-ray induced photoemission spectroscopy. They have drawn two conclusions from their studies: 1) the location of the Zn *3d* level in ZnO has been unambiguously determined and 2) the discrepancy between the measured values and theoretically determined energy values was angular momentum dependent.

By considering the Zn *3d* states as the core levels, Local Density Approximation (LDA) and tight binding methods were employed to simplify the calculation. Satisfactory agreement with qualitative valence band dispersions was achieved with this assumption. However, quantitative disagreement remained and the location of the Zn *3d* states could not be predicted. Most recently, the advent of computer capabilities allow the consideration of the Zn *3d* level as the valence states. These methods enable us to estimate the position of the Zn *3d* states as well as taking into account the influence of Zn *3d* states on the formation of *s*- and *p*-derived valence bands.

ZnO is a direct band-gap wurtzite type semiconductor with a hexagonal crystal structure similar to GaN. From the band structures calculation, the wurtzite ZnO conduction band is mainly constructed from the *s*-like state having Γ_7 symmetry whereas the valence band is mostly *p*-like state which is split into three bands due to the influence of crystal field and spin-orbit coupling interactions. The near band-gap intrinsic absorption and emission spectra are therefore dominated by transition from these three valence bands. The three valence bands are labeled as A-, B-, and C-hole from top to bottom. There is ambiguity about the symmetry ordering of ZnO valence band states.^{27,28,29} However, based on Thomas' interpretation²⁸ and later supported by Lambrecht *et al.*,⁴⁴ the valence bands symmetry assignment are A- Γ_7 , B- Γ_9 , and C- Γ_7 which is due to negative spin-orbit interaction energy. The negative spin-orbit energy in ZnO is related to the influence of Zn *3d* state. The free-excitonic transitions from the conduction band to these three valence bands are denoted as A-, B-, and C-excitons. The schematic energy diagram of ZnO is shown in figure 2.3.

In ZnO, excitonic effects can be sustained even at RT due to its large binding energy (~60 meV). Therefore, the observed optical process in ZnO should be related to excitonic recombination which can be observed up to 550 K. In ZnO, various excitonic processes are commonly observed at low temperature and clearly distinguished from the energy spectrum. The excitonic related recombination mechanisms observed at RT in ZnO are, 1) free-exciton, and 2) exciton-exciton scattering. At very high excitation density, EHP recombination is also observed.

Figure 2.3: Energy band diagram of wurtzite ZnO under the influence of crystal field and spin-orbit interaction. Left, splitting induced only by the crystal field; right, splitting induced only by the spin-orbit interaction; middle, the combined case.

2.4 Stimulated emission in ZnO

Many investigations have reported the observation of efficient excitonic stimulated emission from ZnO at and above RT. Stimulated emission sustained inside ZnO can be attributed to exciton-exciton scattering under low excitation lower than that of the EHP recombination. At very high excitation intensity, the EHP forms beyond the Mott's density which can be estimated by

$$n_{Mott} = \frac{k_B T}{2a_B^3 E_B^{ex}} \sim 3.7 \times 10^{19} \text{ cm}^{-3} \quad (2.6)$$

where $T = 300 \text{ K}$, $a_B = 18 \text{ \AA}$ and $E_B^{ex} = 60 \text{ meV}$ can be used in the calculation. Özgür *etal*⁴⁵ have shown that ZnO layers deposited directly on *c*-plane sapphire substrates by

Chapter 2: Literature Review

rf magnetron sputtering could have optical quality sufficient for excitonic stimulated emission. Pulsed excitation, time integrated photoluminescence (PL) was performed using 100 fs pulses at RT with average excitation energy densities varying between 5 and 700 $\mu\text{J}/\text{cm}^2$. To deduce the stimulated emission threshold, the spectrally integrated PL intensities were plotted as a function of the pump energy density. Stimulated emission features were observed for the samples annealed above 800 $^{\circ}\text{C}$; however, the as-grown sample did not show any sign of stimulated emission for the maximum energy density used. The spectrally resolved time integrated PL for the sample annealed at 1000 $^{\circ}\text{C}$ is shown in inset figure 2.4. For excitation density above 50 $\mu\text{J}/\text{cm}^2$, sharp feature (i.e., stimulated emission emerges at 3.167 eV) on the lower energy side of the spontaneous emission peak is observed and grows superlinearly. This stimulated emission peak has been attributed to exciton-exciton scattering and lies below the free-exciton energy by an exciton binding energy plus the mean kinetic energy $(3/2) k_{\text{B}}T$ where $k_{\text{B}}T$ is the thermal energy. This peak is then slightly red-shifted to 3.160 eV (~ 392.4 nm) since the inelastic exciton-exciton scattering leaves one exciton in an excited state which in turn reduces the emission energy of the recombining exciton. As the excitation density is increased above 250 $\mu\text{J}/\text{cm}^2$, a second peak emerges at 3.133 eV (~ 395.8 nm) due to stimulated emission from EHP. At these higher excitation densities, exciton wave functions start to overlap due to the increase in their density. Phase-space filling and Coulomb interaction cause excitons to lose their individual character by ionization and eventually EHP is formed. This EHP induced stimulated emission peak shifts and broadens with increasing excitation as a result of band gap renormalization. The coexistence of the exciton-exciton scattering and the EHP (i.e., the exciton-exciton scattering and EHP induced stimulated

Figure 2.4: Room temperature spectrally integrated PL for ZnO samples normalized to the spontaneous emission. The inset shows the spectrally resolved PL for 1000⁰ C sample for different excitation densities. The downward pointing arrow in the inset indicates the exciton-exciton scattering induced stimulated emission peak. (The image is taken from ref. 45).

emission), which is originated from the spatial non-uniformity of the samples and pump beam profile, may come from different regions of the sample excited by the laser. From figure 2.4, it is also observed stimulated emission peak due to exciton-exciton scattering for sample annealed at 950⁰ C but not for the sample annealed at 800⁰ C. Due to the existence of exciton-exciton scattering, pump threshold for the 950 and 1000⁰ C samples (i.e., 49 and 58 $\mu\text{J}/\text{cm}^2$, respectively) were significantly lower than that for the 800⁰ C sample (130 $\mu\text{J}/\text{cm}^2$).

Furthermore, the exciton-exciton scattering and EHP induced stimulated emission in ZnO are also observable even at temperature as high as 550 K as reported by Bagnall *etal*^{46,47} from ZnO film deposited using plasma enhanced Molecular Beam Epitaxy (MBE) on *c*-plane sapphire. The existence of excitons at high temperature is made possible by the high exciton binding energy of ZnO. For excitation intensity exceeding 400 kW/cm², the exciton-exciton scattering related stimulated emission peak appeared at 3.18 eV (~389.9 nm) and grew superlinearly as observed at RT. At higher excitation intensity, the EHP peak appeared at 3.14 eV (~394.9 nm) and broadened as well as red-shifted due to band gap renormalization with further increased of excitation intensity. The thresholds for the stimulated emission lines were 1.2 and 1.9 MW/cm² for the exciton-exciton scattering and EHP mechanism, respectively. Figure 2.5 shows the stimulated emission observed at 550 K.

Bagnall *etal*⁴⁸ also reported optically pumped RT lasing from cleaved ZnO cavities even though they were unable to observe the longitudinal cavity modes directly. In their later study, they could clearly see a very strong and stable mode structure of the RT EHP emission peak in ZnO epitaxial layers.⁴⁷ Although its origin was not explicitly identified, the lasing was claimed to be produced by naturally formed or ‘accidental’ ~ 70 μ m cavity as calculated from the 0.5 nm mode spacing. In the same samples, pump probe measurements revealed that the optical gain forms when photo-excited hot carriers cool down to an EHP state.⁴⁹

Kawasaki *etal*⁵⁰ and Zu *etal*⁵¹ investigated the effects of nanocrystal size on stimulated emission in ZnO thin films fabricated on *c*-plane sapphire substrates by laser MBE. The films having small nanocrystal size of about 50 nm showed excitonic stimulated emission as well as the stimulated emission from EHP. The spontaneous

Figure 2.5: Normalized PL intensities spectra for various excitation intensity at 550 K. (The image is taken from ref. 46).

emission generated by exciton-exciton collisions, which showed quadratic intensity dependence was followed by stimulated emission from the same process at higher excitation intensities exhibiting eight-power dependence. With further increase of the excitation intensity the Coulomb interaction leads to ionization of excitons and the formation of a dense EHP. Therefore, the intensity of the excitonic stimulated emission peak is observed to reduce. This was not observed in previously mentioned reports due to the sample's inhomogeneity. Another important observation was that, unlike the

EHP induced stimulated emission, the exciton-exciton scattering induced stimulated emission was not present in the films having larger nanocrystal size. Kawasaki *etal*⁵⁰ concluded that there is an optimum hexagonally shaped microcrystallite size of (50 nm)³ for observing excitonic stimulated emission. Ohtomo *etal*⁵² speculated that the excitonic stimulated emission is due to giant oscillator strength that can occur in high quality nanocrystals with dimension larger than the exciton Bohr's radius (~2 nm) but smaller than the optical wavelength (390 nm). For large grain samples, the exciton superradiance effect becomes weak such that the exciton-exciton collision process should not occur. Thus the grain boundaries between nanocrystals are considered to serve as barriers resulting in the confinement of excitons in nanocrystals.

2.5 Random lasing in ZnO polycrystalline films

In wurtzite ZnO, the design of conventional laser cavity is found to be an engineering challenge for forming mirror by conventional cleaving method. This is due to the hexagonal structure of ZnO crystal has prevented smooth cleaving to form facets. However, a new optical feedback mechanism is recently discovered which make use multiple scattering of light as the feedback mechanism. This new type of laser system is known as 'random laser'.

Cao *etal* observed random lasing in ZnO polycrystalline films at RT.^{53,54} Figure 2.6 shows the evolution of the emission spectra with increasing pump intensity. At low excitation intensity, the spectra consisted of a single broad spontaneous emission peak. As the pump power increased, the emission peak become narrower due to the preferential amplification near the maximum of the gain spectrum. Above a certain threshold, very narrow peaks appear in the emission spectrum. The linewidth of

Chapter 2: Literature Review

these peaks was less than 0.3 nm, which was more than 30 times smaller than the linewidth of the amplified spontaneous emission peak below threshold. When the pump intensity increased further, more sharp peaks appeared. The frequencies of the sharp peaks depend on the sample position, that is, when the excitation spot was moved across the film the frequencies of the sharp peaks changed. Above threshold, the integrated intensity increased much more rapidly with increasing pump intensity and the emission is highly polarized indicating that laser action has occurred in the ZnO films. Bear in mind that in ZnO polycrystalline, the spontaneous emission of ZnO

Figure 2.6: Spectra of emission from the ZnO powder when the excitation intensities are 400, 562, 763, 875, and 1387 kW/cm² (from bottom to top). The inset is a schematic diagram showing the formation of a closed-loop path for light through recurring scattering in the powder. (The image is taken from ref. 54).

Chapter 2: Literature Review

can be resolved as transverse electric (TE) and transverse magnetic (TM) polarization modes. From lasing measurement, the TE mode has lower (higher) threshold (intensity) compare to TM mode. This is due to the origin of spontaneous emission where TE mode is contributed by A- and B-exciton while TM mode is only contributed by C-exciton.

In random lasing, the physical origin of random lasing modes with multimode and unequal mode spacing behavior is due to the formation of different closed loop path. Closed loop path is defined as the path of light that get scattered by a scatterer, experience multiple scattering process in the medium and return back to its original position with constructive interference behavior. The characteristics of this random lasing in semiconductor polycrystalline films exhibit remarkable differences from that of a conventional laser. First of all, the laser emission from the ZnO polycrystalline films can be observed in all direction and the emission spectra and intensities vary with emission angle. Second, the pump intensity required to reach the lasing threshold depends on the excitation area. As the excitation area decreases, the lasing threshold increases and when the excitation area is below a critical size, lasing stops as the closed-loop is too short and the amplification is not high enough to achieve lasing. When the lasing area increased, more lasing peaks appeared as more than one closed-loop path can be formed. The shape and size of the laser cavities changed as the excitation spot is moved across the film. The size and shape of the laser cavities are determined by the optical gain coefficient, the grain size and distribution, the scattering cross section, and the boundary conditions, so the lasing spectrum vary across the film. Third, the modes separation is independent of the cavity size. Since there is no fixed cavity length, the modes separation is randomly spaced which is determined by the

number of closed-loop formed unlike conventional laser cavity where the mode separation is determined by cavity length.

Random laser can be distinguished into two types, which account to their feedback mechanisms, namely *incoherent* and *coherent* random lasers. For polycrystalline ZnO random lasing, the observed random lasing is considered as coherent random lasing as evidenced by very narrow linewidth of less than 0.3 nm. Many theoretical works have been dedicated to understand the nature of random lasing since its origin due to scattering process is physically unique and usually considered detrimental in conventional laser system. On the other hand, many works have been dedicated to make ZnO random laser feasible for commercial applications. It is shown in recent studies that performance of random lasers can be improved by making use of waveguide structures^{55,56,57}. It is desired to design random laser structure to have comparable performance to that of the conventional laser structure. Therefore, works on investigating high power single mode random laser with better directionality still very much required to show it can be used for commercial applications.

2.6 Concluding Remarks

In summary, excitonic process in ZnO has been reviewed. Optical properties of wurtzite ZnO semiconductor are studied theoretically by modeling the corresponding electronic band structure. Hence, it is found that the main feature of ZnO band-edge optical properties are the formation of A-, B-, and C-excitons which have been revealed through the study of electronics band structures. Furthermore, it is noted that the free-exciton model is still not accurate enough to study the many body effects in ZnO especially at the condition of higher carrier density. Therefore, models based on

Chapter 2: Literature Review

exciton-exciton scattering and EHP processes are used to describe the optical characteristics of ZnO materials.

ZnO has potential to be used to fabricate wide band-gap optoelectronic devices. It is also desirable to realize ZnO LDs with excitonic radiative recombination. The excitonic induced stimulated emission (i.e., due to exciton-exciton scattering and EHP) has been observed from ZnO films and nanocrystals. It was found that the lasing threshold due to exciton-exciton scattering is smaller than that of EHP in ZnO lasers. The emission characteristics of ZnO polycrystalline films were also reviewed in this chapter. It is explained that multiple scattering feedback mechanism or random lasing inside highly disordered ZnO polycrystalline films could be the solution to form ZnO laser cavity. Reports on the possibilities to generate coherent UV lasing from ZnO random media are also described.

Chapter 3

Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

3.1 Introduction

ZnO materials have drawn considerable attention for the application in ultraviolet (UV) optoelectronics due to their large excitonic transition energy (~ 3.37 eV) and binding energy (~ 60 meV). Furthermore, considerable improvements on these excitonic characteristics of bulk ZnO materials is possible if ZnO-based Quantum Wells (QWs) structures are constructed.⁵⁸ Recent investigations on the excitonic characteristics of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs growth on ScAlMgO_4 substrate have reported the increment of excitonic transition energy (> 3.6 eV) as well as the reduction of excitation threshold (≤ 17 kW/cm²).⁵⁹ Physical models, inclusive of the influence of exciton-phonon interaction as formulated by Pollmann-Büttner potential⁶⁰, have been developed to interpret the excitonic transition characteristics of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs.⁶¹ Furthermore, spontaneous and piezoelectric polarization effects have been taken into the investigations of the optical characteristics of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs.^{62,63} However, the theoretical study of the excitonic gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs especially with the influence of exciton-phonon interaction has been limited in the literature.

In this chapter, the electronics band structures of bulk wurtzite ZnO were deduced using Empirical Pseudopotential Method (EPM). This involved an iteration

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

process to determine the potential form factors by matching the calculated result with the experimental data at the high symmetry point. After good convergence of the solution is obtained, the full band structures can be calculated with the consideration of spin-orbit (SO) coupling.

The conduction and valence band structures of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs are then modeled by a simple single parabolic band and 6-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian, respectively. The effective mass parameters of the Hamiltonian are deduced from the EPM. The electron and hole wave functions are approximated by plane wave expansion method.⁶⁴ The valence energy dispersion of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is then deduced and the importance of the inclusion of A-, B- and C- holes states for the study of exciton states is then discussed.

The exciton energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is then deduced by variational calculation with exciton-phonon interaction taken into consideration. The corresponding momentum matrix elements and the excitonic optical gain of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs are therefore calculated. The calculated excitonic transition energy of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is subsequently compared with the experimental results for validation purposes. Hence, the band gap offset ratio and conduction band deformation constant are estimated for the calculation of excitonic gain. Furthermore, the optimum design of the optical gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs under the influence of biaxial strain is investigated.

This chapter is organized as follows: In section 3.2, the electronics band structures of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs are studied. It is then followed by the study of excitonic optical gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs in section 3.3. Finally, section 3.4 gives the summary of this chapter.

3.2 Electronics Band structures of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

3.2.1 Theory

The fundamental concept involved in a pseudopotential calculation is that the ion core can be omitted. Computationally this is crucial for it means that the deep core potential has been removed and a simple plane wave basis will yield rapid convergence.⁶⁵ The pseudopotential Hamiltonian for a wurtzite semiconductor crystal is given by Fan *etal*⁶⁶, Cohen and Chelikowsky⁶⁷ as

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (3.1)$$

where $V(r)$ is the pseudopotential of the crystal and is the sum of all the atomic local pseudopotential. The $V(r)$ can be expanded in reciprocal lattice vectors $\mathbf{G}$. For wurtzite structure, this yields

$$V(r) = \sum_{\mathbf{G}} \left(V^S(\mathbf{G}) S^S(\mathbf{G}) + i V^A(\mathbf{G}) S^A(\mathbf{G}) \right) e^{i\mathbf{G} \cdot \mathbf{r}} \quad (3.2)$$

where S^S and S^A are the symmetric and antisymmetric pseudopotential structure factors. The V^S and V^A are the symmetric and antisymmetric pseudopotential form factors of binary wurtzite compound respectively and can be written as

$$V^S(\mathbf{G}) = \frac{1}{2} [V_1(\mathbf{G}) + V_2(\mathbf{G})] \quad (3.2a)$$

$$V^A(\mathbf{G}) = \frac{1}{2} [V_1(\mathbf{G}) - V_2(\mathbf{G})] \quad (3.2b)$$

where the subscripts 1 and 2 indicate the cation and anion in the lattice, respectively. The form factors are determined empirically by fitting the calculated band structures to the experimental data. They depend on the magnitude of $\mathbf{G}$. As the pseudopotential is slowly changing with r , we can ignore those terms with large momentum component, i.e. V_1 and V_2 may be assumed to be zero for $|\mathbf{G}| > \sqrt{7\frac{3}{8}}$. We represent the form factor

of the atom pseudopotential with a continuous function of the magnitude of wave vector $q = |G|$ by the Schluter's formula⁶⁸

$$V(q) = \frac{v_1(q^2 - v_2)}{\exp[v_3(q^2 - v_4)] + 1} \quad (3.3)$$

where the unit of q is au and the unit of $V(q)$ is Ry. There are four parameters v_1 - v_4 for the Zn atom and others four parameters for O atom.

To obtain explicit expressions for the wurtzite structure factors, we choose standard primitive translation vectors and place atoms of one type at $r_1 = [1/6, 1/6, (1/2 + u)/2]$ and $-r_2 = [-1/6, -1/6, -(1/2 - u)/2]$. Atoms of the second type are located at $+r_2$ and $-r_1$. Then, the symmetric and antisymmetric pseudopotential structure factors are given by

$$S^S(G) = \cos[G \cdot (r_1 + r_2)/2] \cos[G \cdot (r_2 - r_1)/2] \quad (3.4a)$$

$$S^A(G) = \cos[G \cdot (r_1 + r_2)/2] \sin[G \cdot (r_2 - r_1)/2] \quad (3.4b)$$

We then include SO interactions in our calculation. The contribution of the SO matrix element to the pseudopotential Hamiltonian is introduced in our calculation follows the work by Chelikowsky *etal*⁶⁵

$$H_{GG'}^{SO}(k) = (K \times K') \sigma_{SS'} [-i\lambda^S S^S(G - G') + \lambda^A S^A(G - G')] \quad (3.5)$$

where $K = k + G$ and $K' = k + G'$ and $\sigma_{SS'}$ is the Pauli's spin matrix. λ^S and λ^A are the symmetric and antisymmetric contributions to the SO Hamiltonian given by

$$\lambda^S = (\lambda_1 + \lambda_2)/2 \quad (3.6a)$$

$$\lambda^A = (\lambda_1 - \lambda_2)/2 \quad (3.6b)$$

where $\lambda_1 = \mu B_{nl}^1(K) B_{nl}^1(K')$ and $\lambda_2 = \alpha \mu B_{nl}^2(K) B_{nl}^2(K')$. μ is the adjustable parameter and α is the fixed ratio of the SO split-off parameters of the free anion and cation atoms. The B_{nl} is defined as

$$B_{nl} = \beta \int_0^\infty j_{nl}(Kr) R_{nl}(r) r^2 dr \quad (3.7)$$

where j_{nl} is the spherical Bessel's function of the l^{th} angular momentum, R_{nl} is the radial part of the outermost p -core wavefunction and β is a normalization constant as in ref. 69. The parameter μ can be varied to give the correct spin splitting of the valence band at the Γ point.

The optical properties of direct band gap semiconductors such as ZnO is important to be analyzed at the vicinity of Γ point of the band structures. This is usually done using $\mathbf{k.p}$ method which is known to give accurate result near the band-edge. Therefore, it is useful to have a $\mathbf{k.p}$ model for wurtzite ZnO to analyze its optical properties at the Γ point. The effective mass Hamiltonian and the cubic approximation for wurtzite semiconductors are used by adopting the effective mass Hamiltonian derived by Chuang and Chang using the $\mathbf{k.p}$ method. The result is a 6-band $\mathbf{k.p}$ Hamiltonian for the valence holes including SO coupling. The 6-band Hamiltonian of the valence bands for wurtzite semiconductor including strain effect is given by⁷⁰

$$H_{6 \times 6}^v = \begin{bmatrix} F & -K^* & -H^* & 0 & 0 & 0 \\ -K & G & H & 0 & 0 & \Delta \\ -H & H^* & \lambda & 0 & \Delta & 0 \\ 0 & 0 & 0 & F & -K & H \\ 0 & 0 & \Delta & -K^* & G & -H^* \\ 0 & \Delta & 0 & H^* & -H & \lambda \end{bmatrix} \quad (3.8)$$

where

$$F = \Delta_1 + \Delta_2 + \lambda + \theta, \quad G = \Delta_1 - \Delta_2 + \lambda + \theta, \quad \Delta = \sqrt{2}\Delta_3,$$

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

$$\begin{aligned}
 \lambda &= \frac{\hbar^2}{2m_0} [A_1 k_z^2 + A_2 (k_x^2 + k_y^2)] + D_1 \varepsilon_{zz} + D_2 (\varepsilon_{xx} + \varepsilon_{yy}), \\
 \theta &= \frac{\hbar^2}{2m_0} [A_3 k_z^2 + A_4 (k_x^2 + k_y^2)] + D_3 \varepsilon_{zz} + D_4 (\varepsilon_{xx} + \varepsilon_{yy}), \\
 K &= \frac{\hbar^2}{2m_0} A_5 (k_x + ik_y)^2 + D_5 \varepsilon_+, \\
 H &= \frac{\hbar^2}{2m_0} A_6 (k_x + ik_y) k_z + D_6 \varepsilon_{z+}.
 \end{aligned} \tag{3.9}$$

In (3.9), A_1 is the crystal field split energy, A_2 and A_3 account for the spin-orbit interaction, ε_{ij} is an element of the strain tensor, $\varepsilon_+ = \varepsilon_{xx} + 2i\varepsilon_{xy} - \varepsilon_{yy}$, $\varepsilon_{z+} = \varepsilon_{xz} + i\varepsilon_{yz}$, A_{1-6} are the effective-mass parameters, and D_{1-6} are the deformation potentials. For biaxial strained QWs, the strain tensor in the well region comprises of $\varepsilon_{xx} = \varepsilon_{yy} = (a_0 - a)/a$, $\varepsilon_{zz} = -2C_{13}\varepsilon_{xx}/C_{33}$ and $\varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{zx} = 0$, where a_0 and a are the lattice constants of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ barrier and ZnO well layers, respectively. C_{13} and C_{33} are the stiffness constants of the ZnO well layer.

The problem now is to determine A_{1-6} parameters used in the Hamiltonian. This can be done by using curve fitting of the Hamiltonian with the energy bands calculated using EPM with SO coupling but ignoring the biaxial strain effect. The curve fitting can be done using least square algorithm. In our case, we employed the least square method provided in MATLAB from Mathworks to get the A_{1-6} values. Based on the model using 6-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian, we can study the valence bands structure of wurtzite ZnO with the inclusion of SO coupling and biaxial strain.

The electronics band structures of wurtzite ZnO developed above can be used to study the optical properties of 2-dimensional ZnO system such as ZnO QW using $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ as the barriers. The electronics band structures of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

can be investigated based on plane wave expansion method. Figure 3.1 shows the schematic of the wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs used in the model. If the z -axis is assumed to be along the growth direction, the wave function $\psi_{n,k}^c(z)$ for the electron can be written as⁷¹

$$\psi_{n,k}^c(z) = \sum_{\eta=\uparrow,\downarrow} \varphi_n(z, \mathbf{k}) |S, \eta\rangle \quad (3.10)$$

where n indexes the number of conduction subbands, η is electron spin and $|S, \eta\rangle$ is the Bloch function transforming like s-state atomic wavefunctions and $\mathbf{k}$ is the wave vector. Using plane wave expansion, the normalized envelope function can be written as

$$\varphi_n(z, \mathbf{k}) = e^{i(k_x x + k_y y)} \sum_p g_{n,p,k_x,k_y} \cdot \frac{1}{\sqrt{L}} e^{i(k_z + p \cdot (2\pi/L))z} \quad (3.11)$$

where $i = \sqrt{-1}$, $L = L_w + L_b$, L_w is the well width of the QW, L_b is the width of the barrier region, and p is an integer running through the plane-waves that construct the z -dependent envelope function. The eigen-equation of electron envelope function can be expressed as

$$(H^c + V_c(z))\varphi_n(z, \mathbf{k}) = E_n^c(\mathbf{k})\varphi_n(z, \mathbf{k}) \quad (3.12)$$

where $H^c = \frac{1}{2} \hbar^2 ((k_x^2 + k_y^2)/m_e^\parallel + k_z^2/m_e^\perp) + P_c(z)$ and $V_c(z)$ is the QWs profile of the unstrained conduction band energy. $m_e^\parallel$ and $m_e^\perp$ are the electron effective masses parallel and perpendicular to the in-plane direction, respectively and $\hbar$ is the Planck's constant. The hydrostatic deformation potential term, $P_c(z)$, is assumed equal to $P_c(z) = a^c(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$ inside the well region and $P_c(z) = 0$ inside the barrier region. a^c is the conduction band deformation potential constant to be determined. If the barrier width of the QWs is large, the energy dispersion $E_n^c(\mathbf{k})$ in the calculation can be approximated by $E_n^c(k_x, k_y)$ as the dependence of $E_n^c(\mathbf{k})$ on k_z is insignificant.

Figure 3.1: Schematic diagram of a $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QW with the lowest energy subbands. Excitons transition energy, E_X (where $X = \text{A}, \text{B}, \text{or C}$) and binding energy, $E_{X,\text{bind}}$ are also shown in the figure.

Based on a 6-band $\mathbf{k.p}$ Hamiltonian, the QWs valence holes state can be described by⁷¹

$$\Psi_{m,k}^v(z) = \sum_{j=-6} \phi_m^{(j)}(z, \mathbf{k}) |u_j\rangle \quad (3.13)$$

The basis set, $|u_{1-6}\rangle$, for the valence bands are chosen to be

$$\begin{aligned} |u_1\rangle &= -\frac{1}{\sqrt{2}}|X+iY, \uparrow\rangle, |u_2\rangle = \frac{1}{\sqrt{2}}|X-iY, \uparrow\rangle, |u_3\rangle = |Z, \uparrow\rangle, \\ |u_4\rangle &= \frac{1}{\sqrt{2}}|X-iY, \downarrow\rangle, |u_5\rangle = -\frac{1}{\sqrt{2}}|X+iY, \downarrow\rangle, |u_6\rangle = |Z, \downarrow\rangle. \end{aligned} \quad (3.14)$$

where $|X\rangle$, $|Y\rangle$, and $|Z\rangle$, are the Bloch functions at the Γ point transforming like the p_x , p_y and p_z atomic wavefunctions, respectively. The envelope function of valence band holes of the QWs is evaluated by diagonalizing

$$\sum_{j=1}^6 (H_{jj}^v + \delta_{jj} V_v(z)) \phi_m^{(j)}(z, k) = E_m^v(z, k) \phi_m^{(j)}(z, k) \quad (3.15)$$

where $j' = 1, 2, \dots, 6$, m indexes the valence subbands and $V_v(z)$ is the potential profile of the unstrained valence-band energy. Strain-induced band-edge shifts in the well are accounted in the diagonal terms of the Hamiltonian $H_{jj'}^v$. The 6-dimensional envelope functions, $\phi_m^{(j)}(z, \mathbf{k})$ are described by

$$\phi_m^{(j)}(z, \mathbf{k}) = e^{i(k_x x + k_y y)} \sum_p a_{m,p,k_x,k_y}^{(j)} \frac{1}{\sqrt{L}} e^{i(k_z + p \cdot (2\pi/L))z} \quad (3.16)$$

3.2.2 Result and Discussion

In this section, we first analyze the electronics band structures of wurtzite ZnO calculated using EPM. From EPM calculation, the 8 parameters of atomic pseudopotential form factors for Zn and O atoms were calculated with Schluter's formula and the electronics band structures of wurtzite ZnO was then calculated. The Zn and O form factors were deduced by iteration of fitting process between the calculation and the experimental data. Subsequently, 6-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian was used to fit the three top most valence bands which have been calculated using EPM with SO coupling. Effective mass parameters of 6-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian were then extracted from the fitting. Based on the 6-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, the valence band structures of $Mg_xZn_{1-x}O/ZnO$ QWs were then studied for different well width and Mg mole fraction.

Compared to zinc-blende semiconductors, wurtzite semiconductors have more complicated band structures due to lack of inversion symmetry. For wurtzite ZnO, the crystal field and SO splitting energies lead to a three edge structure near the top of the valence band known as A- Γ_7 , B- Γ_9 , and C- Γ_7 holes from top to bottom. This assignment of states differs from the usual GaN wurtzite crystals (i.e., A- and B- states

Chapter 3: Investigation of Excitonic Optical Gain in $Mg_xZn_{1-x}O/ZnO$ Quantum Wells

have Γ_9 and Γ_7 symmetries, respectively). This is because the presence of Zn 3d band induces negative spin-orbit split-off energy in ZnO.⁴⁴ This energy is given as

$$E_A(\Gamma_7) - E_B(\Gamma_9) = -\frac{\Delta_{so} + \Delta_{cf}}{2} + \frac{\sqrt{(\Delta_{so} + \Delta_{cf})^2 - \frac{8}{3}\Delta_{so}\Delta_{cf}}}{2} \quad (3.17a)$$

$$E_A(\Gamma_7) - E_C(\Gamma_7) = \sqrt{(\Delta_{so} + \Delta_{cf})^2 - \frac{8}{3}\Delta_{so}\Delta_{cf}} \quad (3.17b)$$

For ZnO, the experimental data gives $E_A - E_B = 0.0024$ eV, and $E_C = 0.0404$ eV as obtained from low temperature two photon absorption (TPA) measurement.⁷² Solving equations (3.17a) and (3.17b) using the experimental data, we have the crystal field splitting energy $\Delta_{cf} = 0.0391$ eV and SO splitting energy $\Delta_{SO} = -0.0035$ eV. By comparing the calculated energy bands with previous theoretical result^{73, 74} and experiment,^{72, 75} as shown in Table 3.1, we obtained that the Zn atom pseudopotential parameters v_1 - v_4 in equation (3.3) are 0.11003, 1.79208, 0.7708, and 4.25370, respectively. For the O atom v_1 - v_4 parameters, we obtained 0.19629, 4.90951, 1.24475, and 3.60095, respectively. The lattice constant, a and c of ZnO used in our calculation are 3.25 Å and 5.21 Å, respectively.

Table 3. 1: Band-edge energies at Γ point, crystal field and spin-orbit splitting energies for wurtzite ZnO

	Present work without SO	Present work with SO	Experimental results	Other calculation results
E_g (eV)	3.4421	3.4409	3.44 ⁷²	0.93(LDA) ⁷⁶ , 4.23(GW) ⁷⁶ , 3.437 ⁴⁴
E_A (eV)	0	0	0	0
E_B (eV)	0	-0.0023	-0.0024 ⁷²	-0.013 ⁴² , -0.010 ⁴⁴
E_C (eV)	-0.0391	-0.0406	-0.0404 ⁷²	-0.018 ⁴² , -0.044 ⁴⁴
Δ_{cf} (eV)	0.0391	0.0391	0.188 ⁷⁷	0.027 ⁴² , 0.040 ⁷⁸ , 0.038 ⁴⁴
Δ_{so} (eV)	0	-0.0035	-0.0035 ⁷⁷	-0.019 ⁴² , -0.007 ⁷⁸ , -0.00915 ⁴⁴ , -0.01359 ⁴⁴

Based on these obtained Schluter's parameters v_1-v_4 , the atoms pseudopotential form factors $V(q)$ as a function of q for Zn and O in ZnO are calculated and shown in figure 3.2. We can see that the O atom has a deeply negative potential well and the Zn atom has large positive potential well.

Based on the deduced form factors and taking into account the SO interaction, the energy bands of ZnO can be calculated by EPM. The SO parameters $\alpha = 0.0842$ and $\mu = 0.1336$ are used in our calculations. μ is an adjustable parameter, α is the ratio of SO splitting of the free anion atom to that of the free cation atom. Figure 3.3 shows the band structures of wurtzite ZnO including SO interaction.

Figure 3.4 shows the valence band structures of ZnO materials obtained from EPM calculation with SO coupling taken into consideration and fitted with 6-band $k.p$ Hamiltonian. The ordering of ZnO valence band symmetry is assigned to be A-state (Γ_7 symmetry), B-state (Γ_9 symmetry) and C-state (Γ_7 symmetry) in descending

Figure 3.2: Form factors of the atom pseudopotentials for Zn and O.

order.^{28,44} The symmetry at the valence band-edge in the spin-orbit coupled states is defined by the Bloch basis function, $|u_j\rangle$ ($j = 1, 2, \dots, 6$). Based on these basis functions, the A- and C- states are formed by a mixture of $|u_2\rangle$ and $|u_3\rangle$ states ($|u_5\rangle$ and $|u_6\rangle$ states for the degenerate state) whereas the B-state is only composed of the $|u_1\rangle$ ($|u_4\rangle$) state. The difference between the A- and C-states is that the A-state is dominated by $|u_2\rangle$ ($|u_5\rangle$) state whereas the C-state is comprised mostly of $|u_3\rangle$ ($|u_6\rangle$) state. These different compositions, as shown later in the next section on optical gain calculation, affect the exciton's optical transition polarization properties formed by the conduction band electron with the A-, B- or C- holes states due to the symmetry of the wavefunctions properties.

The effective mass parameters can be extracted from the EPM calculation of the valence band structures by using least square fitting method. We adjust the 6-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian effective mass parameters to obtain the best-fitted results without

Figure 3.3: Band structures of wurtzite ZnO including SO interaction.

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

biaxial strain taken into consideration. Figure 3.4 shows the fitting of the valence band structures and the deduced effective mass parameters, together with other parameters used for the calculations are listed in Table 3.2. Our calculations of the effective mass parameters are found in agreement with previously reported results.⁴⁴

Table 3.2: Parameters for calculation of the valence subbands in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs

Parameters	ZnO	$\text{Mg}_x\text{Zn}_{1-x}\text{O}$
Lattice constant (Å)		
a	3.250 ⁷⁹	$3.250 + 0.036x$ ⁷⁹
c	5.213 ⁷⁹	—
Energy parameters		
E_g (eV) @ 300 K	3.42 ⁸⁰	$3.42 + 2.00x$ ⁸⁰
$\Delta_1 (= \Delta_{cr})$ (meV)	39.10	—
Δ_{so} (meV)	−3.50	—
$\Delta_2 = \Delta_3 = \Delta_{so}/3$ (meV)	−1.17	
Conduction-band effective mass (m_0)		
$m_e^{\parallel}$	0.24	
$m_e^{\perp}$	0.24	
Valence-band effective mass parameters		
A_1	−6.68036 (our work)	
A_2	−0.45388 (our work)	
A_3	6.12750 (our work)	
A_4	−2.70374 (our work)	
A_5	−2.76690 (our work)	
A_6	−4.62566 (our work)	
Deformation potentials (eV) ⁸¹		
D_1	−2.66	
D_2	2.82	
D_3	−1.34	
D_4	1.00	
D_5	0.00	
D_6	0.00	
Elastic stiffness constants (GPa) ⁸²		
C_{13}	105.1	
C_{33}	210.9	

The in-plane valence band dispersion curves of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ strained QWs are calculated using the 6-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian including the biaxial strain effect. The in-plane lattice constant of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ is $a(\text{Mg}_x\text{Zn}_{1-x}\text{O}) = 3.250 + 0.036x$.⁷⁹ The band gap of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, is assumed to be $E_g(\text{Mg}_x\text{Zn}_{1-x}\text{O}) = 3.42 + 2.00x$.⁸⁰ In our

Figure 3.4: ZnO valence bands computed by EPM (solid squares) and 6 band $k.p$ Hamiltonian (dashed lines) calculation for the case without biaxial strain. The three hole-bands, which are A-state (Γ_7 symmetry), B-state (Γ_9 symmetry) and C-state (Γ_7 symmetry), are indicated from top to bottom.

calculation, we assume that the effective mass parameters are the same for ZnO well and MgZnO barrier. The band offset ratio is taken as 60/40 for conduction band over valence band which will be justified in the next section. Assuming that the barrier material and the substrate are the same, there is no strain in the barrier region. Hence, only the ZnO well will experience strain due to the barrier.

The analysis of the valence bands energy dispersion for $15\text{\AA}$ well width and $100\text{\AA}$ barrier width of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is plotted in figure 3.5. The calculated energy dispersion for the QWs without biaxial strain effect is also included in the figure for comparison. Mole fractions of Mg with $x=0.12$ and 0.27 , are used in the

Figure 3.5: In-plane valence bands energy dispersion of 15 Å well width and 100 Å barrier width $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $x = 0.12$ and 0.27 . Solid (dashed) lines are the calculation with (without) the influence of biaxial strain.

calculation. The amount of Mg in the QWs affects different potential barrier heights and biaxial strains on the valence subbands. To label the subbands, we follow the bulk ZnO notation of A-, B-, and C-hole states at the Γ point with the subbands level indices, $m = 1, 2, 3, \dots$. From our calculation, it is showed that the A1 hole composition is mostly of $|u_2\rangle (|u_5\rangle)$ state (with probability > 0.998) and small part of $|u_3\rangle (|u_6\rangle)$ state (with probability < 0.002) for both of $x=0.12$ and $x=0.27$ cases. B1 is purely consist of $|u_1\rangle (|u_4\rangle)$ state at $k = 0$.

Figure 3.6 shows the valence subbands of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with Mg mole fraction of $x = 0.2$ and well width varied from 40, 60, and 80 Å, respectively. The

Figure 3.6 In-plane valence bands energy dispersion of (a) 40, (b) 60 , and (c) 80 Å well width and 100 Å barrier width of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $x = 0.2$.

barrier width is fixed about 100 Å. The quantum size effect (QSE) incorporated with the biaxial strain is clearly observed. When the well width is 80 Å, the valence subbands are very close together. With reducing well width, the valence subbands start to move away from each other. However, the pair of A_i - B_i ($i = 1, 2, 3, \dots$) is clearly seen still close which indicated that the biaxial strain effect is not significant to repel the A_i and B_i subbands to move away from each other.

3.3 Excitonic Optical Gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

3.3.1 Theory

In wurtzite ZnO semiconductors, the excitonic states still exist even at high temperature. Therefore, it is necessary to have a model that can describe this interaction with optical transition. Furthermore in ZnO bulk and QWs materials, the

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

interaction between exciton and phonon is found significant due to the polar nature of ZnO. It has been shown that the exciton binding energy in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is greatly enhanced by exciton-phonon interaction.⁶¹ This is because the strong confinement of longitudinal phonons enhances the coupling between excitons and phonons inside the QWs. However, the analysis of exciton-phonon coupling in QWs using three phonon modes (i.e., at the well, barrier and their interface) is very complicated.⁸³ Therefore, we simplified the calculation by considering the exciton-bulk phonon interaction to approximate the total interaction of exciton with all the phonon modes.^{84,85} This is possible because the exciton-bulk phonon interaction can be correctly described by the Coulomb interaction using the Pollmann-Büttner potential.⁶⁰

Based on the above assumption, the exciton Hamiltonian, H_X , in the center mass coordinate system at the Γ point is given by^{86,87}

$$H_X = H_e + H_h - \frac{\hbar^2 \nabla^2}{2\mu} + V_{PB} \quad (3.18)$$

where $H_e (= H^c + V_c)$ and $H_h (= H^v + V_v)$ are the electron and hole Hamiltonians at the Γ point, respectively, without Coulomb interaction. The 3rd term on the right-hand-side of (3.18) represents the kinetic energy of electrons and holes. V_{PB} , which takes into account of the exciton-phonon interaction, is the Pollmann-Büttner potential. V_{PB} can be written explicitly as⁶⁰

$$V_{PB}(r) = -\frac{e^2}{4\pi\epsilon_s\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right) \\ \times \left[\frac{C^4}{B^4} - \frac{m_e h_1}{\Delta m} e^{-rA_1/R_1} + \frac{m_h h_2}{\Delta m} e^{-rA_2/R_2} - \left(h_\mu + \frac{C^3 r}{2B^3 a_{exc}} \right) e^{-rB/R_\mu} \right] \quad (3.19)$$

Chapter 3: Investigation of Excitonic Optical Gain in $Mg_xZn_{1-x}O/ZnO$ Quantum Wells

$$\begin{aligned}
 R_1 &= \sqrt{\frac{\hbar}{2m_e\omega}}, \quad R_2 = \sqrt{\frac{\hbar}{2m_h\omega}}, \quad R_\mu = \sqrt{\frac{\hbar}{2\mu\omega}}, \\
 A_1^2 &= 1 + \frac{R_1^2}{a_{exc}^2}, \quad A_2^2 = 1 + \frac{R_2^2}{a_{exc}^2}, \quad B^2 = 1 + \frac{R_\mu^2}{a_{exc}^2}, \quad C^2 = \frac{R_\mu^2}{a_{exc}^2}, \\
 h_1 &= 1 + \left(\frac{m_h R_1}{m_e a_{exc}} \right)^2, \quad h_2 = 1 + \left(\frac{m_e R_2}{m_h a_{exc}} \right)^2, \quad h_\mu = \frac{C^4}{B^4} - \left(\frac{m_e}{m_h} + \frac{m_h}{m_e} \right) C^2, \\
 \Delta m &= m_h - m_e, \quad r = \sqrt{(z_e - z_h)^2 + \rho^2}, \tag{3.20}
 \end{aligned}$$

where m_e is the bulk electron effective mass, m_h (for A-, B-, or C- valence bands) is the bulk hole effective mass, μ is the bulk exciton reduced effective mass, and a_{exc} is the bulk exciton Bohr's radius. ϵ_s ($= 8.1$) is the static dielectric constant, ϵ_∞ ($= 4.0$) is the high frequency dielectric constant and $\hbar\omega$ ($= 72$ meV) is the LO phonon energy.⁶¹

For anisotropic crystal like ZnO, we can relate the effective mass parameters and the holes effective masses for the parallel and perpendicular effective mass to the in-plane direction as follows⁸⁸

$$\begin{aligned}
 m_A^\parallel &= -(A_2 + A_4 + A_5)^{-1}, \quad m_A^\perp = -(A_1 + A_3)^{-1}, \\
 m_B^\parallel &= -(A_2 + A_4 - A_5)^{-1}, \quad m_B^\perp = -(A_1 + A_3)^{-1}, \\
 m_C^\parallel &= -A_2^{-1}, \quad m_C^\perp = -A_1^{-1}. \tag{3.21}
 \end{aligned}$$

It is noted that the effective masses of A- and B- holes given above are different to that in ref. 88. This is because the arrangement of the valence bands symmetry of A- and B-holes in ZnO is in reverse order to that of the GaN. The calculated hole effective masses are tabulated in Table 3.3. The exciton reduced effective mass in the direction parallel (perpendicular) to the in-plane direction is given as

$$\frac{1}{\mu_i^\parallel (\mu_i^\perp)} = \frac{1}{m_e^\parallel (m_e^\perp)} + \frac{1}{m_{h,i}^\parallel (m_{h,i}^\perp)}, \quad \text{where } m_e^\parallel (m_e^\perp) \text{ is the parallel (perpendicular)}$$

Chapter 3: Investigation of Excitonic Optical Gain in $Mg_xZn_{1-x}O/ZnO$ Quantum Wells

electron effective mass, $m_{h,i}^{\parallel}$ ($m_{h,i}^{\perp}$) is the parallel (perpendicular) holes effective mass

and $i = A, B$, or C . Hence, the bulk exciton reduced effective mass is then given as

$$\mu_i = \sqrt{\mu_i^{\parallel} \mu_i^{\perp}}^{89} \text{ and the bulk exciton Bohr's radius can be written as } a_{exc}^i = \frac{4\pi\epsilon_s\epsilon_0\hbar^2}{e^2\mu_i}$$

for the i^{th} excitons. The bulk electron and holes effective masses are then given by

$$m_e = \sqrt{m_e^{\parallel} m_e^{\perp}} \text{ and } m_{h,i} = \sqrt{m_{h,i}^{\parallel} m_{h,i}^{\perp}}, \text{ respectively.}$$

Table 3.3: Hole effective masses of wurtzite ZnO.

Hole effective mass (m_0)	
$m_A^{\parallel}$	0.17
$m_A^{\perp}$	1.81
$m_B^{\parallel}$	2.56
$m_B^{\perp}$	1.81
$m_C^{\parallel}$	2.20
$m_C^{\perp}$	0.15

As the optical properties of ZnO materials are determined by the optical transition at the centre of Brillouin zone, Γ , the exciton states at Γ point can be analyzed by variational method. This can be done by using a trial function, Ψ ^{86, 87}

$$\Psi = \varphi_n(z)\phi_m(z)\psi(\rho), \quad (3.22)$$

$$\psi(\rho) = (2/\pi)^{1/2} \frac{1}{\lambda} \exp(-\frac{\rho}{\lambda}), \quad (3.23)$$

where $\varphi_n(z)$ and $\phi_m(z)$ are the electron and hole envelope functions, respectively, without Coulomb interaction. $\psi(\rho)$ is the trial wavefunction for 1s bound exciton, ρ is

the in-plane coordinate and λ is the trial parameter. If the exciton transition energy, $E_X(\lambda)$, can be minimized with suitable selection of λ using^{86, 87}

$$\begin{aligned} E_X(\lambda) &= \min \frac{\langle \Psi | H_X | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &= (E_g + P_c) + E_n^c(0) + E_m^v(0) + E_{X,bind}(\lambda) \end{aligned} \quad (3.24)$$

We can deduce the realistic value of E_X . In (3.24), E_g is the band gap of ZnO well, $E_n^c(0)$ and $E_m^v(0)$ are the eigenvalues of conduction and valence bands at Γ point, respectively and $E_{X,bin}(\lambda)$ is the binding energy calculated by the variational method. The binding energy of different X (related to A, B, or C hole bands) corresponds to the ground state energy of A-, B- or C-excitons.

To calculate the excitonic gain, we assumed that the total optical gain of the ZnO QWs is contributed by the bound exciton and continuum states. We can calculate the bound exciton states by using the variational method. For the continuum states, the calculation is assumed to be similar to that of the band-to-band transition calculation with the inclusion of Sommerfeld's enhancement factor. The momentum matrix element for the band-to-band transition of ZnO QWs is given by⁷¹

$$\mathbf{M}_{nm}(k_x, k_y) = \langle \Psi_{m,k_x,k_y}^v | \hat{p} | \Psi_{n,k_x,k_y}^c \rangle \quad (3.25)$$

where we have neglected the dispersion in the k_z direction. The momentum matrix can be resolved into TE polarization and can be written as

$$\begin{aligned} \hat{x} \cdot \mathbf{M}_{nm}(k_x, k_y) &= \langle \Psi_{m,k_x,k_y}^v | \hat{p}_x | \Psi_{n,k_x,k_y}^c \rangle \\ &= \langle S | \hat{p}_x | X \rangle \cdot \sum_p \frac{1}{\sqrt{2}} \left(-a_{m,p,k_x,k_y}^1 + a_{m,p,k_x,k_y}^2 + a_{m,p,k_x,k_y}^4 - a_{m,p,k_x,k_y}^5 \right) g_{n,p,k_x,k_y}^* \end{aligned} \quad (3.26a)$$

Chapter 3: Investigation of Excitonic Optical Gain in $Mg_xZn_{1-x}O/ZnO$ Quantum Wells

For TM polarization, the momentum matrix can be expressed as

$$\begin{aligned}\hat{z} \cdot \mathbf{M}_{nm}(k_x, k_y) &= \langle \psi_{m,k_x,k_y}^v | \hat{p}_z | \psi_{n,k_x,k_y}^c \rangle \\ &= \langle S | \hat{p}_x | Z \rangle \cdot \sum_p (a_{m,p,k_x,k_y}^3 + a_{m,p,k_x,k_y}^6) g_{n,p,k_x,k_y}^* \end{aligned} \quad (3.26b)$$

In (3.26), the band-edge momentum matrix elements, $\langle S | \hat{p}_x | X \rangle$ and $\langle S | \hat{p}_z | Z \rangle$ for the wurtzite structure, are given as ⁷⁰

$$|\langle S | \hat{p}_x | X \rangle|^2 = \frac{m_0}{2} \left(\frac{m_0}{m_e^\parallel} - 1 \right) \frac{E_g [(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - 2\Delta_3^2]}{(E_g + \Delta_1 + \Delta_2)(E_g + \Delta_2) - \Delta_3^2}, \quad (3.27)$$

$$|\langle S | \hat{p}_z | Z \rangle|^2 = \frac{m_0}{2} \left(\frac{m_0}{m_e^\perp} - 1 \right) \frac{[(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - 2\Delta_3^2]}{(E_g + 2\Delta_2)}. \quad (3.28)$$

Hence, the excitonic gain of the bound exciton states, g_{bound} , at Γ point can be expressed as ^{90, 91}

$$g_{bound}(E) = \frac{2e^2 \pi \hbar}{n_r c \epsilon_0 m_0^2 L_w E} \left| \sum_X \psi_X(\rho=0) I_{nm} \hat{e} \cdot \mathbf{M}_{nm}(0) \right|^2 \frac{1}{\pi} \frac{\hbar / \tau}{(E_X - E)^2 + (\hbar / \tau)^2} (f_n^c + f_m^v - 1) \quad (3.29)$$

and that of the continuum states, g_{cont} , is given by

$$g_{cont}(E) = \frac{e^2 \pi \hbar}{n_r c \epsilon_0 m_0^2 L_w E} S(E) \sum_{nm} \iint \frac{dk_x dk_y}{(2\pi)^2} |\hat{e} \cdot \mathbf{M}_{nm}(k_x, k_y)|^2 \frac{1}{\pi} \frac{\hbar / \tau}{(E_{nm} - E)^2 + (\hbar / \tau)^2} (f_n^c + f_m^v - 1) \quad (3.30)$$

where $n_r (=2.1)$ is the refractive index of ZnO, c is the speed of light in free space, ϵ_0 is free space permittivity, e is the electron charge and, E_{nm} is the band-to-band transition energy equal to $E_{nm}(k_x, k_y) = (E_g + P_c) + E_n^c(k_x, k_y) + E_m^v(k_x, k_y)$. I_{nm} is the overlap integral for electron and hole, $\hat{e}$ is the electric field polarization vector (TE or TM) and $S(E)$ is the Sommerfeld's enhancement factor⁹⁰. Comparing to ref. 91, our expression of optical gain in the continuum states gain is differed by a Sommerfeld's enhancement factor. To account of the broadening effect, we have assumed a

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

Lorentzian function with broadening lifetime τ of 0.1 ps. The Fermi function for electron, f_n^c , and that for hole, f_m^v , can be expressed as ⁷¹

$$f_n^c(k_x, k_y) = \left[1 + \exp\left(\frac{E_n^c(k_x, k_y) - F_c}{k_B T}\right) \right]^{-1}, \quad (3.31a)$$

$$f_m^v(k_x, k_y) = \left[1 + \exp\left(\frac{E_m^v(k_x, k_y) - F_v}{k_B T}\right) \right]^{-1}, \quad (3.31b)$$

where k_B is the Boltzmann constant and T ($= 300\text{K}$) is the temperature. F_c and F_v is the Fermi level in conduction and valence bands respectively. It must be noted that the values of F_c and F_v are dependent on the amount of external injection of carrier concentration. n_s and p_s , which are defined as the surface carrier injection density (in cm^{-2}) of electrons for the conduction bands and holes for the valence bands, respectively, can be expressed as ⁷¹

$$n_s = \frac{m_e^* k_B T}{\hbar^2 \pi} \sum_n \ln \left[1 + \exp\left(\frac{F_c - E_n^c(0)}{k_B T}\right) \right], \quad (3.32a)$$

$$p_s = \sum_m \iint \frac{1}{4\pi^2} (1 - f_m^v(k_x, k_y)) dk_x dk_y. \quad (3.32b)$$

3.3.2 Result and Discussion

In this section, the excitonic transition energy is analyzed and compared to experimental data. In the calculation, conduction band deformation potential and band gap offset ratio are assumed adjustable parameters. Subsequently, the excitonic optical gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs is deduced for different Mg mole fraction. Finally, a linear relationship between transparency surface carrier density and differential gain is calculated.

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

We analyze the excitonic transition energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs by the variational method. As mentioned in ref. 61, the effect of exciton-phonon coupling in ZnO gives a more accurate calculation of exciton binding energy. However, their calculations have neglected the influence of biaxial strain between the well and barriers of the QWs. In figure 3.7, we calculated the excitonic transition energies for the Mg mole fraction $x=0.12$ and $x=0.27$ of the ZnO QWs with the effect of biaxial strain taken into consideration. The effect of overlapping between the lowest states of A1- and B1-exciton peaks, which cannot be resolved due to very close energy separation, is also considered in the calculation. Our calculations are then compared with that given in ref. 61 and experimental result given in ref. 59. In our calculations,

Figure 3.7: Excitonic transition energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs for (a) $x = 0.27$ and (b) $x = 0.12$ Mg mole fraction as a function of well width. Solid (dashed) lines are the calculation with (without) the influence of biaxial strain. It is noted that the computed results of excitonic transition energy given in ref. 61 are similar to our calculation without biaxial strain (i.e., dashed lines). Experimental data (solid squares) obtained from ref. 59 is also plotted in the figure. The inset shows the resulting peak position as a consequence of A1- and B1-excitons overlapping.

Chapter 3: Investigation of Excitonic Optical Gain in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells

the band offset ratio and the conduction deformation constant are the adjustable parameters, which allowed to be changed in order to match with the experimental results. The values of band offset ratio and conduction deformation constant are found to be 60/40 and -6.8 eV, respectively, by fitting the calculated excitonic transition energies to the experimental results as shown in figure 3.7.

It is noted that the band offset ratio deduced from ref. 61 is 60/40 and the conduction deformation constant recorded from ZnO nanowires is -6.05 eV.⁹² This indicated that our calculation results are consistent with the available data reported in the literatures. It is observed from figure 3.7 that the inclusion of biaxial strain, which decreases the conduction-band energy of the ZnO well as well as increases $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ potential barrier, has lowered the exciton transition energy in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs. In addition, the increase of well width will further decrease the energy level of the confined excitons. We have shown that the biaxial strain in the QWs affects the excitonic transition energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs and therefore it is important to include such effects into the computation.

In order to deduce the optimum well width for the maximum peak gain of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs, we calculate the corresponding oscillator strength. The oscillator strength, f_x , is defined as⁹³

$$f_x = \frac{2}{m_0 E_x} \left| \sum_x \psi_x(\rho=0) I_{nm} \hat{e} \cdot \mathbf{M}_{nm}(0) \right|^2. \quad (3.33)$$

It must be noted that due to the symmetry properties of the wurtzite ZnO crystals, A- and B-excitons transition will mainly contribute to the excitonic gain in TE polarization. Furthermore, the influence of C-exciton transition is ignored in our investigation, as it is far away from the valence band maximum. Therefore, only the

Figure 3.8: Total oscillator strength of A1- and B1-excitons of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs for $x = 0.12$ and 0.27 as a function of well width. The optimum value of $L_w = 15 \text{\AA}$ is observed for a wide range of Mg mole fraction.

transitions of A- and B-excitons, which are mainly of TE polarization, were taken into calculation. Figure 3.8 shows the total oscillator strength per unit area of the lowest state of A1- and B1-excitons for $x=0.12$ and $x=0.27$ with the inclusion of biaxial strain. The optimum well width is found to be $15 \text{\AA}$ for a wide range of Mg mole fraction. The existence of an optimum well width is attributed to the electronic confinement of excitons, which is dependant on the amount of overlapping between the electron and hole wave functions.

Figure 3.9 plots the corresponding peak excitonic gain versus surface carrier density for the range of x . The solid (dashed) lines represent the calculation with (without) the influence of biaxial strain taken into consideration. As expected, the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs exhibited large excitonic gain (in order of 10^5 cm^{-1}), which is

Figure 3.9: Peak excitonic gain versus surface carrier density of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs for x varies from 0.05 to 0.30 and $L_w = 15\text{Å}$. Solid (dashed) lines are the calculation with (without) the influence of biaxial strain. The inset shows the gain spectra versus surface carrier density of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $x = 0.12$ and $L_w = 15\text{Å}$.

an order higher than that of the GaN-based QWs. For $x = 0.05$, it is observed that biaxial strain has negligible effect on the peak gain due to small lattice mismatched between ZnO and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$. For $x > 0.05$, the peak gain (threshold surface carrier density) is increased (reduced) due to the presence of biaxial strain. The biaxial strain induces the enhancement of 1) excitonic confinement inside the QWs and 2) the density of states of the first conduction band so that the peak excitonic gain is improved for the increase of x . The inset of figure 3.9 shows the gain spectra versus surface carrier density of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $x = 0.12$. The redshift of gain spectra indicates the importance of the consideration of the biaxial strain. The expression of Mott's density of the QWs can be written as⁹⁴,

$$n_{\text{mott}} = (\pi a_{\text{exc}}^2)^{-1} \text{ (cm}^{-2}\text{)} \quad (3.34)$$

where a_{exc} ($\sim 20 \text{ \AA}$) is Bohr's radius of excitons. For our $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs, the corresponding Mott's density is found to be $\sim 79 \times 10^{11} \text{ cm}^{-2}$, which is well above the surface carrier density used in our calculations. Hence, neglecting of electron hole plasma recombination in the calculation of MgZnO/ZnO QWs is valid.

From figure 3.9, we can approximate the low-injection excitonic peak gain, g ($= g_b(E_X) + g_c(E_X)$) by a linear expression, $g = g_N(N - N_0)$, where g_N is defined as differential gain constant, N is the injected surface carrier density and N_0 is the surface carrier density at transparency. Figure 3.10 plots the dependence of g_N and N_0 on the

Figure 3.10: The dependence of differential gain constant, g_N and transparency surface carrier density, N_0 , of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $L_w = 15 \text{ \AA}$ versus the mole fraction of Mg. Solid (dashed) lines are the calculation with (without) the influence of biaxial strain.

value of x for the $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs with $L_w = 15\text{\AA}$. The value of $g_N(N_o)$ increases (decreases) with increasing values of x and saturates for $x > 0.27$. Increasing values of x improve the electronic confinement due to greater potential barrier. However, the enhancement of electronic confinement becomes saturated for $x > 0.27$ therefore this causes the saturation of the excitonic gain.

3.4 Summary

In summary, the electronics band structures of wurtzite ZnO have been calculated using EPM. The parameters of the Zn and O atoms pseudopotential form factors were obtained by fitting with experimental data. The calculated band gap, the crystal field splitting energy, and the SO splitting energy were found to be 3.4409 eV, 0.0391 eV, and -0.0035 eV, respectively. These correspond to the band-edge energies $E_A = 0$, $E_B = -0.0023$ eV, and $E_C = -0.00406$ eV. The calculated results were found in good agreement with the experimental results. The A_{1-6} effective masses parameters from 6-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian have also been obtained by fitting from the EPM result.

The excitonic gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs has also been investigated theoretically. The influence of biaxial strain and exciton-phonon interaction was taken into consideration. The band offset ratio and conduction band deformation constant were also extracted from the experimental data. Hence, the influence of biaxial strain on the peak excitonic gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs was investigated. It is found that the excitonic gain can be maximized for x varies between 0.27 and 0.30 if well width is chosen to be $15\text{\AA}$. For $x > 0.30$, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ will change phase to cubic structure so that the value of x larger than 0.30 is not considered.

Chapter 4

Excitonic Recombination and Random Lasing in Highly Disordered ZnO Polycrystalline Films

4.1 Introduction

Room-temperature (RT) stimulated emission has been demonstrated from ZnO polycrystalline thin films under optical excitation.^{46,53,95,96} Radiative recombination due to exciton-exciton scattering (EES) at ~390 nm and electron hole plasma (EHP) at ~395 nm can be observed from ZnO thin films that have undergone different fabrication processes.^{46, 95, 96} Free-exciton (FE) radiative recombination at ~380 nm has also been reported in ZnO microclusters (agglomerated by 50 nm nanocrystallites)⁹⁷ and nanowires.⁹⁸ ZnO thin films deposited on sapphire, silicon, and fused silica substrates have shown UV excitonic lasing at RT under optical excitation. With binding energy of ~60 meV, it is also expected that ZnO films can also sustain excitonic lasing at high temperature.⁴⁶ Recent studies of ZnO epilayers have observed spontaneous emission from FE radiative recombination as well as stimulated emission from EES and EHP radiative recombination at temperature up to ~550 K.⁴⁶ ZnO nanosheets can also sustain photoluminescence (PL) at ~870 K.⁹⁹ These studies have suggested the potential of using ZnO to fabricate high-temperature UV excitonic lasers.

However, it has yet been explained how the different mechanisms of radiative recombination can be occurred in ZnO thin films and nanostructures. It must be noted that the understanding of radiative recombination mechanisms is essential for the

design of high-performance ZnO-based optoelectronics devices. Furthermore, investigations on the temperature dependence of stimulated excitonic emission from ZnO films and ZnO/MgZnO superlattices have shown that the corresponding characteristic temperature, which reflects the quality of high-temperature performance of lasers, is less than 90 K in a narrow range of temperature between 294 and 377 K.¹⁰⁰ In order to obtain high-quality excitonic lasing at high temperature, it is necessary to improve the characteristic temperature of the ZnO lasers.

On the other hand, it is observed that the excitation of coherent random lasing in highly disordered ZnO polycrystalline thin films is due to the formation of closed-loop random cavities.⁵³ The selection of high-quality (i.e., low loss and high gain) scattering paths, which controls the size and location of the random cavities, has been suggested to be the formation mechanism.¹⁰¹ Hence, it is concluded that the available size of the random cavities is determined by a critical cavity length¹⁰² and it is strongly related to the material properties of the random media. This conclusion is based on the assumptions that 1) the pump excitation is uniform distributed over the random media and 2) the small diffusion length of carriers has insignificant influence on the profile of optical gain inside the random media, as the excitation area is usually large.^{95,103} However, what will happen if these assumptions are not applicable in some other ZnO random media?

In this chapter, we will investigate the optical properties of wurtzite ZnO polycrystalline films experimentally. Firstly, the influence of strain on the radiative recombination process of highly disordered ZnO polycrystalline films is studied. Strain is introduced through thermal annealing of the ZnO films deposited on Si substrate with different buffer layers. It is found that the strain-dependence of Mott's density⁴¹ is

Chapter 4: Excitonic Recombination and Random Lasing in Highly Disordered ZnO films

attributed to the variation of lasing wavelengths under optical excitation at RT. Furthermore, strained highly disordered ZnO polycrystalline films with nanostructures are proposed to sustain coherent random lasing at high temperature. It is found that the highly disordered ZnO polycrystalline films can achieve lasing up to 570 K and the corresponding characteristic temperature can be as high as 127 K. This is because the formation of 1) ZnO nanostructures prevents the spreading of excited carriers over the pumped region and 2) closed-loop path of light by random laser action allows the size variation of random cavities. Therefore, lasing can be obtained from the highly disordered ZnO polycrystalline films at high temperature.

The formation mechanism of closed-loop random cavities inside ZnO polycrystalline films is also studied. We can show that the excitation pump, which intensity distribution in fact has a Gaussian profile, can modify the optical gain of the random media (i.e., highly disordered ZnO polycrystalline films). This also implies that the size and location of the random cavities can be controlled externally. In addition, the optical gain profile of the random media with rib waveguide structure can be altered especially for carriers with small diffusion length due to the increase of non-radiative recombination at the side of the rib waveguide. Therefore, the formation characteristics of the closed-loop random cavities are not mainly determined by the material properties of the random media.

This chapter is organized as follows: In section 4.2, strain dependence random lasing mechanisms in highly disordered ZnO polycrystalline films is studied. It is followed by the study of high temperature lasing of highly disordered ZnO polycrystalline films in section 4.3. Finally in section 4.4, closed loop formation of

random lasing in highly disordered ZnO polycrystalline films is discussed. Section 4.5 gives the summary of this chapter.

4.2 Strain Dependence Random Lasing Mechanisms in Highly Disordered ZnO Polycrystalline Films

4.2.1 Experimental Procedure

ZnO polycrystalline films were deposited on Si (100) substrate with a ~400 nm thick SiO₂ layer by the FCVA technique as described in appendix A. During the deposition, the substrate temperature and chamber pressure were set to 230 °C and 9×10^{-4} Torr, respectively. In this experiment, two types of samples were fabricated, i.e. sample *a* and sample *b*. Sample *a* had structures of ZnO(100 nm)/SiO₂(400 nm)/Si (substrate) meanwhile sample *b* had structures of ZnO(100 nm)/MgO(200 nm)/ZnO(100 nm)/SiO₂(400 nm)/Si (substrate). In these samples, the top 100 nm-ZnO thin layer with (002) orientation acts as the active layer to provide radiative recombination. In sample *a*, the 400 nm-SiO₂ film is the buffer layer to allow the transverse confinement of light into the active layer. Similarly in sample *b*, the MgO (200 nm) film is also a buffer layer. The bottom 100 nm-ZnO layer in sample *b* allows the deposition of high-quality MgO (200 nm) film by the FCVA technique. These as-grown samples were then annealed in open air at 900 °C for 2 hours in a standard Lindberg type furnace using a quartz tube reactor. Hence, highly disordered ZnO polycrystalline films with strain can be formed to sustain random laser action.

The optical characteristics of these samples were studied under optical excitation by a frequency-tripled Nd:YAG laser at excitation wavelength of 355 nm and pulsed operation of 6 ns pulse width and 10 Hz repetition rate. The optical pump

was focused using a cylindrical lens to a stripe of length 5 mm and width 50 μm on the sample surface. The stripe pumping was used to give gain guiding effect as well as to enable edge emission measurement. The laser emission of ZnO films was then measured from the edge of the samples. The spectrum of the emission is resolved using grating monochromator.

4.2.2 Result and Discussion

Figure 4.1 shows the lasing spectra and light-light curves of samples *a* and *b*.

Figure 4.1: Emission spectra of the ZnO films (a) without and (b) with the MgO-buffer. The insets are the light-light curves.

Chapter 4: Excitonic Recombination and Random Lasing in Highly Disordered ZnO films

Based on the samples' structure and random laser theory,^{96,97} the lasing phenomena observed from both samples are due to random laser action. Figure 4.1(a) shows the lasing characteristics of sample *a* with threshold $P_{th} \sim 0.4 \text{ MW/cm}^2$ and lasing peaks around 391 nm. This is due to EES and EHP radiative recombination. At higher excitation intensities above threshold, more sharp peaks are excited and EHP is dominant over the lasing spectrum with peak wavelength at $\sim 395 \text{ nm}$. Furthermore, the increase in pump intensity red-shifts the emission peak to $\sim 400 \text{ nm}$. These lasing characteristics are similar to the previous reports on the ZnO films grown on SiO_2/Si ⁹⁶ and sapphire substrates.^{46,95} Figure 4.1(b) shows the lasing characteristics of sample *b* with threshold $P_{th} \sim 0.34 \text{ MW/cm}^2$. We observed that the lasing peaks emerge at $\sim 380 \text{ nm}$, which is close to the expected energy level of FE radiative recombination in ZnO at RT.⁴⁶ At high pump intensities, FE radiative recombination is still dominant in the lasing spectra. This is because the exciton's density is clamped at the threshold due to the lasing mechanism and the triggering of EHP radiative recombination is suppressed. It is noted that the lasing linewidth is broaden by the overlapping of many individual random lasing modes.

The difference in lasing wavelength between samples *a* and *b* can be attributed to strain (i.e., mismatch in lattice constant and different degree of thermal expansion between the active and buffer layers) induced variation of radiative recombination process in ZnO films. We rule out the possibility that the variation of lasing wavelength is due to the difference in size distribution of random cavities in both samples. This is because from the scanning electron microscopy images as given in figures 4.2(a) and 4.2(b), it is observed that the size distribution of ZnO irregular grains for both samples is similar (i.e., mean diameter of ZnO grains is $\sim 150 \text{ nm}$). This

indicates that the scattering mean-free path of ZnO random cavities of both samples generated by thermal annealing is similar. This is evidenced by the coherent backscattering experiment.

In figure 4.2(c), a typical mud-cracking pattern appears in sample *b*, which implies that the sample is under biaxial in-plane tension.¹⁰⁴ The lattice constant c of samples *a* and *b* is estimated to be 0.5250 and 0.5184 nm, respectively. The strain along the c axis of the films perpendicular to the substrate is defined by $\epsilon_{zz}=(c-c_0)/c_0$ (%), where c_0 (~0.5205 nm) is the lattice constant in the unstrained crystal. ϵ_{zz} for samples *a* and *b* is estimated to be 0.9 % and -0.4 %, respectively. Hence, it is shown that sample *a* is in tensile strain and sample *b* is in compressive strain.

It must be noted that the resonance energy of excitons in strained ZnO films normally blue-shifts with the increase of ϵ_{zz} (from compressive to tensile strain)^{105,106}

Figure 4.2: Scanning electron microscope images of ZnO films (a) without and (b) with the MgO buffer layer. (c) Bird-eye view of (b).

but the lasing peaks from our sample with tensile strain are red-shifted. Furthermore, the difference in resonance energy of excitons (observed from the spontaneous emission spectra) between the samples *a* and *b* is ~10 meV, which is smaller than that reported in refs. 105,106 (i.e., ~ 20 to ~ 30 meV). Therefore, the change in lasing wavelength of our samples cannot be attributed to the strain-induced change of exciton energies and the large difference in lasing energy (i.e., ~120 meV) between samples *a* and *b* is due to the change of radiative recombination process.

It is known that ϵ_{zz} can vary the effective mass of holes, $m_h^{//,\perp}$ ($//$ and $\perp$ denote the direction parallel and perpendicular to the *c*-axis, respectively) and thus, the reduced mass, m_r , as delineated in the equation: $1/m_r^{//,\perp} = 1/m_e^{//,\perp} + 1/m_h^{//,\perp}$, where $m_e^{//,\perp}$ is the effective mass of electron. The change in ϵ_{zz} affects the mechanism of radiative recombination as the Mott's density, n_{Mott} depends on ϵ_{zz} . Therefore, we investigate the strain dependence of the lasing characteristics of the ZnO films on the effective hole-mass of different excitons (i.e., A-exciton of Γ_7 band and B-exciton of Γ_9 band). In the calculation, C-exciton is not considered, as the corresponding oscillator strength is normally weak at RT. The effective hole mass of A- and B- excitons (i.e., $m_A^{//,\perp}$ and $m_B^{//,\perp}$), can be expressed as¹⁰⁷

$$\frac{m_0}{m_A^{//,\perp}} = A_{1,2} + \frac{1}{2}A_{3,4} + \frac{1}{4} \left[\left(\Delta_1 - \Delta_2^{//,\perp} + \left(D_3 - \frac{C_{33}}{C_{13}} D_4 \right) \epsilon_{zz} \right)^2 + 2\Delta_2^{//,\perp 2} \right]^{-1/2} \left[\Delta_1 - \Delta_2^{//,\perp} + \left(D_3 - \frac{C_{33}}{C_{13}} D_4 \right) \epsilon_{zz} \right] A_{3,4} \quad (4.1)$$

$$\frac{m_0}{m_B^{//,\perp}} = A_{1,2} + A_{3,4} \quad (4.2)$$

where m_0 is the free-electron mass, A_{1-4} is the Luttinger parameters, C_{ij} is the components of the elastic stiffness constant, $\Delta_{1,2}$ is the crystal-field splitting energy and

D_{1-4} is the deformation potential constants. It should be noted that the indices A and B in all expressions given in Ref. 107 for GaN are inverted when applied to ZnO due to the inverse order of the upper Γ_7 and Γ_9 subbands.⁴⁴

Figure 4.3(a) plots $m_A^{\parallel,\perp}$ and $m_B^{\parallel,\perp}$ versus ϵ_{zz} . It is shown that $m_A^{\parallel,\perp}$ has a strong

Figure 4.3: The strain ϵ_{zz} dependence of (a) the effective hole mass, m_h , and (b) the Mott's density, n_{Mott} , of the A- and B-exciton in strained ZnO film. The estimated values of exciton density, n_{ex} , for different samples a , b , c , d , and e are also shown in (b).

Chapter 4: Excitonic Recombination and Random Lasing in Highly Disordered ZnO films

correlation with ϵ_{zz} , while $m_B^{//,\perp}$ is independent of ϵ_{zz} . Our calculated values of $m_{A,B}^{//,\perp}$ for the case of strain-free ZnO materials match well with that given in Ref. 44. The Mott's density, n_{Mott} , can be calculated from $n_{\text{Mott}} = m_r^2 e^2 k_B T / 4\pi\hbar^4 \epsilon_r \epsilon_0$,⁴¹ where the anisotropy of the dielectric constant, ϵ_r , and effective mass, m_r , are replaced by $(\epsilon_r^{//} \epsilon_r^{\perp})^{1/2}$ and $(m_r^{\perp} m_r^{//})^{1/2}$, respectively. Figure 4.3(b) plots n_{Mott} versus ϵ_{zz} for A- and B-exciton. It is noted that the n_{Mott} value for B-exciton ($\sim 2.63 \times 10^{19}/\text{cm}^3$) is independent of ϵ_{zz} . For A-exciton, the n_{Mott} value is large for $\epsilon_{zz} \leq 0$ (i.e., compressive strain) and extends to the maximum value of $2.62 \times 10^{19}/\text{cm}^3$ with the decrease in ϵ_{zz} . However, n_{Mott} decreases abruptly with the increase in ϵ_{zz} (i.e., tensile strain) and it reduces to $1.95 \times 10^{19}/\text{cm}^3$ for $\epsilon_{zz} > 3\%$.

From our experiment, it is estimated that sample *a* and *b* has ϵ_{zz} equal to 0.9% and -0.4% respectively. From figure 4.3(b), the values of n_{Mott} of A-exciton for sample *a* (■) and *b* (●) are found to be $\sim 2.39 \times 10^{19}/\text{cm}^3$ and $\sim 2.60 \times 10^{19}/\text{cm}^3$, respectively. The excited exciton density, n_{ex} , of samples *a* and *b* at threshold can be estimated by using the rate equation: $\eta \lambda P_{\text{th}} / d h c \approx n_{\text{ex}} / \tau_{\text{FE}}$ where P_{th} is the pump threshold, λ ($=355$ nm) is the pump wavelength, h is the Planck's constant, c is the velocity of light in vacuum, d (~ 100 nm) is the thickness of active layer, τ_{FE} (~ 0.8 ns) is the radiative lifetime of free-exciton at RT,¹⁰⁸ and η (~ 0.435) is the coupling efficiency. η is deduced by assuming only 87% of light is transmitted into the film and at most 50% of pump intensity is converted into optical gain. It is found that the value of n_{ex} for sample *a* is $\sim 2.49 \times 10^{19}/\text{cm}^3$ (i.e., □ in figure 4.3(b)) which is higher than the calculated n_{Mott} of the A-exciton in the same sample. This implies that the density of photoexcited excitons can easily exceed the relatively low n_{Mott} value for A-exciton, and hence part of the

excitons will transfer to EHP for the radiative recombination process (i.e., lasing spectrum around 395 nm). Consequently, due to the enhancement of the screening Coulomb interaction by the free-carriers from the ionized excitons, all the photoexcited excitons tend to transfer completely to EHP. Therefore, EHP radiative recombination process is dominated in ZnO polycrystalline films with larger tensile strain. On the other hand, it is found that n_{ex} for sample *b* is $\sim 2.12 \times 10^{19} / \text{cm}^3$ (i.e., $\circ$ in figure 4.3(b)) which is smaller than the calculated n_{Mott} of the A-exciton with ϵ_{zz} of -0.4% . This indicates that the high n_{Mott} value for ZnO polycrystalline with compressive strain allows the excitonic state to be sustained and the lasing mechanism is dominated by FE radiative recombination (i.e., lasing at ~ 380 nm).

It is noted that the role of strain in the ZnO polycrystalline films is to determine the mechanism of radiative recombination. Therefore, optical gain of the samples is mainly dependent on the corresponding radiative recombination process. It is observed from figure 4.1 that the optical gain of FE radiative recombination is higher than that of the EHP radiative recombination (i.e. sample *b* has lower threshold than sample *a*). This is expected as the gain of excitonic laser action is known to be much higher than that of EHP lasers.^{46,95} Hence, our explanations on the strain dependence of the lasing characteristics in the ZnO polycrystalline films are consistent.

In order to verify our explanation, lasing characteristics of other annealed ZnO samples with various substrates, sample *c*: ZnO(100 nm)/Zn_xSi_{1-x}O(80 nm)/silicon, sample *d*: ZnO(100 nm)/sapphire, and sample *e*: ZnO(100 nm)/quartz, have been investigated. It is found that the residual strain, ϵ_{zz} , (lasing peaks excited near threshold) of samples *c*, *d*, and *e* are $\sim -0.2\%$, $\sim 0.5\%$ and $\sim 1.3\%$ (~ 386 nm, ~ 388 nm, and ~ 396 nm), respectively. It is estimated that for samples *c* and *d*, the values of n_{ex}

are lower than the calculated values of n_{Mott} of A-exciton. The values of n_{ex} (n_{Mott}) for samples c and d are labeled in figure 4.3 with symbols Δ and ∇ ($\blacktriangle$ and $\blacktriangledown$), respectively. This implied that samples c and d exhibit excitonic lasing and the corresponding wavelength of lasing peaks (~ 386 and ~ 388 nm) has supported our claim. On the other hand, sample e has value of n_{ex} ($\diamond$) higher than the calculated value of n_{Mott} of A-exciton ($\blacklozenge$). This indicates that EHP radiative recombination is the dominant mechanism and this can be justified by the corresponding wavelength of lasing peak (~ 396 nm). Furthermore, it is observed that the gain of samples with FE radiative recombination is higher than that with EHP radiative recombination. Hence, the strain dependence of lasing mechanisms in the ZnO polycrystalline films has been explained and verified.

4.3 High Temperature Random Lasing in Highly Disordered ZnO Polycrystalline Films

4.3.1 Experimental Procedure

Two ZnO polycrystalline films, sample A – ZnO(100 nm)/SiO₂(400 nm)/Si (substrate) and sample B – ZnO(100 nm)/MgO(200 nm)/ZnO(100 nm)/SiO₂(400 nm)/Si (substrate), were fabricated by the FCVA technique. During the deposition, the substrate temperature and chamber pressure were set to 230 °C and 9×10^{-4} Torr, respectively. These as-grown samples were then annealed in open air (900 °C, 2 hours) in a standard Lindberg type furnace using a quartz tube reactor. After annealing, highly disordered closely-packed ZnO grains (with size varying between 100 and 150 nm) were formed on the top ZnO active layer of both samples. It is shown that the top

(002)-oriented ZnO active layer of sample A (sample B) experiences tensile (compressive) strain along the c -axis.⁸⁹

The optical characteristics of these samples were studied under optical excitation by a frequency-tripled Nd:YAG laser (at 355 nm) at pulsed operation (6 ns, 10 Hz). The corresponding laser beam has a Gaussian profile with beam-width of ~4 mm. The pump beam was focused on to the sample surface by using a cylindrical lens to a pump stripe which width has a Gaussian shape with beam-width of ~20 μm . The laser emission was measured from the edge of the samples.

For the heating experiments, the samples were mounted on an electrical ceramic heating element of size $1 \times 1 \text{ cm}^2$ and the temperature is allowed to vary between 300 and 600 K. The heating element was a thermocouple attached into the sample holder. The temperatures of the samples were controlled by the voltage applied to the thermocouple using a DC power supply.

The RT I - V characteristics of sample A before and after annealing were measured by deposition of Ni gate contacts (with thickness ~100 nm and area $\sim 100^2 \mu\text{m}^2$) on the top ZnO layer of the sample. The side-to-side separation of the gate contacts was ~ 200 μm . The contacts were underwent rapid thermal annealing at ~500°C for 2 minutes to achieve ohmic behavior as explained in appendix A.

4.3.2 Result and Discussion

Figure 4.4 shows the lasing spectra versus temperature, T , for the two samples under optical excitation at $\sim 2 \times I_{\text{th}}$, where I_{th} is the pump threshold at the corresponding T . It can be shown that sample A (sample B) demonstrates RT EHP (FE) radiative recombination with the discrete peaks at ~393 nm (~380 nm) and the corresponding

Figure 4.4: Lasing spectra for (a) sample A and (b) sample B at different temperatures, T taken under the excitation intensity of $2 \times I_{th}$, where I_{th} is the pump threshold intensity at T . 'LE' and 'SE' refer to lasing and spontaneous emissions, respectively.

lasing mechanism is attributed to the random laser action.⁸⁹ With the increase of temperature, the shrinkage of bandgap red-shifts the lasing peaks. Furthermore, it is observed that the full-width at half-maximum of the lasing peaks for both samples remains less than 0.4 nm for T up to 570 K. Hence, it is shown that coherent random lasing, which is arisen from the formation of closed-loop paths of lights,¹⁰⁹ can be sustained inside the annealed ZnO polycrystalline films with nanostructures at high T . It is also noted that the lasing intensity is reduced faster than spontaneous emission intensity with increasing temperature.

Figure 4.5 plots the peak energy of lasing 'LE' and spontaneous 'SE' emissions versus T for both samples. The data for temperature-dependent stimulated emission of ZnO film deposited on sapphire (i.e., obtained from ref. 46) is also plotted in figure 4.5 for comparison. It is observed that the 'LE' of sample A ($\blacktriangle$) is red-shifted

Figure 4.5: Energy positions of LE and SE as a function of T for samples A and B. The dashed lines represent the linear fit of the experimental data. The data from Bagnall *et al* is also plotted for comparison.

with T at a rate of -1.03 meV/K for the whole range of T and coincides with that of the EHP emission ($\circ$) observed from the ZnO/sapphire film. Hence, it is shown that EHP lasing is sustained in sample A at high T . On the other hand, the ‘LE’ of sample B ($\triangle$) is red-shifted at a rate -0.94 meV/K for T varying between 300 K and 510 K. However, the slope of the ‘LE’ ($\triangle$) increases to -0.53 meV/K for T larger than 510 K. When comparing with the FE and EES emissions ($\circ$) of the ZnO/sapphire film, it is noted that ‘LE’ ($\triangle$) overlaps with FE (EES) emission for $T < 320$ K (> 500 K). This implies that sample B underwent transition from FE to EES lasing for increase of T from 320 K to 500 K. This is because the probability of collision (scattering) between excitons is

proportional to $T^{1/2}$ and therefore the amount of transition from FE to EES radiative recombination is also increased with T . Hence, the corresponding recombination process for T varying between 320 K and 510 K is a mixture of FE and EES radiative recombination. The transition from FE to EHP lasing, however, has not been observed from sample *B*. This is because although the density of excitons is increased with T , the corresponding Mott's density is also increased,⁴¹ so that the density of excitons is less than the Mott's density at $T < 570$ K.

Figure 4.6 plots the high T emission spectra of samples *A* and *B* versus excitation intensity. As the center lasing wavelength of sample *A* is red-shifted with the increase of optical excitation, EHP emission should be the dominant process. However, the lasing wavelength of sample *B* remains unchanged with the increase of excitation intensity so that the corresponding dominant process is excitonic recombination. Hence, the recombination processes of samples *A* and *B* at high T have been clarified.

Figure 4.6: Lasing spectra for (a) sample *A* and (b) sample *B* at temperatures of 500 and 540 K, respectively, versus different excitation intensities.

Figure 4.4 also shows the appearance of broad emission spectra on the shorter wavelength side of the lasing peaks at T greater than 400 K (labeled as ‘SE’ of sample A (▼) and ‘SE’ of sample B (▽) in figure 4.5). The broad emission of sample B (▽) is attributed to FE recombination in ZnO films. The energy overlapping when compared with that of the FE emission (○) as shown in figure 4.5 supports our claim. On the other hand, the origin of the ‘SE’ of sample A (▼) is still not clear although its feature is similar to that of EES emission except having a corresponding lower emission energy.

Figure 4.7(a) shows I_{th} of the two samples versus T . It is expected that the value of I_{th} for sample A is slightly higher than that of sample B from RT to 400 K. This is because the optical gain of EHP radiative recombination is lower than that of the FE radiative recombination near RT.⁸⁹ For T higher than 450 K, I_{th} of sample A increases more rapidly than that of sample B. Nevertheless, the variation of I_{th} with T for both samples followed an exponential dependence. The solid lines plotted in figure 4.7(a) represent the best fitted of the experimental data with an empirical formula $I_{th}(T) = I_0 \exp(T/T_c)$ where I_0 and T_c are the threshold current at $T = 0$ K and the characteristic temperature, respectively. T_c of sample A (sample B) was estimated to be 95 K (127 K). This implies that sample B has lower temperature sensitivity than that of sample A and hence random laser actions supported by excitonic recombination are more effective than that by EHP recombination at high T .

Investigations on the temperature dependence of stimulated EES emission of the ZnO films on sapphire and the ZnO/MgZnO superlattices on ScAlMgO₄ have found that the corresponding T_c are 67 K and 87 K, respectively.¹⁰⁰ These samples (i.e., without grain boundaries) show smaller values of T_c (i.e., poorer high T performance)

Figure 4.7: (a) Plot of I_{th} versus T for sample A and B. The insets give the cross-sectional transmission electron microscopy (TEM) image of sample A (right) and the high-resolution TEM image of the ZnO grain (left). Circles show the location of the nanocrystals. (b) RT current-voltage (I - V) characteristics of sample A before and after annealing. The insets show the schematic diagram of sample A (top) and the enlargement of the I - V curve at low bias voltage for the annealed sample (bottom).

than that of our ZnO polycrystalline films. This is because the increase in T causes the spreading of excited carriers over the non-uniformly pumped region, which leads to the reduction of optical gain, and hence the corresponding value of T_c is small. In contrast, the formation of ZnO grains inside our ZnO polycrystalline films (see the inset of

figure 4.7(a)) confines the excited carriers over the pumped region so that the optical gain can be maintained at high T , and hence the value of T_c is higher. This is because the potential barrier appearing at the grain boundaries¹¹⁰ blocks the diffusion of optically excited carriers/excitons across the pumped region. On the other hand, the presence of nano-crystals inside the ZnO grains could also contribute to the capture of carriers/excitons.

The above confinement of carriers/excitons can be verified by measuring the current-voltage (I - V) characteristics of sample A. This is possible because if the external injection of carriers can be trapped inside the ZnO grains, similar confinement of optically generated carriers/excitons should occur. Figure 4.7(b) shows the RT gate-to-gate I - V curves of sample A before and after annealing. The I - V curve of sample A before annealing (i.e., with very small and closely-packed grains) exhibits linear I - V relationship. However, the I - V curve of sample A after annealing exhibits fast (slow) oscillation with period of ~ 2 mV ($\sim 40 - 50$ mV), which indicates there is charging and discharging of injected carriers¹¹¹ inside the ZnO grains (ZnO nanocrystals inside the grains). The occurrence of oscillations is due to the Coulomb blockade from the nanostructures, and the corresponding Coulomb energy, E_c , can be calculated from $E_c = e^2/2C$, where e is the electron charge and C is the capacitance. The capacitance of ZnO grains and nano-crystals (i.e., assuming that they work like spherical capacitors) can be expressed as $C \approx 4\pi\epsilon_0\epsilon_r r/\alpha$,¹¹² where ϵ_0 is the permittivity in free space, ϵ_r (≈ 7.4) is the relative permittivity, r is the radius of nanostructures, and α is the correction factor. If $r \approx 60$ nm ($r \approx 4$ nm) and $\alpha = 1$ ($\alpha = 1.54$) are used to calculate the capacitance of ZnO grains (nanocrystals), the corresponding value of E_c is found to be ~ 1.6 meV (~ 38 meV), which is close to V_f (V_s) measured from the I - V curve. Hence,

we can conclude that the confinement of injected carriers is mainly due to the presence of nanostructural ZnO grains which support Coulomb blockade at room temperature. This also implies that the confinement of optically excited carriers/excitons at high T can be achieved.

Non-radiative recombination, which is caused by the trapping of carriers/excitons (i.e., by the defects from grain boundaries, surface, vacancies/interstitials, etc) inside the ZnO nanostructures, can also affect the UV lasing of the ZnO polycrystalline films. This is because at elevated temperature, the increase of the number of non-radiative recombination centers further reduces the intensity of radiative recombination so that UV lasing will be suppressed. However, higher pump intensity can generate more excited carriers to compensate the loss due to the non-radiative recombination. As a result, high temperature UV lasing still can be observed from the ZnO polycrystalline films at the expense of higher pump threshold.

Random laser action can also play an important role in maintaining the optical gain of the random cavities inside the ZnO polycrystalline films at high T . This can be demonstrated by investigating the length of the random cavities, L_c (i.e., length of the closed-loop paths of light), of the ZnO polycrystalline films under the influence of T . L_c can be obtained from the lasing spectra as given in figure 4.8(a) by Fourier transform (FT).¹⁰² Figure 4.8(a) plots the corresponding value of L_c (i.e., fundamental resonator of random lasing) for samples A and B versus T . As an example, the FT distribution of the lasing spectra of sample B at $T = \text{RT}$ and 475 K is shown in figure 4.8(a). It is found that the value of L_c decreases from 6~8 μm at RT to 2~4 μm at high T . Figure 4.8(b) explains the reason for the dependence of L_c on T . As the optical excitation has a Gaussian profile (i.e., high gain at the middle of the pump stripe),

random cavities with short L_c will only experience high average optical gain at the region near the middle of the pump stripe to sustain lasing at high T . For region away from the middle of the pump stripe, the average optical gain at high T is not large enough to overcome the scattering loss of long random cavities (i.e., long L_c). On the other hand, the average optical gain at low T is still sufficient to support random cavities with long L_c to achieve coherent lasing. This phenomenon of self-compensation maintains the optical gain of the random cavities and hence short (long) L_c is observed from the samples operating at high (low) T .

Figure 4.8: (a) Plot of L_c versus T for samples A and B. The inset shows the FT spectra of the LE spectra of sample B taken at RT and 475 K. (b) The formation of closed-loop random cavities inside the ZnO films at low and high T .

4.4 Closed Loop Formation of Random Lasing in Highly Disordered ZnO Polycrystalline Films

4.4.1 Experimental Procedure

The ZnO films, which are made of ZnO (~180 nm)/SiO₂ (~400 nm)/ Si (substrate), were fabricated by FCVA technique and post growth thermal annealing at 900 °C and 2 hours. Rib waveguides with a fix length of ~0.1 cm and different width were defined on the ZnO films by photolithography and ion-beam etching. Detailed descriptions on the fabrication procedures of the rib waveguide random lasers have also been given in appendix A.

The lasing characteristics of the ZnO films can be studied under optical excitation by a frequency-tripled Nd:YAG laser (at 355 nm) at pulsed operation (6 ns, 10 Hz). The optical pump was focused using a cylindrical lens to a stripe of length 1 mm and width 50 µm on the surface of the ZnO films. Hence, the lasing emission can be measured from the edge of the films. It must be noted that the intensity profile of the pump stripe has a Gaussian profile.

4.4.2 Result and Discussion

Figure 4.9 shows the lasing spectra of the ZnO films with and without rib waveguide structure. Uniform excitation can be obtained from the ZnO film with rib waveguide structure of width equal to 2.5 µm. It is observed that the lasing spectra red-shift with the increase in temperature due to band-gap shrinkage.¹¹³ In addition, the number of lasing peaks decreases with the increase in temperature especially for the films with rib waveguide structure. This implies that the number of random cavities formed inside the random media is reduced with the increase of temperature. As the

pump intensity remains unchanged, the optical gain of the random media reduces with the increase of temperature. This is because the corresponding threshold pump intensities, which have the same characteristic temperature of ~ 95 K, increase

Figure 4.9: Lasing spectra for the highly disordered ZnO films (a) without and (b) with a rib waveguide structure at pump intensities of ~ 0.4 and ~ 0.6 MW/cm^2 , respectively, for different temperatures.

exponentially with T . Therefore, random cavities with relative higher cavity loss will first disappear from the emission spectra. It is not sure whether the random cavities, which are assumed to have circular shape, with long or short cavity length will be suppressed at high temperature. However, it is believed that the formation of the closed-loop random cavities is mainly dependent on the optical gain profile, which is a function of operation temperature and pump intensity, inside the random media. Hence, we investigate the influence of temperature and pump intensity on the size of the random cavities in order to understand the corresponding formation mechanism.

We performed Fourier transform of the lasing spectra to evaluate the dominant cavity length of the random cavities.¹⁰² Figure 4.10 plots the fundamental cavity length, L , versus temperature, T , at different pump intensity for the ZnO films with and without rib waveguide structure. The threshold pump intensities of the random media with and without rib waveguide structure are equal to ~ 0.26 and ~ 0.36 MW/cm², respectively at $T = 300$ K. It is observed that L reduces with the increase of T for the case without rib waveguide. In addition, the increases in pump intensities increase the value of L . However, for the case with rib waveguide, the dependence of L on T and pump intensities is more complicated. In general, L reduces with the increase in T . However, L reduces (increases) with the increase in pump intensities for T lower (larger) than 340 K. We have repeated the experiment for the rib waveguide laser waveguide width of 6.5 μm . It is found that the dependence of L on T and pump intensities is similar to that of ZnO films without rib waveguide structure. From the experiments, it is noted that 1) the size of the random cavities dependent strongly on the magnitude and profile of the optical gain inside the random media, 2) the presence of waveguide structure will alter the formation of random cavities only if the width of

the waveguide is equal or shorter than $2.5\ \mu\text{m}$, and 3) the scattering loss of the random cavities is less dependent on L (i.e., small variation of optical gain can alter the resonant conditions in the random media).

In order to further understand the formation mechanism of the closed-loop random cavities, we studied the distribution of carrier concentration (i.e., equivalent to study the optical gain profile) over the pump region of the random media. This can be

Figure 4.10: Fundamental cavity length (obtained from Fourier transform to the lasing spectra) versus temperature under different pump intensities for highly disordered ZnO films (a) without and (b) with a rib waveguide structure.

Chapter 4: Excitonic Recombination and Random Lasing in Highly Disordered ZnO films

done by solving the 1-dimensional (1D) rate equation of carrier concentration, N , given as $\partial N / \partial t = I - N / \tau_n + D_n \partial^2 N / \partial x^2$ where x is the direction across the pump stripe, I is pump intensity, τ_n ($=1$ ns) is the carrier lifetime, $D_n (= L_n^2 / \tau_n)$ is the diffusion coefficient and L_n is the diffusion length.

It is noted that the pump beam has a Gaussian profile (all the commercial available frequency-tripled Nd:YAG lasers have output beam of a Gaussian profile, however, most of the lasing experiments reported in the literatures have ignored this fact)¹¹⁴ so that the pump intensity can be written as $I = I_o \exp(-x^2 / \omega^2)$, where I_o is the peak pump intensity, and ω ($= 9 \mu\text{m}$) is the radius of the Gaussian beamwidth. For the case of ZnO films without rib waveguide structure, it is assumed that N decreases exponentially outside the pump region with the increase of x . On the other hand, for the ZnO films with a rib waveguide structure, N at the side of the waveguide has to satisfy the boundary condition $\partial N / \partial x + v_{\text{sur}} N / D_n = 0$ where v_{sur} ($= 1 \times 10^3$ cm/s) is the surface recombination velocity. The above 1D rate equation of N is accurate enough to study the threshold characteristics of the random cavities as the influence of stimulated recombination is not significant.

Figure 4.11(a) plots the normalized values of $N(x)$ versus x for the random media without waveguide and only half of the distributions of N is shown in the figures as they are symmetric at $x = 0$. We assumed that the value of L_n used in the calculated varies from 0.1 to 1.0 μm . This is because the presence of ZnO grains inside the random media confines the diffusion of carriers to a distance of 0.1 μm (i.e., minimum size of grains). On the other hand, it is reported that the value of L_n in ZnO films can change from ~ 0.5 to $\sim 1.0 \mu\text{m}$ for T increases from 300 to > 600 K,

respectively.¹¹⁵ It is observed that for L_n reduces from 1.0 to 0.1 μm , there is an increase in N at $x < 9 \mu\text{m}$ especially at the center ($x = 0$) of the excitation region. The optical gain of the random cavities, G , can be approximated linearly by $G \approx A^{-1} \int a_n(N(x) - N_0) |\Psi(x, y)|^2 dx dy$, where A is the modal area, a_N is gain coefficient, N_0 is the carriers at transparency and $\Psi(x, y)$ is the optical field profile of

Figure 4.11: Normalized carrier concentrations versus distance across the pump stripe for different values of L_n for highly disordered ZnO films (a) without and (b) with a rib waveguide structure.

the random cavities. The expression of G has indicated that the optical gain 1) is high at region near to the middle of the pump stripe and 2) can be improved for the random media with small value of L_n .

Figure 4.11(b) plots the normalized values of N versus x for the films with rib waveguide structure of width equal to $2.5\ \mu\text{m}$. It is observed that the distribution of optical gain across the rib waveguide is less dependent on the intensity distribution of the pump beam. However, the presence of non-radiative recombination at the side of the rib waveguide affects the uniformity of the optical gain especially for the case with small L_n . In fact, this is the reason why the formation mechanism of closed-loop random cavities in ZnO films with narrow rib waveguide is different to that without rib waveguide (i.e., as indicated in figure 4.10). For the calculation of $L_n = 0.1\ \mu\text{m}$ (equivalent to the rib waveguide operating at $T < 320\ \text{K}$), optical gain is significantly reduced (when compared to that without rib waveguide) near the side of the rib waveguide especially at high pump intensities. Therefore, L is restricted to a small value due to the large different in optical gain between the regions near the middle and the side of the rib waveguide. On the other hand, the optical gain is more uniform for the calculation of large L_n (equivalent to the rib waveguide operating at $T > 360\ \text{K}$). In this case, the increase of L with pump intensity is observed from figure 4.10(b) at $T > 360\ \text{K}$ as the gain different between the regions near the middle and the side of the rib waveguide is less significant.

The expression of G for the random media without rib waveguide structure can be evaluated by assuming that the closed-loop random cavities formed a circular path of radius a at a distance c from the middle of the pump stripe and $N(x) \approx N_b \exp(-x^2/\omega^2)$ where N_b is a constant. Hence, G can be expressed as

$G \approx (2\pi a \delta)^{-1} [g(a + \delta, c) - g(a, c)]$ where δ is the equivalent width of $|\Psi|^2$ and $g(a, c) = 2a_N \int_{c-a}^{c+a} \sqrt{a^2 - (x - c)^2} (N_b \exp(-x^2 / \omega^2) - N_o) dx$. Figure 4.12 plots the normalized average gain, $G/(a_N N_b)$, of the random cavities versus a . It is observed that the normalized gain has a maximum at $a = \sim 0.8 \mu\text{m}$ which is equivalent to $L = \sim 5 \mu\text{m}$. This value is close to that the measured value of L for the random media at high T (see figure 4.10(a)). This shows that at high T where G is reduced, only random cavities of size $\sim 5 \mu\text{m}$ (i.e., coinciding with the peak gain) will have sufficient gain to sustain lasing. Hence, this also explains the reason why the reduction of L ceases at a constant value for $T > 360 \text{ K}$. This is because the increase of T reduces G so that only the size of closed-loop random cavities match the peak gain (shown in figure 4.12) will still have sufficient gain to sustain lasing. It is also observed from figure 4.12 that the value

Figure 4.12: Normalized average gains versus the radius of the circular closed-loop random cavities at distance c away from the middle of the pump stripe for the highly disordered ZnO films without a rib waveguide structure.

of G reduces with the increase of c (i.e., equivalent to the formation of random cavities away from the middle of the pump stripe). This indicates that the closed-loop random cavities should form near to the middle of the pump stripe, as the corresponding average optical gain is higher than the other region.

4.5 Summary

In summary, highly disordered ZnO polycrystalline films have been studied experimentally. Based on our investigation, we can explain the general observation of FE lasing in nano-materials.^{97,98} It is due to the weak interaction between the ZnO nano-materials and substrates that results in strain-free nano-materials. However, ZnO thin films deposited on various substrates (e.g., sapphire, Si, SiO₂/Si, MgO/ZnO/Si, and quartz) under different growth and annealing processes usually experience strong tensile strain or compressive strain so that different emissions from EHP or FE can be observed at RT. It is demonstrated that the type of strain experienced by the ZnO active layer, resulting in different values of n_{Mott} , plays an important role in determining the recombination process in the ZnO polycrystalline films.

We have also studied the influence of temperature on the lasing characteristics of the ZnO polycrystalline films with nanostructures. It is found that the characteristic temperature of the annealed ZnO polycrystalline films can be as high as 127 K which is almost doubles to that of the ZnO films on sapphire substrate without nanostructures.¹⁰⁰ We have shown that the improvement of characteristic temperature is due to 1) the confinement of excited carriers inside the ZnO grains (i.e., related to the potential barrier formed at grain boundaries) so that the spreading of excited carriers can be minimized, and 2) the size flexibility of the random cavities so that the

optimum gain for the closed-loop path of light can be obtained. As a result, lasing can be maintained in the ZnO polycrystalline films at high T . Our investigation has shown that the ZnO polycrystalline films can allow “temperature tuning” of the lasing wavelength from UV to purple (red-shifted by more than 30 nm) and the process is reversible and repeatable. Therefore, this unique behavior of the proposed ZnO polycrystalline films will lead to the development of novel wide-tunable-range ZnO UV lasers under the control of substrate temperature.

We have found that the Gaussian profile of pump intensity, which is usually ignored in the study of random lasing action in ZnO films, has significant influence on the size and location of the closed-loop random cavities inside the random media. The formation of random cavities can also be modified by a small value of L_n , which existence is often neglected in the consideration, for the random media with a small waveguide structure. Furthermore, the formation of the size and location of the closed-loop random cavities is shown to be dependent on the profile of the optical gain inside the random media. This implies that the lasing characteristics of the random media can be controlled. Hence, our understanding of the formation characteristics of random cavities will help to design ZnO random lasers to achieve better operation efficiency in order to suit for practical applications.

Chapter 5

Design of Random Lasers

5.1 Introduction

ZnO has attracted considerable attention to realize high internal quantum efficiency UV lasers due to its 1) wide band-gap and high excitonic binding energy at RT^{39,116} and 2) random lasing action from highly disordered ZnO films.^{53,54,117,118} Furthermore, recent experimental investigations have resulted in a renewed believe to make use of random structures as laser cavities for device application.^{57,119} For example, planar microcavity lasers with ultra narrow linewidth and low threshold lasing have been achieved by using organic random media as the active layer.¹²⁰ However, the practical application of ZnO films random media as the active layer in semiconductor lasers is still a major challenge.⁵³ It is believed that the improvement of transverse optical confinement in the highly disordered ZnO films can achieve better optical conversion efficiency.

The process of out-of-plane scattering, which is usually observed from the rough surface of the highly disordered ZnO films, prevents further increase of optical conversion efficiency for edge emission laser structure. Hence, deposition of MgO cladding layer on the ZnO films has been proposed to minimize the influence of out-of-plane scattering so that the corresponding scattering loss and slope efficiency of light-light curves can be reduced and enhanced, respectively.⁵⁷ However, the process

of out-of-plane scattering remains unchanged due to the presence of rough MgO/ZnO interface.

On the other hand, it is also necessary to improve the external conversion efficiency of the lasers in order to achieve better performance for surface emission laser structure. Recently, enhancement of spontaneous emission efficiency has been obtained by surface plasmons mediated surface emission from rough metal surface.^{121,122} However, this has yet been demonstrated in ZnO for the improvement of UV lasing emission.

In this chapter, we investigated two possible designs of ZnO random cavities to achieve low threshold and high conversion efficiency UV lasing emission from the edge and surface of highly disordered ZnO films. For edge emission random laser, we reduce the surface roughness of the highly disordered ZnO films by ion-beam milling in order to achieve better optical conversion efficiency. It can be shown that the corresponding scattering loss can be reduced by more than 70% and the slope efficiency can be increased by more than 3 times for the cases with and without MgO cladding layer. Hence, we can realize practical UV semiconductor lasers by using ZnO random media and the difficulty of achieving conventional Fabry Perot laser cavities by cleaving and polishing of smooth facets can be avoided.

We also studied the possibility to enhance the UV lasing efficiency of surface emission random laser from highly disordered ZnO films by surface plasmons resonance (SPR). It was found that the presence of rough Ag coating on ZnO films supports SPR and random lasing action simultaneously so that the corresponding lasing performance can be improved. On the other hand, reduction of lasing intensity was observed from the Ag-coated ZnO films with relatively smooth surface (i.e.,

suppression of SPR coupling). Hence, we have verified that SPR can be used to facilitate UV lasing from ZnO lasers.

This chapter is organized as follows: In section 5.2, we discuss the influence of surface roughness on the edge emission of highly disordered ZnO random laser. It is followed by the discussion of the effect of SPR to improve lasing characteristics of surface emission ZnO random laser in section 5.3. Finally, section 5.4 gives summary of this chapter.

5.2 Influence of Surface Roughness on Lasing Performance in Highly Disordered ZnO Polycrystalline Films

5.2.1 Experimental Procedure

ZnO films with thickness of ~250 nm was deposited on quartz substrate by the FCVA technique and followed by thermal annealing in open air at 900 °C for 2 hours. After the realization of the highly disordered ZnO films, Ar⁺ ion-beam milling was used to reduce the corresponding surface roughness. The ZnO films were placed perpendicularly with distance ~20 cm on top of the low energy ion beam source (~1 kV, ~ 60 mA). It is found that the etching rate of ZnO by using ion-beam milling is ~5 nm/min.

The lasing characteristics of the ZnO films are studied under optical excitation using frequency-tripled Nd: YAG pulsed laser (355nm, 6ns, 10Hz) at RT. A cylindrical lens was used to focus the pumped beam into a stripe of length $L \sim 2$ mm and width ~ 8 μ m on the surface of the ZnO films. The lasing emission was then collected from the edge of the ZnO films.

5.2.2 Result and Discussion

Figure 5.1 shows the atomic force microscope (AFM) images of the surface profile of the highly disordered ZnO films before and after 3 minutes of ion-beam milling. The ZnO film before ion-beam milling has closely packed grains, which show pillar-like structure with bumped shape on the top surface, with size ranging from ~50 to ~200 nm in diameter.¹²³ On the other hand, the ZnO film after ion-beam milling exhibits significant reduction of surface roughness. This is because the rms roughness of the ZnO films after 3 minutes of ion-beam milling has been reduced from ~15 to ~5 nm. Furthermore, due to low etching rate of ion-beam milling, the optical properties (i.e., optical confinement and gain) of the ZnO films after ion-beam milling will not have any noticeable change.

Figure 5.1: AFM images of the highly disordered ZnO films (a) without and (b) with ion-beam milling. The schematic diagram shows the cross section view of the films without and with ion-beam milling.

Figure 5.2 shows the lasing characteristics of the ZnO films before and after 3 and 8 minutes of ion-beam milling. It is observed that the excitation of lasing peaks with linewidth of ~ 0.4 nm represents the closed-loop random cavities.⁴⁶ The formation of closed-loop path of light (i.e., total round-trip length of the lasing peaks) inside the ZnO films is also explained in the inset of figure 5.2(a). The pumped threshold intensity, I_{th} , of the ZnO films, which can be estimated from the corresponding light-light curves, reduce from ~ 0.34 MW/cm² to ~ 0.23 MW/cm² by ion-beam milling. In addition, the corresponding slope efficiency of the light-light curves is enhanced by more than three times. It must be noted that the lasing characteristics of the ZnO films under 3 and 8 minutes of ion-beam milling show no distinct difference. This is because low energy ion-beam milling is more effective to remove bumped structure of the ZnO grains along the growth direction. Figure 5.2(b) shows the emission spectra (at

Figure 5.2: (a) Light-light characteristics and (b) emission spectra of ZnO films before (■) and after (▲, ●) ion-beam milling. The corresponding value of I_{th} is ~ 0.34 MW/cm² (~ 0.23 MW/cm²) before (after) ion-beam milling condition. The inset shows the Fourier transform spectra of the corresponding lasing emission.

excitation intensity of $\sim 0.42 \text{ MW/cm}^2$) of the ZnO films before and after 3 minutes of ion beam milling. It is observed that the corresponding profiles of the lasing spectra are relatively unchanged except the intensity is increased. This is clearly shown that the corresponding Fourier transform (FT) spectra of the lasing emission have similar profile, see the inset of figure 5.2(b).¹⁰² Since the lasing resonator is determined by the harmonics of FT profile, the result confirms that the optical feedback mechanism of the random media has not been changed after ion-beam milling.

The rough surface of highly disordered ZnO polycrystalline films will contribute to scattering loss radiated into the surface. In conventional semiconductor lasers, cladding layer is used to enhance the transverse optical confinement of the laser cavities. The idea using cladding layer is also used to improve the optical confinement of light inside the ZnO polycrystalline films. Hence, lasing characteristics of the highly disordered ZnO films with MgO film as the cladding layer was studied. The MgO film with thickness of $\sim 150 \text{ nm}$ was deposited on to the surface of the ZnO films by FCVA technique.⁵⁷ The deposition conditions of MgO films are similar to that of ZnO films. Figure 5.3 plots the lasing characteristics of the highly disordered ZnO films (with and without undergone of ion-beam milling) with the deposition of MgO cladding layer. It is observed that the value of I_{th} reduces from $\sim 0.30 \text{ MW/cm}^2$ to $\sim 0.21 \text{ MW/cm}^2$ for the ZnO films undergone 3 and 8 minutes of ion-beam milling. However, the profiles of the lasing spectra do not change much after ion-beam milling. Similarity between the two corresponding FT spectra as given in the inset of figure 5.3(b) confirmed our claim. When compared to figure 5.2, the presence of MgO cladding layer further reduces (enhances) I_{th} (slope efficiency) of the ZnO films with ion-beam milling. This implies that our method is an important process before the deposition of cladding layer.

Figure 5.3: (a) Light-light characteristics and (b) emission spectra of ZnO films with MgO cladding layer before (■) and after (▲, ●) ion-beam milling. The corresponding value of I_{th} before (after) ion-beam milling is ~ 0.30 MW/cm² (~ 0.21 MW/cm²). The inset shows the Fourier transform spectra of the corresponding lasing emission.

We can deduce the scattering loss, α_{scat} , of the ZnO films by assuming that the corresponding threshold gain, g_{th} , is expressed as $g_{th} = \alpha_{scat} + f(L)$ where $f(L)$ is the L dependent random cavity loss. Based on the first-order approximation of one-dimensional random cavities, $f(L)$ can be approximated by $f(L) \sim \chi L^{-1}$ where χ is defined as the normalized cavity loss.¹²⁴ From the rate equation of carrier concentration, it can be shown that the value of g_{th} is proportional to I_{th} .⁵⁷ Hence, the expression of g_{th} can be re-written as $I_{th} b_N = \alpha_{scat} + \chi L^{-1}$ where $b_N (= \eta a_N \tau \lambda / d h c)$. η ($=0.134$) is the coupling efficiency, which is estimated with the assumption that only 54% of incidence pump is transmitted into the ZnO film and at most 25% is converted into the optical gain. $a_N (=2 \times 10^{-16}$ cm²) is the differential gain, τ ($=0.4$ ns) is the carrier lifetime,¹⁰⁸ λ ($=355$ nm) is the pump wavelength, d ($=250$ nm) is the thickness of ZnO

Chapter 5: Design of Random Lasers

films, h is the Planck's constant and c is the speed of light. Hence, b_N is calculated to be $0.77 \times 10^{-3} \text{ cmW}^{-1}$. Therefore, the value of α_{scat} , can be deduced by measuring I_{th} as a function of L .

Figure 5.4 plots $I_{\text{th}}b_N$ against L^{-1} for the ZnO films before and after ion-beam milling and for the structures with and without MgO cladding layer. From the intercept at the y-axis of figure 5.4, the value of α_{scat} for the ZnO films before ion-beam milling and without (with) MgO cladding layer is found to be $\sim 105 \text{ cm}^{-1}$ ($\sim 82 \text{ cm}^{-1}$). Furthermore, the value of α_{scat} for the ZnO films after ion-beam milling and without (with) MgO cladding layer is found to be $\sim 32 \text{ cm}^{-1}$ ($\sim 25 \text{ cm}^{-1}$). This indicated that the use of ion-beam milling can reduce the value of α_{scat} by more than 70 % for the cases with and without MgO cladding layer. The result is expected as the out-of-plane

Figure 5.4: Plot of $I_{\text{th}}b_N$ against L^{-1} for different ZnO films. The slopes of the fitted lines, χ , are found to be ~ 31 .

scattering loss has been significantly reduced by the smooth surface morphology. Also, the gradient of the plot (i.e., the value of $\chi \sim 31$) in figure 5.4 is the same for all samples imply that the feedback mechanism for in-plane scattering process is the same. This is expected as the radiation modes (out-of-plane scattering) are not in resonance with the longitudinal modes of the lasing process.

As it is difficult to cleave perfect facets in ZnO (i.e., wurtzite structured materials) films as compared to that of zinc-blende structured materials, the fabrication of conventional Fabry-Perot laser cavities using ZnO films required further polishing of smooth facets. However, our simple and effective method to reduce scattering loss in ZnO random media allows the fabrication of conventional ZnO laser cavities without the requirement of smooth facets. Hence, low-cost and high-efficiency practical UV ZnO random lasers can be realized.

5.3 Enhancement of Ultraviolet Lasing from Ag-coated Highly Disordered ZnO Polycrystalline Films by Surface Plasmons Resonance

5.3.1 Experimental Procedure

Two sets of ZnO films, which have thickness of ~ 200 and ~ 120 nm, were deposited onto quartz substrates by FCVA technique at RT. The films were annealed at ~ 900 °C for ~ 2 hours in open air to form highly disordered ZnO films to sustain random lasing action. As the two sets of ZnO films have different thickness, the same annealing process will produce ZnO grains with different size and density. It is expected that thinner ZnO film can produce smaller and more closely packed grains (i.e., rougher surface morphology) than that of the thicker one. The ZnO films were then cut into few ~ 1 cm² samples for the deposition of Ag by Ar⁺ ion beam sputtering.

Chapter 5: Design of Random Lasers

The ion-beam energy and current of the Kaufmann type ion-beam source were set to ~ 1 keV and 60 mA, respectively during the deposition. The deposition rate of Ag was found to be ~ 2 nm/min at a chamber pressure of $\sim 3 \times 10^{-4}$ Torr.

A transmission electron microscope (TEM) cross-section image of an annealed ZnO (~ 200 nm) film coated with ~ 40 nm thick Ag is shown in figure 5.5(a). It is noted that the slow deposition rate of Ag coating preserved the surface profile of ZnO grains. The AFM images before and after the deposition of Ag coatings have shown similar surface morphology. This indicated that the surface morphology of Ag coating follows the surface profile of ZnO films. Hence, by controlling the size and density of ZnO grains, different surface roughness of Ag coating can be obtained. A layer of $\text{Zn}_x\text{SiO}_{1-x}$ was also formed due to the inter-diffusion between ZnO and quartz substrate during the thermal annealing process.

Figure 5.5: (a) TEM image of a Ag-coated (~ 40 nm) ZnO (~ 200 nm) film deposited on quartz substrate. (b) Schematic diagram of the optical measurement setup.

Figure 5.5(b) shows the schematic of the optical measurement set-up used to analyze the emission characteristics of the ZnO samples below and above lasing threshold. A frequency-tripled Nd:YAG pulsed laser (355 nm, 10 Hz) with spot size of ~ 1 mm in diameter was used to excite the samples at RT. Large beam diameter (i.e., low optical density) is used to avoid laser ablation of the Ag coatings. Radiation emitted from the surface of the samples was then collected through a pinhole of diameter ~ 250 μm at different emission angle, θ , by a monochromator-detector setup. The monochromator-detector setup was placed on a rotating stage while the sample and excitation laser were kept stationary during the experiment so that the spectra of the surface radiation can be studied spatially. To prevent oxidation of the Ag coating, the samples were kept inside vacuum prior to the measurement.

5.3.2 Result and Discussion

Figure 5.6(a) plots the spontaneous emission intensities versus θ of the ~ 200 nm thickness ZnO films without and with different thickness of Ag coating. The samples were optically pumped at ~ 0.1 MW/cm^2 (i.e., below lasing threshold). Only half of the emission profile is plotted since the emission profile is symmetric about the normal direction. It is observed that two distinct spontaneous emission peaks emerged at $\theta = 0^\circ$ and $\sim 60^\circ$. The emission peak emitted at $\theta = 0^\circ$ resembles the typical dipole emission of direct band gap semiconductor materials. The peak at $\theta \sim 60^\circ$ is due to diffraction of the spontaneous emission by the random distribution of ZnO grains. The inset of the figure 5.6(a) plots the corresponding spontaneous emission spectra at $\theta \sim 60^\circ$. The peak emission is centered at ~ 380 nm which corresponding to free-exciton recombination of ZnO at RT. It is noted that the emission spectra at $\theta \sim 0^\circ$ is similar to

that at $\theta \sim 60^\circ$. On the other hand, the intensity of surface spontaneous emission reduces with the increase of Ag thickness for all emission direction. For Ag coating thicker than 60 nm, most of the emission was either reflected or absorbed at the Ag/ZnO interface.

Figure 5.6: (a) Spontaneous emission intensity of ~ 200 nm thickness Ag-coated ZnO films versus emission angle, θ . Inset: (left) Spontaneous emission spectra measured at $\theta \sim 60^\circ$ and (right) AFM image of a ~ 20 nm thick Ag layer deposited on a ~ 200 nm thick ZnO film. (b) Spontaneous emission intensity of ~ 120 nm thickness Ag-coated ZnO films versus emission angle, θ . Inset: (right) Spontaneous emission spectra measured at $\theta \sim 45^\circ$ and (left) AFM image of a ~ 20 nm thick Ag layer deposited on a ~ 120 nm thick ZnO film. Emission characteristics of bare ZnO films are also included for comparison.

Figure 5.6(b) plots the spontaneous emission intensities versus θ of the ~120 nm thickness ZnO films without and with different thickness of Ag coating. It is observed that two distinct spontaneous emission emerged at $\theta = 0^\circ$ and $\sim 45^\circ$. Furthermore, the intensity of spontaneous emission increases with the thickness of Ag and the enhancement of emission intensity can be more than 10 times for thick Ag coating. This is because thick Ag coating adjusts the SPR energy closer to that of the ZnO emission and hence increases the Purcell enhancement factor.¹²⁵ The inset of the figure 5.6(b) plots the corresponding spontaneous emission spectra at $\theta \sim 45^\circ$. The emission energy and the amount of enhancement in emission intensity have suggested that SPR interaction contributes to the coupling of spontaneous emission from ZnO films to Ag/air interface via surface plasmons. This is found to be dependent on the surface roughness of Ag which can be controlled by the ZnO surface morphology. The AFM images of the ~20 nm thick Ag surface coated on the ZnO films have shown that only the highly dense rough Ag surface on ZnO films with average ZnO grains size of ~50 nm (i.e., inset of figure 5.6(b)) will exhibit enhancement of surface emission. However, relatively less dense rough Ag surface on ZnO films with average ZnO grains size of ~150 nm (i.e., inset of figure 5.6(a)) suppress surface emission intensity. In fact, these observations are consistent with the recent studies on the use of rough metal surface to enhance surface emission.^{122,125}

We have shown that the formation of highly disordered ZnO films can provide a template to form rough Ag coating for the realization of SPR. The presence of ZnO grains and voids can also sustain random lasing action inside the highly disordered ZnO films. Hence, we further studied the random lasing characteristics of the Ag coated ZnO films. Figure 5.7(a) plots the lasing intensities versus θ of the ~200 nm

Chapter 5: Design of Random Lasers

thickness ZnO films without and with different thickness of Ag coating. The samples were optically pumped at $\sim 0.35 \text{ MW/cm}^2$ (above threshold). It is noted that lasing emission was only detected at $\theta \sim 60^\circ$. This value of θ is similar to the case of surface spontaneous emission given in figure 5.6(a). This verified that the diffraction of spontaneous emission is due to the presence of ZnO grains and voids. However, the presence of Ag coating suppresses the lasing intensities and no lasing emission was detected for Ag coating thicker than $\sim 60 \text{ nm}$.

Figure 5.7: (a) Lasing emission intensity of $\sim 200 \text{ nm}$ thickness Ag-coated ZnO films versus angle, θ . Inset: Lasing emission spectra measured at $\theta \sim 60^\circ$. (b) Lasing emission intensity of $\sim 120 \text{ nm}$ thickness Ag-coated ZnO films versus angle, θ . Inset: (right) Lasing emission spectra measured at $\theta \sim 45^\circ$ and (left) rms roughness density of Ag-coated surface versus average ZnO grains size. Lasing characteristics of bare ZnO films are also included for comparison.

Figure 5.7(b) plots the lasing intensities versus θ of the ~120 nm thickness ZnO films without and with different thickness of Ag coating. Random lasing action is only recorded at $\theta \sim 45^\circ$ (i.e., this value is similar to that measured from the spontaneous emission, see figure 5.6(b)) and the presence of Ag coating enhances lasing intensities especially for thick Ag coating. This is because thick Ag coating increases the coupling of lasing emission from ZnO random cavities into surface emission via SPR. Both SPR and random lasing action were supported simultaneously inside the highly disordered Ag-coated ZnO films. Furthermore, the random lasing modes show very broad emission linewidth (i.e., many overlapped lasing modes) due to large pump area. To determine the influence of surface roughness density (i.e., defined as rms roughness per grain area) on the enhancement of the UV lasing emission, the lasing experiment was repeated for Ag-coated ZnO samples with different ZnO grains size (i.e., by varying the thickness of the ZnO films). The inset of figure 5.7(b) plots the corresponding rms roughness density of Ag (with thickness ~20 nm) versus ZnO grains diameter. It is noted that there is a minimum value of rms roughness density that can sustain SPR for the enhancement of lasing emission from the rough Ag coating.

Figure 5.8 shows the light-light curves of the ~120 nm thick ZnO samples without and with Ag coating of different thickness. It is observed that the lasing threshold (slope efficiency) of sample can be reduced (increased) by more than 2 (5.5) times with the presence of thick Ag coating. The expression of lasing threshold, P_{th} , and slope efficiency, η , of the samples can be approximated by $P_{th} \propto \alpha_{scatt} + \alpha_{SPR} + L^{-1} \ln(1/R) + \alpha_{abs}$ and $\eta \sim (\alpha_{SPR} + L^{-1} \ln(1/R)) / (\alpha_{scatt} + \alpha_{SPR} + L^{-1} \ln(1/R))$, respectively, where α_{scatt} is the scattering loss experienced by the random cavity modes, α_{SPR} is the emission loss related to SPR and, α_{abs} is the internal absorption loss of ZnO. L is the

Chapter 5: Design of Random Lasers

length and R is the effective reflectivity of the random cavities. It is noted that the values of α_{abs} , L and R will not be changed by the presence of Ag coating as they are mainly dependent on the ZnO random cavities. As α_{SPR} is defined as the radiation loss related to the surface emission via SPR, the value of α_{SPR} should increase with the thickness of Ag. In order to satisfy the reduction (increase) of P_{th} (η) with the increase of Ag thickness as observed in figure 5.8, the value of α_{scatt} should reduce with the increase of Ag thickness. As α_{scatt} is defined as the radiation loss not coupled to surface plasmons, the presence of Ag coating will reduce the value of α_{scatt} (i.e., improve the optical confinement of the random cavity modes). In addition, if the surface roughness of Ag coating can be reduced with the increase of thickness of Ag coatings, the value of α_{scatt} should also be reduced. The inset of figure 5.8 plots the rms surface roughness of the Ag deposited on the ~ 120 nm thick ZnO sample versus the thickness of Ag

Figure 5.8: Light-light characteristics of ~ 120 nm thickness Ag-coated ZnO films. Inset: The surface rms roughness of ~ 120 nm thickness Ag-coated ZnO films versus different thickness of Ag coating. Lasing characteristics of bare ZnO films are also included for comparison

coating. It is noted that the surface rms roughness reduces with the increase of the Ag thickness as Ag fills up the voids. This indicated that the presence of Ag-coating reduces the surface roughness of air/Ag interface so that the value of α_{scatt} should reduce with the increase of Ag thickness. However, the reduction of surface roughness is still rough enough to excite SPR.

5.4 Summary

In summary, the lasing performance of edge-emitted highly disordered ZnO films with improvement of the surface quality has been studied. It is found that the scattering losses of the ZnO films after ion-beam milling can be reduced by more than 70% (i.e., from ~ 105 to $\sim 32 \text{ cm}^{-1}$) and the slope efficiency of light-light curves can be enhanced by three times. Similar improvement in lasing performance has been observed from the ZnO films with MgO as the cladding layer (i.e., α_{scat} reduces from ~ 82 to $\sim 25 \text{ cm}^{-1}$). Furthermore, we have shown that the application of ion-beam milling do not change the mechanism of random laser action inside the ZnO films.

Furthermore, we have verified that UV random lasing action obtained from the surface of the highly disordered ZnO films can be improved significantly by SPR. This can be realized by depositing Ag coating on the surface of ZnO films with average grains diameter of $\sim 50 \text{ nm}$ or less. As a result, both SPR and random lasing action can be supported simultaneously inside the Ag-coated ZnO films. It is noted that the Ag thickness of $\sim 60 \text{ nm}$ is sufficient to improve the lasing efficiency of the ZnO films by more than a double. Furthermore, the improvement of lasing performance was interpreted as the increase of spontaneous emission via SPR (i.e., increase α_{SPR}) as

Chapter 5: Design of Random Lasers

well as reduction of scattering loss (i.e., reduce α_{scatt}) that experienced by the random cavity modes.

Chapter 6

Conclusion and Recommendations

6.1 Conclusion

In this thesis, we have studied the excitonic processes in wurtzite ZnO semiconductors. The electronics band structures of wurtzite ZnO have been calculated using Empirical Pseudopotential Method (EPM). The parameters of the Zn and O atoms pseudopotential form factors were obtained by fitting with experimental data. The results have revealed the existence of A-, B-, and C-holes due to crystal field and spin-orbit (SO) coupling interaction. The calculated band-gap energy, the crystal field splitting energy, and the SO splitting energy were found to be 3.4409 eV, 0.0391 eV, and -0.0035 eV, respectively. These correspond to the band-edge energies $E_A = 0$, $E_B = -0.0023$ eV, and $E_C = -0.00406$ eV. Furthermore, the calculated results were found in good agreement with the experimental results. The A_{1-6} effective masses parameters from 6-band $k \cdot p$ Hamiltonian have also been obtained by fitting with the EPM result.

The excitonic gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ Quantum Wells (QWs) has also been investigated theoretically. The influence of biaxial strain and exciton-phonon interaction was taken into consideration. The band offset ratio and conduction band deformation constant, which were extracted from the available experimental data, were found to be 60/40 and -6.8 eV, respectively. Hence, the influence of biaxial strain on the peak excitonic gain of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ QWs was investigated. It is found that the excitonic gain can be maximized for x varies between 0.27 and 0.30 if well width is

Chapter 6: Conclusion and Recommendations

chosen to be 15Å. For $x > 0.30$, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ will change phase to cubic structure so that the value of x larger than 0.30 is not considered.

On the other hand, highly disordered ZnO polycrystalline films have been studied experimentally. Based on our investigation, we can explain the general observation of free-excitonic lasing in nano-materials. It is due to the weak interaction between the ZnO nano-materials and substrates that results in strain-free nano-materials. However, ZnO thin films deposited on various substrates (e.g., sapphire, Si, SiO_2/Si , $\text{MgO}/\text{ZnO}/\text{Si}$, and quartz) under different growth and annealing processes usually experience strong tensile strain or compressive strain so that different emissions from free-exciton or EHP can be observed at room-temperature (RT). It is demonstrated that the type of strain experienced by the ZnO active layer, resulting in different values of Mott's density plays an important role in determining the recombination process in the ZnO polycrystalline films.

We also have studied the influence of temperature on the lasing characteristics of the ZnO polycrystalline films with nanostructures. It was found that the characteristic temperature of the annealed ZnO polycrystalline films can be as high as 127 K which was almost doubles to that of the ZnO films on sapphire substrate without nanostructures. We have shown that the improvement of characteristic temperature was due to 1) the confinement of excited carriers inside the ZnO grains (i.e., related to the potential barrier formed at grain boundaries) so that the spreading of excited carriers can be minimized, and 2) the size flexibility of the random cavities so that the optimum gain for the closed-loop path of light can be obtained. As a result, lasing can be maintained in the ZnO polycrystalline films at high temperature. Our investigation has shown that the ZnO polycrystalline films can allow "temperature

Chapter 6: Conclusion and Recommendations

tuning” of the lasing wavelength from UV to purple (red-shifted by more than 30 nm) and the process was reversible and repeatable. Therefore, this unique behavior of the proposed ZnO polycrystalline films will lead to the development of novel wide-tunable-range ZnO UV lasers under the control of substrate temperature.

We have found that the Gaussian profile of pump intensity, which was usually ignored in the study of random lasing action in ZnO films, has significant influence on the size and location of the closed-loop random cavities inside the random media. The formation of random cavities can also be modified by a small value of L_n , which existence is often neglected in the consideration, for the random media with a small waveguide structure. Furthermore, the formation of the size and location of the closed-loop random cavities was shown to be dependent on the profile of the optical gain inside the random media. This implied that the lasing characteristics of the random media can be controlled. Hence, our understanding of the formation characteristics of random cavities will help to design ZnO random lasers to achieve better operation efficiency in order to suit for practical applications.

The coherent excitonic random lasing emitted from edge and surface of highly disordered ZnO polycrystalline films were investigated. The influence of surface quality on the edge emission characteristics of highly disordered ZnO films was studied. It was found that the scattering losses of the ZnO films after ion-beam milling can be reduced by more than 70% (i.e., from ~ 105 to ~ 32 cm^{-1}) and the slope efficiency of light-light curves can be enhanced by three times. Similar improvement in lasing performance has been observed from the ZnO films with MgO as the cladding layer (i.e., scattering loss was reduced from ~ 82 to ~ 25 cm^{-1}). We have

shown that the application of ion-beam milling do not change the mechanism of random laser action inside the ZnO films.

Furthermore, we have verified that UV random lasing action obtained from the surface of highly disordered ZnO films can be improved significantly by SPR. This can be realized by depositing Ag coating on the surface of ZnO films with average grains diameter of ~50 nm or less. As a result, both SPR and random lasing action can be supported simultaneously inside the Ag-coated ZnO films. It is noted that the Ag thickness of ~60 nm is sufficient to improve the lasing efficiency of the ZnO films by more than a double. Furthermore, the improvement of lasing performance was interpreted as the increase of spontaneous emission via SPR as well as reduction of scattering loss that experienced by the random cavity modes.

6.2 Recommendation for further research

Extensive progress in ZnO research has been achieved from the past decade. Better understanding of the electrical and optical properties in ZnO material has been obtained. Low temperature photoluminescence study of excitonic spectra has revealed the fine structure of ZnO energy levels. However, theoretical interpretation on the room-temperature optical properties of ZnO material is still unclear to explain the available experimental results.

Researchers (including the author of this thesis) have attributed the origin of RT lasing mechanism in ZnO to exciton-exciton scattering. However, a recent review article written by Klingshirn *etal* has questioned about the origin of RT luminescence. In the article, it is argued that RT lasing in ZnO is not due to exciton-exciton scattering but it is more related to the recombination of 1) an electron-hole pair under emission of

Chapter 6: Conclusion and Recommendations

one or more plasmon-phonon mixed state quanta or 2) an electron-hole pair under inelastic scattering of a free carrier (i.e., electron).¹²⁶ This conclusion is based and supported by the compiled experimental data that have been reported in literature as well as their experiment on temperature dependent study of ZnO luminescence. Based on the proposed mechanism, the experimental data at room and elevated temperatures can be fitted with the theoretical prediction and are fairly in good agreement. However, there is still very few published works in the literature to support this claim. Therefore, it is still considered an open question whether *the exciton-exciton scattering* or *the proposed mechanisms* is the correct mechanism to explain the RT luminescence in ZnO. For future research works, theoretical study of the new mechanisms can be considered as a new challenge in theoretical study to further understand the optical properties of ZnO semiconductor. Therefore, it is then desirable to further analyze these new mechanisms and subsequently verify or falsify it based on advanced many-body theoretical study using methods such as tight binding, Green's function or variational calculation.

On the other hand, ZnO nanostructures have been attracting a lot of attention for many possible applications (i.e., gas sensors, optoelectronics devices, display, etc.). Considering nanostructures have relatively a small dimension, there is possibility to have excitons confinement if the physical size is comparable to Bohr's radius. In addition, the boundaries of the nanostructure could act as a potential barrier to further enhance the confinement effect. This will improve the near band-edge emission of ZnO nanostructures. Therefore, we can further study the excitonic characteristics of ZnO nanostructures in order to enhance radiative recombination in ZnO under external

Chapter 6: Conclusion and Recommendations

excitation. The possibilities for random lasing can also be explored since nanostructures could also act as light scatterers.

Furthermore, the study of the surface plasmon interaction with band-edge emission of ZnO requires further investigation. We have shown that the size and density of the random ZnO grains affect the coupling efficiency of UV emissions via surface plasmon at Ag/air interface. The experiment related to surface plasmon interaction can be repeated using ZnO nanostructures (i.e., ZnO nanorods, ZnO nanoneedles, etc.) with more controllable size and density to study the coupling process in a more systematical manner.

From these recommendations, it shows that excitonic processes in ZnO at elevated temperature still need to be investigated. The reason is that the room temperature excitonic processes of ZnO must be understood in order to allow us to design optoelectronics devices such as laser diodes. Finally, there is a theoretical prediction of Bose-Einstein Condensation (BEC) of ‘exciton polariton’ at RT which can only be realized by the ZnO excitons existence at elevated temperature. This could realize what will be called ‘RT polaritonic laser’ which theoretically shows the possibility to have threshold-less lasing characteristics.

Author's Publications

1. H.D. Li, S.F. Yu, **A.P. Abiyasa**, Clement Yuen, S.P. Lau, H.Y. Yang, and Eunice S.P. Leong, 'Strain dependence of lasing mechanisms in ZnO epilayers', *Appl. Phys. Lett.*, **86**, 261111, 2005.
2. W.J. Fan, J.B. Xia, **A.P. Abiyasa**, S.T. Tan, S.F. Yu, and X.W. Sun, 'Band parameters and electronic structures of wurtzite ZnO and ZnO/MgZnO quantum wells', *J. Appl. Phys.*, **99**, 013702, 2006.
3. W.J. Fan, **A.P. Abiyasa**, S.T. Tan, S.F. Yu, X.W. Sun, J.B. Xia, Y.C. Yeo, M.F. Li, and T.C. Chong, 'Electronic structures of wurtzite ZnO and MgZnO quantum well', *J. Cryst. Growth*, **287**, 28, 2006.
4. H.D. Li, S.F. Yu, S.P. Lau, Eunice S.P. Leong, H.Y. Yang, T.P. Chen, **A.P. Abiyasa**, and C.Y. Ng, 'High temperature lasing characteristics of ZnO epilayers', *Adv. Mater.*, **18**, 771, 2006.
5. Eunice S.P. Leong, S.F. Yu, **A.P. Abiyasa**, and S.P. Lau, 'Polarization characteristics of ZnO rib waveguide random lasers', *Appl. Phys. Lett.*, **88**, 091116, 2006.
6. **A.P. Abiyasa**, S.F. Yu, W.J. Fan, and S.P. Lau, 'Theoretical investigation of excitonic gain in ZnO-Mg_xZn_{1-x}O strained quantum wells', *IEEE J. Quantum Electron.*, **42**, 455, 2006.
7. S.F. Yu, H.D. Li, **A.P. Abiyasa**, Eunice S.P. Leong, and S.P. Lau, 'The formation characteristics of closed-loop random cavities inside highly disordered ZnO polycrystalline thin films', *Appl. Phys. Lett.*, **88**, 121126, 2006.

Author's Publications

-
8. H.Y. Yang, S.P. Lau, S.F. Yu, **A.P. Abiyasa**, M. Tanemura, T. Okita, and H. Hatano, 'High temperature random lasing in ZnO nanoneedles', *Appl. Phys. Lett.*, **89**, 011103, 2006.
 9. **A.P. Abiyasa**, S.F. Yu, Clement Yuen, and S.P. Lau, 'Influence of surface roughness on the lasing performance of highly disordered ZnO films', *IEEE Photon. Technol. Lett.*, **18**, 2380, 2006.
 10. **A.P. Abiyasa**, S.F. Yu, Eunice S.P. Leong, S.P. Lau, and H.Y. Yang, 'Enhancement of ultraviolet lasing from Ag-coated ZnO highly disordered ZnO films by surface-plasmon-resonance', *Appl. Phys. Lett.*, **90**, 231106, 2007.

Appendix A

Appendix A

I. Fabrication Method

I.1 Filtered Cathodic Vacuum Arc

The Filtered Cathodic Vacuum Arc (FCVA) coating system was first developed in Russia and was intensively studied in NTU since 1993 to fabricate ta-C films. Currently, the FCVA technique has been extended to develop both carbon and metal oxide materials. It can be regarded as a physical vapor deposition method as the working principles are related to arcing at low pressure (i.e., 1×10^{-6} Torr) and the coating species are pure ions that have tunable energy.

We briefly discuss the FCVA deposition system and the basic working principle for film deposition. It is mainly consisted of three parts, i.e. the target chamber, the filter bend, and the deposition chamber. The schematic diagram of this system is shown in figure A.1. In the target chamber, the cathode metal target (e.g., Zn, Mg, etc.) is attached to a copper metal plate. It is shielded by ceramic plate to prevent spurious plasma generation. When the plasma has been initiated (i.e., by connecting anode voltage to the cathode target), magnetic field generated by cathodic and anodic coils are used to stabilize and confine the plasma inside the target chamber. Cooling water is circulated below the metal holder to absorb the heat in the cathodic target generated during the deposition process.

The filtering bend is an Off Plane Double Bend (OPDB) torus coils which generate magnetic field with curvilinear path. The plasma will then follow the

Appendix A

Figure A.1 Schematic diagram of the Filtered Cathodic Vacuum Arc system

magnetic field path whereas the macroparticle (MP) has a straight line path.¹ The OPDB further serve to prevent MP bouncing forth and back due to collision with the wall and reaching the substrate. In the deposition chamber, the substrate was placed on a metal holder 10 cm away from the filter exit. The oxygen pipe is placed near the exit so that the chemical reaction (i.e., due to collision of gas molecules with the high

¹ X. Shi, B.K. Tay, H.S. Tan, E. Liu, J. Shi, L.K. Cheah, and X. Jin, *Thin Solid Films*, **345**, 1, 1999

Appendix A

energy ions plasma) can take place and subsequently deposited on the substrate as films.

1.2 ZnO deposition

The ZnO films were deposited on substrates (e.g., Si, SiO₂, glass, quartz, etc.) which were mounted perpendicular to the direction of the plasma beam. The substrates were cleaned ultrasonically using acetone, methanol and de-ionized water consequently, and then blown dry with nitrogen gas. The deposition chamber was then evacuated to a base pressure of 5×10^{-6} Torr using Roughing Pump and followed by Cryo Pump. Oxygen gas (purity 99.99%) was used as the reactive gas; its flow rate was controlled by a mass flow controller during deposition.

The Zn target was then pre-discharged by potential of 20 V and ignited using arc current of 60 A. To sustain the plasma, cathodic and anodic coils with current of 10 A formed magnetic fields to confine the plasma inside the target chamber before entering the filters. The filters coils with current of 20 A was used for optimum filtering of the Zn plasma. At the exit, focusing coils with current of 10 A formed magnetic fields used to direct the plasma into the substrate. Due to high energy deposition process, the ZnO film can be grown at low temperature substrate with deposition rate of ~20 nm/min when the oxygen flow rate was ~60 sccm.

ZnO deposited using FCVA technique has shown 1) high deposition rate, 2) low temperature deposition, and 3) good films quality. From XRD analysis, the ZnO films have shown polycrystalline structure with (002) orientation showed the highest

Appendix A

diffraction peaks.² Photoluminescence of the ZnO films also showed strong near band edge emission and low defect-related luminescence.²

1.3 Post growth annealing

After ZnO deposition, post growth annealing using standard Lyndberg type furnace was done. The ZnO sample was placed inside a quartz tube reactor and put at the centre of the tube. The annealing process was done at atmospheric pressure at open air. The sample was annealed for 2 hours and let to cool down for 10 hours at atmospheric pressure. After the annealing process, the sample forms highly disordered ZnO polycrystalline films.³ From PL measurement, the near band edge emission is much higher than defect level emission as a sign of high crystal quality.

In our experiment, the random grain size distribution of highly disordered ZnO polycrystalline films was controlled by the temperature of the annealing process. In Figure A.2, we show the grain size distribution against different annealing temperature. The annealing time was 2 hour with ZnO film thickness of ~ 200 nm on quartz substrate. The grain size distribution was analyzed using atomic force microscope (AFM). The (“■”) is the average diameter size while the “line” indicates the range of minimum and maximum diameter size. It shows that the average grain diameter will increase with annealing temperature. However, the increase of the grain size distribution will saturate at temperature ~ 800 °C and above. From lasing measurement,

² Y.G. Wang, S.P. Lau, H.W. Lee, S.F. Yu, B.K. Tay, X.H. Zhang, K.Y. Tse, and H.H. Hng, *J. Appl. Phys.*, **94**, 1597, 2003

³ Y.G. Wang, S.P. Lau, X.H. Zhang, H.H. Hng, H.W. Lee, S.F. Yu, and B.K. Tay, *J. Cryst. Growth*, **259**, 335, 2003

Appendix A

Figure A.2. Grain size distribution for different annealing temperature

we can see lasing behavior only for the sample annealed above 400 °C while below 400 °C there is no lasing behavior was observed.

1.4 Metal contact deposition

In our I-V measurement experiment, Ni was deposited onto ZnO film using e-beam evaporator and annealed by rapid thermal annealing process to form ohmic contact. From the literature, the work function of Ni and ZnO is taken as 5.1 eV⁴ and 5.3 eV⁵, respectively. The ZnO electron affinity is 4.35 eV⁶ and its band gap is 3.37 eV.

⁴ <http://www.iue.tuwien.ac.at/phd/ayalew/node56.html>

⁵ T. Minami, T. Miyata, and T. Yamamoto, "Work function of transparent conducting multicomponent oxide thin films prepared by magnetron sputtering", *Surf. And Coating Tech.*, 108, 583, 1998

⁶ J.A. Aranovich, D. Golmayo, A.L. Fahrenbruch, and R.H. Bube, "Photovoltaic properties of ZnO/CdTe heterojunctions prepared by spray pyrolysis", *J. Appl. Phys.*, 51, 4260, 1980

Appendix A

Figure A.3. Ni-ZnO interface band diagram (a) before and (b) after contact

The contact potential between Ni and ZnO is calculated to be $\sim 0.75 \text{ eV}$ as shown in Figure A.3. From the band diagram, we can confirm that the Ni and ZnO interface form an ohmic contact as required in our experiment.

1.5 Ar^+ Ion Beam Source

The ion beam source is of Kaufmann type of KLAN-103M with the power supply units of SEF-103MC. The schematic diagram of the ion beam source is shown in figure A.4. The ion source consists of a filament cathode, a discharge chamber, ion optics and a cathode-neutralizer. The filament is made of tungsten wire. The discharge chamber contains a frame, an anode and a magnet system. The ion optics includes

Appendix A

screen and accelerator grids and also a ring grounded electrode. The neutralizer is an immersed filament made of tungsten wire.

The power supply includes a cathode heating power unit (CPU), a discharge power unit (DPU), an ion beam power unit (BPU), an accelerator power unit (APU), a neutralizer heating power unit (NhPU) and a neutralizer coupling power unit (NcPU). The principle of operation of the ion beam source can be described as follows. At a gas feed (e.g., Argon gas) to the discharge chamber followed by a feed of voltage to the cathode filament (from CPU) and between the cathode and the anode (from DPU), the discharge appears in the discharge chamber. A low pressure dependent discharge with magnetic field takes place in the discharge chamber. Electrons from the cathode and plasma electrons ionize atoms of the operating gas. All electrons come to the anode while the ions from plasma fall down on walls of the discharge chamber and in holes of the screen grid of the ion optics. At a feed of positive potential from BPU to the anode and a negative potential from APU to the accelerator grid, ions are being accelerated while passing through the holes in the grids of the ion optics and form ion beams. By heating the filament of the neutralizer using current from NhPU followed by applying a bias voltage using NcPU, electrons are created and move to the ion beams providing a neutralization of a space charge of the ion beams.

In our system, the ion beam source was operated in manual control mode. The ion beam energy was controlled by setting the voltage and the current of the power supply manually. The operation procedure can be described as follows. Initially, the chamber was evacuated to a base pressure of 5×10^{-6} Torr using a Rotary Pump followed by a Turbo Pump. Argon gas with flow rate of 4 to 8 sccm is then fed through into the chamber until the chamber pressure is $\sim 3 \times 10^{-4}$ Torr.

Appendix A

Figure A.4 Schematic diagram of the Ion Beam Source system

The high potential and high voltage parts from the power supply were then turned on. When all the power supply was on, we started to increase the DPU voltage to 50 V initially. We then adjusted the CPU current up to about 16-19 A until DPU current appeared. When there was DPU current, we adjusted the CPU current regulators until DPU current was 0.5 A. After that, we set the DPU voltage to 40 V (i.e., the ionization voltage for Argon gas is ~ 40 V). The system is now in a 'discharge' state.

When there was already ion beam appeared in the chamber, we can start adjusting the ion beam energy. We set the BPU voltage to 700 V and at the same time increase APU voltage to 300 V. The ion beam energy corresponds to BPU voltage (700 V of BPU is equal to 700 eV ion beam energy). With this setting, the APU

Appendix A

current should be around 2-5 mA. The ion source is now in ‘ion beam’ state. We adjusted the NhPU regulator, increased NhPU (i.e., heating current) up to 7-12 A until NcPU (i.e., emission) current appeared. Then we set the NcPU current equal to BPU current. The ion source is now in ‘ion beam and neutralization’ state.

1.6 Ion beam etching/milling and sputtering

The Ar^+ ion beam system was used for etching/milling of the ZnO films as well as sputtering of Ag metal deposited on top of ZnO films. For etching/milling, the sample was put on top of the ion beam source at a distance of 20 cm. Using approximately 1 keV ion beam energy, the etching rate of the ion beam was found to be ~ 5 nm/min.

For waveguide design, the ridge structure was defined using UV photolithography technique (Quintel Q2001 CT mask-aligner). The details of the photolithography process are shown in Table A.1. After the formation of the stripe mask, the unmasked ZnO areas were etched away using ion beam source. A low ion beam current and voltage were used to prevent hardening of the photoresist and surface damage to the unmasked region. Several rib structures were developed with length ~ 0.1 cm and width vary from ~ 1.7 μm to 6.5 μm .

Table A.1: UV photolithography recipe

Photoresist	UV lamp Intensity	Pre-baking process	Exposure time	Developing time	Post-baking process
AZ 5214	5 mW/cm ²	90 °C, 2 min	20 sec	30 sec	120 °C, 5 min

Appendix A

The ion beam source can also be used for sputtering. In our application, the ion beam source was used to sputter Ag metal target and deposited it on top of ZnO film. The Ag target was put on top of the ion beam source. When the ion beam strikes the metal target, the metal will be sputtered away from the target surface. We placed our ZnO sample below the target and let the sputtered Ag to be deposited on top of our ZnO samples. In our experiment, ~1 keV ion beam energy was used which gave the Ag deposition rate of ~2 nm/min.

II. Optical Characterization Method

II.1 Photoluminescence

The schematic diagram of the photoluminescence setup is shown in figure A.5. It consisted of Nd:YAG pulse laser source (frequency tripled 355 nm, 10 Hz), harmonic generator, attenuator, mirrors, lenses and monochromator-photodetector set up. The output of the Nd:YAG laser was pumped into the sample at 90°, focused by a cylindrical lens of focal length 10 cm. The emission at the facet of the sample was collimated into a slit input assembly of a monochromator, through a 5 cm plano-convex lens. Beam exited at the slit was detected by a built-in trans-impedance amplifier silicon detector, mounted at the slit exit. Signal output from the

Figure A.5 Schematic diagram of the Photoluminescence measurement setup

Appendix A

photodetector can be detected using either a Merlin 70100 or a SR510 analog lock-in amplifier. Reference signal from the laser pulse synchronize the photodetector and lock-in amplifier reading. The spectrum of the sample output was obtained by the diffraction grating in the monochromator. The data was fed into the computer, recorded and analyzed using a computer program written in Labview.

II.2 Fourier Transform Analysis for Coherent Random Lasing

If the emission peaks are coherent, that implies there is a feedback in the system. Applying Fourier Transform (FT) to the emission spectrum, we could deduce physical length of the coherence system. The unit of the emission spectrum must be in wavenumber (1/length) hence after FT process the data will be shown in unit length. The idea is clearly shown in the case of FP resonator which has a fix two parallel mirror as optical feedback. If we take FT of FP laser spectrum, we get equally spaced harmonics with decreasing amplitude. The separation of this harmonics is given exactly by $n_{\text{eff}}L/\pi$ where n_{eff} is the effective refractive index, L is the mirror separation. For random lasing spectrum, we can make analogy to ring resonator since it is observed in experiment. In the ring resonator case, the mirror separation length, L is equivalent to the half-circumference of the ring and the harmonic separation is multiple of $n_{\text{eff}}D/2$ where D is the ring diameter.⁷

In our random lasing experiment, the spectrum data was collected as intensity against wavelength, λ . We then convert the wavelength into wave number, $\beta = 2\pi/\lambda$ and calculate $\Delta\beta$ by subtracting two adjacent data. To calculate the Fourier Transform, we used FFT algorithm in MATLAB by creating $N (=2^m)$ sampling point. The

⁷ D. Hofstetter and R.L. Thornton, *Appl. Phys. Lett.*, **72**, 404, 1998

Appendix A

sampling frequency (correspond to the harmonic separation) array is then calculated as, $d = ([0 \text{ to } N-1]/N) \times \Delta\beta$. The final Fourier Transform data is then plotted as FFT of intensity against d which gives our Fourier Transform plot of random lasing spectrum. The cavity length, L_c is calculated from d using, $L_c = (\pi/n_{\text{eff}}) \times d$. The random cavity length is determined as the first harmonic position in the Fourier Transform plot measured in μm .

References

- ¹ M.A. Hasse, J. Qui, J.M. De Puydt, and H. Cheng, *Appl. Phys. Lett.*, **59**, 1272, 1991
- ² R.M. Park, M.B. Trofer, C.M. Rouleau, J.M. DePuydt, and M.A. Haase, *Appl. Phys. Lett.*, **57**, 2127, 1990
- ³ K. Ohkawa, T. Karasawa, and T. Mitsuyu, *Jpn. J. Appl. Phys.*, **30**, L152, 1991
- ⁴ H. Jeon, J. Ding, A.V. Nurmikko, H. Luo, M. Smarth, and J.K. Furdyna, *Appl. Phys. Lett.*, **59**, 1293, 1991
- ⁵ H. Nakata, T. Yodo, and K. Yamashita, *Jpn. J. Appl. Phys.*, **29**, L720, 1990
- ⁶ M. Kunz, T. Pier, R.N. Bhargava, A. Reznitsky, V.I. Kozlovskii, G. Muller-Vogt, J.C. Pfister, J.L. Pautrat, and C. Klingshirn, *J. Cryst. Growth*, **101**, 734, 1990
- ⁷ I. Pelant, D. Ohlmann, O. Cregut, R.L. Aulombard, O. Briot, B. Honerlage, and R. Levy, *Solid State Commun.*, **82**, 486, 1992
- ⁸ I.M. Catalano, A. Cingolani, M. Ferrara, and M. Lugara, *Solid State Commun.*, **43**, 371, 1982
- ⁹ P.R. Newbury, K. Shazard, and D.A. Cammack, *Appl. Phys. Lett.*, **58**, 1065, 1991
- ¹⁰ Y. Fujii, I. Suemune, Y. Kuroda, M. Fujimoto, and M. Yamanishi, *Jpn. J. Appl. Phys.*, **31**, L693, 1992
- ¹¹ S. Nakamura, M. Senoh, S. Nagahana, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, *Appl. Phys. Lett.*, **70**, 868, 1997
- ¹² S. Strite and H. Morkoc, *J. Vac. Sci. Technol. B*, **10**, 1237, 1992
- ¹³ M.A. Khan, D.T. Olson, J.M. Van Hove, and J.N. Kuznia, *Appl. Phys. Lett.*, **58**, 1515, 1991
- ¹⁴ K. Yung, J. Yee, J. Koo, M. Rubin, N. Newman, and J. Ross, *Appl. Phys. Lett.*, **64**, 1135, 1994
- ¹⁵ X.H. Yang, T.J. Schmidt, W. Shan, J.J. Song, and B. Goldenberg, *Appl. Phys. Lett.*, **66**, 1, 1995
- ¹⁶ S. Nakamura, M. Senoh, S. Nagahana, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, *Appl. Phys. Lett.*, **70**, 1417, 1997
- ¹⁷ H. Haug and S.W. Koch, *Phys. Rev. A*, **39**, 1887, 1989
- ¹⁸ D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, and T. Goto, *Appl. Phys. Lett.*, **70**, 2230, 1997
- ¹⁹ D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, M.Y. Shen, and T. Goto, *Appl. Phys. Lett.*, **73**, 1083, 1998
- ²⁰ Y. Chen, N.T. Tuan, Y. Segawa, H. Ko, S. Hong, and T. Yao, *Appl. Phys. Lett.*, **78**, 1469, 2001
- ²¹ S. Cho, J. Ma, Y. Kim, Y. Sun, G.K.L. Wong, and J.B. Ketterson, *Appl. Phys. Lett.*, **75**, 2761, 1999
- ²² P. Yu, Z.K. Wang, G.K.L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, *J. Cryst. Growth*, **184**, 601, 1998
- ²³ C.W. Bunn, *Proc. Phys. Soc. London*, **47**, 835, 1935
- ²⁴ R.B. Heller, J. McGannon, and A.H. Weber, *J. Appl. Phys.*, **21**, 1283, 1950
- ²⁵ G.P. Mohatny and L.V. Azaroff, *J. Chem. Phys.*, **35**, 1268, 1961
- ²⁶ R.R. Reeber, *J. Appl. Phys.*, **41**, 5063, 1970
- ²⁷ D.C. Reynolds and T.C. Collins, *Phys. Rev.*, **185**, 1099, 1969
- ²⁸ D.G. Thomas, *J. Phys. Chem. Solids*, **15**, 86, 1960
- ²⁹ Y.S. Park, C.W. Litton, T.C. Collins, and D.C. Reynolds, *Phys. Rev.*, **143**, 512, 1965

- ³⁰ W.Y. Liang and A.D. Yoffe, *Phys. Rev. Lett.*, **20**, 59, 1968
- ³¹ T.C. Damen, S.P.S. Porto, and B. Tell, *Phys. Rev.*, **142**, 570, 1966
- ³² C.A. Arguello, D.L. Rousseau, and S.P.S. Porto, *Phys. Rev.*, **181**, 1351, 1969
- ³³ J.M. Calleja and M. Cardona, *Phys. Rev. B*, **16**, 3753, 1977
- ³⁴ M.L. Moody, 'Blue semiconductor lasers', literature seminar, Dept. Chemistry, The University of Alabama, 2002, http://www.alabama.ua.edu/~chem/seminar/student_seminars/fall02/moody-semf02.doc
- ³⁵ A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, *Nat. Mater.*, **4**, 42, 2005
- ³⁶ Y.R. Ryu, J.A. Lubguban, T.S. Lee, H.W. White, T.S. Jeong, C.J. Youn, and B.J. Kim, *Appl. Phys. Lett.*, **90**, 131115, 2007
- ³⁷ R. Kehl Sink, 'Cleaved-facet group-III nitride lasers', PhD Thesis, University of California, Santa Barbara, Dec 2000
- ³⁸ H.C. Ong, J.Y. Dai, A.S.K. Li, G.T. Du, R.P.H. Chang, and S.T. Ho, *J. Appl. Phys.*, **90**, 1663, 2001
- ³⁹ E.S.P. Leong and S.F. Yu, *Adv. Mater.*, **18**, 1685, 2006
- ⁴⁰ C. Klingshirn and H. Haug, *Phys. Rep.*, **70**, 315, 1981
- ⁴¹ C. Klingshirn, 'Semiconductor Optics', *Springer-Verlag, Berlin*, 1995
- ⁴² U. Rössler, *Phys. Rev.*, **184**, 733, 1969
- ⁴³ D.W. Langer and C.J. Vesely, *Phys. Rev. B*, **2**, 4885, 1970
- ⁴⁴ W. R. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall, and B. K. Meyer, *Phys. Rev. B*, **65**, 075207, 2002
- ⁴⁵ U. Özgür, A. Teke, C. Liu, S.J. Cho, H. Morkoç, and H.O. Everitt, *Appl. Phys. Lett.*, **84**, 3223, 2004
- ⁴⁶ D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen, and T. Goto, *Appl. Phys. Lett.*, **73**, 1038, 1998
- ⁴⁷ D.M. Bagnall, Y.F. Chen, M.Y. Shen, Z. Zhu, T. Goto, and T. Yao, *J. Cryst. Growth*, **184-185**, 605, 1998
- ⁴⁸ D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, *Appl. Phys. Lett.*, **70**, 2230, 1997
- ⁴⁹ A. Yamamoto, T. Kido, T. Goto, Y. Chen, T. Yao, and A. Kasuya, *Appl. Phys. Lett.*, **75**, 469, 1999
- ⁵⁰ M. Kawasaki, A. Ohtomo, I. Ohkuba, H. Koinuma, Z.K. Tang, P. Yu, G.K.L. Wong, B.P. Zhang, and Y. Segawa, *Mater. Sci. Eng. B*, **56**, 239, 1998
- ⁵¹ P. Zu, Z.K. Tang, G.K.L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, *Solid State Commun.*, **103**, 459, 1997
- ⁵² A. Ohtomo, M. Kawasaki, Y. Sakurai, Y. Yoshida, H. Koinuma, P. Yu, Z.K. Tang, G.K.L. Wong, and Y. Segawa, *Mater. Sci. Eng. B*, **54**, 24, 1998
- ⁵³ H. Cao, Y. G. Zhao, H. C. Ong, S. T. Ho, J. Y. Dai, J. Y. Wu, and R. P. H. Chang, *Appl. Phys. Lett.*, **73**, 3656, 1998

- ⁵⁴ H. Cao, Y. G. Zhao, S. T. Ho, E.W. Seelig, Q.H. Wang, and R. P. H. Chang, *Appl. Phys. Lett.*, **82**, 2278, 1999
- ⁵⁵ S.F. Yu, Clement Yuen, S.P. Lau, and H.W. Lee, *Appl. Phys. Lett.*, **84**, 3244, 2004
- ⁵⁶ E.S.P. Leong, S.F. Yu, A.P. Abiyasa, and S.P. Lau, *Appl. Phys. Lett.*, **88**, 091116, 2006
- ⁵⁷ C. Yuen, S. F. Yu, E. S. P. Leong, H. Y. Yang, S. P. Lau, N. S. Chen, and H. H. Hng, *Appl. Phys. Lett.*, **86**, 031112, 2005
- ⁵⁸ H. D. Sun, T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, , *J. Appl. Phys.*, **91**, 1993, 2002
- ⁵⁹ T. Makino, C. H. Chia, N. T. Tuan, H. D. Sun, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, *Appl. Phys. Lett.*, **77**, 975, 2000
- ⁶⁰ J. Pollmann and H. Büttner, *Phys. Rev. B*, **16**, 4480, 1977
- ⁶¹ G. Coli and K. K. Bajaj, *Appl. Phys. Lett.*, **78**, 2861, 2001
- ⁶² S. H. Park and D. Ahn, *Appl. Phys. Lett.*, **87**, 253509, 2005
- ⁶³ D. Ahn, S. H. Park, E. H. Park, and T. K. Yoo, *IEEE Photon. Technol. Lett.*, **18**, 349, 2006
- ⁶⁴ W. J. Fan, M. F. Li, T. C. Chong, and J. B. Xia, *J. Appl. Phys.*, **80**, 3471, 1996
- ⁶⁵ J.R. Chelikowsky and M.L. Cohen, *Phys. Rev. B*, **14**, 556, 1976
- ⁶⁶ W.J. Fan, M.F. Li, T.C. Chong, and J.B. Xia, *J. Appl. Phys.*, **79**, 188, 1996
- ⁶⁷ M.L. Cohen and J.R. Chelikowsky, 'Electronic Structure and Optical Properties of Semiconductors', *Springer, Berlin*, 1988
- ⁶⁸ I.C. Schluter and M. Schlutter, *Phys. Stat. Sol. B*, **57**, 145, 1973
- ⁶⁹ K.L. Teo, Y.P. Feng, M.F. Li, T.C. Chong, and J.B. Xia, *Semicond. Sci. Technol.*, **59**, 349, 1994
- ⁷⁰ S.L. Chuang and C.S. Chang, *Phys. Rev. B*, **54**, 2491, 1996
- ⁷¹ Y. C. Yeo, T. C. Chong, M. F. Li, and W. J. Fan, *IEEE J. Quantum Electron.*, **34**, 526, 1998
- ⁷² A. Mang, K. Reimann, and S. Rubenacke, *Solid State Commun.*, **94**, 251, 1995
- ⁷³ S. Bloom and I. Ortenburger, *Phys. Stat. Sol. B*, **58**, 561, 1973
- ⁷⁴ J.R. Chelikowsky, *Solid State Commun.*, **22**, 351, 1977
- ⁷⁵ K. Hummer, *Phys. Stat. Sol. B*, **56**, 249, 1973
- ⁷⁶ S. Massidda, R. Resta, M. Posternak, A. Baldereschi, *Phys. Rev. B*, **52**, 169777, 1995
- ⁷⁷ Landolt-Bornstein, in K.H. Hellwedge (Ed.), 'Numerical Data and Functional Relationships in Science and Technology', vol. 22a, Group III, *Springer, Berlin*, 1982
- ⁷⁸ L.C.L.Y. Yan, M. Willatzen, M. Cardona, *Phys. Rev. B*, **63**, 703, 1996
- ⁷⁹ A. Ohtomo, M. Kawasaki, I. Ohkuba, H. Koinuma, T. Yasuda and Y. Segawa, *Appl. Phys. Lett.*, **75**, 980, 1999
- ⁸⁰ A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. sakurai, Y. Yoshida, T. Yasuda and Y. Segawa, *Appl. Phys. Lett.*, **72**, 2466, 1998
- ⁸¹ J. E. Rowe, M. Cardona and F.H. Pollak, *Solid State Commun.*, **6**, 239, 1968
- ⁸² Landolt-Bornstein, 'Numerical Data and Functional Relationships in Science and Technology', vol. 17, *Springer, Berlin*, 1982, p. 35

- ⁸³ R. S. Zheng and M. Matsuura, *Phys. Rev. B*, **58**, 10769, 1998
- ⁸⁴ N. Mori and T. Ando, *Phys. Rev. B*, **40**, 6175, 1989
- ⁸⁵ L. F. Register, *Phys. Rev. B*, **45**, 8756, 1992
- ⁸⁶ P. J. Mares and S. L. Chuang, *J. Appl. Phys.*, **74**, 1388, 1993
- ⁸⁷ S. L. Chuang, S. Schmittrink, D. A. B. Miller, and D. S. Chemla, *Phys. Rev. B*, **43**, 1500, 1991
- ⁸⁸ Y. C. Yeo, T. C. Chong, and M. F. Li, *J. Appl. Phys.*, **83**, 1429, 1998
- ⁸⁹ H.D. Li, S.F. Yu, A.P. Abiyasa, Clement Yuen, S.P. Lau, H.Y. Yang, and Eunice S.P. Leong, *Appl. Phys. Lett.*, **86**, 261111, 2005
- ⁹⁰ S.L. Chuang, 'Physic of Optoelectronic Devices', *New York: Wiley*, 1995
- ⁹¹ F. Jain and W. Huang, *IEEE J. Quantum Electron.*, **32**, 859, 1996
- ⁹² W. Shan, W. Walukiewicz, J. W. Ager, K. M. Yu, Y. Zhang, S. S. Mao, R. Kling, C. Kirchner, and A. Waag, *Appl. Phys. Lett.*, **86**, 153117, 2005
- ⁹³ C. Y. P. Chao and S. L. Chuang, *Phys. Rev. B*, **48**, 8210, 1993
- ⁹⁴ S. L. Chuang, *IEEE J. Quantum Electron.*, **32**, 1791, 1996
- ⁹⁵ Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, *Appl. Phys. Lett.*, **72**, 3270, 1998
- ⁹⁶ S. F. Yu, Clement Yuen, S. P. Lau, and H. W. Lee, *Appl. Phys. Lett.*, **84**, 3244, 2004
- ⁹⁷ H. Cao, J. Y. Xu, E. W. Seeling, and R. P. H. Chang, *Appl. Phys. Lett.*, **76**, 2997, 2000
- ⁹⁸ M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science*, **292**, 1897, 2001
- ⁹⁹ S. J. Chen, Y. C. Liu, C. L. Shao, R. Mu, Y. M. Lu, J. Y. Zhang, D. Z. Shen, and X. W. Fan, *Adv. Mater.*, **17**, 586, 2005
- ¹⁰⁰ A. Ohtomo, K. Tamura, M. Kawasaki, T. Makino, Segawa, Z. K. Tang, G. K. L. Wong, Y. Matsumoto, and H. Koinuma, *Appl. Phys. Lett.*, **77**, 2204, 2000
- ¹⁰¹ A.L. Burin, M.A. Ratner, H. Cao, and R.P.H. Chang, *Phys. Rev. Lett.*, **87**, 215503, 2001
- ¹⁰² R. C. Polson, and Z. V. Vardeny, *Phys. Rev. B*, **71**, 045205, 2005
- ¹⁰³ S. Cho, J. Ma, Y. Kim, Y. Sun, G.K.L. Wong, and J.B. Ketterson, *Appl. Phys. Lett.*, **75**, 2761, 1999
- ¹⁰⁴ V. Srikant and D. R. Clarke, *J. Appl. Phys.*, **81**, 6357, 1997
- ¹⁰⁵ T. Makino, T. Yasuda, Y. Segawa, A. Ohtomo, K. Tamura, M. Kawasaki, and H. Koinuma, *Appl. Phys. Lett.*, **79**, 1282, 2001
- ¹⁰⁶ Th. Gruber, G. M. Prinz, C. Kirchner, R. Kling, F. Reuss, W. Limmer, and A. Waag, *J. Appl. Phys.*, **96**, 289, 2004
- ¹⁰⁷ A. Shikanai, T. Azuhata, T. Sota, S. Chichibu, A. Kuramata, K. Horino, and S. Nakamura, *J. Appl. Phys.*, **81**, 417, 1997
- ¹⁰⁸ A. Teke, Ü. Özgür, S. Dogan, X. Gu, H. Morkoç, B. Nemeth, J. Nause, and H. O. Everitt, *Phys. Rev. B*, **70**, 195207, 2004
- ¹⁰⁹ H. Cao, J. Y. Xu, D. Z. Zhang, S. H. Chang, S. T. Ho, E. W. Seelig, X. Liu, and R. P. H. Chang, *Phys. Rev. Lett.*, **84**, 5584, 2000

-
- ¹¹⁰ F. Greuter and G. Blatter, *Semicond. Sci. Technol.*, **5**, 111, 1990
- ¹¹¹ T. P. Chen, J. Y. Huang, M. S. Tse, S. S. Tan, C. H. Ang, and S. Fung, *Appl. Phys. Lett.*, **82**, 3113, 2003
- ¹¹² M. Krcmar, W.M. Saslow, and A. Zangwill, *Appl. Phys. Lett.*, **77**, 3797, 2000
- ¹¹³ Eli Kapon (editor), 'Semiconductor Lasers II: Materials and Structures', *Academic Press*, 1999
- ¹¹⁴ A. Yariv, 'Optical Electronics, 3rd edition', *Holt-Saunders International Editions*, 1985
- ¹¹⁵ O. Lopatiuk, L. Chernyak, A. Osinsky, J.Q. Xie and P.P. Chow, *Appl. Phys. Lett.*, **87**, 162103, 2005
- ¹¹⁶ S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, and T. Steiner, *J. Vac. Sci. Technol. B*, **22**, 932, 2004
- ¹¹⁷ R. V. Ambartsumyan, N.G. Basov, P.G. Kryukov, and V.S. Lethokov, *IEEE J. Quantum Electron.*, **2**, 442, 1966
- ¹¹⁸ N. M. Lawandy, R. M. Balachandran, A. S. L. Gomez, and E. Sauvain, *Nature*, **368**, 436, 1994
- ¹¹⁹ E. S. P. Leong, S. F. Yu, M. K. Chong, O. K. Tan, and K. Pita, *IEEE Photon. Technol. Lett.*, **17**, 1815, 2005
- ¹²⁰ Q.H. Song, L.Y. Liu, S.M. Xiao, X.C. Zhou, W.C. Wang, and L. Xu, *Phys. Rev. Lett.*, **96**, 033902, 2006
- ¹²¹ S. Wedge, J.A.E. Wasey, W.L. Barnes, and I. Sage, *Appl. Phys. Lett.*, **85**, 182, 2004
- ¹²² K. Okamoto, I. Niki, A. Shvarts, Y. Narukawa, T. Mukai and A. Scherer, *Nat. Mater.*, **3**, 601, 2004
- ¹²³ H. D. Li, S. F. Yu, S. P. Lau, E. S. P. Leong, H. Y. Yang, T. P. Chen, A. P. Abiyasa, and C. K. Ng, *Adv. Mat.*, **18**, 771, 2006
- ¹²⁴ Y. Ling, H. Cao, A.L. Burin, M.A. Ratner, X. Liu, and R. P. H. Chang, *Phys. Rev. A*, **64**, 063808, 2001
- ¹²⁵ C. W. Lai, J. An, and H.C. Ong, *Appl. Phys. Lett.*, **86**, 251105, 2005
- ¹²⁶ C. Klingshirn, R. Hauschild, J. Fallert, and H. Kalt, *Phys. Rev. B*, **75**, 115203, 2007