Zinc oxide based nanostructures : fabrication, characterization and applications

Yang, Hui Ying

2007

Yang, H. (2007). Zinc oxide based nanostructures : fabrication, characterization and applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/46955>

<https://doi.org/10.32657/10356/46955>

Nanyang Technological University

Downloaded on 26 Apr 2023 22:01:55 SGT

9477814

Zinc Oxide Based Nanostructures: Fabrication, Characterization and Applications

Yang Hui Ying

School of Electrical & Electronic Engineering

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

2007

QC
176.8
•N35
Y22
2007

To Shixing and our beloved parents.

Acknowledgments

First of all, I express my deepest and special gratitude to my supervisor, Prof. Lau Shu Ping, Daniel, who offered me this opportunity to pursue my PhD degree. I really appreciate his invaluable efforts, endless patience and kind encouragement in guiding me to be a real researcher in the past three years. His unique idea, commitment and determination to research inspired me. I also learnt from him the disciplines in study and life, which will benefit my whole life.

I must be thankful to Prof. Yu Siu Fung from the bottom of my heart for his generosity in sharing all his valuable knowledge with me. I would like to express my sincere thanks to Prof. Masaki Tanemura, Nagoya Institute of Technology, Japan, for providing me with unique and interesting nanostructured samples. I am grateful to Dr. Zhang Xin Hai, Institute of Materials Research and Engineering, for the photoluminescence measurements and discussions. I would like to thank Dr. Teng Kar Seng, Vincent, University of Swansea, for the x-ray photoelectron spectroscopy analysis.

I would like to thank Prof. Tay Beng Kang, Prof. Sun Chang Qing, and Prof. Sun Xiao Wei at Ion Beam Processing Lab for their assistances and instructions. I am grateful to all staff and students in Ion Beam Processing lab, Dr. Li Hongdong, Dr. Huang Lei, Mr. Clement Yuen, Ms. Ji Xiaohong, Ms. Leong Sok Ping, Mr. Herng Tun Seng, Mr. Agus Putu Abisaya, Mr. Chen Nanshu, Ms. Neo Bee Geok, Ms. Teh Hsieh Foong and Mr. Hasman for all the help they gave me.

Finally, I will forever be sincerest gratitude to my parents for their deep love, great understanding and unconditional support during my education as well as life.

My sister, Yang Zihan, who grows along with me as a life-long friend, has shared with me all the beauties from life. My husband, Yan Shixing, is always a true companion beside me. His love, wisdom, kindness and positive attitude have been delighting my life full of miracles and happiness.

Summary

Summary

As a functional oxide material, zinc oxide (ZnO) has substantial research importance for its superior optical and electrical properties, which may lead a race for the innovation in the next decade. The fabrication, characterization, and applications of ZnO based nanostructures are the central issues of this thesis. Emphasis is devoted to realize the high-efficient, mechanical-flexible and wavelength-tunable lasers and field emitters by ZnO based nanostructures.

A filtered cathodic vacuum arc (FCVA) technique has been used to fabricate ZnO thin films. Thermal annealing was used to optimize the crystal quality and optical properties of the as-grown ZnO thin films. Ultraviolet (UV) lasing emission was found in the annealed ZnO polycrystalline thin films, the mechanism of which has attributed to the formation of random laser cavities by ZnO grains and grain boundaries. A zinc silicate layer was formed after the annealing process which was found to be effective for light confinement in a laser cavity. The photoluminescence (PL) peak of the ZnO thin film was blueshifted 47 meV after prolong annealing of 10 hours, which was attributed to the formation of ZnO quantum dots (QDs). Based on the spectrally integrated PL analysis, the exciton radiative lifetime of the ZnO QDs was determined to be 65 ps at 4.3 K, which is much shorter than the exciton radiative lifetime of 322 ps in bulk ZnO.

Flexible UV lasers on plastic substrates were demonstrated by utilizing ZnO thin films and nanoparticles. The performance of the lasers has been evaluated by measuring the lasing threshold at different curvature radius of the plastic. It was found that the pumping threshold intensity increased from 0.8 to 1.1 MW/cm² as the radius of curvature decreases from 100 to 3 cm. This is the first time that the discrete cavity

Summary

modes of random lasers have been fabricated on flexible substrates, and the scattering efficiency of nanoparticles has been captured.

One-dimensional ZnO nanoneedles were prepared selectively on silicon and plastic substrates by an ion-beam technique at room temperature. Optical pumped UV random lasing has been observed in these ZnO nanoneedle arrays with a characteristic temperature (T_c) of 138 K in the temperature range from 300 to 615 K. The temperature dependence of the cavity length of the random lasers was determined by Fourier transform spectroscopy. The optical gain of the ZnO nanoneedle lasers at high temperature was attributed to the high-crystal-quality of the nanoneedles, enhancement of oscillator strength in nanostructures, and a self-compensation mechanism in random laser cavities.

Bandgap-tunable ZnMgO thin films have been successfully fabricated by the FCVA. ZnMgO nanoneedles were then formed by irradiating the corresponding ZnMgO thin films by an ion beam source. The photoluminescence emission energies of the ZnMgO nanoneedles can linearly increase from 3.28 eV to 3.58 eV with Mg contents ranging from 0 to 21 at. %. Random laser action was observed in the ZnMgO nanoneedles at temperature ranging from 300 K to 470 K, whereas the lasing mechanism is electron-hole plasma.

Using the similar ion-beam technique mentioned above, large-area ZnO nanoneedles were deposited on plastic substrates for field emission experiments. Excellent field emission characteristics have been obtained with a threshold voltage of ~ 4.1 V/ μm at a current density of $1 \mu\text{A}/\text{cm}^2$. The field enhancement factor was determined to be ~ 1134 . The ZnO nanoneedles on plastic substrates have also been used as field emitters to generate x-ray for x-ray radiography application.

Table of Contents

Table of Contents

ACKNOWLEDGMENTS	IV
SUMMARY	VI
TABLE OF CONTENTS.....	VIII
LIST OF FIGURES	XI
LIST OF TABLES.....	XVIII
ABBREVIATIONS	1
CHAPTER 1 INTRODUCTION	1
1.1 Motivations and Objectives	1
1.2 Major Contributions.....	2
1.3 Organization.....	3
CHAPTER 2 LITERATURE REVIEW	5
2.1 Properties of ZnO.....	5
2.2 Growth of ZnO.....	11
2.3 Random Laser Action in ZnO Thin Film and Nanoparticles.....	13
2.4 ZnO Nanostructures and Its Applications.....	17
CHAPTER 3 EXPERIMENTAL AND METHODOLOGY	21
3.1 Filtered Cathodic Vacuum Arc	21
3.2 Ion Beam Sputtering	23
3.3 Sample Characterization Methodology.....	26
3.3.1 Transmission Electron Microscopy	26
3.3.2 Field Emission Scanning Electron Microcopy	26
3.3.3 Atomic Force Microscopy	27
3.3.4 X-ray Diffraction	27
3.3.5 Spectrophotometer	28
3.3.6 Photoluminescence Spectroscopy	28
3.3.7 X-ray Photoelectron Spectroscopy	30

Table of Contents

3.3.8	Field Emission	31
3.3.9	Lasing Measurement	32
CHAPTER 4 FORMATION OF RANDOM LASER CAVITIES BY THERMAL ANNEALING		34
4.1	Introduction	34
4.2	Experimental Details	36
4.3	Results and Discussions	36
4.3.1	Microstructure and Optical Properties of Annealed ZnO	36
4.3.2	Self-generated Guiding Effect in ZnO Thin Film without Buffer Layer	48
4.3.3	Optical Properties of ZnO Quantum Dots	52
4.4	Conclusions	59
CHAPTER 5 RANDOM LASERS BASED ON NANOPARTICLES		60
5.1	Introduction	60
5.2	Design and Fabrication of Flexible Random Lasers	60
5.3	Results and Discussion	61
5.4	Conclusions	66
CHAPTER 6 RANDOM LASERS IN ZnO NANONEEDLES		67
6.1	Introduction	67
6.2	Experimental Details	68
6.3	Results and Discussion	68
6.3.1	Random Lasing from ZnO Nanoneedles on SiO ₂ /Si	68
6.3.2	Random Lasing from ZnO Nanoneedles on Plastic Substrates	73
6.3.3	High Temperature Random Lasing in ZnO Nanoneedles	75
6.4	Conclusions	80
CHAPTER 7 WAVELENGTH-TUNABLE RANDOM LASERS IN Zn _{1-x} Mg _x O NANONEEDLES		81
7.1	Introduction	81
7.2	Experimental Details	82
7.3	Results and Discussions	82
7.3.1	Structure and Optical Properties of Zn _{1-x} Mg _x O Thin Films	82
7.3.2	Random Lasing Emission from Zn _{1-x} Mg _x O Nanoneedles	86

Table of Contents

7.4	Conclusions.....	94
CHAPTER 8 ZnO NANONEEDLES AS FLEXIBLE FIELD EMITTER		95
8.1	Introduction.....	95
8.2	Experimental Details.....	96
8.3	Results and Discussion	98
8.3.1	Field Emission Property.....	98
8.3.2	X-ray Generation Using ZnO Nanoneedles on Plastic Substrate	102
8.4	Conclusions.....	104
CHAPTER 9 CONCLUSIONS AND FUTURE WORK RECOMMENDATIONS		105
9.1	Conclusions.....	105
9.2	Recommendations for Further Research.....	107
9.2.1	Electrical Pumped ZnO Nanoneedles based UV Light Emitting Devices.....	107
9.2.2	To Develop ZnO Nanomaterial with Tunable Size	107
APPENDIX I: LIST OF PUBLICATIONS.....		109
APPENDIX II: BIBLIOGRAPHY		112

List of Figures

Figure 2.1 Schematic illustration of a wurtzitic ZnO structure with lattice constant c in the basal direction.	6
Figure 2.2 Optical and structural properties of $\text{Cd}_y\text{Zn}_{1-y}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy films mapped out in a plane of a -axis length and room-temperature band-gap energy. The same curves for (In, Ga)N and (Al, Ga)N alloys are also shown. The alloy compositions are shown on the top axis. ^[22]	10
Figure 2.3 (a) The lasing feedback mechanisms, (b) typical incoherent random lasing spectrum with a pumping intensity $2 \times I_{th}$ and $0.5 \times I_{th}$, (c) typical coherent random lasing spectrum with a pumping intensity $2 \times I_{th}$ and $0.5 \times I_{th}$	15
Figure 3.1 Schematic illustration of a FCVA system.	22
Figure 3.2 Schematic diagram of the nanoneedle fabrication setup.	24
Figure 3.3 Schematic diagram of the nanoneedle formation process.	25
Figure 3.4 Main physical processes of a semiconductor excited by light with equal to or higher than band gap energy, i.e., I: photo-excited process; II: band to band PL process; III: excitonic PL process; IV: non-radiative transition process.	29
Figure 3.5 Standard field emission model from a field emitter, showing the potential barrier and the corresponding energy distribution (i.e., energy on the vertical axis, current on the horizontal logarithmic axis).	31
Figure 3.6 A schematic illustration of the layout of lasing measurement.....	33
Figure 4.1 XRD patterns of the ZnO thin films annealed at different temperatures...	37

List of Figures

Figure 4.2 The plotting of calculated values of (a) FWHM of the (0002) peak, and (b) the lattice constant c and the estimated percentage strain of the ZnO films from the XRD patterns.....	38
Figure 4.3 FESEM images of the ZnO thin films (a) as-grown, (b) 600 °C annealed and (c) 900 °C annealed.	39
Figure 4.4 $2 \times 1 \mu\text{m}^2$ AFM topographs of ZnO thin films (a) as-grown, (b) 600 °C annealed and (c) 900 °C annealed. All the topographs share the same color scale bar with the maximum height of 40 nm, and the corresponding rms roughness of the films is indicated in the figure.....	39
Figure 4.5 TEM image of the as-grown ZnO thin films in cross-sectional ((a) and (b)) and plain view ((c) and (d)). The insets show the corresponding SAD patterns.	40
Figure 4.6 TEM images of ZnO thin film annealed at 900 °C in cross-sectional ((a) and (b)) and plain view ((c) and (d)). The arrow shows the grain boundary between two grains.	41
Figure 4.7 PL spectra of the ZnO thin films annealed at different temperatures from 600 °C to 1000 °C. The PL of the as-grown ZnO thin film is also included for comparison.	42
Figure 4.8 (a) NBE peak intensity and peak position as a function of annealing temperature. (b) Intensity ratio of the NBE emission to the DL green emission and the FWHM of NBE emission position as a function of annealing temperature.	44
Figure 4.9 Emission spectra of the ZnO/SiO ₂ /Si sample annealed at 900 °C taken from TE and TM polarizations as a function of pump intensity.....	46
Figure 4.10 (a) Emission spectra from 30°, 45°, and 60° from the sample surface. The pump intensity is $\sim 1.0 \text{ MW/cm}^2$ and the excitation area is kept at $3 \times 10^{-3} \text{ cm}^2$. (b)	

List of Figures

Emission spectra of the sample with different excitation areas. The excitation intensity is $\sim 1.0 \text{ MW/cm}^2$.	47
Figure 4.11 Emission spectra of the ZnO/Si sample annealed at 900 °C taken from TE and TM polarizations as a function of pump intensity.	49
Figure 4.12 TEM investigations of the interfacial area of the ZnO samples as-grown (a), 600°C (b) annealed, 800°C (c) annealed and 900°C (d) annealed.	50
Figure 4.13 (a) EDS spectra of the new phase formed after 900 °C annealing, (b) HRTEM image of the new phase.	51
Figure 4.14 (a) Schematic illustration of the annealed sample. The far field images of the (a) ZnO/ SiO ₂ /Si and (b) ZnO/ Si samples annealed at 900 °C record from a CCD camera.	52
Figure 4.15 TEM images of the sample. The cross-sectional TEM image (a) clearly shows the existence of the ZnO QDs. (b) is the high resolution TEM image of a single ZnO QD. (c) is the fast Fourier transform pattern of the single ZnO QD. The standard indexed diffraction pattern for hcp crystals in the (001) beam direction is also presented as a reference (d).	53
Figure 4.16 XRD profile of the ZnO QDs.	54
Figure 4.17 The formation mechanism of ZnO QDs in ZnO/SiO ₂ /Si structure.	55
Figure 4.18 The TIPL spectra of the ZnO QDs and as-grown ZnO thin film measured at 4.3 K.	56
Figure 4.19 The time evolution of spectrally integrated PL of the ZnO QDs measured at 4.3 K.	57
Figure 4.20 Exciton lifetime as a function of temperature.	58
Figure 4.21 The time and spectrally integrated PL intensity (solid squares) as a function of excitation density. The linear fitting is also plotted in the figure.	58

List of Figures

Figure 5.1 (a) Photoluminescence spectra at room temperature from ZnO and In ₂ O ₃ nanoparticles on Si substrates. (b) Schematic diagram of the nanoparticles embedded in the ZnO films. (c) Cross-sectional FESEM image of the device bent inwardly with a radius of curvature of 3 cm. (d) Surface morphology of the device.	62
Figure 5.2 Evolution of emission spectra with pump intensity ranging from 0.6 to 2.5 MW/cm ² (a) ZnO nanoparticles and (b) In ₂ O ₃ nanoparticles embedded in ZnO thin films on plastic substrate. Insets: the linewidth and output intensity versus the input power intensity. Curves A, B and C represent pump intensities of 2.5, 1.6 and 0.6 MW/cm ² respectively.	64
Figure 5.3 (a) Plot of $A_{th}^{2.3}$ versus P_{th}^{-1} . (b) Lasing thresholds versus the radius of curvature of the device bent inwardly. The pump intensity and excitation area are 2.6 MW/cm ² and 3×10 ⁻³ cm ² respectively.	66
Figure 6.1 (a) FESEM image of the as-grown ZnO thin film. FESEM images of the ZnO nanoneedle arrays after (b) 30 min and (c) 60 min ion irradiation. (d) High magnification FESEM image of the ZnO nanoneedles. (e) TEM image of a single nanoneedle. (f) High-resolution TEM image of the nanoneedle and (g) the corresponding electron-diffraction pattern.	69
Figure 6.2 (a) EDX analysis, and (b) XRD pattern of the ZnO nanoneedles.	70
Figure 6.3 Schematic diagram of the laser measurement setup.	71
Figure 6.4 (a) Light-light curves of the samples after various ion irradiation times. The inset shows the maximum emission intensity of the TE mode as a function of polarization angles. (b) Emission spectrum of the as-grown ZnO thin film under pump power of 1.6 M/cm ² . (c) Evolution of emission spectra of the 30-min	

List of Figures

irradiated sample under different pump intensities. (d) Emission spectrum of the sample irradiated for 60 min under pump power of 1.6 M/cm^2	72
Figure 6.5 (a) Low and (b) high magnification FESEM images of ZnO nanoneedles on plastic substrate. (c) Emission spectrum under 2.8 MW/cm^2 pump intensity. The inset shows the light-light curve of ZnO nanoneedles on plastic substrate. .	74
Figure 6.6 (a) Lasing emission spectra at different temperatures from ZnO nanoneedles; the emission spectra were obtained under an excitation density of $2 \times I_{th}$, where the I_{th} represents the lasing threshold at a corresponding temperature. (b) Light-light curves of ZnO nanoneedles at different temperature.	76
Figure 6.7 Temperature dependence of lasing peak emission ($\blacktriangle$) and temperature dependence of lasing threshold ($\blacksquare$) in ZnO nanoneedles samples. The solid line represents the best result of the least-squares fit to the experimental data. The characteristic temperatures are derived from the fit.	78
Figure 6.8 Fourier transform of typical lasing spectra of the ZnO nanoneedles taken at 300 K, 400 K and 550 K as shown in Figure 6.6(a). (b) Schematic diagram of the formation of closed-loop laser cavities at high and low temperature.	79
Figure 7.1 XRD patterns of the as-grown $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films with different Mg concentration.....	83
Figure 7.2 The plotting of calculated lattice constant c obtained from the XRD peaks as shown in Figure 7.1.	84
Figure 7.3 Room temperature transmittance spectra for the films with different Mg concentration.....	84
Figure 7.4 The $(\alpha h\nu)^2$ plots of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films as a function of photon energy.	85

List of Figures

Figure 7.5 The variation of the band gap energy of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films as a function of Mg content.....	86
Figure 7.6 (a) TEM image of the as-grown $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ thin film. (b) TEM image of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles. (c) TEM image of a single nanoneedle. (d) High-resolution TEM image of the nanoneedle and the corresponding selected area electron diffraction pattern of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles sample.....	87
Figure 7.7 FESEM image of the as-grown $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles.....	88
Figure 7.8 Normalized PL spectra of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles with various Mg contents. The inset shows the PL peak energy as a function of composition x of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles.....	89
Figure 7.9 Room temperature lasing emission spectra at different excitation intensities from the (a) $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ and (b) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}$ nanoneedles. The insets show the corresponding light-light curve of each of the sample.	90
Figure 7.10 Lasing emission spectra at different temperatures from the (a) $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles and (b) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}$ nanoneedles; the emission spectra were obtained under an excitation density of $2 \times I_{th}$	91
Figure 7.11 Temperature dependence of lasing peak emission and lasing threshold of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles. The solid line represents the best result of the least-squares fit to the experimental data.....	93
Figure 8.1 (a) Low magnification FESEM image of the flexible field emitter. (b) FESEM image of the ZnO nanoneedles. (c) TEM image of a single nanoneedle. (d) High-resolution TEM image of the nanoneedle.....	97
Figure 8.2 Emission current density vs applied electric field from the ZnO nanoneedles grown on polyimide foil.....	99
Figure 8.3 The FN plots of the I-V data as shown in Figure 8.2.	100

List of Figures

Figure 8.4 The stability test of the flexible emitter.....	100
Figure 8.5 Schematic diagram of the emitter and the anode in a mock-up lay-out. (b) Photograph of the flexible field emitter.....	103
Figure 8.6 (a) The x-ray transmission images of a Bougainvillea flower taken at 15 kV using the flexible emitter as an electron source. (b) An enlargement image of the stigma area as indicated by the white square.	104
Figure 9.1 Schematic diagram of the proposed ZnO nanoneedle LED.	107

List of Tables

Table 2.1 Basic properties of ZnO. 7

Table 2.2 Valence and ionic radii of candidate dopant atoms for ZnO. 8

Table 2.3 Crystal parameters of MgO, ZnO, and CdO.¹⁷ 9

Table 2.4 Lattice parameters of a number of prospective substrate materials for ZnO.
..... 12

Table 2.5 Crystallographic geometry of functional oxide nanobelts 19

Table 7.1 The Mg content comparison at .% from the Zn_{1-x}Mg_x target and Zn_{1-x}Mg_xO
thin films deposited by FCVA technique..... 82

Table 8.1 Key performance parameters of some ZnO nanostructures field emitters
reported in the literature and this work. The threshold field at 0.1 μA/cm² and the
field at current densities of 1.0 mA/cm² are listed, respectively, unless otherwise
stated. 101

Abbreviations

Abbreviations

1D	One dimensional
AFM	Atomic force microscopy
ASE	Amplified spontaneous emission
DLE	Deep level emission
EDS	X-ray energy-dispersive spectroscopy
E_g	Bandgap energy
FCVA	Filtered cathodic vacuum arc
FE	Field emission
FESEM	Field emission scanning electron microscopy
FT	Fourier transform
FWHM	Full width at half maximum
I_{th}	Threshold pumping intensity
L_c	Length of the closed-loop paths of light
LED	Light emitting diode
MBE	Molecular-beam epitaxy
M_s	Saturation magnetization
MOCVD	Metal-organic chemical-vapor deposition
NBE	Near band emission
PLD	Pulsed-laser deposition
PECVD	Plasma-enhanced chemical vapor deposition
UV	Ultraviolet
T_a	Annealing temperature
T_c	Characteristic temperature

Abbreviations

TEM	Transmission electron microscopy
XRD	X-ray diffraction
PL	Photoluminescence
TIPL	Time-integrated photoluminescence
TRPL	Time-resolved photoluminescence
QDs	Quantum dots
RT	Room temperature
SAD	Selected area diffraction
SE	Stimulated emission
SPE	Spontaneous emission
XPS	X-ray photoelectron diffraction

CHAPTER 1 Introduction

1.1 Motivations

Nanomaterials have attracted increasing interest recently, because of their specific structure, important properties that differ from their solid counterparts, and wide applications in chemistry, biotechnology, and materials science.^[1,2,3] Considerable research efforts have been devoted into the optical and electronic properties of 1D ZnO based nanostructures, which has few key advantages among the known nanomaterials. First, the cylindrical geometry and strong confinement of electrons, holes and photons make 1D ZnO nanostructure particularly attractive as potential building blocks for nanoscale UV lasers and electron emitters. Second, it exhibits both semiconductor and piezoelectric properties that can form the basis for electromechanically coupled sensors and transducers. Finally, ZnO is relatively biosafe and biocompatible, and it can be used for biomedical applications with little toxicity. Yang *et al* demonstrated UV lasing emission from ZnO nanowires, as a result of the breakthrough in the fabrication method and successful development of nanoscale laser diode.^[1]

To realize efficient short-wavelength laser devices, high quality and efficient structure should be fabricated. In order to fabricate highly efficient nanostructures based laser device, the present work has focused in the fabrication, characterization and application of ZnO based nanostructures. In the mean time, the advancement of these optical devices has been proceeded in parallel with the fundamental investigations of optical and structural properties of these nanomaterials. Although

mechanical flexibility can be achieved in organic semiconductor lasers,^[4,5] they lacked the stability to be incorporated into inorganic semiconductor structures. ZnO nanostructure lasers with mechanical flexibility are still not available so far. Another key challenge in nanolaser devices is to tune the emission wavelength, and to select suitable wavelength according to different application purpose. From the viewpoint of practical applications, the laser device should also have the ability to sustain high temperature. However, there is no report about the nanostructured laser devices operated at high temperature. This thesis is attempted to due with the above issues.

1.2 Objectives

The main objectives of this thesis are to provide:

1. Investigation in the formation of random laser cavities in ZnO thin films.
2. Fabrication and characterization of ZnO nanostructured lasers and field emitters on Si and plastic substrates.
3. Study of high temperature laser action in 1D ZnO nanostructures.
4. Wavelength tunable laser device using 1D ZnMgO nanostructures.

1.3 Major Contributions

The main contributions of this work are as follows:

1. The formation of random laser cavities in ZnO thin films was investigated.
2. It is the first time that ZnO nanoparticles based inorganic flexible UV laser device has been developed.
3. An ion-beam technique has been employed to fabricate nanoscale needle-like structures in ZnO thin films on Si and plastic substrates at room temperature.
4. High temperature lasing in ZnO nanoneedle arrays was studied.

5. Wavelength-tunable laser devices based on 1D $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles were fabricated. High-temperature lasing properties of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles were investigated.
6. Flexible field emitters and x-ray source based on ZnO nanoneedles on plastic substrates were fabricated and characterized.

1.4 Organization

Chapter 2 gives a brief review of the fabrication methods of ZnO thin film, ZnO nanostructures and their device applications as well as the general properties of ZnO. The fundamental of random laser action will be explained as well.

Chapter 3 describes the fabrication methods and characterization approaches adopted in this work.

In chapter 4, the formation of random laser cavities in annealed ZnO thin films is investigated. The secondary phase produced in the post-grown annealing process is also presented.

Chapter 5 presents the design and characterization of flexible UV random lasers based on nanoparticles and ZnO thin films on plastic substrates.

Chapter 6 presents the fabrication of ZnO nanoneedles on Si substrate and the random laser action observed from these nanoneedles. The high temperature random laser properties have been studied as well.

Chapter 7 describes the wavelength-tunable lasers based on ZnMgO thin films and 1D nanoneedles.

ZnO nanoneedles prepared on flexible plastic substrate as field emitter and x-ray source are presented in Chapter 8.

Chapter 1 Introduction

The thesis ends in Chapter 9 with a summary of the main conclusions and recommendations for further research.

CHAPTER 2 Literature Review

Recent research efforts in the wide-bandgap semiconductors throughout the world have resulted in substantial contributions to the intriguing field of ZnO based devices. ZnO has a wide direct bandgap (~ 3.4 eV), which is suitable for ultraviolet (UV) optoelectronic devices.^[6,7] Its extremely large exciton binding energy (~ 60 meV),^[8,9] is 2.4 times that of the room-temperature (RT) thermal energy ($k_B T = 25$ meV).^[10] Current optical research works in ZnO have been focused on the properties of stimulated emissions using electron beam pumping and optical pumping.^[8,11,12,13] ZnO has high-energy radiation stability and amenability to wet chemical etching, which provides an opportunity for fabrication of small-size devices. Furthermore, recent advance in fabrication and characterization methods bring broad attention to the field of nanostructured ZnO.^[14,15] With reduction in size, novel electrical, mechanical, chemical and optical properties are found in these materials, which are largely believed to be the result of surface and quantum confinement effects.^[16,17,18,19] In this section, a brief review on the growth, properties and recent progress of ZnO and its nanostructure will be given.

2.1 Properties of ZnO

The crystal structures shared by ZnO are wurtzite (B4), zinc blende (B3), and rocksalt (B1). At ambient conditions, the thermodynamically stable phase is wurtzite.^[20] The wurtzite structure has a hexagonal unit cell with two lattice parameters, a and c , in the ratio of $c/a = 1.633$ and belongs to the space group of C or $P6_3mc$. A schematic representation of the wurtzitic ZnO structure is shown in Figure

2.1. The structure is composed of two interpenetrating hexagonal-close-packed (hcp) sublattices, each of which consists of one type of atom displaced with respect to each other along the threefold c -axis by the amount of $u=3/8=0.375$ (in an ideal wurtzite structure) in fractional coordinates (the u parameter is defined as the length of the bond parallel to the c axis, in units of c). In a ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the c/a ratio or the u value.

Figure 2.1 Schematic illustration of a wurtzitic ZnO structure with lattice constant c in the basal direction.

The quality of the crystal and theoretical approximation are of primary importance for the precise determination of the physical properties. The basic properties of ZnO are listed in Table 2.1.^[21,22,23,24,25]

Chapter2 Literature Review

Property	Value
Lattice parameters at 300 K	
a_0	0.324 95 nm
c_0	0.520 69 nm
a_0/c_0	1.602 (ideal hexagonal structure shows 1.633)
u	0.345
Density	5.606 g/cm ³
Stable phase at 300 K	Wurtzite
Melting point	1975 °C
Thermal conductivity	0.6, 1–1.2 W/cmK
Linear expansion coefficient(/C)	a_0 : 6.5×10^{-6}
	c_0 : 3.0×10^{-6}
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy gap	3.4 eV, direct
Intrinsic carrier concentration	$<10^6$ cm ⁻³
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron Hall mobility at 300 K for low n -type conductivity	200 cm ² /Vs
Hole effective mass	0.59
Hole Hall mobility at 300 K for low p -type conductivity	5–50 cm ² /Vs

Table 2.1 Basic properties of ZnO.

Electron doping can be achieved in undoped ZnO due to Zn interstitials, oxygen vacancies, or hydrogen. Many kinds of atoms have been recognized as potential candidates for doping in ZnO, as shown in Table 2.2. Normally, n-type conductivity is relatively easy to be realized via excess Zn or with Al, Ga, or In doping. The main

obstacle to the development of ZnO has been the lack of reproducible and low-resistivity *p*-type ZnO. The growth of reproducible *p*-type ZnO films is only reported in few groups so far.^[26,27,28] Moreover, the electron Hall mobility in ZnO single crystals is on the order of $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature.

Atom	Valence	Ionic radius ($\text{\AA}$)
Zn	2+	0.60
Sn	4+	0.55
Li	1+	0.59
Ag	1+	1.00
Mn	2+	0.66
Cr	3+	0.62
Fe	2+	0.63
Co	2+	0.38
V	3+	0.64
Ni	2+	0.55
Mg	2+	0.57

Table 2.2 Valence and ionic radii of candidate dopant atoms for ZnO.

With respect to *p*-type doping, ZnO displays significant resistance to the formation of shallow acceptor levels. On the other hand, ZnO is considered as a prospective material for fabricating light emitting diode (LED) structures emitting in the UV region, because of its excellent optical properties.^[29,30] Therefore, *n*-type ZnO grown on other available and comparable *p*-type materials could provide an alternative way for realizing ZnO based short-wavelength LED. Many groups have been pursuing this subject by using various *p*-type materials such as Si,^[31] GaN,^[32,33] AlGaN,^[34] SrCu₂O₂,^[35] CdTe,^[36] SiC,^[37,38] and ZnRh₂O₄.^[39] These *p-n* heterojunctions

also have important applications as UV photodetectors due to its good electrical and optical properties.

The band gap of ZnO can be tuned via divalent substitution on the cation site. Cd substitution leads to a reduction in the band gap to ~ 3.0 eV.^[22,40] Substituting Mg on the Zn site in epitaxial films can increase the band gap to approximately 4.0 eV while still maintaining the wurtzite structure.^[41,42] The crystal parameters and elastic constants of ZnO, MgO and CdO are summarized in Table 2.3.

Parameters	MgO	ZnO	CdO
a (Å)	3.199	3.250	3.660
c (Å)	5.086	5.205	5.589
C_{11} (Gpa)	298	207	...
C_{12} (Gpa)	96	117	...
C_{44} (Gpa)	42.5	148	...

Table 2.3 Crystal parameters of MgO, ZnO, and CdO.²²

According to Vegard’s law, Figure 2.2 shows the lattice parameter, a , as a function of room-temperature E_g values in $\text{Cd}_y\text{Zn}_{1-y}\text{O}$ and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys. It can be seen that a -axis lengths are monotonically increasing functions of concentrations in $\text{Cd}_y\text{Zn}_{1-y}\text{O}$ and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys. This is one important advantage compared to $\text{Ga}_x\text{In}_{1-x}\text{N}$ or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ in fabricating quantum well structures. The same parametric plots in $\text{Ga}_x\text{In}_{1-x}\text{N}$ or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ are shown by dashed curves. In the case of quantum well structures, if the lattice constant of the well layer differs from that of the barrier layer, strain and a piezoelectric field will exist inside the well layers, which are key factors to downgrade the whole structures and make the excitonic properties complicated.^[43]

Figure 2.2 Optical and structural properties of $\text{Cd}_y\text{Zn}_{1-y}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy films mapped out in a plane of a -axis length and room-temperature band-gap energy. The same curves for $(\text{In}, \text{Ga})\text{N}$ and $(\text{Al}, \text{Ga})\text{N}$ alloys are also shown. The alloy compositions are shown on the top axis.^[22]

With the significant advancement of the materials engineering of thin-film and nanoscale heterostructures, a great deal of ferromagnetic semiconductors with high Curie temperature (T_c) well beyond room temperature has been observed.^[44] To date, the existences of diluted magnetic semiconductors (DMSs) based on Mn ,^[45] Cu ,^[46] Fe ,^[47] Co ^[48] doped ZnO bulk materials and thin films have been demonstrated by various fabrication methods.^[49,50,51] By combining magnetic, electronic and optical functionality, ZnO based DMSs have the high potential to be used in a variety of short wavelength optical devices, such as spin-polarized light emitters, spin-laser diodes and optical switches and modulators.^[52,53]

A goal of research in ZnO is to fabricate ZnO based optoelectronic devices operating in the UV spectral region.^[6] Compared to other wide bandgap semiconductors, the large exciton binding energy of ZnO allows the survive of excitons at room temperature and above.^[9] Thus the excitons play an important role in the optical properties of ZnO . The optical properties of ZnO have been studied by

many groups using photoluminescence (PL), photoconductivity, and absorption, which can efficiently reflect the intrinsic direct band gap, bound exciton state, and gap states due to point defects.^[54,55,56] The strong room temperature near-band-edge (NBE) UV photoluminescence peak at ~ 3.2 eV has been attributed to an exciton state.^[57] In addition, visible emission is also observed due to defect states. A blue-green emission, centered at around 500 nm in wavelength, has been explained within the context of transitions involving self-activated centers formed by a doubly ionized zinc vacancy and an ionized interstitial Zn^{2+} . Oxygen vacancies and donor–acceptor pair recombination may also involve as impurity acceptor.^[58,59,60] A broad orange-red photoluminescence emission at ~ 1.9 eV has been observed by some groups in undoped ZnO thin films, which was assigned to defect states.^[61]

2.2 Growth of ZnO

Growth of large-area and high-quality ZnO crystals is important not only for materials science but also for many device applications. The depositions of high-quality ZnO films are mainly carried out by a number of methods, such as rf magnetron sputtering,^[62] molecular-beam epitaxy (MBE),^[63,64] pulsed-laser deposition (PLD),^[65,66] metal-organic chemical-vapor deposition (MOCVD),^[67,68] and filtered cathodic vacuum arc (FCVA) technique.^[69,70] These growth methods are mainly belong to three mechanisms: hydrothermal, vapor phase, and melt grown. Because of its high vapor pressure, growth of ZnO from the melt is difficult,^[70] and growth by vapor-phase deposition is difficult to control. On the other hand, techniques involving gas phase are the most widespread method for ZnO deposition, which can produce high quality epitaxial growth and can be directly applied in industry. Among these know fabrication methods, we selected FCVA for its unique merits as simple, large-scale production, cost-effective, and integration with the silicon-based industry.

Chapter2 Literature Review

Material	Crystal structure	Lattice parameters a (Å) c (Å)	Lattice mismatch (%)	Thermal-expansion coefficient, α (K ⁻¹) α_a (10 ⁻⁶) α_c (10 ⁻⁶)
ZnO	Hexagonal	3.252 5.213	...	2.9 4.75
GaN	Hexagonal	3.189 5.185	1.8	5.17 4.55
AlN	Hexagonal	3.112 4.980	4.5	5.3 4.2
α -Al ₂ O ₃	Hexagonal	4.757 12.983	(18.4% after 30° in-plane rotation)	7.3 8.1
6H-SiC	Hexagonal	3.080 15.117	3.5	4.2 4.68
Si	Cubic	5.430	40.1	3.59
ScAlMgO ₄	Hexagonal	3.246 25.195	0.09	
GaAs	Cubic	5.652	42.44	6.0

Table 2.4 Lattice parameters of a number of prospective substrate materials for ZnO.

ZnO thin films has a strong tendency to grow with strong (0001) preferential orientation, which has been successfully deposited on various kinds of substrates, including glass,^[71] sapphire,^[72] GaN,^[73] silicon, diamond^[74],and ScAlMgO₄.^[75] as shown in Table 2.4. Although high-quality ZnO substrates are available, our current research is paving the way to deposit high quality ZnO thin films on Si or plastic substrate, due to its low-cost, availability as large-area wafers, and multiple applications. ZnO single-crystal substrates could also be useful for heteroepitaxy of GaN-based active layers. The stacking order of ZnO is the same as that of GaN, with a

lattice mismatch of only 1.8%,^[73] which result in a new generation of hybrid heterostructure optical devices.

2.3 Random Laser Action in ZnO Thin Film and Nanoparticles

“LASER” is an acronym for Light Amplification by Stimulated Emission of Radiation. Stimulated Emission is the key process to realize lasers, which was proposed in 1917 by Albert Einstein. However, no one realized the incredible potential of this concept until the 1950's, when practical research was first performed on applying the theory of stimulated emission to making lasers. In 1964, Townes, Basov and Prokhorov shared the Nobel Prize for their fundamental work about the construction of lasers. It was not until 1960, the first functioning laser was built by Maiman, out of synthetic ruby. To date, many ideas for laser applications follow the early pioneers of laser technology have revolutionized a number of industries, from communications to medicine.

Stimulated emission from bulk ZnO at room temperature was first reported by Zu *et al* in 1997,^[76] to be followed by the achievement of room-temperature lasing in thin films.^[8] Moreover, Bagnall *et al* found that the stimulated emission and lasing in ZnO thin film can survive even at temperatures as high as 550 K.^[6] Chen *et al* measured the optical gain spectrum of ZnO thin films by varying the stripe length method.^[77] Based on the one-dimensional optical amplifier mode for excited media, the result can be fitted to the equation:

$$I(E) = \frac{I_0}{g} (e^{gL} - 1) \quad (2.1)$$

where g is the optical gain coefficient and L is the length of the excitation stripe. Moreover, the thickness effect on the optical gain is also investigated by Yu *et al*,^[78] it

was found that the film forms the propagation medium in the waveguide structure, and its thickness determines the mode of propagation. This is attributed to the large gain for the modification of the spontaneous emission rate by the dielectric planar waveguide structure of air ($n_1=1$)/ ZnO($n_2=2.45$)/ sapphire ($n_3=1.8$). The film thickness values d , below which a guided mode of order m ceases to exist, can be calculated using the expression:

$$\left(\frac{d}{\lambda}\right)_{TE} = \frac{1}{2\pi\sqrt{(n_2^2 - n_3^2)}} \left[m\pi + \tan^{-1} \left(\frac{n_3^2 - n_1^2}{n_2^2 - n_3^2} \right)^{\frac{1}{2}} \right] \quad (2.2)$$

where λ is the wavelength in ZnO. There is an optimum thickness where the emission rate is maximum, and for thinner films this rate decreases rapidly and reaches zero at a cutoff value.

The laser action in disordered media was first found by Ambartsumyan in 1966.^[79] Since then, there has been considerable interest in the stimulated emission processes in disordered media.^[80,81,82,83] It has been shown that optical nonlinearity can modify light transport in disordered medium.^[84] In 1998, Cao *et al* demonstrated an efficient random laser at room temperature from ZnO nanoparticles,^[85] which show the possibility to modify light transport in disordered medium.^[86] More recently, different kinds of lasing process in disordered semiconductor powder and polycrystalline films were reported.^[87,88,89,90]

There are three distinct characters of this kind of laser action.^[91] First, sharp lasing peaks appear when the gain or the length of the system is over a well-defined threshold value. In this system, a drastic spectral narrowing is observed, but discrete lasing modes were missing. Second, more peaks appear when the gain or the system size further increases over the threshold. Third, the spectra of the lasing system is

direction dependent, not isotropic. So in the random laser action, the classical optical theoretical ideas cannot fully explain this phenomenon.

Figure 2.3 (a) The lasing feedback mechanisms, (b) typical incoherent random lasing spectrum with a pumping intensity $2 \times I_{th}$ and $0.5 \times I_{th}$, (c) typical coherent random lasing spectrum with a pumping intensity $2 \times I_{th}$ and $0.5 \times I_{th}$

As shown in Figure 2.3(a), based on the feedback mechanisms, random lasers are classified into two categories: ^[80] random lasers with incoherent (or non-resonant) feedback, also called incoherent random lasers and random lasers with coherent (or resonant) feedback, also called coherent random lasers. There are two essential components in the laser, gain medium and cavity. The gain medium amplifies light through stimulated emission, and the cavity provides positive feedback. For example in Fabry–Perot cavity mode, there are two mirrors in parallel. Light returns to its original position after traveling one round trip between the mirrors. Thus only light at the resonant frequencies spends a long time in the cavity. The long dwell time in the cavity facilitates light amplification. The laser action with closed-loop scattering is called random laser with coherent feedback. However, if one mirror is replaced by a scattering surface, light in the cavity suffers multiple scattering and its direction is

changed every time it is scattered. Thus light does not return to its original position after one round trip. The dwell time of light is not sensitive to its frequency. The feedback in such a laser is used merely to return part of the energy or photons to the gain medium. That is what we call laser with incoherent feedback. There is no resonant in this mode, the feedback is energy or intensity feedback. In the typical laser spectrum (see in Figure 2.3 (b) and (c)), the full width at half maximum (FWHM) of the emission peaks with a pumping intensity at half of pumping threshold (I_{th}) are all about 16-20 nm. However, when the pumping intensity exceeds the I_{th} (i.e., $2 \times I_{th}$), the coherent random laser spectrum is observed with sharp peaks. The FWHM ratio of coherent and incoherent random lasers is $\sim 1:10$, which implies a much higher gain and intense light emission.

Lately, time-dependent theoretical model is widely considered as the main fundamental theory for random laser.^[92] The gain medium is separated to four several electronic levels according to this theory. In the scattering process, random medium are surrounded by air and the spontaneous emission can be detected through the boundary of the random media. Even though, when we treat quantum confined random laser and chaotic cavity laser, we need to use special theory such as quantum theory and chaotic laser theory to fully explain the laser action.

Because of the random scattering, random laser can be detected in all directions. In other words, there are many different lasing modes when the pump angles are different. In addition, the lasing threshold also depends on the pump area. The changing of pump areas is realized by moving a cylinder lens before the sample to change the size of the pump beam spot on the sample.

The random laser is a non-conventional laser whose feedback mechanism is based on random scattering, as opposed to the reflective feedback by the mirrors of a

conventional laser. This alternative feedback mechanism has important application to lasers in the spectral regime where an efficient conventional mirror is not available. Furthermore, the low fabrication cost, sample specific wavelength of operation, small size, flexible shape and substrate compatibility of random laser lead to many potential applications. On the other hand, random laser action has high scattering losses, non-axial lasing radiation and multi-longitudinal-mode lasing, which are obstacles for its applications in practical lasers. Moreover, the pump threshold of random laser is relatively higher as compared to conventional laser, which is another key baffle for the electrical pumped random laser. These shortcomings can be overcome by suitable design of random laser cavities.^[93] It has been reported that single-longitudinal mode emission can be obtained from highly disordered ZnO films if the distribution of photon density can be controlled along the laser cavity, which has been obtained by the design of coupled-cavity ZnO thin-film waveguide.^[94] In addition, it has been found that MgO capped layer can be used to prevent non-axial emission and to reduce scattering loss, in highly disordered ZnO thin-film ridge waveguide.^[95]

ZnO based random lasers have been fabricated in polycrystalline thin film and nanostructured samples.^[96,97,98] The laser cavities were formed by closed-loop optical scattering in the lateral facets of the irregular ZnO grains or nanoparticles. This approach has opened up a new way to construct laser devices. Furthermore, the investigations of ZnO nanostructure random lasers on Si or plastic substrates may have many applications in the optical-electrical field.^[99,100]

2.4 ZnO Nanostructures and Its Applications

The discovery of carbon nanotubes attracts scientists' interests into a novel research field: nanotechnology, which is diverse and colorful with endless new

phenomena and applications.^[101] Exploration of nanostructures that show functionality is the key to nanotechnology. Theoretically, it has been shown that the exciton-photon coupling in ZnO nanostructure is particularly strong and the exciton radiative recombination rate drastically varies with the particle size.^[102] It is due to this quantum confinement effects, nanostructures promise application potentials in UV lasers,^[14] nanocantilevers,^[103] chemical sensors,^[104] nanogenerators,^[105] light-emitting diodes^[106] and field emitters (FEs).^[107]

Since the finding of oxide nanobelts in 2001,^[108] many nanostructures based on the functional semiconductors, such as CdS,^[109] SnO₂,^[110] GaN,^[111] InN,^[112] ZnO,^[113] and TiO₂,^[114] have been fabricated for different applications. Among them, nanostructured ZnO shows interesting electrical, optical, acoustic and chemical properties, due to its excellent optical and electrical properties based on its bulk material counterpart.^[115] One-dimensional (1D) ZnO nanostructure systems are the ideal systems with intense interests for studying, which have a well-defined and uniform geometrical shape. It is of benefit not only for understanding the fundamental phenomena in low-dimensional systems but also for developing new generation nanodevices with high performance.

The growth of patterned and aligned 1D nanostructures with high crystallinity is important for device applications. The crystallographic geometry of functional oxide nanobelts has been summarized in Table 2.5. Various kinds of ZnO nanostructures have been fabricated, for example, Wang's group have reported fabrication of single-crystal nanobelts,^[108] nanorings,^[116] nanohelices^[117] and bicrystalline nanowires.^[118] Yang's group have demonstrated ZnO nanowires fabricated using gold catalyst.^[11] In the above cases, high-temperature vapor-phase evaporation was used as synthesized method. Aligned 1D nanostructures can also be achieved by laser ablation-

Chapter2 Literature Review

catalytic,^[119] oxide-assisted,^[120] template-induced,^[121] solution-liquid-solid ^[122,123] in organic solvents and MOVPE growth.^[124] More importantly, Haupt *et al.* ^[125] were able to reduce the average diameter of the nanowires below 30 nm using a vapor transport process, which may help to fabricate 1D nanowire in a controllable fashion. Although interesting nanostructures can be produced via these techniques, future incorporation into nanoscale devices would suffer from a major drawback; the inability to grow the nanostructures in different kinds of substrates and design its position with nanoscale precision. Ion beam sputtering technique may offer the possibility to solve these problems, which can selectively fabricate 1D nanostructure on any solid substrates.^[99] More details about the ion beam sputtering technique as a controlled process to fabricate 1D ZnO based nanoneedles will be presented later in this thesis.

Nanobelts	Crystal structure	Growth direction	Top surface	Side surface
ZnO	Wurtzite	[0001] or [01 $\bar{1}$ 0]	$\pm(21\bar{1}0)$ or $\pm(2\bar{1}10)$	$\pm(01\bar{1}0)$ or $\pm(0001)$
Ga ₂ O ₃	Monoclinic	[001] or [010]	$\pm(100)$ or $\pm(010)$	$\pm(010)$ or $\pm(10\bar{1})$
t-SnO ₂	Rutile	[101]	$\pm(10\bar{1})$	$\pm(010)$
o-SnO ₂ wire	Orthorhombic	[010]	$\pm(100)$	$\pm(001)$
In ₂ O ₃	C-rare earth	[001]	$\pm(100)$	$\pm(010)$
CdO	NaCl	[001]	$\pm(100)$	$\pm(010)$
PbO ₂	Rutile	[010]	$\pm(201)$	$\pm(10\bar{1})$

Table 2.5 Crystallographic geometry of functional oxide nanobelts¹²⁶

1D ZnO semiconductor nanowires and nanorods are important building blocks for nanometer-scale electronic and photonic devices for their excellent physical properties.^[127] Recent observation of room temperature UV lasing emission from ZnO nanorod and nanoneedles shows the possibility to fabricate ZnO based nanolasers.^{[14,}

Chapter2 Literature Review

^{99,128]} The discoveries of 1D ZnO nanostructures also bring a revolution in electron emitting sources because of their large aspect ratios comparable to CNTs and the degradation of field emission characteristics by residual gas may be reduced for an oxide surface of ZnO.^[129,130,131] In addition, 1D ZnO nanostructures have also attracted considerable attention for solid-state gas sensors and humidity sensors with great potential for overcoming fundamental limitations due to their ultrahigh surface-to-volume ratio.^[132,133, 134]

CHAPTER 3 Experimental and Methodology

3.1 *Filtered Cathodic Vacuum Arc*

Filtered cathodic vacuum arc (FCVA) technique belongs to the family of arc plasma deposition, which is first proposed by Thomas Edison in 1892.^[135] The cathodic arc is a low-voltage, high-current plasma discharge that takes place between two electrodes in vacuum. It is also called a metal vapor vacuum arc or vacuum arc. Ever since the metal coatings deposited from vacuum arc by Kikushi *et al.*,^[136] vacuum arc has aroused worldwide interest as a deposition tool for thin films. To date, vacuum arc deposition equipment is one of the most important commercial-available technique for high quality thin films deposition.

However, the thin films deposited by vacuum arc are suffered from the generation of macroparticles,^[137] which hinder their advanced usage as optics and microelectronics devices. To overcome this obstacle, Aksenov *et al.*^[138] designed a magnetic filter in the cathodic vacuum arc system in 1980, that is what we call later “FCVA”. In the past two decades, various metal (e.g. Zn, Al, Ti, W, Si, Fe, Co) oxide thin films with superior optical and electrical properties have been deposited by FCVA technique, which recognized it as a promising technology.^[139,140] Compare with other deposition methods, such as chemical vapor deposition, spray pyrolysis, MOCVD, and atomic layer deposition,^[141,142,143,144] the advantages of the FCVA technique include: (1) deposition on lattice mismatched substrate or plastic substrate, (2) low-temperature deposition, (3) high deposition rate (~50 nm/min), (4) the use of large substrate (i.e., substrate diameter can be as large as 8”), and (5) environmental friendly (non-toxic precursor).

Figure 3.1 provides a schematic illustration of FCVA system used in this study. The system mainly consists of three parts: a cathodic arc source, a plasma-filtering duct, and a deposition chamber. A rotary-cryogenic pump system is connected to the chamber for pumping down to the desired pressure during the deposition. The cathodic vacuum arc source has five main parts: the anode wall, the power supply, the arc trigger, the target, and the target cooling system.

Figure 3.1 Schematic illustration of a FCVA system.

The filtering duct is the most important part of the FCVA system as it can effectively remove macroparticles from the metal-oxide plasma. The exterior wall of the filtering duct is surrounded by a set of magnetic coils for the generation of magnetic field to guide the plasma ions. High purity, typically 99.99%, metal target (i.e., Zn and ZnMg alloy targets for ZnO and ZnMgO deposition, respectively) was used as the cathode material and oxygen was used as the reactant gas. Typically, the base pressure was kept at approximately 2×10^{-6} Torr, and the pressure during

deposition is about 10^{-4} Torr. When the trigger is struck on the metal target with an arc current of 60 A, energetic plasma ions from the metal target are formed. The plasma ions are then guided by the magnetic field inside the plasma-filtering duct. Oxygen is introduced inside the filtering duct through an outlet along the filter such that metal-oxide plasma can be formed. The oxygen partial pressure in the deposition process is set to 2×10^{-4} Torr. Although the substrate temperature in the FCVA system can be tuned in the range from RT to ~ 400 °C, a substrate temperature of 200 °C is sufficient to produce high-crystal-quality ZnO thin films.

3.2 Ion Beam Sputtering

Currently, different methods have been reported for the fabrication of 1D ZnO nanostructures, including template, thermal-evaporation, vapor-transport, condensation, MOCVD, buffer-layer-precoated, solution and laser-ablation methods.^[14, 124, 127] However, previous efforts to synthesize vertically aligned 1D ZnO have usually produced impurity materials, needed expensive substrates, or complex experimental procedures, or used catalysts, additives to control their growth. Exploring simple, cheap, catalyst-free, low-temperature methods of synthesizing vertically aligned 1D ZnO nanostructures remains a challenge. Energetic ions are an excellent tool for the creation of nanostructures on a surface or in the surface-near region of any kind of solid at room temperature.^[145] The fabrication mechanism induced by sputtering of solid surfaces and the formation kinetics is mainly determined by etching instead of growth.^[149] In an established sputtering model, surface atoms are ejected into a vacuum from an ion-impacting point via a collision cascade in the projectile-implanted subsurface. The ion beam sputtering technique has been proved to entail the formation of nanosized ripples, pyramids, conical protrusions and whiskers structures of carbon, Si and Au.^[146, 147, 148]

In this study, ion beam sputtering technique was used to fabricate ZnO and ZnMgO nanostructures. Two types of the experimental systems are employed for different fabrication purposes. (1) To fabricate nanoneedles as optical devices, the experimental systems is an ultra-high vacuum (UHV) system comprised by differentially pumped micro-beam ion gun (JEOL; MIED) and an arc-plasma gun (ULVAC; APG-1000).^[149,189] The ion gun operated under an UHV ambient, is located with an incidence angles at 55° from the normal to the surface, as shown in Figure 3.2. Prior to ion beam irradiation, a thin carbon layer was deposited onto the ZnO films which enhances the formation of nanostructures during sputtering. An Ar^+ ion (i.e., 3 keV) beam with $380\ \mu\text{m}$ beam-diameter was used to irradiate the ZnO and ZnMgO thin films. The inset of Figure 3.2 is the ion beam intensity spectrum, which shows that the intensity of ion beam is in a Gaussian profile (i.e., the center of ion beam is 3 keV). The chamber was pumped down to $\sim 10^{-7}$ Torr, and the pressure remained at 10^{-6} Torr during the sputtering process. Prior to characterization, the residue of carbon layer was removed by ethanol.

Figure 3.2 Schematic diagram of the nanoneedle fabrication setup.

(2) To fabricate large area ZnO nanoneedles as field emission devices, a Kaufman-type ion gun (Ion Tech. Inc. Ltd., model MPS 3000 FC) was used instead of the micro-beam ion gun. ZnO thin films with thickness of about 650 nm were first deposited on polyimide foils by the FCVA technique. A thin carbon layer was also deposited onto the ZnO films before ion beam irradiation. The sample with a dimension of 4 cm x 1.5 cm was then irradiated at room temperature for 60 min by 1 keV Ar^+ ions with a beam diameter of 6 cm in a high vacuum system with base and working pressure of 1.5×10^{-5} Torr and 1×10^{-2} Torr, respectively. Finally, the residue of carbon layer was removed by ethanol.

Figure 3.3 Schematic diagram of the nanoneedle formation process.

Figure 3.3 shows the formation processes of the ZnO nanoneedles. The ZnO thin film is protected by a thin layer of carbon. As described in reference [149], Ar^+ ion irradiation onto a carbon film can form carbon protrusions, which can act as a protection against the sputter erosion of the tips of ZnO nanoneedles. Further ion-irradiation sputter the carbon film away and form slender needle-like structures of ZnO. After the irradiation, the residue of carbon layer will be removed by ethanol.

Ion beam bombardment of thin films surfaces provides a controlled and cost effective process for the formation of regular array of nanostructures, which offers several advantages over other fabrication methods: (1) room temperature fabrication, (2) catalyst-free, (3) selectively growth of nanostructures, and (4) on any substrates.

3.3 Sample Characterization Methodology

3.3.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is one of the most useful and precise tools for microstructure characterization of thin films and nanomaterials. It provides the information of size, shape and arrangement of the particles in the sample as well as their relationship to each other on the scale of atomic diameter. The arrangement of atoms in the sample can also be shown in their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter. The detailed study of the TEM in this work was done by using TEM (JEOL TEM-2010) operating at 200 kV.

The preparation of the cross-section TEM specimens was first by ultrasonically cutting two pieces of sample of the size of 4 x 5 mm². The samples were then glued face to face. It was introduced into a copper grid and secured with epoxy. The composite was sliced into 600 µm thick disks with the low speed diamond saw. The disks were then mechanically ground with a disk grinder to a thickness of about 100 µm. The centre portions of these disks were further grounded by the dimple grinder to approximately 20 µm. The samples were then thinned in the precision ion polishing system with argon ions at an accelerating voltage of 5 kV which incident at both surfaces at an angle of 4°. A hole is finally created at the center of the specimen to provide larger transparent areas for observation.

3.3.2 Field Emission Scanning Electron Microscopy

Field emission scanning electron microscopy (FESEM) forms an image of the surface of materials by scanning a fine electron beam. Both secondary and backscattered electrons can be collected giving information about the surface topography and atomic weight of the sample. The surface morphologies of our

samples were studied using FESEM (JEOL JSM-6340F) with an X-ray spectrometer for elemental identification, which has a resolution of 1 nm at 15 kV and above accelerating voltages and 2.5 nm at 1 kV.

3.3.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is used to analyze the surface morphology of the films in tapping mode (Digital Instruments NanoScope IIIa) with Si tip. The resolution of root mean square (RMS) roughness is 0.1 nm.

3.3.4 X-ray Diffraction

X-ray Diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials, which provides information on structures, phases, preferred crystal orientations (texture) and other structural parameters such as average grain size, crystallinity, strain and crystal defects. All the XRD measurements were carried out by CuK α ($\lambda = 0.154$ nm) radiation on X-ray diffractometer (Rigaku Ultima) (40 kV, 40 mA). The grain size can be calculated from Scherrer's equation:

[150]

$$t = \frac{C\lambda}{B \cos \theta}$$

where λ is the x-ray wavelength (nm), B is the full width at half maximum (FWHM) of the peak (radians) corrected for instrumental broadening, θ is the Bragg angle, C is a factor (typically 1.0) that depends on the crystallite shape, and t is the crystallite size (nm).

3.3.5 Spectrophotometer

Transmittance was measured by UV-Vis spectrophotometer (HP 8453, 190 nm ~1100 nm) and UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 900, 200 ~ 3500 nm). The transmittance was automatically calibrated against a bare quartz substrate as a reference sample, and the absorption coefficient was obtained from the transmittance. Absorption coefficient α was calculated from the relation:

$$T = A \exp(-\alpha d)$$

where T is the transmittance of thin film, A is a constant and d is the film thickness.

3.3.6 Photoluminescence Spectroscopy

The light energy can be dissipated as radiation, which results in a luminescence emission of semiconductor material, called photoluminescence (PL). PL is a very important technique used to study the electronic band structure of semiconductors. The intensity and spectral content of PL is a direct measure of various important material properties.^[151]

As shown in Figure 3.3, there are four main possible processes when the semiconductors excited by light with no less than the band gap energy. Process I is the photo-excited process in which the electrons from the valence band (VB) are promoted to the conduction band (CB) with different energy levels to become different excited states, with simultaneous generation of holes (h^+) in the VB under irradiation. In fact, the excited electrons with different energy levels in the CB easily transfer firstly to the CB bottom via non-radiative transitions; subsequently, the processes II, III or IV will possibly occur. In process II (i.e., band to band), electron transit from the CB bottom to the VB top and simultaneously release photon energy, which equals to the band gap energy. Process III is the excitonic PL in which the non-

radiative transitions of excited electrons from the CB bottom to different sub-bands (or surface states) occur first, and subsequent radiative transitions from the sub-band to the VB top can take place. In addition, the excited electrons at the CB bottom can come back to the VB directly or indirectly by non-radiative transitions, which is the process IV.

Figure 3.4 Main physical processes of a semiconductor excited by light with equal to or higher than band gap energy, i.e., I: photo-excited process; II: band to band PL process; III: excitonic PL process; IV: non-radiative transition process.

The PL measurement system consists of a 325 nm He-Cd laser with 100 fs pulses operate at room temperature and a streak scope with a spectral coverage of 300 nm–1100 nm. The luminescence was collected in a conventional back-scattering geometry. One of the most widely used methods to quantify the energy loss rate of hot carriers in semiconductors is by measuring time-resolved photoluminescence (TRPL) spectra and time-integrated photoluminescence (TIPL) spectra. The free-carrier or exciton lifetime, an important parameter related to material quality and device performance, can be measured by TRPL spectroscopy. The exciton lifetimes will vary

with crystal quality, becoming longer as the quality improves. The efficiency of the radiative recombination is strongly related to the decay time of the particular transition. In a TRPL measurement, the spectra in the time domain are converted to the energy domain, resulting in a family of PL versus energy spectra at various times following the excitation. The carrier temperature is then calculated by fitting each spectrum to a Fermi–Dirac carrier distribution, which also gives the carrier temperature as a function of time and the decay time can be calculated.^[152]

TRPL and TIPL were conducted with the excitation of 150 fs pulses centered at 325 nm from an optical parametric amplifier, which was driven by a 1 kHz Ti:sapphire regenerative amplifier. The luminescence was collected in a conventional back-scattering geometry. For the TIPL measurement, the PL was dispersed in a 50 cm monochromator and detected with a photomultiplier using standard lock-in amplification. For the TRPL measurement, the luminescence was dispersed in a 25 cm monochromator and detected with a streak camera. The total time resolution of the setup is 20 ps. The sample was secured in a close-cycle He gas cryostat for temperature-variable measurements.

3.3.7 X-ray Photoelectron Spectroscopy

The Mg concentration in the ZnMgO samples was determined by x-ray photoelectron spectroscopy (XPS). The XPS experiment was carried out by a Kratos-Axis spectrometer with Dual-Anode Al Ka (1486.6 eV) X-ray radiation (150 W, 15 kV and 10 mA) and hemispherical electron energy analyzer on the surface of the samples. The base vacuum of the chamber is 2×10^{-9} Torr. The survey spectra in the range of 0–1100 eV were recorded in 1 eV step followed by high-resolution spectra over different element peaks in 0.1 eV step, from which the detailed composition was calculated.

3.3.8 Field Emission

Field emission (i.e., Fowler-Nordheim tunneling) is the process whereby electrons tunnel through a barrier in the presence of a high electric field. As shown in Figure 3.4, the emitted current depends directly on the local electric field at the emitting surface, E , and on its work function, ϕ . In fact, a simple model (the Fowler-Nordheim model) shows that the dependence of the emitted current on the local electric field and the work function is exponential-like. Therefore, a small variation of the shape or surrounding of the emitter (geometric field enhancement) and/or the chemical state of the surface has a strong impact on the emitted current.

Figure 3.5 Standard field emission model from a field emitter, showing the potential barrier and the corresponding energy distribution (i.e., energy on the vertical axis, current on the horizontal logarithmic axis).

Field emission experiment was carried out in a parallel plate configuration (vacuum chamber at $\sim 8.0 \times 10^{-7}$ Torr) at room temperature. ZnO nanoneedles deposited on plastic substrate are the cathode. Indium tin oxide coated glass was used as the anode, which was separated by a 100 μm thick Teflon spacer. The sample area

was 0.28 cm^2 . A voltage was applied between the anode and cathode to supply an electric field, sweeping from 300-1600 V. The emission current was monitored by a Keithley 6517A electrometer.

3.3.9 Lasing Measurement

The lasing measurement system consists of a Nd: YAG laser (Surelite III-10Hz), the Surelite Separation Package (SSP), the monochromator (Oriel 77200 1/4m grating), lens and mirrors, which are adjusted to the same height with respect to the optical table and secured, as shown in Figure 3.5. The 10 Hz, tripling 355nm output of the Nd: YAG laser was optically pumped into the sample at 90° , focused by a cylindrical lens of focal length 5~10 cm. The emission at the facet of the sample was collimated into a slit input assembly of a monochromator, via a plano convex lens (i.e., focal length 5 cm). Beam exited at the slit was detected from a built-in transimpedance amplifier Si detector, mounted at the slit assembly. Signal output can be detected using either a Merlin 70100 or a SR510 analog lock-in amplifier. The reference signal fed into the lock-in amplifier was output from a circuit discussed afterward. The data obtained was recorded and analyzed, using a computer program written in Labview. For high temperature lasing experiments, the samples were mounted on an electrical ceramic heater with surface area of $1 \times 1 \text{ cm}^2$ and the temperatures can be varied from 300 to 700 K.

The Fourier transform of the lasing emission spectrum gives an accurate analysis of laser cavity, which is a powerful technique to investigate the emission lines.^{[153][54]} The expected intensity of the Fourier transform of a Fabry–Perot laser cavity has been derived by Hofstetter *et al*,^[155] which consists of a series of equally spaced diminishing lines given by

$$I(d) = \left| 1 - R \exp(2i\phi) \right|^2 \sum_{m=0}^{\infty} \sum_{l=0}^{\infty} \frac{R^{l+m} \exp[-2i\phi(l-m)]}{kL(l+m+1) + i[\pi d + nL(l-m)]}$$

where k is the wavevector, $k = 2\pi/\lambda$, d is the conjugate variable to wavevector, l, m are integers, ϕ is the phase change upon reflection at the mirrors, and R is the mirror reflectivity. The important part of this expression is that peaks are produced whenever the imaginary part of the denominator goes to zero. This occurs when d is a multiple of nL/π , or $nD/2$ with the circular geometry used here. In a random laser, we assume that the closed-loop paths of the coherent photon are approximately circles, then the optical path $2L$ is replaced by the circumference of the loop, and the resultant FT harmonics appear at the multiples of $nD/2$, where D is the loop diameter.

Figure 3.6 A schematic illustration of the layout of lasing measurement.

CHAPTER 4 Formation of Random Laser Cavities by Thermal Annealing

4.1 Introduction

Realizing ZnO in highly oriented/epitaxial thin-film form is currently a subject of active research. This interest stems from the strong commercial desire for blue and UV light emitters and detectors. It is due to the wide band gap and large exciton binding energy, ZnO has potential applications in UV optoelectronic devices, such as UV laser, optical waveguide, and exciton-related devices.^[8, 29, 96] However in these applications, it is imperative to grow high-crystal-quality thin films of ZnO especially on substrates of the most used electronic material, i.e., Si, albeit it is totally lattice mismatched.

The luminescence of ZnO films typically consists of a near-band-edge (NBE) emission (around 380 nm) and a deep-level (DL) emission.^[21] The mechanism of NBE has been attributed to free excitons, donor-or acceptor-bound excitons, and their phonon replicas.^[21] To explain the DL emission, various models have been suggested. For example, Vanheusden proposed that the green emission is the recombination of oxygen vacancies (V_O) electrons with photoexcited holes in the valence band, based on electron paramagnetic resonance, optical absorption, and photoluminescence spectroscopy.^[156] Lin *et al.* assigned the green luminescence to an electron transition from the bottom of the conduction band to the antisite defect O_{Zn} level.^[157] Wu *et al.* attributed the violet, green, and yellow emissions to the radiative recombination of delocalized electrons close to the conduction band with deeply trapped holes in V_{Zn}^- , V_O^+ , and O_i^- centers, respectively.^[158] Among the different mechanisms proposed to

explain the DL luminescence, green emission is commonly observed in oxygen deficient ZnO samples, while orange emission is seen in oxygen-rich films obtained by annealing in oxygen.^[159]

In general, the different growth methods and postgrowth treatments result in different concentration and spatial distribution of intrinsic or extrinsic defects. The postgrowth annealing is an important method for improving the quality of thin films and changing its luminescence characteristics.^[160] Moreover, Yu et al. demonstrated that random lasing cavities can be formed in ZnO on Si substrate by thermal annealing.^[96] ZnO thin film waveguide structure on Si, which is a pre-requisite for laser devices as well as for device efficiency,^[93] has also been reported. In order to confine light on Si substrate, a buffer layer is inserted between ZnO and Si. This is required because the refractive index of Si (~ 3.45) is higher than that of ZnO (~ 2.1). Silicon dioxide (SiO_2) is selected as the buffer layer because it has a refractive index of ~ 1.45 so that transverse optical confinement can be achieved in a ZnO thin film with minimum absorption loss. The effect of the buffer layer undergone thermal annealing on the optical properties of ZnO needs further investigations.

ZnO with particles or grains in nanoscale diameter exhibit a so-called quantum size effect, an enlargement of the band gap that is typically measured by the blueshift of light absorbance.^[161] Novel devices can be fabricated based on ZnO quantum dots (QDs). ZnO QDs are made typically by wet chemistry involving a series of steps that require close attention as ZnO continuously grows (ages),^[162] which suffer from undesirable impurities. Another way for synthesis of ZnO nanoparticles is embedding them in transparent silica matrices, aerogels, or spray granule.^[163, 164, 165] These wet preparation techniques require large amounts of solvents, multiple process steps, and

minute control on composition. In our experimental results, we found a one-step synthesis of stable ZnO QDs by thermal annealing.

In this chapter, the as-grown films have been treated by annealing at different temperatures in air. We examine (i) the effect of annealing on the structural as well as optical properties of the ZnO films, (ii) the role of buffer layer on the optical properties of the ZnO, and (iii) the formation conditions of ZnO QDs and their optical properties. Significant improvement in the crystal quality and PL properties has been observed in the annealed films. The observation of laser action in the annealed films is one of the major outcomes of annealing. The significance of a self-generate buffer layer is also formed in the annealed ZnO films on Si substrate without a thick SiO₂ layer.

4.2 Experimental Details

ZnO thin films were deposited on Si substrates using the FCVA technique at room temperature. The deposition of ZnO films has been described in details in chapter 2. The substrates were *n*-type (100) with a thin native oxide layer. Prior to depositing ZnO, a ~ 400 nm SiO₂ layer was grown on some Si substrates by dry oxidation at 1000 °C. The as-grown films were then annealed in air for 2 h with various temperatures up to 1000 °C. In order to grow ZnO QDs, the ZnO/SiO₂/Si samples were annealed for 10 h at 900 °C.

4.3 Results and Discussions

4.3.1 Microstructure and Optical Properties of Annealed ZnO

Figure 4.1 shows the XRD patterns of the ZnO thin films on SiO₂/Si substrate annealed at different temperatures from 400 °C to 900 °C. The XRD spectrum of the

as-deposited ZnO thin film indicates no preferred orientation and crystal structure. The annealed ZnO samples are highly *c*-axis oriented. The FWHM (2θ) of the (0002) peak decreases with an increase in T_a , indicating the enhancement in the crystallite sizes of ZnO. On the other hand, the increase in (0002) peak intensities show noticeable improvement in the crystalline quality with an increase in T_a . Furthermore, a small peak at 24.5° is found in the films with $T_a \geq 700^\circ\text{C}$, which indicates the appearance of a new phase.

Figure 4.1 XRD patterns of the ZnO thin films annealed at different temperatures.

The out-of-plane lattice constant (c) of the ZnO thin films was calculated as shown in Figure 4.2(a). The c values are found to decrease with an increase in annealing temperature, T_a . The films annealed at 400°C have a c value very close to the theoretical value ($c_0 = 0.5205\text{ nm}$). Hence, we assume it is the reference for comparison of the strain in the thin film. The percentage strain along the c axis of the films perpendicular to the substrate is defined by $\epsilon_{zz} = \frac{c - c_0}{c_0}$, where $c_0 = 0.5205\text{ nm}$

is the lattice constant in the unstrained crystal.^[166] The annealed films with $T_a > 600$ °C have c values greater than the theoretical value, which indicates a tensile strain in the films and released with increase of the annealing temperature, as shown in Figure 4.2(b).

Figure 4.2 The plotting of calculated values of (a) FWHM of the (0002) peak, and (b) the lattice constant c and the estimated percentage strain of the ZnO films from the XRD patterns as a function of annealing temperature.

The FESEM micrographs in Figure 4.3 show the effect of annealing temperature on the grain size for the as-grown, 600 °C and 900 °C annealed ZnO thin films. It is noted that the as-grown ZnO thin film is smooth without noticeable feature, as shown in Figure 4.3(a). On comparing the micrographs of 600 °C and 900 °C annealed films,

the enhancement of the grain size with T_a is clearly observed. This observation supports the XRD results shown in Figure 4.2, wherein the FWHM decreases with T_a .

Figure 4.3 FESEM images of the ZnO thin films (a) as-grown, (b) 600 °C annealed and (c) 900 °C annealed.

To observe the changing in roughness of the thin films with annealing temperatures, AFM topographs of the as-grown and annealed films were also taken. The root-mean-square (RMS) roughness of the ZnO films was measured using the NanoScope III software (attached to the AFM machine). As shown in Figure 4.4, the grain size and surface roughness increases with an increase in T_a . The sample annealed at 900 °C has a RMS roughness of 10.7 nm, which is much larger than that of the as-grown film (1.3 nm).

Figure 4.4 AFM topographs of ZnO thin films (a) as-grown, (b) 600 °C annealed and (c) 900 °C annealed. All the topographs share the same color scale bar with the maximum height of 40 nm, and the corresponding RMS roughness of the films is indicated in the figure.

Figure 4.5 shows the cross-sectional and plain view TEM micrographs of the as-grown ZnO thin film. As shown in Figure 4.5 (a) and (b), the interface between the ZnO film and SiO₂ layer is atomically sharp and coherent. The selected area diffraction (SAD) pattern confirms that the growth direction of ZnO grain is along *c*-axis and perpendicular to the substrate. As shown in Figure 4.5 (c) and (d), the film is consisted of quasi-spherical shape ZnO grains with average size ~ 10 nm. The SAD pattern (Figure 4.5 (c)) exhibits several separated rings and are identified as wurtzite structure of ZnO.

Figure 4.5 TEM image of the as-grown ZnO thin films in cross-sectional ((a) and (b)) and plain view ((c) and (d)). The insets show the corresponding SAD patterns.

Figure 4.6 shows the TEM images of the ZnO thin film annealed at 900 °C. After annealing, the ZnO grains obtained thermal kinetic energy, which drive the aggregation of the nearby grains to coalescence. As a result, long-range crystallinity is dominated in the sample. ZnO grains with average size of ~150 nm can be clearly seen in Figure 4.6(a). Figure 4.6(b) shows the HRTEM image and the corresponding SAD pattern of a typical ZnO grain. The lattice spacing ($c = 5.26 \text{ \AA}$) matches well with a hexagonal ZnO. As shown in Figure 4.6 (c) and (d), sharp ZnO grain boundaries can be observed, as labeled by the arrow in Figure 4.6(d).

Figure 4.6 TEM images of ZnO thin film annealed at 900 °C in cross-sectional ((a) and (b)) and plain view ((c) and (d)). The arrow shows the grain boundary between two grains.

As shown in Fig. 4.6(a), a 150 nm thick zinc silicate ($\text{Zn}_x\text{Si}_{1-x}\text{O}$) layer is formed between ZnO and SiO_2 layers. The formation of this layer can be attributed to the ZnO diffused into SiO_2 layer at high temperature. The growth of $\text{Zn}_x\text{Si}_{1-x}\text{O}$ can be expressed in a simple chemical reaction as:^[167]

The structure evolution and effects of this $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer on the ZnO/Si sample will be discussed later.

Figure 4.7 PL spectra of the ZnO thin films annealed at different temperatures from 600 °C to 1000 °C. The PL of the as-grown ZnO thin film is also included for comparison.

Figure 4.7 shows the room temperature PL spectra of the as-grown ZnO thin films annealed at different temperatures in the range from 600 °C to 1000 °C. The luminescence can be attributed to the NBE emission and the DL emission. The NBE emission in the as-grown sample is centered at ~ 374 nm, which blue-shift 6 nm (~56

meV), as compared with the typical PL of bulk ZnO (i.e., ~380 nm) crystal. The energy shift is probably due to a quantum-confinement-induced energy gap enhancement.^[168] The energy gap under quantum confinement effect can be expressed as:^[169]

$$E_g \approx E_{g0} + \frac{h^2 \pi^2}{2\mu d^2} - \frac{1.8e^2}{\epsilon d}$$

where E_{g0} is the energy gap for bulk materials, d is the particle size, $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$ (m_e and m_h is the electron and hole effective masses, respectively), and ϵ is the dielectric constant. For ZnO, the effective masses of electrons and holes are $0.38m_0$ and $1.80m_0$,^[170] respectively, and the dielectric constant is 8.75.^[63] Thus, we obtain $E_g(eV) \approx E_{g0} + 75.885d^{-2}(nm)^2 - 1.902d^{-1}(nm)$. Therefore, the enhanced band gap can be written as $\delta E(eV) \approx 75.885d^{-2}(nm)^2 - 1.902d^{-1}(nm)$. The calculated enhanced band gap in ZnO of grain in 10 nm diameter is ~56.8 meV, which is in good agreement with our results.

As the annealing temperature increases from 600 °C to 900 °C, the NBE peak position is similar to that of a typical bulk ZnO. The NBE emission intensity increases remarkably and the DL peaks become weaker, while a FWHM of the NBE emission decreases gradually, as shown in Figure 4.8(b). The strongest NBE emission with the smallest FWHM of ~10 nm is observed at around 378 nm (3.28 eV) for the films annealed at 900 °C, as shown in Figure 4.8 (a). An important method to evaluate the concentration of structural defects in ZnO films is to compare the PL intensity ratio of the NBE emission to the DL green emission.^[171] The reported epitaxial thin films grown by other fabrication methods^[142,172] showed relatively weaker DL emissions, with ratios of 20 to 60, respectively. The intensity ratio of the NBE emission to the DL

green emission is shown in Figure 4.8(b). The highest ratio in our experiment is 82 from the sample annealed at 900 °C, from which the DL emission band at around 2.5 eV is highly suppressed. It suggests that the ZnO films annealed at 900 °C are of superior quality.

Figure 4.8 (a) NBE peak intensity and peak position as a function of annealing temperature. (b) Intensity ratio of the NBE emission to the DL green emission and the FWHM of NBE emission position as a function of annealing temperature.

As shown in the Figure 4.8, a red-shift of 0.02 eV is observed in the UV range peak for the sample annealed at 1000 °C as compared to the 900 °C annealed sample. In addition, both the emission intensity and intensity ratio of the I_{NBE} to I_{DL} decrease

at this annealing temperature. This phenomenon has been reported by some groups [171, 173] and no satisfactory consensus about the origins is proposed so far. We have given our own explanation as follows. Firstly, a high annealing temperature (above 900 °C) facilitates the migration of grain boundaries and promotes the coalescence of small crystals, and thus favors a decrease of the concentration of nonradiative recombination centers. Therefore, the red-shift may deduce by a shrinkage of the energy band gap with an increase in particle size. Secondly, high temperature increases the probability of the formation of radiative defects, which will compete with excitonic recombination and decrease UV emission efficiency. The redshifting and broadening may mainly resulted by these two mechanisms.^[173]

It is obvious that the cleaved facets of the annealed thin film are too rough to provide sufficient optical feedback for sustaining UV lasing. However, in the absence of any fabricated mirrors, we observed lasing in the annealed ZnO films. Figure 4.9 shows the RT emission spectra from the edge of the ZnO thin film annealed at 900 °C under 355 nm excitation. It should be noted that lasing emission can be detected from the ZnO/SiO₂/Si sample with $T_a \geq 600$ °C. At low pump intensities, single-broad spontaneous emission peak with a FWHM of ~15 nm can be detected from both polarizations. When the pump intensities exceeding a threshold value (i.e., ~0.34 MW/cm²), lasing modes of both polarizations are excited at around 390 nm with linewidth less than 0.4 nm. The number of lasing modes (of both polarizations) increases with an increase of pump intensities. It should be noted here that the emission above the threshold were measured to be strongly polarized (i.e., light emission intensity from TE polarization was much higher than TM polarization), which is optical confinement effect due to the ZnO/SiO₂/Si waveguide structure.^[96] A

broad emission spectrum is also found in the TM mode, which is attributed to the spontaneous emission.^[166]

The lasing characteristics of the annealed ZnO films show remarkable differences from that of a conventional laser. As shown in Figure 4.10(a), the laser emission from the ZnO films could be observed in all directions. The laser emission spectrum varied with the observation angle. Furthermore, the lasing emission threshold is dependent of the excitation area. Figure 4.10(b) shows the variation of emission spectra with excitation area from $\sim 1 \times 10^{-3} \text{ cm}^2$ to $\sim 3 \times 10^{-3} \text{ cm}^2$ for constant pump intensity of 1.0 MW/cm^2 . As the excitation area decreases, the lasing threshold density increases. When the excitation area was increased, more lasing peaks emerged in the emission spectra. On the contrary, when the excitation area was reduced to below a critical size (i.e., $\sim 1 \times 10^{-3} \text{ cm}^2$), laser oscillation ceased.

Figure 4.9 Emission spectra of the ZnO/SiO₂/Si sample annealed at 900 °C taken from TE and TM polarizations as a function of pump intensity.

Figure 4.10 (a) Emission spectra from 30°, 45°, and 60° from the sample surface. The pump intensity is $\sim 1.0 \text{ MW/cm}^2$ and the excitation area is kept at $3 \times 10^{-3} \text{ cm}^2$. (b) Emission spectra of the sample with different excitation areas. The excitation intensity is $\sim 1.0 \text{ MW/cm}^2$.

According to random laser theory,^[80] laser cavities formed by multiple scattering could have different output directions. Lasing modes observed at different angles may be different. In addition, the lasing modes from these cavities could be observed in different directions. When the excitation area increases, there are more closed-loop paths for light, and thus, the number of lasing modes increases. On the other hand, when the excitation area is reduced to below a critical size, laser oscillation stops because the closed-loop paths are too short, and the amplification along the loops is not sufficient to achieve lasing. That is why the pump intensity required to reach lasing threshold increases with a decrease of the excitation area.^[98,97] From the above measurement, all of the essential characteristics of random laser action have been observed from the sample. Therefore, the observed self-formation laser cavities are attributed to the strong optical scattering in the annealed ZnO thin films.

4.3.2 Self-generated Guiding Effect in ZnO Thin Film without Buffer Layer

As mentioned earlier: the 400 nm SiO₂ buffer layer is necessary to provide transverse optical confinement for laser action. Therefore, it was presumed that no laser action can be detected from ZnO/Si structure due to the high absorption of Si. However, it is very interesting that lasing emissions can be detected from the annealed ZnO/Si with $T_a \geq 700$ °C. Figure 4.11 shows the light–light curves and emission spectra of the ZnO/Si sample annealed at 900 °C, which is found to be similar to the results obtained from the ZnO/ SiO₂/ Si sample annealed at 900 °C. Threshold pump intensity was found to be about 0.45 MW/cm². For both polarizations, single-broad emission spectra with a FWHM of about 15 nm are observed. When the excitation exceeds the threshold, sharp lasing peaks of a linewidth less than 0.4 nm are emerged from the single-broad emission spectra. A further increase in pump intensity increases the number of lasing modes. The appearance of sharp lasing peaks is in fact caused by the formation of closed-loop paths for light through recurrent scattering (i.e., coherent feedback). In addition, the lasing intensity of the TM polarization is weaker than that of the TE polarization, which is due to the light confinement effect. However, such random laser emission is not detected in annealed ZnO/Si sample with $T_a \leq 600$ °C (not shown here). In order to investigate the reason of the light confinement from the structure without the buffer layer, a detailed TEM work was carried out.

Figure 4.11 Emission spectra of the ZnO/Si sample annealed at 900 °C taken from TE and TM polarizations as a function of pump intensity.

HRTEM images at the interfacial of the ZnO/Si samples annealed at different temperatures are shown in Figure 4.12. An amorphous SiO₂ layer having a thickness of 8 nm is found on the silicon substrate (Fig. 4.12(a)). In order to provide efficient optical confinement, a SiO₂ layer with a thickness of ~ 400 nm is required.^[96] It is obvious that the 8 nm SiO₂ is not enough to confine the light. Despite the grains enhancement, the native SiO₂ layer after 600 °C annealing remains 8 nm (Figure 4.12(b)). Figure 4.12(c) shows the TEM images of the sample annealed at 800 °C. The high contrast in the layered structure illustrates that a new phase different from SiO₂ was formed between the interface of ZnO and Si. Figure 4.12(d) reveals a self-generated layer of ~60 nm from the sample annealed at 900 °C.

Figure 4.12 TEM investigations of the interfacial area of the ZnO samples as-grown (a), 600°C (b) annealed, 800°C (c) annealed and 900°C (d) annealed.

Figure 4.13(a) shows the x-ray energy-dispersive spectroscopy (EDS) analysis of the newly formed layer. The peak at 0.53 keV and 1.74 keV is from oxygen and silicon, respectively. All other peaks at 0.995, 8.63, and 9.58 keV are from Zn. Only Zn, Si and O signals in the sample were detected, which confirms the chemical components in this new phase. Figure 4.13(b) shows a HRTEM image of the newly formed layer. ZnO quantum dots (QDs) with diameter of ~10 nm embedded in the $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer can be observed. The TEM observations suggest that the newly formed $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer was the most possible reason to cause the self-generated optical confinement.

Figure 4.13 (a) EDS spectra of the new phase formed after 900 °C annealing, (b) HRTEM image of the new phase.

As report by Xu et al, the $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer may exhibit a green emission at 525 nm, which is undesirable for ZnO/Si heterojunction.^[174, 175] On the other hand, the refractive index of $\text{Zn}_x\text{Si}_{1-x}\text{O}$ (~ 1.7) is smaller than that of ZnO (~ 2.1),^[174] so that total internal reflection can occur and confine the light in the ZnO layer. This could be the reason for the light confinement and the observation of lasing emission.

To evaluate the light confinement efficiency of the $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer, the divergence angles of the 900 °C annealed ZnO/SiO₂/Si and ZnO/Si samples were measured and compared. The divergence angle is a measured angle from one side of the emission light to the central axis of the light beam in the far field, as shown in Figure 4.14(a). A CCD camera was used to record far field image of the emitted lasing spot on a screen 5.2 cm away from the edge. When the pump intensity was above the threshold, a bright emitted spot was observed from the edge of the waveguide. As shown in Figure

4.14(b) and (c), the divergence angle is $\sim 3^\circ$ in the ZnO/SiO₂/Si sample, which is surprisingly small, especially in the vertical plane direction. However, the divergence angle increases to $\sim 7.2^\circ$ in the ZnO/Si sample under the identical measurement. The lights with large propagation angle have larger loss, since they will be scattered by the rough surface more times. Therefore, our observations show that optical confinement effect of the structure without buffer layer have more scattering loss than the buffered structure.^[176] The observation of self-generated light confinement effect of Zn_xSi_{1-x}O layer in the random laser cavities are certainly intriguing and further work is needed to achieve high optical confinement efficiency.

Figure 4.14 (a) Schematic illustration of the annealed sample. The far field images of the (a) ZnO/ SiO₂/Si and (b) ZnO/ Si samples annealed at 900 °C record from a CCD camera.

4.3.3 Optical Properties of ZnO Quantum Dots

As mentioned in section 4.3.2, ZnO QDs can be formed in Zn silicate layer by a simple thermal annealing technique. In order to prepare high density ZnO QDs, the sample, ZnO (100 nm)/ SiO₂ (400 nm)/ Si, was annealed at 900 °C for 10 hours.

Figure 4.15 TEM images of the sample. The cross-sectional TEM image (a) clearly shows the existence of the ZnO QDs. (b) is the high resolution TEM image of a single ZnO QD. (c) is the fast Fourier transform pattern of the single ZnO QD. The standard indexed diffraction pattern for hcp crystals in the (001) beam direction is also presented as a reference (d).

Figure 4.15 presents the TEM images of the annealed sample. The cross-sectional TEM image (Fig. 4.15(a)) clearly shows the formation of ZnO QDs. The density of the ZnO QDs is estimated as $1.7 \times 10^{18} / \text{cm}^3$. Figure 4.15(b) is the high resolution TEM image of a typical ZnO QD. It is seen that the QD has a crystalline structure with a dimension that measures 12.8 nm in length and 10.3 nm in height. Since the dimension of the QDs is much larger than the bulk exciton Bohr radius $a_B = 1.8$ nm, this is the regime of weak confinement. Figure 4.15(c) is the fast Fourier transform (FFT) pattern of the ZnO QD, which is identical to the standard indexed diffraction pattern for hexagonal closed packed (hcp) crystals in the (001) beam direction (Figure

4.15(d)). From the TEM analysis, the ZnO QD has the wurtzite structure with the lattice parameters $a = 3.17 \text{ \AA}$ and $c = 5.17 \text{ \AA}$.

Figure 4.16 demonstrates the XRD profiles of the ZnO QDs. The diffraction peaks and their relative intensities of spectra all coincide with JCPDS card no. 36-1451, so that the observed patterns can be unambiguously attributed to the presence of hexagonal wurtzite. The crystalline size can be estimated to be 12 nm by using the Scherer formula, which is in good agreement with our TEM results. Moreover, a $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer is discernable from the XRD pattern.

Figure 4.16 XRD profile of the ZnO QDs.

Figure 4.17 shows the formation procedures of the ZnO QDs embedded in $\text{Zn}_x\text{Si}_{1-x}\text{O}$ matrix. ZnO diffuses into the SiO_2 matrix via interstitial sites, forcing SiO_2 to occupy the interstitial sites in turn, leading to a modification of the ZnO thin films. Firstly, between ZnO and SiO_2 , a $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer was formed. After thermal annealing for 10 h, the $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer is saturated to form a stable layer. ZnO continually diffused and accumulated into this saturated $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer, therefore,

Chapter 4 Formation of Random Laser Cavities by Thermal Annealing

ZnO crystalline was preserved and formed in the $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer. The key step in the sample preparation is the formation of $\text{Zn}_x\text{Si}_{1-x}\text{O}$ layer in the precursor, which provides a template for the intercalated growth of the ZnO QDs. It also serves to stabilize the ZnO QDs and to passivate the surface. It is also noted that the refractive indices of $\text{Zn}_x\text{Si}_{1-x}\text{O}$ is lower than ZnO ,^[174] hence, the light emission from each ZnO QD is highly confined.

Figure 4.17 The formation mechanism of ZnO QDs in ZnO/SiO₂/Si structure.

In order to determine the exciton lifetime of the ZnO QDs and compare with ZnO bulk material, the optical properties of ZnO QDs were measured using TIPL and TRPL. Figure 4.18 plots the TIPL spectrum of the ZnO QDs measured at 4.3 K. The TIPL spectrum of the 400 °C deposited ZnO film by the FCVA technique is also plotted as a comparison. For the ZnO QDs, a PL band at 3.399 eV is observed, which

blueshifts by 47 meV when compared to that of the ZnO film (3.352 eV). The blueshift of the PL peak is caused by the quantum confinement. It is interesting to note that the FWHM of the ZnO QDs (38 meV) is smaller than that of ZnO film (50 meV) and the PL spectrum of the ZnO QDs has a Gaussian lineshape, suggesting the good uniformity in the size of QDs and the improvement in the crystal quality.

Figure 4.18 The TIPL spectra of the ZnO QDs and as-grown ZnO thin film measured at 4.3 K.

Figure 4.19 presents the time evolution of the spectrally integrated PL intensity of the ZnO QDs measured at 4.3 K. A lifetime of 65 ps was measured at 4.3 K, which is much shorter than the exciton radiative lifetime of 322 ps in bulk ZnO.^[177] Theoretically, it has been shown that the exciton-photon coupling in ZnO QDs is particularly strong and the exciton radiative recombination rate drastically varies with the dot size.^[169] Fonoberov and Balandin^[168] calculated the radiative lifetime of excitons in ZnO nanocrystals and predicted the size dependence of the exciton radiative lifetime. For the dots of 5 nm, they predicted an exciton radiative lifetime of 38 ps. Therefore, the lifetime of 65 ps we measured at 4.3 K is reasonable. To further ensure that the measured shorter lifetime was not caused by nonradiative

recombinations, we measured the exciton lifetimes at different temperatures, which is shown in Figure 4. 20. If the recombination process was dominated by nonradiative channels, the lifetime would decrease with increasing temperature, since the nonradiative channels would play a more important role with increasing temperature. However, within the experimental uncertainties, the measured lifetimes do not change below 15 K. It is also found that the time and spectrally integrated PL intensity remains constant below 15 K. Therefore, it is concluded that the exciton radiative recombination dominates the recombination process below 15 K and the measured lifetimes are exciton radiative lifetimes.

Figure 4.19 The time evolution of spectrally integrated PL of the ZnO QDs measured at 4.3 K.

It is well known that a short PL decay time at low exciton density with weak excitation can be caused by the dominance of nonradiative recombinations. Such a mechanism would cause a nonlinear increase in the time and spectrally integrated PL intensity with the excitation intensity. However, our measurement, as shown in Figure 4. 21, reveals a linear dependence of the time and spectrally integrated PL intensity on the excitation intensity. The linear behavior of the dependence evidences that the

exciton radiative recombination is the dominating channel for the carrier recombination process.

Figure 4.20 Exciton lifetime as a function of temperature.

Figure 4.21 The time and spectrally integrated PL intensity (solid squares) as a function of excitation density. The linear fitting is also plotted in the figure.

The mechanism of the short exciton radiative lifetime has also been investigated. As mentioned earlier, in addition to the size-dependent spectral shifts in the absorption and emission spectra (as is seen in Figure 4.18), the confinement also strongly influences the exciton radiative recombination rate. Superradiance originates from the fact that for systems small compared to an optical wavelength where all oscillator

strength is cooperated in one collective superradiant excited state. This leads to an enhancement of the optical transition oscillator strength and thus to a shortening of the excitation radiative lifetime. Exciton superradiance has been studied in semiconductor nanocrystals^[178] and other geometrically confined systems. Kayanuma^[179] theoretically studied the quantum-size effects of Wannier excitons in semiconductor nanocrystals and found that the exciton radiative lifetime in the weak confinement region (i.e., our case) decreases rapidly with the size of the nanocrystal as a result of exciton coherence effect, in other words, the exciton superradiance. Therefore, the short exciton radiative lifetime in our sample can be explained in terms of exciton superradiance.

4.4 Conclusions

In summary, the microstructure evolutions and optical properties of the ZnO thin films on Si substrates were systematically studied. Three important issues were investigated: (1) high quality grains with sharp grain boundary can be produced after high temperature annealing, which results in efficient random laser cavities. (2) Optical confinement can be realized by a self-generated $\text{Zn}_x\text{Si}_{1-x}\text{O}$ buffer layer in the ZnO/Si structure after the thermal annealing process. (3) ZnO QDs have been fabricated and a short exciton radiative decay time of 65 ps at 4.3 K is observed.

CHAPTER 5 Random Lasers Based on Nanoparticles

5.1 Introduction

As presented in the Chapter 4, random laser does not require a regular cavity but instead depends on a scattering material such as a fine powder, grains or nanostructures.^[80,96,98,99] We have demonstrated random lasers in annealed ZnO thin films, however, the high annealing temperature, usually more than 600 °C, makes it impossible to realize laser on temperature sensitive substrate like plastic. Obviously, a breakthrough in the methods of fabricating inorganic laser on plastic substrate is imminently needed for flexible optoelectronic device.

Organic based semiconductor have received considerable interest due to their ease of fabrication and mechanical flexibility.^[180] Organic semiconductor plays a particularly important role for such devices since it offers prospects for laser sources of virtually any shape, which is not possible with conventional inorganic semiconductor materials. However, electrically pumped organic laser has not been demonstrated and it still suffers from degradation problems similar to the organic light emitting diodes counterpart.^[181] In this Chapter, we report the design, fabrication and characterization of UV random lasers on plastic substrates by utilizing ZnO thin films and nanoparticles.

5.2 Design and Fabrication of Flexible Random Lasers

To create a random laser, light scattering must be combined with light amplification.^[80] For our random laser device, nanoparticles are the scattering centers and high-quality ZnO thin films deposited at low temperature act as optical gain

medium. The high-crystal-quality ZnO films, which serve as gain medium, have been deposited by the FCVA technique at low temperature, where the apparatus of the FCVA has been described in Chapter 3. Nanoparticles of ZnO or In_2O_3 with average diameter of 100 nm, which were used as scattering centers, were first dispersed in distilled water in the proportion of 1: 20. A dispersant (Sokalan CP10, (BASF)) was added in the solution. This mixture was stirred vigorously in an ultrasonic machine. The nanoparticles were then sprayed onto the ZnO film using a spray gun. After drying the sample, another ZnO layer of 200 nm thick was deposited onto it. In our design, the ZnO powder may also serve as a gain medium in UV random lasers.^[80] Hence, In_2O_3 nanoparticles were also used to verify the role of particles in the random laser mechanism.

5.3 Results and Discussion

The room temperature photoluminescence (PL) spectra of the ZnO and In_2O_3 nanoparticles coated on Si substrate were measured and shown in Figure 5.1(a). For the ZnO nanoparticles, the observed sharp peak at around 390 nm and weak peak at 520 nm represent the NBE and defects emission respectively. No NBE is observed for the In_2O_3 particles, which may be due to the poor crystal quality of the particles. However, a broad emission at around 640 nm is detected which may be attributed to the defects or oxygen deficiencies from the In_2O_3 .

Figure 5.1(b) shows the design of the UV laser on plastic substrate where nanoparticles are embedded in the ZnO thin films. Figure 5.1(c) shows the cross-sectional view of SEM image for such a device bent inwardly with a radius of curvature of 3 cm, which shows the flexibility of the device. Polycarbonate with refractive index of 1.59 was used as a transparent and flexible substrate. The low

refractive index of the plastic substrate as compared to ZnO film (~ 2.1) allows transverse optical confinement of light in the ZnO thin film to be achieved with minimum absorption loss.^[93] The nanoparticles were then deposited on the ZnO thin film by a spray method and another 200 nm thick ZnO thin film was further deposited. This layer not only confines the nanoparticles and forms a robust film but also serves as an optical gain medium. The surface morphology of the ZnO nanoparticles embedded in the ZnO film is shown in the inset of Figure 5.1(d). The nanoparticles tend to form large clusters on the film after the spray process.

Figure 5.1 (a) Photoluminescence spectra at room temperature from ZnO and In_2O_3 nanoparticles on Si substrates. (b) Schematic diagram of the nanoparticles embedded in the ZnO films. (c) Cross-sectional FESEM image of the device bent inwardly with a radius of curvature of 3 cm. (d) Surface morphology of the device.

Figure 5.2(a) shows the evolution of the emission spectra from the ZnO nanoparticles embedded in the ZnO films with pump intensity ranging from 0.6 to 2.5 MW/cm^2 at a spot size of $3.0 \times 10^{-3} \text{ cm}^2$. When the pump intensity reaches a threshold,

a significant narrowing occurs. As shown in the inset of Figure 5.2(a), when the incident pump power exceeds $\sim 0.8 \text{ MW/cm}^2$, the linewidth quickly reduces to 5 nm, and the peak emission intensity increases rapidly with the pump intensity. The gain length is the shortest at the peak of the gain spectrum. As the pump intensity increases, the gain length decreases. When the gain length becomes equal to the average path length of light in the gain medium, amplified spontaneous emission (ASE) occurs. Thus, the intensity at the wavelength of gain maximum builds up quickly, which leads to the apparent narrowing of the emission spectrum. Since there is a clear threshold for the ASE, the light amplification is referred to lasing with incoherent feedback.^[80] It should be noted that no lasing was observed from the nanoparticles on the plastic and Si substrate with a 420 nm thick SiO_2 layer. Random lasing with coherent feedback in ZnO nanoparticles can only occur in certain density and size of particles.^[81] Furthermore, it was also found that no lasing emission could be observed from the ZnO thin films alone, even when the pumping power exceeded 2.5 MW/cm^2 .

In order to investigate the role of the nanoparticles in the laser action process, In_2O_3 nanoparticles were also used to fabricate the device structure as shown in Figure 5.1(b). In_2O_3 nanoparticles are chosen because the band gap (3.55 eV) and refractive index (1.95 – 2.15) of In_2O_3 are close to that of ZnO (3.37 eV and 2.1 respectively).^[182] It is due to the broad PL band (Figure 5.1(a)), In_2O_3 nanoparticles cannot be a gain medium at 390 nm in the device. Figure 5.2(b) shows the evolution of emission spectra from the In_2O_3 nanoparticles embedded in the ZnO films as a function of pump intensity. When the pump intensity reaches the threshold, the linewidth of the emission peak at around 390 nm becomes narrower. There is no significant difference between the threshold pump intensity (0.8 MW/cm^2), emission peak position ($\sim 390 \text{ nm}$) and intensity for the two types of nanoparticles samples. It

seems that the role of ZnO nanoparticles is mainly to act as scattering centers as no change in lasing threshold and intensity are observed for the two types of nanoparticles (Figures 5.2(a) and 5.2(b)). Hence, this confirms that the nanoparticles act as scattering centers and the ZnO film serves as an optical gain medium in this design.

Figure 5.2 Evolution of emission spectra with pump intensity ranging from 0.6 to 2.5 MW/cm² (a) ZnO nanoparticles and (b) In₂O₃ nanoparticles embedded in ZnO thin films on plastic substrate. Insets: the linewidth and output intensity versus the input power intensity. Curves A, B and C represent pump intensities of 2.5, 1.6 and 0.6 MW/cm² respectively.

According to random laser theory, the critical volume $V = A_{th}$ (threshold excitation area) $\times d$ (thickness of ZnO) can be related to the threshold gain length l_g and the scattering mean-free path l_s of the highly disordered gain media by: $V = (l_s \times l_g)^{3/2}$, [80,96]

where l_g is inversely proportional to the threshold pump intensity, P_{th} , by $l_g = (\partial l_g^{-1} / \partial P) P_{th}^5$, and $\partial l_g^{-1} / \partial P$ is less dependent on the pump intensity (i.e., variation of threshold pump intensities is less than 6%). Therefore, it is possible to rewrite the above equation as:

$$A_{th}^{2/3} = K P_{th}^{-1} \quad (5.1)$$

where $K = d^{2/3} l_g (\partial l_g^{-1} / \partial P)^{-1}$, and can be considered as a constant. Therefore, the random laser properties of our sample can be evaluated by plotting $A_{th}^{2/3}$ versus P_{th}^{-1} .

As shown in Figure 5.3(a), a linear relationship between $A_{th}^{2/3}$ and P_{th}^{-1} obtained from ZnO nanoparticles sample is in consistent with Equation (5.1). Hence, the threshold characteristic of this sample is in good agreement with the random laser theory. Furthermore, the effect of various pump areas (0.5×10^{-3} to $3.0 \times 10^{-3} \text{ cm}^2$) on the lasing spectrum was also investigated under a constant pump intensity of 2.5 MW/cm^2 . It is observed that before the critical area ($1.0 \times 10^{-3} \text{ cm}^2$) is reached, no narrowing of the linewidth is observed. However, when the excitation area exceeds the threshold, linewidth narrowing occurs. The linewidth decreases as the excitation area increases. This is because in a large excitation area, more closed-loop paths for light can be formed. As a result, random laser action could occur in more cavities formed by scattering. However, if the excitation area was reduced to below a critical size, laser oscillation stopped.

The flexibility of the laser device was also tested by bending the device during optical pumping. There is no significant difference in the lasing spectra when the device is bent inwardly or outwardly. However, the lasing threshold is increased from 0.8 to 1.1 MW/cm^2 as the radius of curvature of the device (bent inwardly) decreases from 100 to 3 cm as shown in Figure 5.3 (b). The increase in the pump threshold is due to the increase in bending loss with the radius of curvature.^[183]

It should be noted that the lasing emission intensity could also be enhanced further if ZnO film deposited at higher temperature ($\sim 200^\circ\text{C}$) could be used. However, this will require the use of high performance plastic substrate. On the other hand, drawbacks of this method are that the incoherent random lasers have low efficiency.

Figure 5.3 (a) Plot of $A_{th}^{2/3}$ versus P_{th}^{-1} . (b) Lasing thresholds versus the radius of curvature of the device bent inwardly. The pump intensity and excitation area are $2.6 \text{ MW}/\text{cm}^2$ and $3 \times 10^{-3} \text{ cm}^2$ respectively.

5.4 Conclusions

Inorganic semiconductor flexible laser in UV region has been designed and fabricated at room temperature. Incoherent random lasers with a threshold of $0.8 \text{ MW}/\text{cm}^2$ were obtained from both ZnO and In_2O_3 nanoparticles embedded in ZnO thin film samples, indicating that nanoparticles act as scattering center apart from gain medium. This method should have significant implication for the future development of inorganic flexible laser.

CHAPTER 6 Random Lasers in ZnO Nanoneedles

6.1 Introduction

In Chapter 5, incoherent random laser action is demonstrated from the nanoparticles embedded in ZnO film. Coherent random laser will be more desirable for its high efficiency and intensity. Fabricating ZnO nanostructures directly on plastic substrates may enable the development of high-performance electronic and photonic devices with the potential to impact a broad spectrum of applications. Despite significant progress in deposition techniques such as vapor-liquid solid (VLS),^[184] thermal evaporation condensation,^[185] and MOCVD,^[186] the synthesis of semiconductor nanostructures still requires growth temperatures of above 400 °C. Although low-temperature (<100 °C) aqueous-solution-based synthesis methods have been demonstrated to grow aligned ZnO nanostructures, a seed layer is required which may lead to contamination.^[187,188] Recently, it was reported that carbon nanofiber could be fabricated by Ar⁺ bombardment a glassy carbon surface.^[189] The ion beam technique should lead to a new approach to fabricate semiconductor nanostructures selectively on any substrate, especially on temperature-sensitive substrates, which may find applications in the emerging plastic electronic and optoelectronic devices. In this chapter, we use ion beam sputtering technique to fabricate ZnO nanoneedles on Si and plastic substrates.

The temperature dependence of emission characteristics of 1D nanostructures is a crucial factor when evaluating the potential of high-temperature nanostructure-based photonic devices. The performance of 1D ZnO based photonic devices is expected to be highly efficient and robust at high temperature as the exciton oscillator strength is

highly enhanced in nanostructure.^[190] Although the photoluminescence of ZnO nanosheets has been demonstrated up to 850 K, high-temperature lasing from 1D nanostructured ZnO has not been reported so far.^[191] In this chapter, we also present UV random laser action in ZnO nanoneedles on Si substrate at high-temperature. The characteristic temperature of the ZnO nanoneedles was derived to be 138 K in the temperature range of 300 – 500 K, which is comparable with GaN thin films and much better than ZnO films (87 K) or ZnO/ZnMgO superlattices (67 K).^[194]

6.2 Experimental Details

An ion beam sputtering system was used to fabricate ZnO nanoneedles from ZnO thin films deposited on SiO₂/Si substrates by FCVA technique. 400 nm thick SiO₂ layer ensures the confinement of the light in a waveguide structure for the laser action measurement. The apparatus of the FCVA and ion beam sputtering technique have been presented in details in Chapter 3. In order to demonstrate the capability of the ion beam technique, plastic substrate is also used. The ZnO nanostructures were formed selectively and uniformly in the ZnO thin films. The growth mechanism of the ZnO nanoneedles may be similar to the sputter-induced CNFs, as reported by Tamenura *et al.*^[189] The formation of nanoneedles is ascribed to the dependence of sputtering yield on the incidence angle of ion-beam measured from the normal to the surface.

6.3 Results and Discussion

6.3.1 Random Lasing from ZnO Nanoneedles on SiO₂/Si

Figure 6.1(a) shows the FESEM image of the as-grown ZnO thin film on SiO₂/Si substrate. Figures 6.1(b) and (c) show the aligned ZnO nanoneedles formed after 30

and 60 min ion-beam irradiation, respectively. No features were observed from the as-grown ZnO thin film. After ion irradiation, sharp tips of cone-like structures were clearly seen (Figure 6.1(d)). The lengths of the cone structures ranged from 200 to 400 nm. The diameter of the nanoneedles in the stem part was around 100 nm, where some of the nanoneedles tend to form in a cluster with similar sharpness at the tip. As the ZnO thin film was only 300 nm thick, the upper part of the cone was ZnO (white contrast as shown in Figure 6.1(d)) and the lower part of the stem was SiO₂. It can be seen that the separation between the nanoneedles was irregular and ranged from a few nanometers to tens of nanometers. The density of the nanoneedles with 30 min irradiation was much higher than the sample irradiated for 60 min, as shown in Figures 6.1(b) and (c). Energy-dispersive x-ray spectroscopy (EDX) shows that there was no residue material or contaminant detected between the nanoneedles (see Figures 6.2(a)).

Figure 6.1 (a) FESEM image of the as-grown ZnO thin film. FESEM images of the ZnO nanoneedle arrays after (b) 30 min and (c) 60 min ion irradiation. (d) High magnification FESEM image of the ZnO nanoneedles. (e) TEM image of a single nanoneedle. (f) High-resolution TEM image of the nanoneedle and (g) the corresponding electron-diffraction pattern.

Figure 6.1(e) shows the TEM image of an individual nanoneedle. The tips of the nanoneedles exhibited an extremely sharp morphology. The interior angle of the nanoneedles was around 20° . The sharpness of the tip was comparable to the ZnO nanoneedles prepared by catalyst-free MOCVD.^[186] Electron diffraction and high-resolution TEM observations indicated that the nanoneedles were in fact single crystals and were indexed to be the wurtzite structure of ZnO with lattice constants of $a=0.32$ nm, $c=0.52$ nm [Figures 6.1(f) and (g)]. This result shows that the nanoneedles maintained the high-crystal quality of the ZnO thin film, which was in good agreement with the XRD pattern of the nanoneedles shown in Figure 6.2(b)

Figure 6.2 (a) EDX analysis, and (b) XRD pattern of the ZnO nanoneedles.

Optical characteristics of the devices at room temperature were studied under optical excitation by a 355-nm frequency tripled Nd: YAG pulse laser (10 Hz, 6 ns pulse width). Optical pump was achieved by using a cylindrical lens to focus a pump stripe of 5 mm length and 60 μ m width onto the sample. A polarizer was set before the detector in order to analyze the polarization properties of the lasing light. Figure 6.3 shows the experimental setup of the room temperature lasing measurement.

Figure 6.3 Schematic diagram of the laser measurement setup.

Figure 6.4 (a) shows the light-light curves of the samples. Only the sample irradiated for 30 min showed a "kink" in the light-light curves which was characteristic of laser action. As shown in Figures 6.4 (b) and (d), the as-grown and 60 min irradiated samples showed only ASE spectra with a peak wavelength and FWHM of about 385 and 12 nm, respectively, at a pump intensity of 1.6 MW/cm^2 . Figure 6.4 (c) shows the evolution of emission spectra of the ZnO nanoneedles sample irradiated for 30 min as a function of pump power. Below the threshold, ASE was observed. When the pump power reached a threshold as high as $\sim 0.34 \text{ MW/cm}^2$, a dramatic emission oscillation in a linewidth as narrow as 0.4 nm emerged from the single-broad emission spectra. As the pump power increased, multiple laser modes with strong coherent feedback at wavelengths between 390 and 400 nm were detected. This phenomenon of emission spectra was attributed to random lasing with coherent feedback.^[80,97] Conventional lasing due to the Fabry-Perot (FP) cavities between the top and bottom natural facets of the ZnO nanoneedles was unlikely to occur. This is because the short length ($< 300 \text{ nm}$) and the sharp top surface of the ZnO nanoneedles

were not able to provide sufficient optical gain and large optical loss, respectively. Hence, the natural FP cavities of the ZnO nanoneedles would not sustain lasing even under a high optical excitation.

Figure 6.4 (a) Light-light curves of the samples after various ion irradiation times. The inset shows the maximum emission intensity of the TE mode as a function of polarization angles. (b) Emission spectrum of the as-grown ZnO thin film under pump power of 1.6 M/cm². (c) Evolution of emission spectra of the 30-min irradiated sample under different pump intensities. (d) Emission spectrum of the sample irradiated for 60 min under pump power of 1.6 M/cm².

Random laser does not require a regular cavity but depends instead on a scattering material. Random laser action is possible for the ZnO nanoneedles as the corresponding gain length and scattering mean-free path along the lateral direction satisfy the requirements of random laser action; that is, the gain length (scattering mean-free path) is long (short) enough to sustain amplified coherent feedback. It is due to the fact that the ZnO nanoneedles were grown on a SiO₂/Si substrate, the refractive index difference in the interface of air ($n_r=1.0$)/ZnO ($n_r\sim 2.1$)/SiO₂ ($n_r\sim 1.45$) allowed strong scattering and amplification along the ZnO tips to achieve random

laser action.^[96] Above the threshold, the emission was strongly polarized, as shown in the inset of Figure 6.4(a).

Random laser action has been observed in ZnO thin films annealed at 900 °C and ZnO nanorod arrays embedded in ZnO thin films.^[98] The threshold pump intensity of the ZnO nanoneedles (~ 0.35 MW/cm²) was comparable to that of ZnO thin films annealed at 900 °C (~ 0.32 MW/cm²), but it was significantly lower than that of ZnO nanorod arrays embedded in ZnO thin films (~ 0.8 MW/cm²). The relatively lower pump threshold of the ZnO nanoneedles compared to that of ZnO nanorod arrays was due to the relatively stronger optical scattering between the air and ZnO interface of the ZnO nanoneedles (Figure 6.1(b)), so that coherent optical feedback could be obtained from relatively low pump intensities. It should also be noted that the threshold pump intensity of ZnO nanoneedles random lasers was significantly lower than the conventional lasing observed in ZnO nanocolumns prepared by an aqueous solution method (~ 3.0 MW/cm²). Our result was also significant as no high-temperature annealing was required in order to form random media in the ZnO thin films. The sample under 60 min irradiation exhibited no lasing. This was attributed to the low density of nanoneedles, which did not satisfy the requirement of random laser action.

6.3.2 Random Lasing from ZnO Nanoneedles on Plastic Substrates

A similar approach was used to fabricate ZnO nanoneedles on flexible plastic substrates. We used 180- μ m-thick commercially available Kapton® polyimide foil as the flexible substrate material. Polyimide foils are commonly used as substrate material for flexible thin-film transistors.^[192] A 520-nm-thick ZnO was deposited on the plastic substrate at 200 °C. Figures 6.5(a) and (b) show the FESEM images of the

ZnO nanoneedles on the plastic substrate. The cone-shape morphology was also obtained after 30 min of ion irradiation. The lengths and diameter (stem) of the nanoneedles were 200–300 nm and 100 nm, respectively, which were very similar to the ZnO nanoneedles on Si substrate (Figure 6.1(b)). However, the tips of the nanoneedles were not as sharp as those for the Si sample, which might be due to the quality of the ZnO film and the softness of the plastic substrate. The optical characterization of the plastic sample was studied.

Figure 6.5 (a) Low and (b) high magnification FESEM images of ZnO nanoneedles on plastic substrate. (c) Emission spectrum under 2.8 MW/cm^2 pump intensity. The inset shows the light-light curve of ZnO nanoneedles on plastic substrate.

Figure 6.5(c) shows the emission spectrum of the nanoneedles on the plastic substrate excited above the threshold at 2.8 MW/cm^2 . Random laser action with

coherent feedback was clearly detected and the resulting threshold pump power density was determined to be $\sim 0.84 \text{ MW/cm}^2$ as shown in the inset of Figure 6.5(c). The lasing threshold of the plastic sample was two times more than that of the nanoneedles on Si (i.e., $\sim 0.34 \text{ MW/cm}^2$). As illustrated in Figure 6.5(c), the ZnO nanoneedles were about 300 nm in length, and there was a 200 nm thick ZnO thin film underneath the nanoneedles so that light could be confined within the ZnO nanoneedle array. However, the relatively high pump intensity of the plastic sample was mainly due to the high optical loss of the substrate as the polyimide substrate absorbed the light with wavelength less than 450 nm. As a result, the corresponding pump threshold was higher than that with Si substrate. Despite all these, coherent random laser action in the ZnO nanoneedles could still be obtained, which demonstrated the usefulness of the ion-beam technique for creating functional nanostructures on flexible plastic substrates.

6.3.3 High Temperature Random Lasing in ZnO Nanoneedles

Figure 6.6(a) shows the lasing spectra of the ZnO nanoneedles as a function of temperature, T , under optical excitation of $\sim 2 \times I_{th}$, where I_{th} represents the pump threshold at the corresponding T . When the pump power reached I_{th} , random laser emission in a linewidth as narrow as 0.4 nm emerged from the single-broad emission spectra at all the temperature. The linewidth of the lasing peaks remained less than 0.4 nm for T up to 615 K. The peak lasing wavelength was red-shifted from 394 to 435 nm as the temperature increased from 300 K to 615 K. It is due to the reduction of bandgap as temperature increases. Moreover, a broad emission band in the shorter wavelength side of the lasing peaks become apparent when temperature higher than 450 K (as labeled by the arrows in Figure 6.6 (a)). The origin of this broad emission

band was not clear. Figure 6.6 (b) shows the typical light-light curve of the ZnO nanoneedles at various temperatures. The spectra showed a “kink” in the light-light curves which was the characteristic of laser action. The lasing threshold at 300 K was $\sim 0.25 \text{ MW/cm}^2$ and it increased to $\sim 2.05 \text{ MW/cm}^2$ at 615 K.

Figure 6.6 (a) Lasing emission spectra at different temperatures from ZnO nanoneedles; the emission spectra were obtained under an excitation density of $2 \times I_{th}$, where the I_{th} represents the lasing threshold at a corresponding temperature. (b) Light-light curves of ZnO nanoneedles at different temperature.

Figure 6.7 plots the peak energy of lasing emission in ZnO nanoneedles as a function of temperature. The emission peak of the ZnO nanoneedles at room temperature is 3.15 eV. It was red-shifted with increasing temperature at a rate of -0.97 meV/K for the entire temperature range. The observed linear relationship between the emission peak energy and temperature of our ZnO nanoneedles is in good agreement with the electron-hole plasma stimulated emission observed from ZnO thin film on sapphire substrate.^[6]

The lasing threshold of ZnO nanoneedles as a function of temperature is also shown in Figure 6.7. It was found that the I_{th} of the ZnO nanoneedles is increased exponentially with temperature. The solid line represents the best fit using least-squares fitting of the experimental data to the empirical formula: $I_{th}(T) = I_0 \exp(\frac{T}{T_c})$, where, I_0 is the threshold pump intensity at $T = 0$ K and T_c is the characteristic temperature.^[193] The T_c of our ZnO nanoneedles sample was determined to be 138 K, which is significantly higher than that of ZnO/sapphire (67 K) and ZnO/Zn_{0.74}Mg_{0.25}O superlattice on ScAlMgO₄ (87 K).^[194] Most importantly, the T_c of the ZnO nanoneedles on Si was comparable to the value (162 K) reported for laser structure based on InGaN/GaN multiquantum well in the temperature range of 175-575 K.^[193] The high operating temperature of our lasers is evident of the high quality of the structures. In this case, the internal loss of the laser should be very low. The optical gain is increased due to the enhancement of oscillator strength in 1D nanostructure. This modified density of states should results in a narrower spread of carriers in energy, a higher peak gain, and thus better temperature stability. The relatively high values of lasing thresholds in the high temperature range effectively eliminate exciton-related effects from consideration of laser mechanisms. Electron-hole plasma is believed to be the dominant lasing mechanism in ZnO nanoneedles for temperature above 300 K. It should also be noted that the changing temperature allows “tuning” of the lasing peak energy of ZnO nanoneedles from UV to the blue spectral region for up to ~300 meV. Remarkably, the high-temperature lasing process of the ZnO nanoneedles is reversible and repetitious, even operated in air.

Figure 6.7 Temperature dependence of lasing peak emission (▲) and temperature dependence of lasing threshold (■) in ZnO nanoneedles samples. The solid line represents the best result of the least-squares fit to the experimental data. The characteristic temperatures are derived from the fit.

To further investigate the closed-loop random laser cavities at high temperature, Fourier transform (FT) of the lasing spectrum is used to determine the change of cavities length L_c (i.e., length of the closed-loop paths of light),^[90] which is also an important factor in retaining the optical gain of the ZnO nanoneedles at high T . The FT distribution of the lasing spectra of ZnO nanoneedles at 300, 400, and 550 K under an excitation density of $2 \times I_{th}$ are shown in Figure 6.8(a). A series of broad peaks of the harmonics in each of the FT transform is observed and the fundamental resonator at each of these three temperatures was determined to be ~ 14 , ~ 8 , and $\sim 2 \mu\text{m}$, respectively. It is found that the length of the cavities reduced as temperature increases. All the estimated values of L_c are much smaller than the spot size of the pumping laser beam on the samples. Figure 6.8 (b) is the schematic diagram of the dependence of L_c on T . The optical excitation has a Gaussian profile, which has a high gain at the middle of the pump stripe. According to Yu *et al.*,^[195] random cavities with

a short L_c will only experience a high optical gain near the middle of pump stripe at high temperature. At low temperature, the long L_c provides a high average optical gain to sustain coherent random lasing.^[80] When T increases, the L_c decreases which reduces the average optical gain and a higher pump power is needed to sustain the lasing. When T is above 615 K, the optical gain is not sufficient to overcome the scattering loss, therefore, lasing ceases. This self-compensation mechanism of random laser cavities maintains the optical gain for lasing emissions at high temperature.

Figure 6.8 Fourier transform of typical lasing spectra of the ZnO nanoneedles taken at 300 K, 400 K and 550 K as shown in Figure 6.6(a). (b) Schematic diagram of the formation of closed-loop laser cavities at high and low temperature.

6.4 Conclusions

In summary, we have demonstrated the fabrication of ZnO nanoneedles directly on Si and plastic substrates using ion beam sputtering technique. Random laser action was observed from these samples. In addition, the increasing temperature allows “tuning” of the lasing peak energy of ZnO nanoneedles from UV to the blue spectral region for up to ~ 300 meV. The high temperature random lasing emissions from ZnO nanoneedles laser cavities were investigated. The T_c of ZnO nanoneedles was derived to be 138 K from the temperature dependence of the lasing emission threshold in the temperature range of 300 – 615 K. The dominant lasing mechanism in the ZnO nanoneedles for temperature above 300 K is believed to be electron-hole plasma. The optical gain maintained in the random laser cavities at high temperature is attributed to a self-compensation mechanism where the cavity length decreases with increasing temperature.

CHAPTER 7 Wavelength-tunable Random Lasers in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles

7.1 Introduction

In the previous few chapters, we investigate the random laser action in annealed ZnO thin films, nanoparticles embedded in ZnO thin films, and ZnO nanoneedles. Nevertheless, all these lasers are with a fixed emission wavelength of ~ 385 nm, which is determined by the NBE of ZnO. Obviously, continuous control of the bandgap of the semiconductor is highly desirable for light-emitter applications. The approach for tuning the width of energy band-gap (E_g) of ZnO has been investigated by the ternary alloy $\text{Zn}_{1-x}\text{Mg}_x\text{O}$.^[196,197,198] Ohtomo et al.^[24] reported the growth of wurtzite structure $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloy films with Mg content up to $x = 0.33$, achieving a band gap of 3.99 eV at room temperature. The UV-luminescent properties of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ has been attributed to radiative recombination of the electron-hole pairs.^[25,199] However, the investigation of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys has been mostly focused on the possibility to prepare quantum wells structures, which can produce blue-green lasers.^[200,201] In contrast to the significant progress in 1D ZnO nanostructures, there is no report on stimulated emissions (SE) or lasing from ZnMgO nanostructure at room temperature so far.^[202,203]

In this chapter, we exploit FCVA technique to grow $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films and then to fabricate $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles using the ion beam technique reported in Chapter 3. The emission wavelength of room-temperature photoluminescence and lasing spectra of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles can be tuned by adjusting the Mg concentration. In addition, the high-temperature dependence of emission

characteristics on the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles was also studied. The characteristic temperature of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles was derived to be 84 K in the temperature range of 300 – 500 K.

7.2 Experimental Details

$\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films were grown by the FCVA technique (i.e., details can be found in Chapter 3) at 300 °C on Si substrates using various $\text{Zn}_{1-x}\text{Mg}_x$ alloy targets containing 15, 20 and 25 at .% of Mg. The corresponding Mg content in the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films was determined by x-ray photoelectron spectroscopy (XPS) to be 7.8, 10 and 21 at .%, respectively, as shown in Table 7.1. The substrate temperature was kept at 300 °C during deposition. It is due to the different vapour pressures between Zn and Mg related species,^[75] the deposition rate for $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films is lower than ZnO thin films for ~2 times. The $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles were fabricated by an ion beam technique which has been described in Chapter 3.

$\text{Zn}_{1-x}\text{Mg}_x$ target		$\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films measured by XPS
Mg content	15%	7.8%
	20%	10%
	25%	21%

Table 7.1 The Mg content comparison at .% from the $\text{Zn}_{1-x}\text{Mg}_x$ target and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films deposited by FCVA technique.

7.3 Results and Discussions

7.3.1 Structure and Optical Properties of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ Thin Films

Prior to the study of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanostructures, the structural and optical properties of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films were investigated. Figure 7.1 shows the XRD

patterns obtained from the as-grown $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ layers deposited on SiO_2/Si substrates. The result of ZnO is also exemplified for comparison. The XRD spectra basically consist of one major peak located at $\sim 34.04^\circ$ to $\sim 34.86^\circ$, suggesting the presence of single-phase crystal in c -axis (0002) orientation. For all the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films, the angle position of the (0002) peak moves toward greater values with increasing Mg content, indicating Zn^{2+} ions are successfully substituted by Mg^{2+} in the ZnO lattice. It is also noticeable that there is no significant decrease in the intensity of the (0002) peak, which shows the high-crystal-quality of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ layers.

Figure 7.1 XRD patterns of the as-grown $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films with different Mg concentration.

The out-of-plane lattice constant of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ layers was calculated using Bragg's law. The (0002) peak positions shifted to higher angles, which indicate the decrease of c and increase of a . The calculated lattice constants using the XRD peak positions were presented in Figure 7.2. It is seen that the length of c -axis of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films decreased linearly with increasing the Mg content up to $x = 0.21$. The trend is in good agreement with the report by others.^[24, 25, 196]

Figure 7.2 The plotting of calculated lattice constant c obtained from the XRD peaks as shown in Figure 7.1.

Figure 7.3 Room temperature transmittance spectra for the films with different Mg concentration.

Figure 7.3 shows the transmittance spectra of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloy films on quartz substrates measured at room temperature by an ultraviolet-visible spectrometer. All the ZnO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films were highly transparent in the visible region from 400 to 600 nm and showed sharp absorption edges in the UV region. The average transmittance was over 80 % for all the films. Oscillations are observed in the

transmittance spectra, which correspond to multi-reflections at the film-air and film-substrate interfaces. The ZnO film has a falloff at 380 nm, while the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ has a broader fall off up to 200 nm. It should be noted that the spectra near the absorption edges of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys are not steep in comparison with the ZnO thin films and there is an obvious shift of the absorption edge to shorter wavelengths with increasing Mg content.

Figure 7.4 The $(\alpha h\nu)^2$ plots of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films as a function of photon energy.

In the high energy spectral range, where the film is strongly absorbent, the absorption coefficient α of the films can be calculated from the transmittance using the relationship:

$$\alpha = -\frac{1}{d} \ln T,$$

where T is the transmittance, and d is the film thickness. It is well known that the absorption coefficient α for allowed direct transitions at a given photon energy $h\nu$ can be expressed as:

$$\alpha \cong A^* (h\nu - E_g)^{1/2},$$

where A^* is a function of the refractive index and hole/electron effective masses. The characteristics of α^2 vs. $h\nu$ (photon energy) were plotted for evaluating the E_g values as shown in Figure 7.4. Figure 7.5 shows the calculated E_g of the samples as a function of Mg concentration. It is observed that E_g increases almost linearly from 3.30 eV to 3.55 eV as Mg content, x , increases from 0 to 0.21. This blueshift of E_g clearly indicate that the optical energy band gap of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films can be precisely tailored between 3.30 and 3.55 eV.^[24] Moreover, the Mg content in these wurtzite structure films was found to be independent of the kinds of substrates used such as, Si or quartz, under the same growth conditions.

Figure 7.5 The variation of the band gap energy of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films as a function of Mg content.

7.3.2 Random Lasing Emission from $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ Nanoneedles

In order to realize random laser cavities based on the ZnMgO samples, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles were fabricated. The morphology and optical properties of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles were investigated. The bright-field cross-sectional TEM of $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ thin film is shown in Figure 7.6(a). Columnar structures are clearly revealed in the micrograph. Figure 7.6(b) shows the cross-sectional view of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedle arrays. The nanoneedles were oriented in the ion beam

direction which is 55° from the surface normal of a sample, as labeled by the dashed arrows in Figure 7.6(b). As the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ thin film was only 300 nm thick, the upper part of the cone was $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ (black contrast) and the lower part of the stem was SiO_2 . Figure 7.6(c) shows the TEM image of an individual nanoneedle, which exhibits sharp-tip morphology. Figure 7.6(d) shows the high-resolution TEM image at the interface of $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ and SiO_2 . The corresponding selective area electron diffraction (SAED) pattern illustrates the high-crystal-quality and wurtzite structure of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ sample. The lattice spacing in (0002) direction of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ was found to be about 5.18 Å.

Figure 7.6 (a) TEM image of the as-grown $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ thin film. (b) TEM image of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles. (c) TEM image of a single nanoneedle. (d) High-resolution TEM image of the nanoneedle and the corresponding selected area electron diffraction pattern of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles sample.

Figure 7.7 shows the high-resolution FESEM image of the as-grown nanoneedles sample. The lengths of the cone structure were ranging from 200 to 400 nm. The diameter of the nanoneedles in the stem part was around 100 nm, where some of the nanoneedles tend to form in a cluster with similar sharpness at the tip. It can be seen that the separation between the nanoneedles was irregular and ranged from a few nanometers to tens of nanometers.

Figure 7.7 FESEM image of the as-grown $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles.

Figure 7.8 shows the normalized room temperature photoluminescence (PL) spectra of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles. The samples were excited by a 325 nm He-Cd laser at room temperature. The observed PL peak wavelengths of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles with 0, 7.8, 10 and 21 at.% of Mg are 378, 363, 359 and 347 nm respectively. The inset in Figure 7.8 shows the variation of PL peak energies as a function of Mg composition. The PL data as a function of Mg content obtained from Ref. 20 and 195 were also included for comparison. Our results are in good agreement with their works. The PL peak energy of $\text{Zn}_{0.79}\text{Mg}_{0.21}\text{O}$ nanoneedles is blue-shifted for 300 meV as compared to ZnO nanoneedles (PL peak energy = 3.28 eV). The FWHM values of the samples are all less than 19 nm. Furthermore, since the recombination process is excitonic the FWHM value of the spectrum only broaden slightly with Mg

content up to 21 at.%. It is also noted that no defect-related green emission can be observed from our $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles although an extremely weak band at around 550 nm can be observed from the ZnO sample.

Figure 7.8 Normalized PL spectra of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles with various Mg contents. The inset shows the PL peak energy as a function of composition x of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles.

The optical characteristics of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ samples were further carried out by a 355 nm Nd:YAG pulse laser. A pumping stripe of length 8 mm and width 10 μm was focused onto the surface of the sample by a cylindrical lens. Laser action in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles with Mg content of up to 10 at.% can be obtained. It is due to the large bandgap (3.58 eV) of the $\text{Zn}_{0.79}\text{Mg}_{0.21}\text{O}$ sample, our laser with energy of 3.5 eV is not sufficient to excite this sample. The lasing spectra of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films at room temperature are exemplified in Figure 7.9 for x values of ~ 0.078 and ~ 0.10 , showing lasing modes centered at 382 nm and 378 nm, respectively. When the

pump power reached a threshold value, a dramatic emission oscillation with coherent feedback emerged from the single-broad emission spectra of all the samples at room temperature. The FWHM of the lasing peaks from all the samples remain less than 0.4 nm. The lasing emissions are arising from closed loop path of light formed by the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles. At higher excitation intensities above the threshold, more lasing modes are excited and these lasing actions can be detected in all directions. The lasing characteristics detected from the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ samples are similar to ZnO nanoneedles.^[99] Based on the structural properties of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles and random laser theory; the observed lasing phenomena are attributed to random laser action.^[91,97] It should be noted that no lasing can be observed from the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films without nanostructures. The insets in Figure 7.9 show the plots of emission intensity versus pumping intensity (i.e., light-light curve), suggesting the clear onset of lasing emission. The lasing threshold of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ ($\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$) was $\sim 0.30 \text{ MW/cm}^2$ ($\sim 0.33 \text{ MW/cm}^2$) at room temperature, which is comparable to ZnO nanoneedles.

Figure 7.9 Room temperature lasing emission spectra at different excitation intensities from the (a) $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ and (b) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}$ nanoneedles. The insets show the corresponding light-light curve of each of the sample.

Figure 7.10 Lasing emission spectra at different temperatures from the (a) $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ nanoneedles and (b) $\text{Zn}_{0.90}\text{Mg}_{0.10}\text{O}$ nanoneedles; the emission spectra were obtained under an excitation density of $2 \times I_{th}$.

High-temperature lasing characteristics in nanostructures is an important factor to evaluate the quality of the nanostructures.^[204] Thus, the temperature dependence of lasing emission on the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles was also investigated. It is remarkable to observe lasing at temperature well above room temperature. Figure 7.10 shows the lasing spectra versus temperature, T , under optical excitation of $\sim 2 \times I_{th}$, where I_{th} represents the pump threshold at the corresponding T . With increasing temperature, the bandgap of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ decreases which red-shift the lasing peaks. The peak lasing wavelength of $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ ($\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$) was red-shifted from ~ 382 nm (~ 378 nm) to ~ 395 nm (~ 394 nm) as the temperature increased from 300 K to 470 K. The lasing emission ceased when the temperature reached 500 K, however, a broad amplified spontaneous emission band remained. The FWHM of the lasing peaks for both

samples remains less than 0.4 nm for temperature up to 470 K. Figure 7.11 plots the peak lasing emission of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles as a function of temperature. The emission peak of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ ($\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$) nanoneedles were red-shifted from ~ 3.24 eV (~ 3.28 eV) to 3.14 eV (~ 3.15 eV) at a rate of -0.67 meV/K (-0.82 meV/K) from room temperature to 470 K. The observed linear relationship between the emission peak energy and temperature of our $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles is in good agreement with the electron-hole plasma stimulated emission observed from ZnO thin film on sapphire substrate.^[11]

The lasing threshold of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles was measured as a function of temperature and plotted in Figure 7.11. It was found that the I_{th} of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles increased exponentially with temperature. The solid line represents the best fit using least-squares fitting of the experimental data to the empirical formula:

$$I_{th}(T) = I_0 \exp\left(\frac{T}{T_c}\right)$$

for the temperature dependence of the threshold, where, I_0 is the

threshold pump intensity at $T = 0$ K and T_c is the characteristic temperature.^[193] The T_c of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ and $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ samples was determined to be 81 K and 84 K, respectively. However, compared with ZnO nanoneedles (~ 138 K), the T_c of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles is significantly lower, which may result from fluctuations in the compound, where localized excitons experience a different Coulomb potential depending on the local concentration and/or arrangement of the substituting elements.^[24,202] It is due to the small Bohr radius of 18 Å, ZnO crystals are more sensitive to local inhomogeneity, which can be largely affected by local (atomic-scale) fluctuations related to Mg content. It can also be seen from Figure 7.11 that the relatively high values of lasing thresholds in the temperature range effectively eliminate exciton-related effects from consideration of laser mechanisms. The free

carrier recombination or electron-hole plasma is the dominant lasing mechanism in the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ for temperature above 300 K.

Figure 7.11 Temperature dependence of lasing peak emission and lasing threshold of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles. The solid line represents the best result of the least-squares fit to the experimental data.

Several factors are believed to contribute to the high operating temperature of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ lasers, including: (1) the high optical quality of the structures, (2) the enhancement of oscillator strength in 1D nanostructure, and (3) the self-compensation ability of random laser cavities.^[205] In our case, the nanoneedles are of high-crystal quality and free of defect-related emission which ensure a high optical gain in the structure. Furthermore, the optical gain can be increased because of the enhancement of oscillator strength in 1D nanostructure. This modified density of states should result in a narrower spread of carriers in energy, a high peak gain, and thus better temperature stability. As reported by Li *et al.*^[206], the average cavity length of a random laser will be reduced as an increase in temperature in order to sustain lasing at high temperature. Similarly the high-temperature random laser action in the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$

$\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles should also be governed by the self-compensation mechanism in laser cavities.

7.4 Conclusions

In summary, highly c -axis $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films were fabricated by the FCVA technique. $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles with tunable lasing emissions were fabricated at room temperature by ion beam sputtering technique. The lasing mechanism was attributed to the random light scattering in the nanoneedles. The T_c of the $\text{Zn}_{0.922}\text{Mg}_{0.078}\text{O}$ and $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ samples was 81 K and 84 K, respectively. The dominant lasing mechanism in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ for temperature above 300 K is believed to be electron-hole plasma.

CHAPTER 8 ZnO Nanoneedles as Flexible Field Emitter

8.1 Introduction

Field emission is one of the most promising applications of 1D ZnO nanostructures for field emission displays, x-ray sources, and highly coherent electron gun in an electron microscope. As a wide band gap semiconductor, 1D ZnO nanostructures has high melting point, high mechanical stability, high conductivity, and high aspect ratio. Recently, several groups have investigated the field emission properties of various 1D ZnO nanostructures, such nanowires, nanotips, nanotubes and nanorods.^[207,208,209,210,211,212,213,214,215,216,217] The results show that the field emission properties are related to several important factors, such as the geometry of tip, the electrode shape, the interelectrode distance, the emitter structure, and the distance between adjacent emitters. The ZnO nanostructures with sharp tip, or surface perturbation exhibits better field emission performance as compared with nanowires with flat surface.

The growth temperatures of most 1D ZnO nanostructures were above 400 °C, making those methods incompatible with low-cost flexible substrates such as plastics. In chapter 3, the growth of small area (~300 μm) ZnO nanoneedles on Si substrate at room temperature has been realized using the ion beam sputtering technique. The similar technique has been used to prepare large-area ZnO nanoneedles on plastic substrates as flexible field emitters.

X-ray imaging has been important to both medical and industrial applications for over 100 years. The ability to reconstruct high-resolution, three-dimensional anatomical images for the detection of tumors, blood clots, and bleeding has had a

major impact in medicine.^[218, 219, 220] Conventional x-ray sources for computed tomography (CT) and digital tomosynthesis are generated by bombarding a rotating metal anode with electrons emitted from a heated tungsten filament (thermionic cathode).^[222] X-ray sources using field emission cathodes (i.e., carbon nanotubes, carbon nanofibers) have several intrinsic advantages over the thermionic x-ray tubes, including low operating temperature, instantaneous response time, and potential for miniaturization.^[223, 224, 225, 226, 227] Therefore, x-ray source based on field emitters have attracted considerable research interests. An x-ray source with compact size, and mechanical flexibility is highly desirable.

In this chapter, the field emission properties from ZnO nanoneedle arrays on plastic substrates are investigated. Superior field emission characteristics have been found with a threshold voltage of ~ 4.1 V/ μm at a current density of $1 \mu\text{A}/\text{cm}^2$. The ZnO nanoneedles on flexible plastic substrate have also been used as a stationary x-ray source for radiography application.

8.2 Experimental Details

ZnO thin films (i.e., 650 nm) were first deposited on polyimide foils with a dimension of 4 cm x 1.5 cm at a substrate temperature of 200 °C. Ion beam irradiation was carried out by a Kaufman-type ion gun under high vacuum to fabricate ZnO nanoneedles. Figure 8.1(a) shows the low magnification FESEM image of the ZnO nanoneedles on plastic substrate, where the substrate is curved with a radius of curvature of 60 mm. Figure 8.1(b) shows the FESEM image of the nanoneedles. It is found that aligned ZnO nanoneedles are formed after the ion beam irradiation.

Figure 8.1 (a) Low magnification FESEM image of the flexible field emitter. (b) FESEM image of the ZnO nanoneedles. (c) TEM image of a single nanoneedle. (d) High-resolution TEM image of the nanoneedle.

The nanostructure is uniformly distributed with diameter ranging from 100 to 300 nm. It is also seen that the nanoneedles are grown preferentially in an angle of around 60° (as labeled in Figure 8.1(b)) with respect to the substrate. The lengths of the nanoneedles are ~ 700 nm, which are higher than the thickness of the ZnO thin film (i.e. 650 nm) deposited on the plastic substrate. If we consider a 700 nm long nanoneedle aligned with an angle of 60° with respect to the substrate, the estimated height of the nanoneedle is about 600 nm. Therefore, there should have about 50 nm thick of ZnO thin film underneath the nanoneedles which ensures the ZnO

nanoneedles in good electrical contact with the thin film. Figure 8.1 (c) shows the TEM image of an individual nanoneedle with sharp tip. High-resolution TEM analysis in Figure 8.1(d) shows the wurtzite structure of the ZnO nanoneedle with lattice constant $c = 0.52$ nm, which indicate high-crystal-quality of the sample.

8.3 Results and Discussion

8.3.1 Field Emission Property

The vast majority of electrons are emitted through a tunneling process from the Fermi level, which is a function of electronic conductivity. Therefore, one of the criteria for good field emission properties is to provide a low electron scattering path (low resistance). The resistivity of as-grown ZnO thin film on the polyimide substrate was measured to be $9.2 \times 10^{-3} \Omega\text{cm}$ by a four point probe method. The obtained resistivity of the ZnO sample is comparable to a typical indium tin oxide film. The resistance within the ion irradiated region was measured to be in the order of 100 k Ω by a multi-meter with a separation of about 3 cm which confirmed that the nanoneedles are in good electrical contact.

Figure 8.2 shows the field emission characteristics of the ZnO nanoneedles. The data were obtained by sweeping the voltage several times from 0 to 1100V, measuring in the up-sweep as well as in the down-sweep. No hysteresis-like behavior was seen. The current density was calculated referring to the anode area. The J-E curve in Figure 8.2 shows a threshold field (E_{th}), i.e. the field for which J is 1 $\mu\text{A}/\text{cm}^2$, is 4.1 V/ μm . The emission current reaches 1 mA/ cm^2 at a field of 9.6 V/ μm . This emission behavior is already better than ZnO nanowires grown on Si using a metal vapor deposition ($E_{th} = 6$ V/ μm),^[207] and ZnO nanoneedles on Ga-doped conductive ZnO film using vapor phase grown ($E_{th} = 20$ V/ μm).^[228] The result compares well to that

observed for carbon nanofibers grown on polyimide substrate at 200 °C ($E_{th} = 4.2$ V/ μm).^[229] As a reference, as-grown ZnO thin film on polyimide substrate was tested at the same conditions and no emission current can be detected for electric field up to 10 V/ μm . Hence, the ZnO thin film contributed to the observed emission current can be excluded.

Figure 8.2 Emission current density vs applied electric field from the ZnO nanoneedles grown on polyimide foil.

In order to understand the emission behavior, the I-V data are also analyzed by applying the Fowler-Nordheim (FN) equation:

$$J = \frac{aV^2\beta^2}{d^2\phi} \exp\left(\frac{bd\phi^{\frac{3}{2}}}{\beta V}\right),$$

where J is the current density (A m^{-2}), V is the applied voltage (V), ϕ is the work function (eV), β is the field enhancement factor, and $a = 1.56 \times 10^{-10} \text{ A eV/V}^2$ and $b = 6.83 \times 10^{-10} \text{ V/m}^{-1} \text{ eV}^{-3/2}$.^[207] The FN emission behavior can be examined from the linearity of curves by plotting $\ln(I/V^2)$ versus $1/V$. The FN plot is shown in Figure 8.3.

It exhibits a linear behavior in the measured range, confirming the emission current in Figure 8.2 is indeed from cold electron emission. Assuming the work function of ZnO is 5.3 eV,^[214] a field enhancement factor was calculated to be ~1134 from the slope of the straight line as shown in Figure 8.3.

Figure 8.3 The FN plots of the I-V data as shown in Figure 8.2.

Figure 8.4 The stability test of the flexible emitter.

Figure 8.3 shows the stability measurement of the flexible ZnO nanoneedle FE emitter operated at 900 V, which suggests a low fluctuation of the FE output. No obvious degradation of current density was observed and the fluctuation of the emission current was less than 10 % within 140 min. The stable FE behavior is suggested to be related to the uniform height of the vertical aligned nanoneedle arrays, which guarantees a uniform field distribution across the device under test.

Reference	ZnO emitter shapes	Turn-on field (V/ μm)	The field at 1mA/cm ² (V/ μm)	β	Stability: testing time and fluctuation	Substrates
Xu <i>et al</i> ^[207]	Nanopins	1.92	5.9	657	----	Si
Yu <i>et al</i> ^[208]	Tetrapod nanoneedles	1.8 at 1 $\mu\text{A}/\text{cm}^2$	3.9	----	8 h, <3%	nickel
Li <i>et al</i> ^[215]	Nanowires	0.97 at 12.7 $\mu\text{A}/\text{cm}^2$	----	3810	----	Si
Jo <i>et al</i> ^[209]	Nanowires	0.2	0.7	4.11×10^4	----	carbon cloth
Yang <i>et al</i> ^[211]	Nanowires	8.0	17	900	----	Si
Lee <i>et al</i> ^[206]	Nanowires	6	11	847	----	Si
Wei <i>et al</i> ^[210]	Nanotubes	7	17.8	910	24 h, <10%	copper plate
Liao <i>et al</i> ^[214]	Nanoscrews	3.6 at 10 $\mu\text{A}/\text{cm}^2$	11.2 at 1.2 mA/cm ²	----	30 min, <10%	Si
Wang <i>et al</i> ^[220]	Nanopencils	3.7 at 10 $\mu\text{A}/\text{cm}^2$	4.6 at 1.3 mA/cm ²	2300	30 min, <10%	Si
Shen <i>et al</i> ^[216]	Nanonails	7.9	----	----	----	Si
Zhu <i>et al</i> ^[213]	Nanoneedles	2.4	7 at 2.4 mA/cm ²	372	----	Si
This work	Nanoneedles	4.1	9.6	1134	140 min, <10%	Plastic

Table 8.1 Key performance parameters of some ZnO nanostructures field emitters reported in the literature and this work. The threshold field at 0.1 $\mu\text{A}/\text{cm}^2$ and the field at current densities of 1.0 mA/cm² are listed, respectively, unless otherwise stated.

For comparison, Table 8.1 tabulates the key performance parameters of the ZnO field emitters reported in the literature. As revealed in Table 8.1, the β of our ZnO nanoneedle is higher than those of the ZnO nanowires ($\beta = 847$)^[207] and nanoneedles ($\beta = 372$)^[214]. The high β value may be attributed to the sharp tip of the nanoneedles. It can be seen that the field emission properties of the ZnO nanoneedles flexible emitter is highly comparable to other ZnO nanostructured emitters prepared at high temperature and deposited on solid substrates.

8.3.2 X-ray Generation Using ZnO Nanoneedles on Plastic Substrate

The x-ray experimental system is an open type x-ray tube with a beryllium window directing the x-ray in a vertically upward direction. The location of the window is at 7 cm away from the target. A high voltage feed-through was used to allow electrical connection to the flexible emitter cathode, which was connected to a pulse voltage generator. The pulse power supply was operated at 600 Hz with output voltage ranging from 10 to 25 kV. The anode used in this experiment was a copper block connected to electrical ground. Figure 8.5(a) is a schematic diagram showing the mock-up arrangement of the flexible emitter and the copper anode when inside the x-ray tube. The surface of the copper anode was angled approximately 45° to assist x-ray emission. The radius of the emitter curl was approximately 3 mm. The photograph of the ZnO nanoneedles on polyimide substrate is shown in Figure 8.5(b), which is used as a field emitter to generate x-ray.

To minimize current fluctuation, the electron-gun chamber would have to be differentially pumped down by a mechanical pump and a turbomolecular pump to a base pressure of 10^{-6} Torr. X-ray was generated by bombarding the Cu target with high-density electron from the emitter. The shadow x-ray image of the specimen is formed on the projection screen by radically propagating x-rays.

Figure 8.5 Schematic diagram of the emitter and the anode in a mock-up layout. (b) Photograph of the flexible field emitter.

Figures 8.6(a) and (b) show the x-ray transmission images of a Bougainvillea flower obtained from the flexible emitter operated at 15 kV after exposing for about 3 min, which reveal veins for nutrition transportation. It is emphasized that this flower was snatched from its tree just before imaging and hence was still not dehydrated. From the images, it can be clearly seen that the ZnO nanoneedles on polyimide

substrate can be used as flexible field emitter to generate x-ray. This result is attributed to the good field emission properties of ZnO nanoneedles and the diode design.

Figure 8.6 (a) The x-ray transmission images of a Bougainvillea flower taken at 15 kV using the flexible emitter as an electron source. (b) An enlargement image of the stigma area as indicated by the white square.

8.4 Conclusions

In summary, the aligned ZnO nanoneedles on flexible plastic substrates can be used as FE emitter for x-ray generation. The ZnO nanoneedles show a low FE threshold field of $4.1 \text{ V}/\mu\text{m}$ and high emission current density of $1 \text{ mA}/\text{cm}^2$ at an applied field of $9.6 \text{ V}/\mu\text{m}$. Moreover, our results show that ZnO nanoneedles flexible emitter can be an efficient electron source for x-ray generation.

CHAPTER 9 **Conclusions and Future Work**

Recommendations

9.1 *Conclusions*

- Polycrystalline ZnO thin films were grown by the FCVA technique at substrate temperatures below 400 °C. The structural and optical properties of the ZnO films on Si were systematically investigated as a function of annealing temperature up to 900 °C. Random laser cavities were formed in the ZnO films after thermal annealing. ZnO grains and their boundaries form natural cavities, which provide sufficient optical gain and coherent feedback to achieve random laser action. The zinc silicate layer, formed between ZnO and Si after thermal annealing, can serve as a light confinement layer for random laser cavities.
- ZnO QDs with diameter of 10-13 nm were formed in the zinc silicate layer when the ZnO/SiO₂ sample was annealed at 900 °C for 10 hours. The near-band-edge PL spectrum of the ZnO QDs blue-shifted 48 meV as compared with the as-grown ZnO film, which is an evidence of quantum confinement effect. A lifetime of 65 ps was determined from the ZnO QDs at 4.3 K, which is much shorter than the exciton radiative lifetime of 322 ps in ZnO thin films. This result has been attributed to the superradiance effect.
- A new method to fabricate mechanical flexible UV laser device has been proposed in this thesis. ZnO and In₂O₃ nanoparticles were used as scattering centers and the ZnO film deposited on plastic substrate served as an optical

gain medium. Both of the ZnO and In_2O_3 nanoparticles based flexible laser devices exhibited incoherent random laser action. The pump threshold and emission intensity of the flexible lasers depend on the radius of curvature of the device.

- Ion beam sputtering method has been successfully applied to fabricate ZnO nanoneedles selectively from ZnO thin films. Optical pumped UV random laser was observed in the ZnO nanoneedle arrays. In the high temperature lasing measurement, a characteristic temperature was derived to be 138 K in the temperature range from 300 K to 615 K. The optical gain of the ZnO nanoneedle at high temperature is attributed to the high-crystal-quality of the nanoneedles, enhancement of oscillator strength in nanostructures, and a self-compensation mechanism in random laser cavities.
- $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles were also fabricated by the ion beam technique at room temperature. The near-band-edge PL emission at room temperature could be readily tuned from 3.28 eV to 3.58 eV by varying the Mg concentration. Random laser action in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles with tunable wavelengths was demonstrated. The temperature dependence of the lasing emission from the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles has been investigated and a characteristic temperature of ~ 84 K was deduced.
- 1D ZnO nanoneedles were grown on plastic substrate by ion beam technique. Excellent field emission properties with a threshold as low as 4.1 V/ μm were achieved, the emission current density can reach 1 mA/ cm^2 at 9.6 V/ μm . The flexible emitters have been acted as electron source to generate x-ray for radiography image.

9.2 Recommendations for Further Research

9.2.1 Electrical Pumped ZnO Nanoneedles based UV Light Emitting Devices

It is highly desirable to fabricate efficient UV light emitting diodes (LED) based on 1D ZnO nanoneedle heterojunction structures. The key step to achieve LED is to fabricate efficient p-n junction such as, n-ZnO/p-ZnO heterojunction structures. The proposed LED structure is shown in Figure 9.1. The principle of this design can also be applied to $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoneedles for wavelength-tunable LED applications.

In addition, an electrically pumped random laser system can be realized based on the design of ZnO random laser devices and LEDs. The scatters used in the electrically pumped random lasers can be in the form of annealed thin films, nanoparticles and 1D nanoneedles. The flexible electrically pumped random lasers should be explored based on plastic substrate as well.

Figure 9.1 Schematic diagram of the proposed ZnO nanoneedle LED.

9.2.2 To Develop ZnO Nanomaterial with Tunable Size

ZnO QDs are of great research interest due to their fundamental importance as a three-dimensional confined system in bridging the gap between bulk matter and molecular species. ZnO QDs have been fabricated by a simple thermal annealing

Chapter 9 Conclusions and Future Work Recommendations

method. In order to control the sizes of ZnO QDs, the annealing parameters should be studied such as annealing time, ambient gaseous etc. A strong and predominant UV luminescence with broad applications could be achieved by ZnO QDs with controllable size.

Furthermore, coherent random laser in ZnO nanoneedles has been observed and reported in Chapter 6. More investigations are needed to carry out in the effect of ZnO nanoneedles size on random lasing properties. More efforts should be focused on finding new fabrication method for the nanoneedles and how to control the size of nanoneedles.

Appendix I: List of Publications

1. **H. Y. Yang**, S. P. Lau, S. F. Yu, M. Tanemura, T. Okita, H. Hatano, K. S. Teng, and S. P. Wilks, "Wavelength-tunable and high-temperature lasing in ZnMgO nanoneedles", *Appl. Phys. Lett.*, **89**, 081107 (2006).
2. **H. Y. Yang**, S. P. Lau, S. F. Yu, A. P. Abiyasa, M. Tanemura, T. Okita, and H. Hatano, "High-temperature ZnO nanoneedle random lasers", *Appl. Phys. Lett.*, **89**, 011103 (2006).
3. **H. Y. Yang**, S. P. Lau, S. F. Yu, L. Huang, M. Tanemura, J. Tanaka, T. Okita, and H. Hng, "Field emission from zinc oxide nanoneedles on plastic substrates", *Nanotechnology*, **16**, 1300 (2005).
4. S. P. Lau, **H. Y. Yang**, S. F. Yu, C. Yuen, E. S. P. Leong, H. D. Li, and H. H. Hng, "Optically pumped flexible UV random laser", *Small*, **1**, 956 (2005).
5. S. P. Lau, **H. Y. Yang**, S. F. Yu, H. D. Li, M. Tanemura, J. Tanaka, T. Okita, and H. H. Hng, "Laser action in ZnO nanoneedles selectively grown on Si and plastic substrates", *Appl. Phys. Lett.* **87**, 013104, (2005). (also selected and published by the *Virtual J. Nanoscale Sci. Tech.* **12**, (2005)).
6. L. Huang, S. P. Lau, **H. Y. Yang**, E. S. P. Leong, and S. F. Yu, "Stable superhydrophobic surface via Carbon nanotubes coated with a ZnO thin film", *J. Phys. Chem. B*, **109**, 7746 (2005).
7. X. H. Ji, S. P. Lau, **H. Y. Yang**, and S. F. Yu, "Aligned InN nanofingers prepared by the ion-beam assisted filtered cathodic vacuum arc technique", *Nanotechnology*, **16**, 3069 (2005). (the published work has been highlighted in *Nanotechnology Journal Highlights* **22** Nov. 2005.)
8. L. Huang, S. P. Lau, **H. Y. Yang**, S. F. Yu, "Local measurement of secondary electron emission from ZnO coated carbon nanotubes", *Nanotechnology*, **17**, 1564 (2006).
9. S. P. Lau, L. Huang, S. F. Yu, **H. Y. Yang**, J. K. Yoo, S. J. An, G. C. Yi, "Enhanced secondary electron emission from III-nitride/ZnO nanorod coaxial heterostructures", *Small*, **2**, 736 (2006).

Appendix I: List of Publications

10. C. Yuen, S. F. Yu, E. S. P. Leong, **H. Y. Yang**, S. P. Lau, N. S. Chen, and H. H. Hng, "Low-loss and directional output ZnO thin-film ridge waveguide random lasers with MgO capped layer", *Appl. Phys. Lett.*, **86**, 031112 (2005).
11. T. T. Tan, H. S. Sim, S. P. Lau, **H. Y. Yang**, M. Tanemura, and J. Tanaka, "X-ray generation using flexible field emitters", *Appl. Phys. Lett.*, **88**, 103105 (2006).
12. C. Yuen, S. F. Yu, E. S. P. Leong, **H. Y. Yang**, S. P. Lau, and H. H. Hng, "Formation conditions of random laser cavities in annealed ZnO epilayers", *IEEE J. Quantum Electronics*, **47**, 970 (2005).
13. T. S. Herng, S. P. Lau, S. F. Yu, **H. Y. Yang**, X. H. Ji, J. S. Chen, N. Yasui, and H. Inaba, "Origin of room temperature ferromagnetism in ZnO:Cu films", *J. Appl. Phys.*, **99**, 086101 (2006).
14. H. D. Li, S. F. Yu, A. P. Abiyasa, C. Yuen, S. P. Lau, **H. Y. Yang**, and E. S. P. Leong, "Strain dependence of lasing mechanisms in ZnO epilayers", *Appl. Phys. Lett.*, **86**, 261111 (2005).
15. H. D. Li, S. F. Yu, S. P. Lau, E. S. P. Leong, **H. Y. Yang**, and A. P. Abiyasa, "High-temperature excitonic lasing in annealed ZnO epilayers", *Adv. Mater.*, **18**, 771 (2006).
16. X. H. Zhang, S. J. Chua, A. M. Yong, S. Y. Chow, **H. Y. Yang**, S. P. Lau, S. F. Yu, "Exciton radiative lifetime in ZnO quantum dots embedded in SiO_x matrix", *Appl. Phys. Lett.*, **88**, 221903 (2006).
17. M. Tanemura, T. Okita, J. Tanaka, M. Kitazawa, K. Itoh, L. Miao, S. Tanemura, S. P. Lau, **H. Y. Yang**, and Lei Huang, "Room-temperature grown and applications of carbon nanofibers: A review", *IEEE Trans. on Nanotechnology*, **5**, 587 (2006).
18. X. H. Zhang, S. J. Chua, A. M. Yong, **H. Y. Yang**, S. P. Lau, S. F. Yu, X. W. Sun, L. Miao, M. Tanemura and S. Tanemura, "Exciton radiative lifetime in ZnO nanorods fabricated by vapor phase transport method" *Appl. Phys. Lett.*, **90**, 013107 (2007).
19. T. S. Herng, S. P. Lau, S. F. Yu, **H. Y. Yang**, L. Wang, M. Tanemura and J. S. Chen, "Magnetic anisotropy in the ferromagnetic Cu-doped ZnO nanoneedles", *Appl. Phys. Lett.*, **90**, 032509 (2007).
20. X. H. Ji, S. P. Lau, S. F. Yu, **H. Y. Yang**, T. S. Herng and J. S. Chen, "Ferromagnetic Cu-doped AlN nanorods", *Nanotechnology*, **18**, 105601 (2007).
21. M. Tanemura, H. Hatano, M. Kitazawa, J. Tanaka, T. Okita, S. P. Lau, **H. Y. Yang**, S. F. Yu, L. Huang, L. Miao and S. Tanemura, and L. Huang, "Room-temperature growth of carbon nanofibers on plastic substrates", *Surf. Sci.*, **600**, 3663 (2006).

Appendix I: List of Publications

22. H. S. Sim, S. P. Lau, **H. Y. Yang**, L. K. Ang, M. Tanemura and K. Yamaguchi, "Reliable and flexible carbon-nanofiber-based all-plastic field emission devices", *Appl. Phys. Lett.*, **90**, 143103 (2007).
23. C. Yuen, S. F. Yu, E. S. P. Leong, S. P. Lau, K. Pita, **H. Y. Yang**, and T. P. Chen, "Room temperature deposition of p-type Arsenic doped ZnO polycrystalline films by laser-assist filtered cathodic vacuum arc technique", *J. Appl. Phys.*, accepted for publication (2007).

Appendix II: Bibliography

Appendix II: Bibliography

- ¹ P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H. J. Choi, "Controlled grown of ZnO nanowires and their optical properties", *Adv. Func. Mater.* **15**, 1911-1914 (2003).
- ² E. Mathiowitz, J. S. Jacob, Y. S. Jong, G. P. Carino, D. E. Chickering, P. Chaturvedi, C. A. Santos, K. Vijayaraghavan, S. Montgomery, M. Bassett, C. Morrell, "Biologically erodable microspheres as potential oral drug delivery systems", *Nature* **386**, 410-414 (1997).
- ³ Z. Y. Jiang, Z. X. Xie, X. H. Zhang, S.C. Lin, T. Xu, S. Y. Xie, R. B. Huang, and L. S. Zheng, "", *Adv. Mater.* **16**, 904-907 (2004).
- ⁴ J. Capmany, D. Pastor, B. Ortega, "New and flexible fiber-optic delay-line filters using chirped Bragg gratings and laser arrays", *IEEE Trans. on Microwave Theory and Techniques* **47**, 1321-1326 (1999).
- ⁵ S. Li, K. T. Chan, "Electrical wavelength tunable and multiwavelength actively mode-locked fiber ring laser", *Appl. Phys. Lett.* **72**, 1954-1956 (1998).
- ⁶ D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen and T. Goto, "Optically pumped lasing of ZnO at room temperature", *Appl. Phys. Lett.* **70**, 2230-2232 (1997).
- ⁷ D. C. Look, "Recent advances in ZnO materials and devices", *Mater. Sci. Eng. B* **80**, 383-387 (2001).
- ⁸ Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, "Room-temperature ultraviolet laser emission from self-assembled ZnO microcrystallite thin films", *Appl. Phys. Lett.* **72**, 3270-3272 (1998).

Appendix II: Bibliography

- ⁹ Y. F. Chen, D. Bagnall, and T. F. Yao, "ZnO as a novel photonic material for the ultraviolet region", *Mater. Sci. Eng. B* **75**, 190-198 (2000).
- ¹⁰ F. Bernardini, V. Fiorentini, and D. Vanderbilt, "Spontaneous polarization and piezoelectric constants of III-V nitrides", *Phys. Rev. B* **56**, 10024-10027 (1997).
- ¹¹ D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen and T. Goto, "High temperature excitonic stimulated emission from ZnO epitaxial layers", *Appl. Phys. Lett.* **73**, 1038-1040 (1998).
- ¹² Y. F. Chen, N. T. Tuan, Y. Segawa, H. Ko, S. Hong, and T. Yao, "Stimulated emission and optical gain in ZnO epilayers grown by plasma-assisted molecular-beam epitaxy with buffers", *Appl. Phys. Lett.* **78**, 1469-1471 (2001).
- ¹³ S. L. Cho, J. Ma, Y. K. Kim, Y. Sun, G. K. L. Wong, and J. B. Ketterson, "Photoluminescence and ultraviolet lasing of polycrystalline ZnO thin films prepared by the oxidation of the metallic Zn", *Appl. Phys. Lett.* **75**, 2761-2763 (1999).
- ¹⁴ M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, "Room-temperature ultraviolet nanowire nanolasers", *Science* **292** 1897-1899 (2001).
- ¹⁵ Y. C. Kong, D. P. Yu, B. Zhang, W. Fang, and S. Q. Feng, "Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach", *Appl. Phys. Lett.* **78**, 407-409 (2001).
- ¹⁶ M. H. Huang, Y. Y. Wu, H. Feich, N. Tran, E. Weber, and P. D. Yang, "Catalytic grown of zinc oxide nanowires by vapor transport", *Adv. Mater.* **13**, 113-116 (2001).

Appendix II: Bibliography

- ¹⁷ Y. C. Kong, D. P. Yu, B. Zhang, W. Fang, and S. Q. Feng, "Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach", *Appl. Phys. Lett.* **78**, 407-409 (2001).
- ¹⁸ B. D. Yao, Y. F. Chan, and N. Wang, "Formation of ZnO nanostructures by a simple way of thermal evaporation", *Appl. Phys. Lett.* **81**, 757-759 (2002).
- ¹⁹ P. D. Yang, H. Q. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. R. He, and H. J. Choi, "Controlled grown of ZnO nanowires and their optical properties", *Adv. Func. Mater.* **12**, 323-331 (2002).
- ²⁰ J. E. Jaffe and A. C. Hess, "Hartree-Fock study of phase changes in ZnO at high pressure", *Phys. Rev. B* **48**, 7903-7909 (1993).
- ²¹ Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doan, V. Avrutin, S. J. Cho, and H. Morko, "A comprehensive review of ZnO materials and devices", *J. Appl. Phys.* **98**, 041301 (2005).
- ²² T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, R. Shiroki, K. Tamura, T. Yasuda, H. Koinuma, "Band gap engineering based on $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_y\text{Zn}_{1-y}\text{O}$ ternary alloy films", *Appl. Phys. Lett.* **78**, 1237-1239 (2001).
- ²³ H. Tabet-Derraz, N. Benramdane, D. Nacer, A. Bouzidi, M. Medles, "Investigations on $\text{Zn}_x\text{Cd}_{1-x}\text{O}$ thin films obtained by spray pyrolysis", *Solar energy mater. solar cells* **73**, 249-259 (2002).
- ²⁴ A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakuraiand, Y. Yoshida, T. Yasuda, and Y. Segawa, " $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ as a II-VI widegap semiconductor alloy", *Appl. Phys. Lett.* **72**, 2466-2468 (1998).
- ²⁵ K. Shama, J. Narayan, J. F. Muth, C. W. Teng, C. Jin, A. Kvit, R. M. Kolbas and O. W. Holland, "Optical and structural properties of epitaxial $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys", *Appl. Phys. Lett.* **75**, 3327-3329 (2005).

Appendix II: Bibliography

- ²⁶ Y. R. Ryu, S. Zhu, D. C. Look, J. M. Wrobel, H. M. Jeong, and H. W. White, "Synthesis of p-type ZnO films", *J. Cryst. Growth* **216**, 330-334, (2000).
- ²⁷ T. Yamamoto, and H. Katayama-Yoshida, "Solution using a codoping method to unipolarity for the fabrication of p-type ZnO", *Jpn. J. Appl. Phys.* **38**, L166-L169 (1999).
- ²⁸ K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga, A. Shimizu, "Grown of p-type zinc oxide films by chemical vapor deposition", *Jpn. J. Appl. Phys.* **36**, L1453-L1455 (1997).
- ²⁹ C. Yuen, S. F. Yu, S. P. Lau, Rusli, and T. P. Chen, "Fabrication of n-ZnO:Al/p-SiC(4H) heterojunction light-emitting diodes by filtered cathodic vacuum arc technique", *Appl. Phys. Lett.*, **86**, 241111 (2005).
- ³⁰ X. L. Guo, J. H. Choi, H. Tabata, and T. K. Kawai, "Fabrication and optoelectronic properties of a transparent ZnO homostructural light-emitting diode", *Jpn. J. Appl. Phys.* **40**, L177-L180 (2001).
- ³¹ I. S. Jeong, J. H. Kim, and S. Im, "Ultraviolet-enhanced photodiode employing *n*-ZnO/*p*-Si structure", *Appl. Phys. Lett.*, **83**, 2946-2948 (2003).
- ³² Q. X. Yu, B. Xu, Q. H. Wu, Y. Liao, G. Z. Wang, R. C. Fang, H. Y. Lee and C. T. Lee, "Optical properties of ZnO/GaN heterostructure and its near-ultravioletV light-emitting diode" *Appl. Phys. Lett.*, **83**, 4713-4715 (2003).
- ³³ Y. I. Alivov, J. E. Van Nostrand, D. C. Look, M. V. Chukichev, and B. M. Ataev, "Observation of 430 nm electroluminescence from ZnO/GaN heterojunction light-emitting diodes", *Appl. Phys. Lett.*, **83**, 2943-2945 (2003).
- ³⁴ Y. I. Alivov, E. V. Kalinina, A. E. Cherenkov, D. C. Look, B. M. Ataev, A. K. Omaev, M. V. Chukichev, and D. M. Bagnall, "Fabrication and characterization of

Appendix II: Bibliography

-
- n*-ZnO/*p*-AlGaIn heterojunction light-emitting diodes on 6H-SiC substrates” Appl. Phys. Lett., **83**, 4719-4721 (2003).
- ³⁵ H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, “Current injection emission from a transparent *p*-*n* junction composed of *p*-SrCu₂O₂/*n*-ZnO” Appl. Phys. Lett. **77**, 475-477 (2000).
- ³⁶ 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**, 4260-4268 (1980).
- ³⁷ Y. I. Alivov, Ü. Özgür, S. Doan, D. Johnstone, V. Avrutin, N. Onojima, C. Liu, J. Xie, Q. Fan, and H. Morkoç, “Photoresponse of *n*-ZnO/*p*-SiC heterojunction diodes grown by plasma-assisted molecular-beam epitaxy”, Appl. Phys. Lett. **86**, 241108 (2005).
- ³⁸ C. Yuen, S. F. Yu, S. P. Lau, Rusli, and T. P. Chen, “Fabrication of *n*-ZnO:Al/*p*-SiC(4H) heterojunction light-emitting diodes by filtered cathodic vacuum arc technique”, Appl. Phys. Lett. **86**, 241111 (2005).
- ³⁹ H. Ohta, H. Mizoguchi, M. Hirano, S. Narushima, T. Kamiya, and H. Hosono, “Fabrication and characterization of heteroepitaxial *p*-*n* junction diode composed of wide-gap oxide semiconductors *p*-ZnRh₂O₄/*n*-ZnO”, Appl. Phys. Lett. **82**, 823-825 (2003).
- ⁴⁰ H. Tabet-Derraz, N. Benramdane, D. Nacer, A. Bouzidi, M. Medles, “Investigations on Zn_xCd_{1-x}O thin films obtained by spray pyrolysis”, Solar energy mater.solar cells **73**, 249-259 (2002).
- ⁴¹ A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakuraiand, Y. Yoshida, T. Yasuda, and Y. Segawa, “Mg_xZn_{1-x}O as a II-VI widegap semiconductor alloy”, Appl. Phys. Lett. **72**, 2466-2468 (1998).

Appendix II: Bibliography

-
- ⁴² K. Shama, J. Narayan, J. F. Muth, C. W. Teng, C. Jin, A. Kvit, R. M. Kolbas and O. W. Holland, "Optical and structural properties of epitaxial $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys", *Appl. Phys. Lett.* **75**, 3327-3329 (2005).
- ⁴³ T. Makino, N. T. Tuan, Y. Segawa, C. H. Chia, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, "Radiative and nonradiative recombination processes in lattice-matched $(\text{Cd,Zn})\text{O}/(\text{Mg,Zn})\text{O}$ multiquantum wells", *Appl. Phys. Lett.* **77**, 1632-1634 (2000).
- ⁴⁴ S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, "Spintronics: A Spin-Based Electronics Vision for the Future", *Science*, **294**, 1488-1491 (2000).
- ⁴⁵ Y. M. Kim, M. Yoon, I. W. Park, Y. J. Park, and J. H. Lyoo, "Synthesis and magnetic properties of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films prepared by the sol-gel method", *Solid State Commun.* **129**, 175 (2004).
- ⁴⁶ T. S. Herng, S. P. Lau, S. F. Yu, H. Y. Yang, X. H. Ji, J. S. Chen, N. Yasui, and H. Inaba, "Origin of Room temperature ferromagnetism in $\text{ZnO}:\text{Cu}$ films on silicon substrate", *J. Appl. Phys.* **99**, 086161 (2006).
- ⁴⁷ T. Monteiro, C. Boemare, M. J. Soares, E. Rita, and E. Alves, "Photoluminescence and damage recovery studies in Fe-implanted ZnO single crystals", *J. Appl. Phys.* **93**, 8995-9000 (2006).
- ⁴⁸ K. Ueda, H. Tabata, and T. Kawai, "Magnetic and electric properties of transition-metal-doped ZnO films", *Appl. Phys. Lett.* **79**, 988-990 (2001).
- ⁴⁹ T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, "Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors", *Science* **287**, 1019-1022 (2000).

Appendix II: Bibliography

-
- ⁵⁰ K. Sato, H. Katayama-Yoshida, "Material design for transparent ferromagnets with ZnO-based magnetic semiconductors", *Jpn. J. Appl. Phys.* **39**, L555-L558 (2000).
- ⁵¹ M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, J. M. D. Coey, "Anisotropic ferromagnetism in substituted zinc oxide", *Phys. Rev. Lett.* **93**, 177206, (2004).
- ⁵² T. Fukumura, Z. W. Jin, M. Kawasaki, T. Shono, T. Hasegawa, S. Koshihara, H. Koinuma, "Magnetic properties of Mn-doped ZnO", *Appl. Phys. Lett.* **78**, 958-960 (2001).
- ⁵³ D. F. Paraguay, M. M. Yoshida, J. Morales, J. Solis, L. W. Estrada, "Influence of Al, In, Cu, Fe and Sn dopants on the response of thin film ZnO gas sensor to ethanol vapour", *Thin solid films* **373**, 137-140 (2000).
- ⁵⁴ K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, "Correlation between photoluminescence and oxygen vacancies in ZnO phosphors", *Appl. Phys. Lett.* **68**, 403-405 (1996).
- ⁵⁵ B. J. Jin, S. H. Bae, S. Y. Lee, and S. Im, "Effects of native defects on optical and electrical properties of ZnO prepared by pulsed laser deposition", *Mater. Sci. Eng. B* **71**, 301-305 (2000).
- ⁵⁶ H. J. Ko, Y. F. Chen, T. Yan, K. Miyajima, A. Yamamoto, T. Goto, "Biexciton emission from high-quality ZnO films grown on epitaxial GaN by plasma-assisted molecular-beam epitaxy", *Appl. Phys. Lett.* **77**, 537-539 (2000).
- ⁵⁷ B. J. Lin, S. Im, and S. Y. Lee, "Violet and ultraviolet luminescence emitted from ZnO thin films grown on sapphire by pulsed laser deposition", *Thin solid films* **366**, 107-110 (2000).
- ⁵⁸ B. X. Lin, Z. X. Fu, and Y. B. Jia, "Green luminescent center in undoped zinc oxide films deposited on silicon substrates", *Appl. Phys. Lett.* **79**, 943-945 (2001).

Appendix II: Bibliography

- ⁵⁹ A. B. Djurišić, Yu Hang Leung, W. C. H. Choy, K. W. Cheah, and W. K. Chan, "Visible photoluminescence in ZnO tetrapod and multipod structures", *Appl. Phys. Lett.* **84**, 2635-2637 (2004).
- ⁶⁰ K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, B. E. Gnade, "Mechanisms behind green photoluminescence in ZnO phosphor powders", *J. Appl. Phys.* **79**, 7983-7990 (1996).
- ⁶¹ S. A. Studenikin, Nickolay Golego, and Michael Cocivera, "Fabrication of green and orange photoluminescent, undoped ZnO films using spray pyrolysis", *J. Appl. Phys.* **84**, 2287-2294 (1998).
- ⁶² K. K. Kim, J. H. Song, H. J. Jung, W. K. Choi, S. J. Park, and J. H. Song, "The grain size effects on the photoluminescence of ZnO/ α -Al₂O₃ grown by radio-frequency magnetron sputtering", *J. Appl. Phys.* **87**, 3573-3575 (2000).
- ⁶³ Y. Chen, D. M. Bagnall, H.-J. Koh, K.-T. Park, K. Hiraga, Z.-Q. Zhu, and T. Yao, "Plasma assisted molecular beam epitaxy of ZnO on *c*-plane sapphire: Grown and characterization", *J. Appl. Phys.* **84**, 3912-3914 (1998).
- ⁶⁴ P. Fons, K. Iwata, S. Niki, A. Yamada, and K. Matsubara, "Grown of high-quality epitaxial ZnO films on α -Al₂O₃", *J. Cryst. Grown* **201–202**, 627-632 (1999).
- ⁶⁵ E. M. Kaidashev, M. Lorenz, H.V-Wenckstern, A. Rahm, H. C. Semmelhack, K. H. Han, G. Benndorf, C. Bundesmann, H. Hochmuth, and M. Grundmann, "High electron mobility of epitaxial ZnO thin films on *c*-plane sapphire grown by multistep pulsed-laser deposition", *Appl. Phys. Lett.* **82**, 3901-3903 (2003).
- ⁶⁶ B. J. Jin, S. Im, and S. Y. Lee, "Violet and ultraviolet luminescence emitted from ZnO thin films grown on sapphire by pulsed laser deposition", *Thin solid films* **366**, 107-110 (2000).

Appendix II: Bibliography

- ⁶⁷ W. W. Wenas, A. Yamada, M. Konagai, and K. Takahashi, "Textured ZnO thin-films for solar-cells grown by metal organic chemical vapor-deposition", *Jpn. J. Appl. Phys. Part 2* **30**, L441-L443 (1991).
- ⁶⁸ Y. Liu, C. R. Gorla, S. Liang, N. Emanetoglu, Y. Lu, H. Shen, and M. Wraback, "Ultraviolet detectors based on epitaxial ZnO films grown by MOCVD", *J. Electronics Mater.* **29**, 69-74 (2000).
- ⁶⁹ X. L. Xu, S. P. Lau, J. S. Chen, G. Y. Chen, and BK Tay, "Polycrystalline ZnO thin films on Si (1 0 0) deposited by filtered cathodic vacuum arc", *J. Cryst. Grown* **223-202**, 201-205 (2001).
- ⁷⁰ Y. G. Wang, S. P. Lau, H. W. Lee, S. F. Yu, B. K. Tay, X. H. Zhang and H. H. Hng, "Photoluminescence study of ZnO films prepared by thermal oxidation of Zn metallic films in air", *J. Appl. Phys.* **94**, 354 -358 (2003).
- ⁷¹ T. Yamamoto, T. Shiosaki, and A. Kawabata, "Characterization of ZnO piezoelectric films prepared by rf planar-magnetron sputtering", *J. Appl. Phys.* **51**, 3113-3120 (1980).
- ⁷² T. Mitsuyu, S. Ono, and K. Wasa, "Structures and SAW properties of rf-sputtered single-crystal films of ZnO on sapphire", *J. Appl. Phys.* **51**, 2464-2470 (1980).
- ⁷³ R. D. Vispute, V. Talyansky, S. Choopun, R. P. Sharma, T. Venkatesan M. He, X. Tang, J. B. Halpern, and M. G. Spencer, Y. X. Li, L. G. Salamanca-Riba, A. A. Iliadis, and K. A. Jones, "Heteroepitaxy of ZnO on GaN and its implications for fabrication of hybrid optoelectronic devices", *Appl. Phys. Lett.* **73**, 348-350 (1998).
- ⁷⁴ C. X. Wang, G. W. Yang, H.W. Liu, Y. H. Han, J. F. Luo, C. X. Gao, and G. T. Zou, "Experimental analysis and theoretical model for anomalously high ideality factors in ZnO/diamond *p-n* junction diode", *Appl. Phys. Lett.* **84**, 2427-2429 (2004).

Appendix II: Bibliography

- ⁷⁵ A. Ohtomo, K. Tamura, K. Saikusa, K. Takahashi, T. Makino, Y. Segawa, H. Koinuma, and M. Kawasaki, "Single crystalline ZnO films grown on lattice-matched ScAlMgO₄(0001) substrates", *Appl. Phys. Lett.* **75**, 2635-2637 (1999).
- ⁷⁶ P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, "Ultraviolet spontaneous and stimulated emissions from ZnO microcrystallite thin films at room temperature", *Solid State Commun.* **103**, 459-463 (1997).
- ⁷⁷ Y. Chen, N. T. Tuan, Y. Segawa, H. J. Ko, S. K. Hong, and T. Yao, "Stimulated emission and optical gain in ZnO epilayers grown by plasma-assisted molecular-beam epitaxy with buffers", *Appl. Phys. Lett.* **78**, 1469-1471 (2001).
- ⁷⁸ P. Yu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, "Room-temperature gain spectra and lasing in microcrystalline ZnO thin films", *J. Cryst. Growth* **184-185**, 601-604 (1998).
- ⁷⁹ R. Ambartsumyan, N. G. Basov, P. G. Kryukov and V. S. Letokhov, "Short-pulse Q-switched laser with variable pulse length", *IEEE J. Quantum Electron.* **2**, 436-441 (1966).
- ⁸⁰ H. Cao, "Lasing in random media", *Waves Random Media* **12**, R1-R39 (2003).
- ⁸¹ H. Cao, Y. G. Zhao, S. T. Ho, E. W. Seelig, Q. H. Wang, and R. P. H. Chang, "Random laser action in semiconductor powder", *Phys. Rev. Lett.* **82**, 2278-2281 (1999).
- ⁸² D. S. Wiersma, and A. Lagendijk, "Light diffusion with gain and random lasers", *Phys. Rev. E* **54**, 4256-4265 (1996).
- ⁸³ D. S. Wiersma, M. P. Vanalbada, and A. Lagendijk, "Random laser", *Nature* **373**, 203-204 (1995).

Appendix II: Bibliography

- ⁸⁴ L. Florescu, and S. John, "Lasing in a random amplifying medium: Spatiotemporal characteristics and nonadiabatic atomic dynamics", *Phys. Rev. E* **70**, 036607 Part 2 (2004).
- ⁸⁵ H. Cao, Y. G. Zhao, H. C. Ong, S. T. Ho, J. Y. Dai, J. Y. Wu, and R. P. H. Chang, "Ultraviolet lasing in resonators formed by scattering in semiconductor polycrystalline films", *Appl. Phys. Lett.* **73**, 3656-3658(1998).
- ⁸⁶ H. Cao, J. Y. Y. Xu, Y. Ling, A. L. Burin, E. W. Seeling, X. Liu, and R. P. H. Chang, "Random Lasers with coherent feedback", *IEEE J. Selected Topics Quantum Electronics* **9**, 111-119 (2003).
- ⁸⁷ D. S. Wiersma, and S. Cavaleri, "Light emission - A temperature-tunable random laser", *Nature* **414**, 708-709 (2001).
- ⁸⁸ R. K. Thareja, and A. Mitram, "Random laser action in ZnO" *Appl. Phys. B lasers Opt.* **71**, 181-184 (2000).
- ⁸⁹ Y. Feng, J. F. Bisson, J. R. Lu, S. H. Huang, K. Takaichi, A. Shirakawa, M. Musha, and K. Ueda, "Thermal effects in quasi-continuous-wave Nd^{3+} : $\text{Y}_3\text{Al}_5\text{O}_{12}$ nanocrystalline-powder random laser", *Appl. Phys. Lett.* **84**, 1040-1042 (2004).
- ⁹⁰ R. C. Polson, Z. V. Vardeny, "Random lasing in human tissues", *Appl. Phys. Lett.* **85**, 1289-1251 (2004).
- ⁹¹ H. Cao, Y. G. Zhao, X. Liu, Seeling, X. Liu, and R. P. H. Chang, "Effect of external feedback on lasing in random media", *Appl. Phys. Lett.* **75**, 1213-1215 (1999).
- ⁹² J. S. Liu, H. Lu, and C. Wang, "Spectral time evolution of quasistate modes in two-dimensional random media", *Acta Physica Sinica* **54**, 3116-3122 (2005).

Appendix II: Bibliography

- ⁹³ C. Yuen, S. F. Yu, S. P. Lau, and G. C. K. Chen, "Design and fabrication of ZnO light-emitting devices using filtered cathodic vacuum arc technique", *J. Cryst. Growth* **287**, 204-212 (2006).
- ⁹⁴ S. F. Yu, and E. S. P. Leong, "High-power single-mode ZnO thin-film random lasers", *IEEE J. Quantum Electron.* **40**, 1186-1189, (2004).
- ⁹⁵ C. Yuen, S. F. Yu, E. S. P. Leong, H. Y. Yang, S. P. Lau, N. S. Chen, and H. H. Hng, "Low-loss and directional output ZnO thin-film ridge waveguide random lasers with MgO capped layer", *Appl. Phys. Lett.* **86**, 031112 (2005).
- ⁹⁶ S. F. Yu, C. Yuen, S. P. Lau, and H. W. Lee, "ZnO thin-film random lasers on silicon substrate", *Appl. Phys. Lett.* **84**, 3244-3246 (2004).
- ⁹⁷ S. P. Lau, H.Y. Yang, S.F. Yu, C. Yuen, E. S. P. Leong, H. D. Li, and H.H. Hng, "Flexible UV random lasers based on nanoparticles", *Small* **1**, 956-959 (2005).
- ⁹⁸ S. F. Yu, C. Yuen, S. P. Lau, W. I. Park and G-C. Yi, "Random laser action in ZnO nanorod arrays embedded in ZnO epilayers", *Appl. Phys. Lett.* **84**, 3241-3243 (2004).
- ⁹⁹ S. P. Lau, H. Y. Yang, S. F. Yu, H. D. Li, M. Tanemura, T. Okita, H. Hatano and H. H. Hng, "Laser action in ZnO nanoneedles selectively grown on silicon and plastic substrates", *Appl. Phys. Lett.* **87**, 013104 (2005).
- ¹⁰⁰ H. C. Hsu, C. Y. Wu, and W. F. Hsieh, "Stimulated emission and lasing of random-grown oriented ZnO nanowires", *J. Appl. Phys.* **97**, 064315 (2005).
- ¹⁰¹ Z. L. Wang, "Mechanic properties of nanowires and nanobelts", *Dekker Encyclopedia of Nanoscience and Nanotechnology*, 1773-1786 (2004).

Appendix II: Bibliography

- ¹⁰² C. M. Mo, Y. H. Li, Y. S. Liu, Y. Zhang and L. D. Zhang, "Enhancement effect of photoluminescence in assemblies of nano-ZnO particles/silica aerogels", *J. Appl. Phys.* **83**, 4389-4391 (1998).
- ¹⁰³ S. G. Nilsson, E. L. Sarwe, and L. Montelius, "Fabrication and mechanical characterization of ultrashort nanocantilevers", *Appl. Phys. Lett.* **83**, 990-902 (2003).
- ¹⁰⁴ J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. J. Dai, "Nanotube molecular wires as chemical sensors", *Science* **14**, 622-625 (2000).
- ¹⁰⁵ Z. L. Wang and J. H. Song, "Piezoelectric nanogenerators based on zinc oxide nanowire arrays", *Science* **14**, 242-246 (2006).
- ¹⁰⁶ H. M. Kim, T. W. Kang, K. S. Chung, H. M. Kim, T. W. Kang, and K. S. Chung, "Nanoscale UV-light-emitting diodes using wide-bandgap gallium nitride nanorods", *Adv. Mater.* **15**, 567-569 (2003.)
- ¹⁰⁷ H. Y. Yang, S. P. Lau, S. F. Yu, L. Huang, M. Tanemura, J. Tanaka, T. Okita and H. H. Hng, "Field emission from zinc oxide nanoneedles on plastic substrates", *Nanotechnology* **16**, 1300-1303 (2005).
- ¹⁰⁸ Z. W. Pan, Z. R. Dai, and Z. L. Wang, "Nanobelts of semiconducting oxides", *Science* **291**, 1947-1949 (2001).
- ¹⁰⁹ Y. K. Liu, J. A. Zapien, Y. Y. Shan, C. Y. Geng, C. S. Lee, S. T. Lee, "Wavelength-controlled lasing in $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ single-crystal nanoribbons", *Adv. Mater.* **17**, 1372-1377 (2005).
- ¹¹⁰ Y. J. Chen, L. Nie, X. Y. Xue, Y. G. Wang, and T. H. Wang, "Linear ethanol sensing of SnO_2 nanorods with extremely high sensitivity", *Appl. Phys. Lett.* **88**, 083105 (2006).

Appendix II: Bibliography

- ¹¹¹ Y. Xie, Y. T. Qian, W. Z. Wang, S. Y. Zhang, and Y. H. Zhang, "A benzene-thermal synthetic route to nanocrystalline GaN", *Science* **272**, 1926-1927 (1996).
- ¹¹² X. H. Ji, S. P. Lau, H. Y. Yang, and S.F. Yu, "Aligned InN nanofingers prepared by the ion-beam assisted filtered cathodic vacuum arc technique", *Nanotechnology* **16**, 3069-3073 (2005).
- ¹¹³ S. P. Lau, L. Haung, S. F. Yu, H. Y. Yang, J. K. Yoo, S. J. An, and G. C Yi, "Enhanced secondary electron emission from III-nitride/ZnO coaxial nanorod heterostructures", *Small*, **2**, 736-740 (2006).
- ¹¹⁴ M. Y. Song, Y. R. Ahn, S. M. Jo, D. Y. Kim, and J. P. Ahn, "TiO₂ single-crystalline nanorod electrode for quasi-solid-state dye-sensitized solar cells", *Appl. Phys. Lett.* **87**, 113113 (2005)
- ¹¹⁵ Z. L. Wang, "Zinc oxide nanostructures: grown, properties and applications", *J. Phys.: Condens. Matter* **16**, R829-R858 (2004).
- ¹¹⁶ X. Y. Kong, Y. Ding, R. Yang, and Z. L. Wang "Single-crystal nanorings formed by epitaxial self-coiling of polar nanobelts", *Science* **303**, 1348 – 1351(2004).
- ¹¹⁷ X. Y. Kong and Z. L. Wang, "Polar-surface dominated ZnO nanobelts and the electrostatic energy induced nanohelices/nanosprings", *Appl. Phys. Letts.*, **84**, 975-977 (2004).
- ¹¹⁸ Y. Dai, Y. Zhang, and Z. L. Wang, "Bicrystalline zinc oxide nanowires", *Chem. Phys. Lett.*, **375**, 96-101(2003).
- ¹¹⁹ Y. Jiang, X. M. Meng, J. Liu, Z. R. Hong, C. S. Lee, and S. T. Lee, "ZnS nanowires with wurtzite polytype modulated structure", *Adv. Mater.* **15**, 1195-1198 (2005).

Appendix II: Bibliography

- ¹²⁰ S. R. C. Vivekchand, G. Gundiah, A. Govindaraj, and C. N. R. Rao, "A new method for the preparation of metal nanowires by the nebulized spray pyrolysis of precursors", *Adv. Mater.* **16**, 1842-1845 (2004).
- ¹²¹ E. C. Greyson, Y. Babayan, and T. W. Odom, "Directed grown of ordered arrays of small-diameter ZnO nanowires", *Adv. Mater.* **16**, 1348-1351 (2004).
- ¹²² R. Könenkamp, R. C. Word, and C. Schlegel, "Vertical nanowire light-emitting diode", *Appl. Phys. Lett.* **85**, 6004-6006 (2004).
- ¹²³ L. Vayssieres, "Grown of arrayed nanorods and nanowires of ZnO from aqueous solutions", *Adv. Mater.* **15**, 464-466 (2003).
- ¹²⁴ W. I. Park, D. H. Kim, S. W. Jung, and G. C. Yi, "Metalorganic vapor-phase epitaxial grown of vertically well-aligned ZnO nanorods", *Appl. Phys. Lett.* **80**, 4232-4234 (2002).
- ¹²⁵ M. Haupt, A. Ladenburger, R. Sauer, K. Thonke, R. Glass, W. Roos, J. P. Spatz, H. Rauscher, S. Riethmüller, and M. Möller, "UV-emitting ZnO nanowhiskers prepared by a vapor transport process on prestructured surfaces with self-assembled polymers", *J. Appl. Phys.* **93**, 6252-6257 (2003).
- ¹²⁶ Z. L. Wang, "Functional oxides nanobelts – Materials, properties and potential applications in nanosystems and biotechnology", *Annual Rev. Phys. Chem.* **55**, 159-196 (2004).
- ¹²⁷ Z. L. Wang, "Nanostructure of zinc oxide", *Mater. Today* **7**, 26-33(2004).
- ¹²⁸ J. H. Choy, E. S. Jang, J. H. Won, J. H. Chung, D. J. Jang, and Y. W. Kim, "Soft solution route to directionally grown ZnO nanorod arrays on Si wafer; room-temperature UV laser", *Adv. Mater.* **15**, 1911-1914 (2003).
- ¹²⁹ Y. B. Li, Y. Bando, and D. Golberg, "ZnO nanoneedles with tip surface perturbations: Excellent field emitters", *Appl. Phys. Lett.* **84**, 3603-3605 (2004).

Appendix II: Bibliography

-
- ¹³⁰ Y. N. Xia, P. D. Yang, and Y. G. Sun, "One-dimensional nanostructures: synthesis, characterization, and applications", *Adv. Mater.* **15**, 353-389 (2003).
- ¹³¹ Q. Zhao, X. Y. Xu, X. F. Song, X. Z. Zhang, D. P. Yu, C. P. Li, and L. Guo, "Enhanced field emission from ZnO nanorods via thermal annealing in oxygen", *Appl. Phys. Lett.* **88**, 033102 (2006).
- ¹³² Y. Zhang, K. Yu, D. Jiang, H. Geng, and L. Luo, "Zinc oxide nanorod and nanowire for humidity sensor", *Appl. Surf. Sci.* **242**, 212-217 (2005).
- ¹³³ Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, X. G. Gao, and J. P. Li, "Positive temperature coefficient resistance and humidity sensing properties of Cd-doped ZnO nanowires", *Appl. Phys. Lett.* **84**, 3085-3087 (2004).
- ¹³⁴ Y. W. Heo, D. P. Norton, L. C. Tien, Y. Kwon, B. S. Kang, and F. Ren "ZnO nanowire grown and devices", *Mater. Sci. Eng. R.* **47**, 1-47 (2004).
- ¹³⁵ T. A. Edison, US Patent 484,582 (October 18, 1892).
- ¹³⁶ M. S. P. Lucas, C. R. Vail, W. C. Stewart and H. A. Owens, "Proceedings of the transactions of the eighth AVS national symposium", p. 988. (1962).
- ¹³⁷ B. K. Tay, Z. W. Zhao and D. H. C. Chua, "Review of metal oxide films deposited by filtered cathodic vacuum arc technique", *Mater. Sci. Eng. R: Reports* **52**, 1-48 (2006).
- ¹³⁸ I. I. Aksenov, V. G. Padalka, N. S. Repalov and V. M. Khoroshikh, "Motion of a plasma stream in a curvilinear plasma-optics system", *Sov. J. Plasma Phys.* **6**, 173-176 (1980).
- ¹³⁹ X. Shi, B. K. Tay, and S. P. Lau, "The double bend filtered cathodic arc technology and its applications", *International J. Modern Phys. B* **14**, 136-153 (2000).

Appendix II: Bibliography

- ¹⁴⁰ 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, "Comprehensive study of ZnO films prepared by filtered cathodic vacuum arc at room temperature", *J. Appl. Phys.* **94**, 1597-1604 (2003).
- ¹⁴¹ S. Bethke, H. Pan and B.W. Wessels, "Luminescence of heteroepitaxial zinc oxide", *Appl. Phys. Lett.* **52**, 138-140 (1988).
- ¹⁴² A. B. M. Almamun Ashrafi, A. Ueta, A. Avramescu, H. Kumano, I. Suemune, Y. W. Ok and T. Y. Seong, "Growth and characterization of hypothetical zinc-blende ZnO films on GaAs(001) substrates with ZnS buffer layers", *Appl. Phys. Lett.* **76**, 550-552 (2000).
- ¹⁴³ Bethke, H. Pan, and B. W. Wesseis, "Luminescence of heteroepitaxial zinc oxide", *Appl. Phys. Lett.* **52**, 138-140 (1988).
- ¹⁴⁴ T. Makino, Y. Segawa, S. Yoshida, A. Tsukazaki, A. Ohtomo and M. Kawasaki, "Gallium concentration dependence of room-temperature near-band-edge luminescence in n-type ZnO:Ga", *Appl. Phys. Lett.* **85**, 759-761. (2004)
- ¹⁴⁵ G. Savigny, J. R. Currie, D. Ila, R. L. Zimmerman, C. I. Muntele, R. Mu and A. Ueda, "Ion beam induced modification of nanolayers containing vanadium and silica", *Surface and Coatings Tech.* **196**, 113-117 (2005).
- ¹⁴⁶ Auciello and R. Kelly, "Ion bombardment modification of surfaces", Elsevier, Tokyo (1984).
- ¹⁴⁷ W. Czanderna, T. E. Madey and C. J. Powell, "Beam effects, surface topography, and depth Profiling in surface analysis", Plenum Press, Chapter 3 (1998).
- ¹⁴⁸ J. Ghatak, B. Satpati, M. Umananda, D. Kabiraj, T. Som, B. N. Dev, K. Akimoto, K. Ito, T. Emoto and P. V. Satyam, "Characterization of ion beam induced nanostructures", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **244**, 45-51(2006).

Appendix II: Bibliography

- ¹⁴⁹ M. Tanemura, T. Okita, J. Tanaka, M. Kitazawa, K. Itoh, L. Miao, S. Tanemura, S. P. Lau, H. Y. Yang, and Lei Huang, "Room-temperature grown and applications of carbon nanofibers: A review", *IEEE Trans. on Nanotech*, **5**, 587-594 (2006).
- ¹⁵⁰ P. Thompson, D. E. Cox, J. B. Hastings, "Riveted refinement of debye-Scherrer synchrotron X-ray data from Al_2O_3 ", *J. Appl. Crystallography* **20**, 79-83 Part 2 (1987).
- ¹⁵¹ L. Jing, Y. Qu, B. Wang, S. Li, B. Jiang, L. Yang, W. Fu, H. Fu, and J. Sun, "Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity", *Solar Energy Mater. and Solar Cells* **90**, 1773-1787 (2006).
- ¹⁵² E. Poles, D. Huppert and Y. Rosenwaks, "A study of super-bandgap time-resolved luminescence in InP", *Semicond. Sci. Technol.* **12**, 1252-1256 (1997).
- ¹⁵³ R. C. Polson, G. Levina, and Z. V. Vardeny, "Spectral analysis of polymer microring lasers", *Appl. Phys. Lett.* **76**, 3858-3860 (2000).
- ¹⁵⁴ R. C. Polson, A. Chipouline, and Z. V. Vardeny, "Random Lasing in π -Conjugated Films and Infiltrated Opals", *Adv. Mater.* **13**, 760-764 (2001).
- ¹⁵⁵ D. Hofstetter and R. L. Thornton, "Loss measurements on semiconductor lasers by Fourier analysis of the emission spectra", *Appl. Phys. Lett.* **72**, 404-406 (1998).
- ¹⁵⁶ K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, "Correlation between photoluminescence and oxygen vacancies in ZnO phosphors", *Appl. Phys. Lett.* **68**, 403-405 (1996).
- ¹⁵⁷ B. Lin, Z. Fu, and Y. Jia, "Green luminescent center in undoped zinc oxide films deposited on silicon substrates", *Appl. Phys. Lett.* **79**, 943-945 (2001).

Appendix II: Bibliography

- ¹⁵⁸ X. L. Wu, G. G. Siu, C. L. Fu, and H. C. Ong, "Photoluminescence and cathodoluminescence studies of stoichiometric and oxygen-deficient ZnO films", *Appl. Phys. Lett.* **78**, 2285-2287 (2001).
- ¹⁵⁹ S. A. Studenikin, N. Golego, and M. Cocivera, "Density of band-gap traps in polycrystalline films from photoconductivity transients using an improved Laplace transform method", *J. Appl. Phys.* **84**, 5001-5004 (1998).
- ¹⁶⁰ Z. Q. Chen, S. Yamamoto, M. Maekawa, A. Kawasuso, X. L. Yuan and T. Sekiguchi, "Postgrowth annealing of defects in ZnO studied by positron annihilation, x-ray diffraction, Rutherford backscattering, cathodoluminescence, and Hall measurements", *J. Appl. Phys.* **94**, 4807-4811 (2003).
- ¹⁶¹ U. Koch, A. Fojtik, H. Weller, and A. Henglein, "Photochemistry of semiconductor colloids. Preparation of extremely small ZnO particles, fluorescence phenomena and size quantization effects", *Chem. Phys. Lett.* **122**, 507-510 (1985).
- ¹⁶² S. Mahamuni, K. Borgohain, B. S. Bendre, V. J. Leppert and S. H. Risbud, "Spectroscopic and structural characterization of electrochemically grown ZnO quantum dots", *J. Appl. Phys.* **85**, 2861-2865 (1999).
- ¹⁶³ B. D. Yao, H. Z. Shi, H. J. Bi, and L. D. Zhang, "Optical properties of ZnO loaded in mesoporous silica", *J. Phys.: Condens. Matter* **12**, 6265-6270 (2000).
- ¹⁶⁴ C. M. Mo, Y. H. Li, Y. S. Liu, Y. Zhang, and L. D. Zhang, "Enhancement effect of photoluminescence in assemblies of nano-ZnO particles/silica aerogels", *J. Appl. Phys.* **83**, 4389-4391 (1998).
- ¹⁶⁵ M. Ikrajuddin, F. Iskandar, K. Okuyama, and F. G. Shi, "Stable photoluminescence of zinc oxide quantum dots in silica nanoparticles matrix prepared by the combined sol-gel and spray drying method", *J. Appl. Phys.* **89**, 6431-6434 (2001).

Appendix II: Bibliography

-
- ¹⁶⁶ H. D. Li, S. F. Yu, A. P. Abiyasa, C. Yuen, S. P. Lau, H. Y. Yang, and E. S. P. Leong, "Strain dependence of lasing mechanisms in ZnO epilayers", *Appl. Phys. Lett.* **86**, 261111 (2005).
- ¹⁶⁷ X. D. Wang, C. J. Summers, and Z. L. Wang, "Mesoporous single-crystal ZnO nanowires epitaxially sheathed with ZnSiO₄", *Adv. Mater.* **16**, 1215-1218 (2004).
- ¹⁶⁸ V. A. Fonoberov and A. A. Balandin, "Origin of ultraviolet photoluminescence in ZnO quantum dots: Confined excitons versus surface-bound impurity exciton complexes", *Appl. Phys. Lett.* **85**, 5971-5973 (2004).
- ¹⁶⁹ L. E. Brus, "Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state", *J. Chem. Phys.* **80**, 4403 (1984).
- ¹⁷⁰ R. E. Dietz, J. J. Hopfield, and D. G. Thomas, "Excitons and the absorption edge of ZnO", *J. Appl. Phys.* **32**, 2282 (1961).
- ¹⁷¹ X. T. Zhang, Y. C. Liu, L. G. Zhang, J. Y. Zhang, Y. M. Lu, D. Z. Shen, W. Xu, G. Z. Zhong, X. W. Fan, and X. G. Kong, "Structure and optically pumped lasing from nanocrystalline ZnO thin films prepared by thermal oxidation of ZnS thin films", *J. Appl. Phys.* **92**, 3293-3298 (2002).
- ¹⁷² Y. Chen, D. M. Bagnall, H. J. Koh, K. T. Park, K. Hiraga, Z. Zhu, and T. Yao, "Plasma assisted molecular beam epitaxy of ZnO on *c*-plane sapphire: growth and characterization", *J. Appl. Phys.* **84**, 3912-3198 (1998).
- ¹⁷³ H. J. Lozykowski and V. K. Shastri, "Excitonic and Raman properties of ZnSe/Zn_{1-x}Cd_xSe strained-layer quantum wells", *J. Appl. Phys.* **69**, 3235-3237 (1991).
- ¹⁷⁴ X. Xu, P. Wang, Z. Qi, H. Ming, J. Xu, H. Liu, C. Shi, G. Lu and W. Ge, "Formation mechanism of ZnSiO₄ crystal and amorphous SiO₂ in ZnO/Si system", *J.*

Appendix II: Bibliography

-
- Phys. Condens. Matter **15**, L607-L613 (2003).
- ¹⁷⁵ K. K. Kim, N. Koguchi, Y. W. Ok, T. Y. Seong, S. J. Park, "Fabrication of ZnO quantum dots embedded in an amorphous oxide layer", Appl. Phys. Lett. **84**, 3810-3812 (2004).
- ¹⁷⁶ Q. H. Song, L. Wang, S. M. Xiao, X. C. Zhou, L. Y. Liu, and L. Xu, "Random laser emission from a surface-corrugated waveguide", Phys. Rev. B **72**, 035424 (2005).
- ¹⁷⁷ D. C. Reynolds, D. C. Look, B. Jogai, J. E. Hoelscher, R. E. Sherriff, M. T. Harris, and M. J. Callahan, "Time-resolved photoluminescence lifetime measurements of the Γ_5 and Γ_6 free excitons in ZnO", J. Appl. Phys. **88**, 2152-2153 (2000).
- ¹⁷⁸ T. Itoh, M. Furumiya, T. Ikehara, and C. Gourdon, "Size-dependent radiative decay time of confined excitons in CuCl microcrystals", Solid State Commun. **73**, 271-274 (1990).
- ¹⁷⁹ K. Misawa, H. Yao, T. Hayashi, and T. Kobayashi, "Superradiance quenching by confined acoustic phonons in chemically prepared CdS microcrystallites", J. Chem. Phys. **94**, 4131-4140 (1991).
- ¹⁸⁰ T. Sekitani, Y. Kato, S. Iba, H. Shinaoka, T. Someya, T. Sakurai, and S. Takagi, "Bending experiment on pentacene field-effect transistors on plastic films", Appl. Phys. Lett. **86**, 073511 (2005).
- ¹⁸¹ D. Wiersma, "Laser physics - The smallest random laser", Nature **406**, 132-135 (2000).
- ¹⁸² A. Murali, A. Barve, V. J. Leppert, S. H. Risbud, I. M. Kennedy, and H. W. H. Lee, "Synthesis and characterization of indium oxide nanoparticles", Nano Lett. **1**, 287-290 (2001).
- ¹⁸³ A. W. Snyder and J. D. Love, "Optical waveguide theory", 1st ed., Chapman and Hall, Part II, section **22** (1983).

Appendix II: Bibliography

-
- ¹⁸⁴ Y. C. Kong, D. P. Yu, B. Zhang, W. Fang, and S. Q. Feng, "Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach", *Appl. Phys. Lett.* **83**, 4288-4290 (2003).
- ¹⁸⁵ S. H. Jo, J. Y. Lao, Z. F. Ren, R. A. Farrer, T. Baldacchini, and J. T. Fourkas, "Field-emission studies on thin films of zinc oxide nanowires", *Appl. Phys. Lett.* **83**, 4821-4823 (2003).
- ¹⁸⁶ W. I. Park, C. G. Yi, M. Kim, and S. Pennycook, "ZnO nanoneedles grown vertically on Si substrates by non-catalytic vapor-phase epitaxy", *Adv. Mater.* **14**, 1841-1844 (2002).
- ¹⁸⁷ K. Govender, D. S. Boyle, P. O. Brien, D. Binks, D. West, and D. Coleman, "Room-temperature lasing observed from ZnO nanocolumns grown by aqueous solution deposition", *Adv. Mater.* **14**, 1221-1224 (2002).
- ¹⁸⁸ J. B. Cui, C. P. Daghlain, U. J. Gibson, R. Pusche, P. Geithener, and L. Ley, "Low-temperature grown and field emission of ZnO nanowire arrays", *J. Appl. Phys.* **97**, 044315 (2005).
- ¹⁸⁹ M. Tanemura, T. Okita, H. Yamauchi, S. Tanemura, and R. Morishima, "Room-temperature grown of a carbon nanofiber on the tip of conical carbon protrusions", *Appl. Phys. Lett.* **84**, 3831-3833 (2004).
- ¹⁹⁰ Y. Kayamura, "Quantum-size effects of interacting electrons and holes in semiconductor microcrystals with spherical shape", *Phys. Rev. B*, **38**, 9797-9805 (1998).
- ¹⁹¹ S. J. Chen, Y. C. Liu, C. L. Shao, R. Mu, Y. M. Lu, J. Y. Zhang, D. Z. Shen, X. W. Fan, "Structural and optical properties of uniform ZnO nanosheets", *Adv. Mater.* **17**, 586-589 (2005).

Appendix II: Bibliography

-
- ¹⁹² H. Gleskova, S. Wagner, and Z. Suo, "Failure resistance of amorphous silicon transistors under extreme in-plane strain", *Appl. Phys. Lett.* **75**, 3011 (1999).
- ¹⁹³ S. Bidnyk, T. J. Schmidt, Y. H. Cho, G. H. Gainer, J. J. Song, S. Keller, U. K. Mishra, and S. P. DenBaars, "High-temperature stimulated emission in optically pumped InGaN/GaN multiquantum wells", *Appl. Phys. Lett.* **72**, 1623-1625 (2000).
- ¹⁹⁴ A. Ohtomo, K. Tamura, M. Kawasaki, T. Makino, Y. Segawa, Z. K. Tang, G. K. L. Wong, Y. Matsumoto, and H. Koinuma, "Room-temperature stimulated emission of excitons in ZnO/(Mg, Zn)O superlattices" *Appl. Phys. Lett.* **77**, 2204-2206 (2000).
- ¹⁹⁵ 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).
- ¹⁹⁶ B. M. A. Ashrafi and Y. Segawa, "Determination of Mg composition in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy: Validity of Vegard's law", *J. Vac. Sci. Technol. B*, **23**, 2030-2033 (2005).
- ¹⁹⁷ W. I. Park, Gyu-Chul Yi, and H. M. Jang, "Metalorganic vapor-phase epitaxial grown and photoluminescent properties of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($0 \leq x \leq 0.49$) thin films", *Appl. Phys. Lett.* **79**, 2022-2044 (2001).
- ¹⁹⁸ K. Sakurai, T. Kubo, D. Kajita, T. Tanabe, H. Takasu, S. Fujita, S. Fujita, "Blue photoluminescence from ZnCdO films grown by molecular beam epitaxy", *Jpn. J. Appl. Phys. Part 2* **39**, L1146-L1148 (2000).
- ¹⁹⁹ Y. Jin, B. Zhang, S. Yang, Y. Wang, J. Chen, H. Zhang, C. Huang, C. Cao, H. Cao, and R. P. H. Chang, "Room temperature UV emission of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films", *Solid state Commun.* **119**, 409-413(2001).

Appendix II: Bibliography

- ²⁰⁰ H. D. Sun, T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, "Biexciton emission from ZnO/Zn_{0.74}Mg_{0.26}O multiquantum wells", *Appl. Phys. Lett.* **78**, 3385-3387 (2001).
- ²⁰¹ W. J. Fan, J. B. Xia, P. A. Agus, S. T. Tan, S. F. Yu, X. W. Sun, "Band parameters and electronic structures of wurtzite ZnO and ZnO/MgZnO quantum wells", *J. Appl. Phys.* **99**, 013702 (2006).
- ²⁰² M. Lorenz, E. M. Kaidashev, A. Rahm, Th. Nobis, J. Lenzner, G. Wagner, D. Spemann, H. Hochmuth, and M. Grundmann, "Mg_xZn_{1-x}O (0 ≤ x ≤ 0.2) nanowire arrays on sapphire grown by high-pressure pulsed-laser deposition", *Appl. Phys. Lett.* **86**, 143113 (2005).
- ²⁰³ R. Kling, C. Kirchner, T. Gruber, F. Reuss and A. Waag, "Analysis of ZnO and ZnMgO nanopillars grown by self-organization", *Nanotechnology* **15**, 1043-1046 (2004).
- ²⁰⁴ H. D. Sun, T. Makino, N. T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, "Temperature dependence of excitonic absorption spectra in ZnO/Zn_{0.88}Mg_{0.12}O multiquantum wells grown on lattice-matched substrates", *Appl. Phys. Lett.* **78**, 2464-2466 (2001).
- ²⁰⁵ H. Y. Yang, S. P. Lau, S. F. Yu, A. P. Abiyasa, M. Tanemura, T. Okita, and H. Hatano, "High-temperature ZnO nanoneedle random lasers", *Appl. Phys. Lett.*, **89**, 011103 (2006).
- ²⁰⁶ H. D. Li, S. F. Yu, S. P. Lau, E. S. P. Leong, H. Y. Yang, and A. P. Abiyasa, "High-temperature excitonic lasing in annealed ZnO epilayers", *Adv. Mater.* **18**, 771-774 (2006).

Appendix II: Bibliography

- ²⁰⁷ C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh, H. J. Lee, "Field emission from well-aligned zinc oxide nanowires grown at low temperature", *Appl. Phys. Lett.* **81**, 3648-3650 (2002).
- ²⁰⁸ C. X. Xu and X. W. Sun, "Field emission from zinc oxide nanopins", *Appl. Phys. Lett.* **83**, 3806-3808 (2003).
- ²⁰⁹ K. Yu, Y. S. Zhang, R. L. Xu, S. X. Ouyang, D. M. Li, L. Q. Luo, Z. Q. Zhu, J. Ma, S. J. Xie, S. H. Han, and H. R. Geng, "Efficient field emission from tetrapod-like zinc oxide nanoneedles", *Mater. Lett.* **59**, 1866-1870 (2005).
- ²¹⁰ S. H. Jo, D. Banerjee, Z. F. Ren, "Field emission of zinc oxide nanowires grown on carbon cloth", *Appl. Phys. Lett.* **85**, 1407-1409 (2004).
- ²¹¹ A. Wei, X. W. Sun, C. X. Xu, Z. L. Dong, M. B. Yu, and W. Huang, "Stable field emission from hydrothermally grown ZnO nanotubes", *Appl. Phys. Lett.* **88**, 213102 (2006).
- ²¹² Y. H. Yang, C. X. Wang, B. Wang, N. S. Xu, and G. W. Yang, "ZnO nanowire and amorphous diamond nanocomposites and field emission enhancement", *Chem. Phys. Lett.* **403**, 248-251 (2005).
- ²¹³ R. Maity, A. N. Banerjee, and K. K. Chattopadhyay, "Low-macroscopic field emission from fibrous ZnO thin film prepared by catalyst-free solution route", *Appl. Surf. Sci.* **236**, 231-235 (2004).
- ²¹⁴ Y. W. Zhu, H. Z. Zhang, X. C. Sun, S. Q. Feng, J. Xu, Q. Zhao, B. Xiang, R. M. Wang, and D. P. Yu, "Efficient field emission from ZnO nanoneedle arrays", *Appl. Phys. Lett.* **83** 144-146 (2003).

Appendix II: Bibliography

- ²¹⁵ L. Liao, J. C. Li, D. H. Liu, C. Liu, D. F. Wang, W. Z. Song, and Q. Fu, "Self-assembly of aligned ZnO nanoscrews: Growth, configuration, and field emission", *Appl. Phys. Lett.* **86**, 083106 (2005).
- ²¹⁶ S. Y. Li, P. Lin, C. Y. Lee, and T. Y. Tseng, "Field emission and photofluorescent characteristics of zinc oxide nanowires synthesized by a metal catalyzed vapor-liquid-solid process", *J. Appl. Phys.* **95**, 3711-3716 (2004).
- ²¹⁷ G. Shen, Y. Bando, B. Liu, D. Golberg, C.J. Lee, "Characterization and field-emission properties of vertically aligned ZnO nanonails and nanopencils fabricated by a modified thermal-evaporation process ", *Adv. Mater.* **16**, 410-416 (2005).
- ²¹⁸ S. Senda, Y. Sakai, Y. Mizuta, S. Kita, and F.Okuyama, "Super miniature x-ray tube", *Appl. Phys. Lett.* **85**, 5679-5681 (2004).
- ²¹⁹ C. M. Tang, and R. D. Deslattes, "Miniature x-ray source", *Secretary of Commerce* **5**, 729 (1998).
- ²²⁰ A. Haga, S. Senda, Y. Sakai, Y. Mizuta, S. Kita, and F. Okuyama, "A miniature x-ray tube", *Appl. Phys. Lett.* **84**, 2208-2210 (2004).
- ²²¹ R. C. Wang, C. P. Liu, J. L. Huang, S.-J. Chen, Y.-K. Tseng, and S.-C. Kung, "ZnO nanopencils: Efficient field emitters", *Appl. Phys. Lett.* **87**, 013110 (2005).
- ²²² M. Yoshimatsu and S. Kozaki, "High Brilliance X-Ray Sources", *X-ray Optics*, Springer (1977).
- ²²³ H. Sugie, M. Tanemura, V. Filip, K. Iwata, K. Takahashi, and F. Okuyama, "Carbon nanotubes as electron source in an x-ray tube", *Appl. Phys. Lett.* **78**, 2578-2580 (2001).
- ²²⁴ O. Zhou and J. P. Lu, U.S. Patent No. 6,553,096 (April 22, 2003).

Appendix II: Bibliography

-
- ²²⁵ Y. B. Zhang, S. P. Lau, L. Huang, and M. Tanemura, "Carbon nanotubes synthesized by biased thermal chemical vapor deposition as an electron source in an x-ray tube", *Appl. Phys. Lett.* **86**, 1231151 (2005).
- ²²⁶ T. T. Tan, H. S. Sim, S. P. Lau, H. Y. Yang, M. Tanemura, and J. Tanaka, "X-ray generation using flexible field emitters", *Appl. Phys. Lett.* **86**, 073511 (2006).
- ²²⁷ T. Matsumoto, and H. Mimura, "Point x-ray source using graphite nanofibers and its application to x-ray radiography", *Appl. Phys. Lett.* **82**, 1637–1639 (2003).
- ²²⁸ Y. K. Tseng, C. J. Huang, H. M. Cheng, I. N. Lin, K. S. Liu and I. C. Chen, "Characterization and field-emission properties of needle-like zinc oxide nanowires grown vertically on conductive zinc oxide films", *Adv. Funct. Mater.* **13**, 811-824 (2003).
- ²²⁹ S. Hofmann, C. Ducati, B. Kleinsorge and J. Robertson, "Direct grown of aligned carbon nanotube field emitter arrays onto plastic substrates", *Appl. Phys. Lett.* **83**, 4661-4663 (2003).