Nanocrystal semiconductor lasers

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Nanocrystal Semiconductor Lasers

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Summary

Summary

Zinc Oxide (ZnO), which has a wide bandgap (~ 3.37 eV) and high exciton binding energy (~ 60 meV), is promising for the development of room-temperature ultra-violet (UV) optoelectronic devices. Currently, the reported ways to obtain laser cavities using ZnO material include: (i) cleaving ZnO films to form Fabry-Perot (FP) structures, (ii) forming microcavities, and (iii) using disordered ZnO films or nano-composite films to exhibit random lasing action. However, the reported ZnO FP structure shows a much higher lasing threshold ($\sim 10\times$) as compared to the ZnO microcavities. This implies that the cleaved facets formed may not be very smooth and introduces large cavity loss. Therefore this may pose a problem when building an electrically-pumped ZnO lasing device. On the other hand, it is not easy to form microcavities that can allow efficient injection of carriers and confinement of light to achieve high enough optical gain.

The realization of ZnO random cavities may be an alternative approach to fabricate low-cost ZnO laser diodes as there is no stringent requirement in the design of the disordered media provided that they can sustain enough optical gain and feedback within the media to achieve random lasing. Nevertheless, ZnO random lasers suffer from some drawbacks such as multimodes operation (i.e., uncontrollable lasing behavior), high threshold and lack of directionality.

In this thesis, two types of optically pumped ZnO UV random lasers: i) nano-composite random lasers containing metal-oxide nano-powders and ii) ZnO disordered film based waveguide lasers were designed, fabricated and tested to tackle the problems of in-directionality and multimodes operation. Furthermore, electrically pumped ZnO UV light emitting devices using these disordered media were also demonstrated.

Summary

Coherent random lasing has been successfully achieved in these structures with directional, polarized output emission and low optical pump threshold. For random lasers containing metal-oxide nanopowders, the key reason lies in the presence of stripes of ZnO nano-powder clusters in nano-composite films to guide the light for reflection between the stripes. This provides lateral confinement of light as well as improved optical gain (i.e., efficient injection of carriers) under electrical injection. These stripes eventually form an important basis as high-quality random media for achieving the ‘world first’ electrically pumped UV random laser operating at low voltage. ZnO master oscillator power amplifier (MOPA) and rib waveguide thin-film random lasers have also been designed to tackle the problem of multimode operation. Reduced number of lasing modes with low pump threshold and directional output emissions have been demonstrated from these random lasers. On the other hand, the use of ZnO disordered films in the fabrication of light emitting devices shows an improvement in the light extraction from the surface of the diodes. Hence, it is verified that it is possible to realize directional UV laser diodes using ZnO random cavities.

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1. Introduction

1.1 Background and Motivation

Semiconductor lasers are widely used in optical communications, optical data storage (i.e., CDs and DVDs players), displays, and bio-sensing applications due to their compactness in size, small power consumption, long lifetime, large volume production and low manufacturing cost.^{1,2} In particular, the global market for short wavelength (<450 nm) semiconductor lasers has been estimated to grow from US\$9 million in 2003 to US\$207 million in 2009, due to the demand in data storage market.³ It is predicted that short wavelength semiconductor lasers will be the essential technology for the development of next generation high-compact optical data storage systems. Furthermore, researchers have foreseen potential applications of ultraviolet (UV) light-emitting devices in the field of communications, defense, water and air purification and chemical processing.⁴ Therefore, they are actively exploring ways to achieve high efficiency UV light emitting devices (i.e., light emitting diodes and lasers).

1.1.1 Choice of UV Material

The design of UV (<390 nm) lasers involves the use of wide bandgap semiconductor materials. The common materials used for UV emission include III-V semiconductors such as GaN and its alloys,^{1,2} and II-VI semiconductors such as ZnO. In fact, GaN is the most widely used material for the fabrication of commercial blue laser diodes. This is because of the realization of *p*-GaN film by activation of Mg acceptors using electron radiation⁵ and thermal annealing⁶ techniques. In addition, two methods have been proposed for mass production of GaN based blue lasers. They are (i) epitaxial lateral overgrowth (ELOG) method

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which involves the deposition of GaN template film followed by SiO₂ mask layer and (ii) hetero-epitaxial lateral overgrowth (HELO) method which refers to the deposition of GaN films directly on substrates such as sapphire, SiC or GaAs. These two methods allow the fabrication of 2-inch GaN based substrates with low dislocation density of 10^6 - 10^7 cm⁻², which is important to minimize non-radiative recombination for high efficiency emission.⁷

The current common techniques to grow *p*- and *n*- GaN films include metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE).⁸ MOCVD technique involves the reaction of trimethyl gallium, which is toxic, air and moisture sensitive, with ammonia, which is also toxic. This requires special handling of the chemicals and proper safety monitoring procedures for ammonia gas, which will add on to the fabrication cost. Moreover, sophisticated design is needed for high temperature (1000 °C) deposition. As for MBE, though lower temperature growth is possible, the technique requires a high-energy plasma source to create nitrogen radical for reaction with gallium. However, this will result in high N ion energy and hinder the reaction process and form defective films. More expensive equipment such as electron cyclotron resonance is then used with MBE to solve the problem.⁸ Moreover, GaN is inert to most chemicals. Therefore, it may be difficult to form waveguides for better confinement of light. Hence, the use of GaN to fabricate semiconductor lasers is not cheap and easy as compared to the fabrication of long-wavelength lasers.

On the other hand, ZnO is also a wide bandgap material of $E_g \sim 3.37$ eV (at room temperature (R.T.)), which is quite similar to that of GaN ($E_g \sim 3.4$ eV). Fairly high quality bulk ZnO single crystals are available and this eliminates the need of expensive substrates such as sapphire or SiC as in the case of GaN film

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growth. Good quality ZnO films can be fabricated at low temperature ($<700\text{ }^{\circ}\text{C}$) and they possess high-energy radiation resistance. This makes the crystal growth much simpler and cheaper than GaN. Moreover, it can be used as a substrate in the epitaxial growth of GaN films.⁹

An important unique property for ZnO is its high binding energy of 60 meV, which implies that excitons are thermally stable for temperature as high as $400\text{ }^{\circ}\text{C}$. This value is twice as large as that of GaN and implies that excitonic recombination process can be sustained and experimental studies on the excitonic mechanism can be carried out. A recent theoretical study on ZnO has also shown that the excitonic gain of ZnO based quantum wells is expected to be at least ten times greater than that of GaN based quantum wells.¹⁰ In addition, the external quantum efficiency of UV ZnO detectors is $\sim 90\%$, which is 3 times higher than that of GaN detectors. Such high efficiency values may also be applicable for the conversion of electrons to photons.¹¹ Thus it is believed that more highly efficient UV light emitting devices can be obtained from ZnO. A comparison on some of the properties between ZnO and GaN is given in table 1.1.¹²

While ZnO has many advantages over GaN, a major obstacle hindering the progress of ZnO lasers is the realization of *p*-type ZnO material. This is important

Table 1.1: Comparison between GaN and ZnO

	GaN	ZnO
Structure	Wurtzite	Wurtzite
Bandgap (eV)	3.4 (R.T.)	3.37 (R.T.)
Binding energy (meV)	28	60
Lattice constant ($\text{\AA}$)	$a=3.186$ $c=5.178$	$a=3.249$ $c=5.206$
Refractive index (n)	$\sim 2.4\text{--}2.5$ ^{ref:13,14}	~ 2.1
Thermal expansion coefficient ($/^{\circ}\text{K}$)	$a=5.59\times 10^{-6}$ $c=7.75\times 10^{-6}$	$a=6.51\times 10^{-6}$ $c=3.02\times 10^{-6}$

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Table 1.2: Comparison of hole concentrations of the p-type materials used for wide bandgap pn junction diodes

	$p\text{-ZnO:N}^{15}$	$p\text{-SiC (4H)}^*$	$p\text{-SiC (6H)}^*$	$p\text{-GaN:Mg}^{**}$
Bandgap (eV)	3.37	3.26	3.03	3.4
Concentration (cm^{-3})	2×10^{16}	$10^{18} - 10^{19}$	$10^{18} - 10^{19}$	$10^{17} - 10^{18}$

*Cree, Inc

** Technologies and Devices International, Inc

as most of the ZnO films fabricated are *n*-type. If reproducible good quality *p*-type ZnO material can be fabricated, homojunction LEDs and laser diodes can be realized with low defect levels (i.e., lattice matched). To date, reproducible *p*-type ZnO has been achieved by a Japanese research group led by M. Kawasaki.¹⁵ The hole concentration obtained is $2 \times 10^{16} \text{ cm}^{-3}$, which is still lower than the commercial *p*-GaN/sapphire and *p*-SiC substrates, (a comparison on the hole concentration is listed in table 1.2) which are normally used for the fabrication of wide bandgap pn junction diodes. Thus much work still needs to be done to improve the hole concentration. Nevertheless, this implies that it is possible to replace the commercially available GaN based blue LEDs with cheaper ZnO based blue or UV LEDs.

1.1.2 Development of ZnO Lasers

Early work on ZnO lasers was pumped by electron beam and lasing was observed at cryogenic temperature.¹⁶ However for more practical applications, R.T. (room temperature) emission is preferred and much progress has been done to improve the quality of ZnO film. In 1997, R.T. optically pumped ZnO laser was first demonstrated.^{17, 18} Subsequently, high temperature excitonic stimulated

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emission and lasing were also observed from ZnO thin films.^{19,20} These works imply that the unique property of having a large binding energy in ZnO allows lasing to sustain even at temperature as high as 550 K. Thus these show that ZnO material is indeed suitable for LEDs and laser diode operation. In the next few paragraphs, a short review on the ZnO lasers will be described to illustrate the development of various forms of ZnO lasers (i.e., film, powder, nanostructures) using different lasing mechanisms.

The first R.T. optically pumped ZnO laser was designed based on the traditional Fabry-Perot (FP) cavity theory.¹⁷ The ZnO film on sapphire substrate was first grown by microwave plasma enhanced (PE) MBE technique and then cleaved into bars of length 5 mm and cavity length in the range of 300-1000 μm to form smooth facets for cavity. The pump source is a pulsed-operated Nd:YAG laser (355 nm, 10 Hz, 6 ns) and is collimated to an excitation stripe of $\sim 50 \mu\text{m}$. A pump threshold of $\sim 240 \text{ kW/cm}^2$ is reported. Nevertheless, ZnO has a wurtzite structure and cleaving to form smooth facets is not an easy task.²¹

With the advent of nanotechnology, nanocrystals (i.e., particles of size in the nanometer range) can also be employed in ZnO devices to improve the lasing efficiency. In the past, the incorporation of nanocrystals (i.e., in size range of $\sim 100 \text{ nm}$) into devices such as photovoltaic solar cells and transistors, have all shown significant improvement in the working performance of the devices (i.e., higher open circuit voltage, higher fill factor, higher conversion efficiency and faster performance).^{22 - 25} In the field of semiconductor lasers, nanocrystals can be employed either as the gain medium or scatterers to improve the efficiency. In fact, most of the current ZnO lasers are also based on nanocrystals design.

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In one reported nanocrystals laser design, researchers tried to form hexagonally shaped ZnO nanocrystals in high-quality ZnO thin films grown on sapphire substrate using laser MBE.^{18,26,27} The size of the nanocrystals can be tuned from 50 to 200 nm. It was proposed that the excitons were confined in the nanocrystals and under optical pump excitation, the boundary of the pumped region, which consists of several nanocrystals, may act as distributed mirrors to confine the photons in the cavity.^{26,27} A low threshold of 24 kW/cm² was obtained for 50 nm size nanocrystal. The threshold is in fact much lower than that of the ZnO FP laser structure. This implies that nanocrystals are indeed better alternatives to conventional laser cavity designs to obtain low pump threshold, and smooth facets are still difficult to achieve in wurtzite ZnO films.

Nanocrystals of size comparable to the emission wavelength can also be used as microcavities to confine light in small dimensions to form microcavity lasers. One example is the demonstration of optically pumped ZnO based microdisk laser on silicon substrate.²⁸ This was done by first fabricating SiO₂ microdisks (of size ~2 – 20 μ m) and on top of which, a thin layer of ~55 nm thick ZnO film was deposited. The size of the ZnO nanocrystals was found to be ~30 nm. Whispering gallery modes are observed due to the microdisk structure that confines the light via total internal reflection.²⁸ In another example, ZnO nanowires, which have well-facetted ends to act as natural resonance cavities, have been reported to emit single-mode emission.²⁹

Although periodic structures are highly desired in some applications such as achieving single-mode emission in distributed feedback (DFB) lasers and photonic crystal lasers, random microcavities may find useful applications in the realization of low-cost semiconductor lasers. In addition, it has been investigated

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recently that disordered materials may result in more efficient operation of nonlinear optical devices as compared to perfectly regular cavities.³⁰ Therefore, nanocrystals may also act as randomly distributed reflectors (i.e., random media) in cavities to improve the lasing efficiency of lasers.³¹ For example, instead of using hexagonal grains in ZnO films to sustain lasing, lasing from ZnO films are still possible if the ZnO film contains disordered grains. Cao *et al*³² first demonstrated that a disordered ZnO film facilitates the scattering of light in the film such that random cavities are formed. If optical gain exceeds the cavity loss of these random cavities, longitudinal modes will emerge from the emission spectrum. This kind of lasing mechanism has been coined as ‘random laser’. This method is inexpensive and is substrate independent.³³⁻³⁷ The size of the grains may vary from ~ 20 nm³⁴ to 150 nm.³² Other than as-deposited disordered ZnO films, random lasing has also been found in oxidized Zn films³⁵ and annealed ZnO films.³⁸ ZnO micro random laser³⁹ of size ~ 1.7 μm has also demonstrated narrow lasing linewidth of 0.22 nm. The optical confinement is believed to be due to disorder-induced scattering and interference of light.

Optically pumped lasing from ZnO powder has also been reported.^{34,40,41} The powder may be electrophoresis deposited to a thick film of 6-15 μm ⁴⁰ or compressed to a pellet with grains ranging from 20-180 nm.⁴¹ In these cases, the lasing mechanism is attributed to the formation of random ring cavities in the ZnO powder. More recently, random lasing action is also observed in ZnO nanostructures such as nanorods,⁴² nanowires⁴³ and nanoneedles.³⁷

From above, we summarize that optical cavities can be formed through (i) smooth cleaved facets, (ii) microcavities and (iii) disordered media. Although lasing can be obtained via optical pumping, ZnO based optical devices will be

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more useful if they can be pumped electrically. This is why much research concentrates on obtaining electroluminescence (EL) from ZnO so that highly efficient ZnO LEDs and LDs will be devised in the future. EL has been realized from ZnO films, nanoparticles,⁴⁴ nanorods,^{45,46} and nanowires.⁴⁷⁻⁴⁹ Reports on the various ZnO based light-emitting homojunction and heterojunction diodes operating at room temperature are summarized in table 1.3 below. Nevertheless, electrically pumped ZnO lasers have yet been demonstrated. This is because the fabrication of the laser cavities are constrained by the material properties and high gain under low voltage operation is difficult to achieve. As such, if ZnO laser diodes can be realized, it will certainly increase the market value for ZnO and make it on par with GaN laser diodes.

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Table 1.3: Literature review on ZnO film based light emitting diodes heterojunction and homojunction operating at room temperature

Structure			n-contact	p-contact	Method	EL Emission (nm)	Turn-on Voltage (V)	Ref.
p	i	n						
150 nm ZnO	10 nm ZnO	400 nm ZnO	10 nm Ti /100 nm Au	5 nm Ni /5 nm Au /10 nm Ni /100 nm Au	Laser MBE	395, 420, 500, 610	5.4, 7	14,49
700 nm CuGaS ₂	50 nm ZnO	600 nm ZnO:Al	Al	Au	MOVPE	477-775	2	50
6H-SiC	-	500 nm ZnO	1 μ m Al /300nm Au	1 μ m Al /300 nm Ni	Plasma assisted MBE	425, 588	8	51
800 nm AlGaIn	-	1 μ m ZnO	Al	Ni	HVPE (p)and CVD (n)	389	3.2	52,53
40 nm AlGaIn	50-100 nm ZnO	150 nm MgZnO	Not stated	Not stated	RF Plasma assisted MBE	390	3.2	54
2 μ m GaN	-	100 nm ZnO	100 nm ITO	-	MOCVD	384, 365.4	10	55
1 μ m GaN	-	1 μ m ZnO	In	Au	MBE (p) CVD (n)	430	3	56,57
300 nm SCO	-	500 nm ZnO	ITO	Ni	PLD	382	3	58
400 nm ZnO	-	1.6 μ m GaN	30 nm Ti /80 nm Al	30 nm NiO/ 50 nm Au	MOCVD (n)/ RF magnetron sputtering (p)	409	5.4	59
4H-SiC	-	100 nm ZnO:Al (3%)	100 nm Ni	25 nm Al /150 nm Ti	FCVA	385	3.8	60
ZnO	-	ZnO	In	Au	N ₂ O PE PLD	600 - 800	0.5	61
1 μ m GaN	30 nm ZnO	1 μ m ZnO	In	Ni/Au	RF reactive magnetron sputtering	386, 620	10	62
2 μ m GaN	-	720 nm ZnO	Ti/Au	Ni/Au	MOCVD (p), RF-MBE (n)	389, 570 (FB), 390 (RB)	6, -7	63

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0.1 μm GaN	-	0.5 μm Zn	In	Pt	MBE	361-391	10	64
300 nm ZnO	-	150 nm ZnO	Al	In	MOCVD	372, 435, 520	30	65
GaN	-	ZnO	Al	Ni/Au	Plasma assisted MBE	430	5	66
	ZnO:N					400	4.5	
	MgO					382	4.5	
0.7 μm GaN	0.4 μm ZnO	0.4 μm GaN	30 nm Au/ 100 nm Al	30 nm Au/ 100 nm Ni	MOCVD (p) Plasma assisted MBE (n)	400-446	3.2	67
1 μm ZnO		ZnO wafer	In/Zn	In/Zn	MOCVD	375, 430-600	2.3	68
1 μm GaN	-	200 nm ZnO	Ti/Au	Ni/Au	MOCVD (p) PLD (n)	375 -381	3.3	69
0.5 – 1.5 μm PEDOT	-	2 μm ZnO nanowire Diameter, $\phi \sim 100\text{-}200$ nm	Fluorine doped-SnO ₂ film	100 nm Au	electrodeposition	393, 620	5-7	46,47
0.7 μm GaN	1 μm ZnO nanowire, $\phi \sim 63$ nm	0.7 μm ZnO	In	In	PE MBE (p) MOCVD (i, n)	386	3.1	48
GaN	-	1 μm ZnO nanorod, $\phi \sim 40$ nm	10 nm Ti/10 nm Au	10 nm Pt/50 nm Au	MOVPE	370, 443, 560	-3	44
Si	-	1 μm ZnO nanorod, $\phi \sim 40$ nm	In	Au	hydrothermal	387, 535	1	45
Pedot	2 μm ZnO nanowire, $\phi \sim 40$ nm	GaN	-	ITO	CVD	383, 430, 640, 748	3	70

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The development of ZnO lasers and LEDs has shown that the use of nanocrystals to form laser structures is a more viable option. In particular, judging by the numerous reports on ZnO random lasers, disordered gain medium proves to be an attractive method to obtain lasing out of ZnO material for the fabrication of low-cost UV lasers. Nevertheless, the studies on random lasers are still at its preliminary stage before the commencement of this research work. Most work emphasizes on the general properties of random laser action and more work is required to further improve the efficiency of ZnO random lasers for more practical applications.

In particular, the use of scattering effect to form random cavities leads to the output emission to be emitted in all directions. Therefore the amount of light collected in a specific direction will be much smaller as compared to conventional lasers. Hence, there is a need to improve the directionality of the output emission so that the collected emission is much higher. A directional beam will also allow easier beam focusing for future possible applications.

Another major problem with random lasers is that many random cavities are formed and as such, many lasing modes may appear from the emission spectrum. This makes the control of the lasing behavior of random lasers difficult. Hence, it is necessary to look into ways to reduce the mode operation of random lasers and yet achieve low pump threshold and high gain. More importantly, the ultimate goal is to investigate the possibility of using random media to produce electrically pumped ZnO lasers.

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1.2 Objectives

The objectives for this thesis are as listed below:

1. To investigate the properties of random lasing from nanocomposite and disordered films.
2. To improve the lasing efficiency (i.e., reduce threshold, improve the directionality and coherence of emission light) of random lasers.
3. To investigate the possibility of achieving electrically pumped random laser devices based on nano-composite and disordered films

1.3 Major Contributions

This research work focuses on the study of the optical properties of ZnO random lasers based on nanopowder and disordered films, which are fabricated using the sol-gel and Filtered Cathodic Vacuum Arc (FCVA) technique, respectively. Both optical and electrical injections have been carried out to investigate the optical properties of the samples. The main contributions of the work done for this thesis are as listed below:

1. In the sol-gel fabrication of ZnO-SiO₂ nanocomposite film, almost parallel stripes of ZnO clusters are formed. It is discovered that directional, coherent random lasing emission from ZnO powder can be obtained under optical excitation if the pump stripe is made at an angle to the powder stripes. This angle dependence differentiates it from other disordered gain medium where the nanocrystals are randomly distributed. The work enables the study on the effect of particles that have dual roles as scatterer and gain on the random lasing properties. Results show different random lasing properties as compared to the case where ZnO powder only acts as scatterer in laser dyes.⁷²

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2. Directional lasing emission has been achieved from as-deposited ZnO film with much lower lasing threshold (by at least three times as compared to the ZnO-SiO₂ nanocomposite waveguide lasers and annealed ZnO films). This is done by depositing a layer of ZnO film on metal-oxide nano-composite film with stripes of metal-oxide powder prepared by the sol-gel technique. The nano-composite layer acts as a scattering layer and the presence of stripe pattern has been proven to be crucial for obtaining directional and coherent random lasing output. It is also important for providing lateral confinement of light to minimize scattering loss. This study shows that the choice of nano-composite film as the scattering layer is important to achieve good lasing emission with low lasing threshold.
3. A ZnO master oscillator power amplifier (MOPA) has been fabricated to operate at single wavelength with strong output emission. This is done by pumping a small ZnO random cavity to obtain less lasing modes and then amplify them with ZnO gain medium. The design allows easier control and pumping of the lasing modes as compared to other ways such as selective excitation⁷³ or injection locking.⁷⁴ In addition, directional coherent emission is also achieved.
4. 2-D ZnO rib waveguide lasers with varying stripe width have been studied. Experiments show that by forming narrower stripe of disordered ZnO film, the modes will be greatly reduced, without affecting too much of the lasing threshold. Both experimental and theoretical studies on these ZnO rib waveguide lasers show that better polarization is attained in narrower stripes and emission is TE dominant. This differs from the TM polarization dominant

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emission from 3-dimensional (3-D) medium. The result implies that the random lasing characteristics for a 2-D medium are different to that of a 3-D medium. This work also gives an insight on the cavity length of the polarization modes of the ZnO rib waveguide lasers.

5. An investigation on the thermal annealing effect to form disordered ZnO film in n -ZnO/ i -ZnO/ p -GaN and n -ZnO/ i -ZnO/ p -SiC heterjunction diodes on the optical properties under electrical excitations have been carried out. The work shows that more efficient light extraction from the LEDs is possible due to the rough surface of the intrinsic layer. However, the formation of grain boundaries also influences the flow of carriers such that the rate of vacancies formation increases (i.e., increased radiative recombination at defect state levels).
6. Surface and edge emitting UV random laser diodes are realized using sol-gel fabricated ZnO-SiO₂ nano-composite as the gain layer. It is the first time that electrically pumped random lasers with low operating voltage have been demonstrated. The work proves that the stripe pattern inside the nano-composite film forms high quality random media. It also shows that the dimension of powder size is important not only in achieving strong scattering of light but also in reducing the series resistance. The formation of random cavities in the nano-composite film can be controlled by improving the confinement of light in the heterojunction diode. This confinement is found to be affected by the index guiding effect of the waveguide structure and the corrugation effect of the nano-composite film. This finding is important for future development of directional random laser diodes.

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1.4 Organization

A background on ZnO lasers, motivations and contributions for this thesis are presented in chapter 1. Chapter 2 briefly discusses the fundamentals of random laser theory and the current state-of-art of the research and development in random lasers. The fabrication and characterization techniques are presented in chapter 3. The reasons and procedures for using these techniques are also stated in this chapter. In chapter 4, the work on optically pumped nano-composite random lasers based on nanopowder is investigated in details. For ZnO disordered film (i.e., with the presence of nanograins) based random lasers, more in-depth study on controlling the mode emission and polarization characteristics of the lasers are presented in chapter 5. Chapter 6 is devoted to the fabrication and experimental study of disordered ZnO film based LEDs. The works on electrically pumped ZnO-SiO₂ nano-composite random laser diodes can be found in chapter 7. Last but not least, the research work done during these 3 years of Ph.D training and recommendations on possible future works will be given in chapter 8.

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2. Literature Review

2.1 Conventional Laser Cavities Design

Lasers have the characteristics of being a spatially, temporally and spectrally coherent source of light. They are directional and brighter than conventional sources such as fluorescent lamps. For lasing to occur, both gain (i.e., gain is greater than cavity loss) and phase conditions (i.e., $\phi \sim m2\pi$) have to be fulfilled. A typical laser requires an amplifying gain medium to be enclosed within a resonant cavity, which is made up of reflective elements. These reflective elements should be as smooth as possible such that scattering, which is detrimental to the lasing operation, is minimal. Generally, optical feedback of laser cavities can be formed via cleaved or etched facets,²¹ deposited reflective metal films at the edges or external pair of mirrors. Pumping is needed to achieve population inversion for stimulated emission and can be done either optically or electrically. In semiconductor lasers, an optical waveguide design is also required for better light confinement. Figure 2.1 shows an example of a slab waveguide laser where an active layer is deposited on a substrate of lower refractive index.

Figure 2.1: Schematic of a slab waveguide laser

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From the phase condition, it can be deduced that the cavity is at resonance when integrals of half wavelength are supported within the cavity, i.e., cavity length, $L=m\lambda/2n$, where m is the mode number and n is the refractive index of the medium. These modes occur along the cavity and are known as longitudinal modes. The existence of these modes is represented by the narrow, sharp peaks (full width at half maximum of <1 nm) in the emission spectrum.

Since light is an electromagnetic wave, it will consist of transverse electric (TE) and transverse magnetic (TM) mode. The TE (TM) mode is parallel (perpendicular) to the active layer while propagation of light (k) is along the active region as shown in figure 2.1. Conventionally, the TE mode lases first due to a lower threshold gain. The design of the cavity length and the gain spectrum affect the number of longitudinal modes and the thickness of the active film, d , and the cavity width determine the number of transverse modes. For a 1D waveguide design, the mode cutoff thickness for the TE mode is given by $d = 2(m\lambda / 4\sqrt{n_2^2 - n_1^2})$. To observe the transverse modes, one can capture the field profile of the emission using a CCD camera. Both near and far field profiles show the number of transverse modes while the far field one will also reveal the divergence of the output emission.

2.2 Basics of Random Lasers

The working mechanisms of semiconductor lasers are already well established over the past 40 years. Many waveguide designs such as ridge, rib, or buried for improving light confinement and more sophisticated structures such as the distributed feedback (DFB), distributed bragg reflector (DBR), coupled cavity, quantum well, and vertical cavity surface emitting lasers (VCSELs) for single

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mode operation have been proposed and realized.⁷⁵ However, as operation wavelength gets shorter, the periodic structure (i.e., $\sim\lambda/4$) to be defined in these designs also gets smaller (i.e., harder to fabricate). Moreover, the easiness of cleaving to form smooth facets is dependent on the material structure. In the case of ZnO material for fabricating UV lasers, the wurtzite structure poses problem in obtaining smooth facets via cleaving. In addition, using UV reflectors as external mirrors is an expensive option.

Recently, a new kind of mirrorless laser has evolved and is known as the random lasers. Random lasers do not require smooth facets for optical feedback. What is needed is only a disordered gain medium that supports coherent feedback for lasing. This provides an easier and cheaper method for achieving UV lasers. Therefore, the studies on UV random lasers form an important basis for this thesis and the literature reviews on random lasers are given in the next few sections.

2.2.1 History of Random Lasers

Random laser theory has evoked much interest in recent years. The history of random lasing can be traced back to 1966 when Ambartsumyan *et al* replaced one mirror of the FP cavity with a scattering surface to realize a different type of laser cavity.⁷⁶ It was later proposed by Letokhov⁷⁷ that the combination of multiple light scattering and light amplification may lead to lasing. This proposition was first realized by Lawandy *et al*⁷⁸ who discovered spectral narrowing (from 70 to 4 nm) in emission, also known as amplified spontaneous emission (ASE) in random laser theory, from a methanol solution of Rhodamine 640 perchlorate and TiO₂ microparticles (diameter $\sim$ 250 nm) and the emission exhibits threshold dependence characteristics. This type of lasing is coined as incoherent random lasing by Cao *et*

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al when their group discovered random laser action with coherent feedback in ZnO powder.⁴⁰ This has led to an interest in investigating the role of particles in gain medium^{72,79} To date, various experiments and modeling of the random laser theory have been devised to investigate the properties of random lasers.⁸⁰⁻⁸⁴

2.2.2 Understanding Random Lasers

Like conventional lasers, random lasers also require an active medium and pumping source to create population inversion. However, while reflecting boundary is required to define equi-spaced lasing modes and scattering of light is considered detrimental to the operation of conventional laser, the lasing mechanism of a random laser is based on scattering. When scattering is strong enough to induce feedback, closed loop paths will be formed in the medium and are reflected by the lasing peaks in the emission spectrum.

The degree of scattering depends on the refractive index contrast between the scatterer and the medium and on the size of the scatterer. There are 3 regimes of scattering, namely, Rayleigh, Mie and Geometric optics,⁸⁵ which are determined by the size parameter, x , where $x=2\pi r/\lambda$ and r is the radius of the particle. In general, $x < 0.1$ in the Rayleigh regime, $0.1 < x < 50$ in the Mie regime and $x > 50$ in the Geometric regime.⁸⁵ It is noted that the scattering is inefficient in the Rayleigh regime. For the Geometric regime, the scattering cross section, σ_{sc} , is twice the geometric area. Usually, stronger scattering effect occurs if the size of the scatterer is of the order of the wavelength in the Mie regime. Generally, σ_{sc} also increases with the refractive index contrast between the scatterer and the medium. This type of scattering is described by the Mie theory where three light transport regions namely the (a) weak scattering (or ballistic) region, $L \leq l_t$ (b) diffusive region,

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$L > l_t > \lambda$ and (c) localization region, $kl_s \approx 1$ ($L > l_t$) are considered. k is defined as the effective wavevector in the random medium, l_s is the scattering mean free path, which refers to the average distance between two scattering events,^{86,87} l_t is the transport mean free path, which is defined as the distance light travels before being randomized and L is the sample size.

In the weak scattering regime, $l_s \sim 1/\rho\sigma_{sc}$ where ρ is the density of the scatterers. Also, l_t is related to l_s by $l_t = l_s(\omega)/(1 - \langle \cos \theta(\omega) \rangle)$, where θ is the scattering angle, $\langle \rangle$ is the angular average weighted by the differential cross-section, the denominator refers to the angular dependence of the scattering cross-section and $\cos \theta(\omega)$ takes into account the change in light propagation. This involves the scattering characteristics of individual scatterers. As this scattering becomes stronger, the interaction between scatterers becomes important and leads to multiple scattering.⁸⁸ Usually, this occurs in the diffusion region.

In a special case, coherent radiation may travel through a disordered medium and encounter multiple diffuse reflections. This leads to an increase in the reflected intensity as the waves interfere constructively when they travel along time-reversed paths.^{87,89} This phenomenon is known as the coherent backscattering and is an example of weak localization. If scattering gets stronger such that $kl_s < 1$, destructive interference will inhibit propagation of waves for length scales larger than the localization length.⁸⁶ This phenomenon is also known as Anderson localization and there is much debate over whether light can actually be localized.⁹⁰

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2.2.2.1 Coherent vs Incoherent Random Lasers

Random lasers are classified into two types: with (i) incoherent and (ii) coherent feedback. The first type is a laser that fulfills the gain condition but not the phase condition. In this kind of random laser, the working mechanism is based on light diffusion with gain. Light does not return to the original path after a round trip. Thus this does not form a closed loop path and will not form a lasing mode. Instead, gain narrowing in the emission spectrum occurs (i.e., ASE) as scattering increases the path length of light travel in the medium. Light is then amplified since $I = I_0 e^{gl}$ where g is the gain and l is the path length traveled by light in the medium. In this case, the dwell time of light is indifferent to the frequency. The feedback mechanism is also known as the energy or intensity feedback as only part of the energy is returned to the gain medium.^{80,86,87}

The second type is one that fulfills both gain and phase conditions. In the multiple scattering regime where a sufficient degree of randomness is present, the feedback may be coherent and resonant as light returns to where it begins.⁹¹ As such, closed loop paths of light are formed and this forms the random cavities in the gain medium. If gain is able to overcome the lossy closed loop path, lasing mode occurs. In this case, interference of light occurs and constructive interference for phase delay of $2m\pi$ is required for sustaining the lasing mode in each cavity. This condition is similar to that in conventional lasers where lasing modes occur at integral multiples of half-wavelengths of each random cavity. Due to interference effect taking place, the feedback mechanism is also known as the field or amplitude feedback.⁸⁰ It is this type of random laser that researchers are more interested in studying, as their properties resemble that of a conventional laser.

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2.3 Properties of Random Lasers

There are various characteristics length scales for random lasers: (i) gain length (i.e., the distance traveled by photon over which the intensity is amplified by a factor of e), (ii) average path length (i.e., distance the photon travels in the medium), (iii) scattering length (i.e., transport and scattering mean free path) and (iv) sample size.⁸⁰ The common way to measure the scattering length, i.e., the transport mean free path, l_t , in the samples is from the coherent backscattering (CBS) experiment. This experiment measures the width of the backscattering cone, from which l_t can be determined. The measurement of l_t provides a gauge on the light transport regime the sample is in (i.e., degree of disorderness). It is believed that light will be localized if $kl_t \sim 1$ and coherent feedback will occur. However, experiments have shown that the value is large and no rounding of the top of backscattering cone is observed. This implies that light may not be localized and hence the origin of the coherent feedback remains a question mark.⁹² Nevertheless, Cao *et al* brought forward the idea that closed loop paths are formed in disordered gain media (for $kl_t \sim 5-14$) so that each loop gives rise to a set of longitudinal modes.^{32,40,72} This idea was further verified by the rings of emission in the amplified images of the excited area of ZnO polycrystalline film³² and has been used by many other research groups in explaining the mechanism of random lasing in their samples.³⁸

On the other hand, Mujumdar *et al* have also observed lasing peaks from 3D random medium consisting of ZnO powder suspension in rhodamine 6G-methanol solution whereby $kl_t \sim 35-5800$.⁹³ Instead of attributing the peaks to the random optical cavities, they propose that the peaks correspond to extremely long light path travel in the sample, which results in strong amplification. However

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more investigations have to be made to see if this is true for lasing from ZnO powder or thin films with large mean free path.⁹³

In general for a coherent random laser, a broad spontaneous emission is observed below pump threshold. As pump intensity increases above threshold, lasing peaks (of linewidth between $<0.2 \text{ nm}^{80}$ to 0.4 nm^{38}) start to emerge from the emission spectrum. With further increase in pump intensity, the number of modes will increase and saturate.^{82,83} This is because the lasing modes may originate from different cavities and if gain is large enough to overcome the cavity loss, lasing from more lossy cavities will occur. At some point, the modes will overlap and form a broad peak.⁹⁴ The lasing threshold also shows a direct relationship with l_t , indicating the importance of scattering on the lasing behavior.⁸⁰ Moreover, the number of lasing modes will also increase with a reduction in l_t .⁸²

The understanding of this behavior is important for more practical applications. Besides lasing threshold and number of lasing modes, other properties such as linewidth, frequency and polarization dependence and directionality of emission are important as well and as such, many experiments and theoretical models have been carried out to examine these properties. A consolidation of the parameters affecting these properties is as listed:

a) Concentration, n : The amount of scatterers will directly affect the path length and transport mean free path, l_t , since $l_t \sim 1/n\sigma_{sc}$. Generally, with higher disorder (i.e., higher n), more scattering occurs and l_t will reduce. This enhances the amplification of light (i.e., lower lasing threshold). It has been estimated that the lasing threshold P_{th} is related to n by $P_{th} \propto n^{-\chi}$.⁹⁵ Cao *et al*⁷² has also demonstrated that the increase in ZnO nanoparticles that act as scatterers in Rhodamine 640 lasing dye solution will cause a transition from incoherent random lasing to

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coherent random lasing. Incoherent feedback occurs when the gain length equals the path length and coherent feedback occurs when the gain exceeds the loss of the random cavities. On a separate experiment, it is found that the increase in n (i.e., higher gain) will also lead to more lasing modes since there are more low-loss cavities.⁸² The regime $l_t \sim \lambda$ is also found to be crucial for minima lasing threshold and maxima number of lasing modes. On the other hand, from the quantum theory point of view, a low concentration of particles will lead to a poor confinement of light and large overlapping modes.⁹⁶

b) Shape, size and position of excitation area: Excitation from an optical pump source can be collimated to a spot or a stripe. In some experiments, it has been reported that a stripe has a higher chance to excite the lasing modes.⁸³ For a pump stripe, the increase in excitation area generally reduces the lasing threshold.³² Also, the number of lasing modes will increase since there are more closed loop paths in a larger excitation area.^{32,40, 94} However there exists a critical area beyond which the lasing threshold is nearly independent of the area and below which no lasing occurs.³² On the other hand, for a pump spot, the area of the spot is increased by shifting the lens at a distance other than the focal length. In this case, the lasing threshold reduces for larger pump area. However the number of lasing modes also reduces with increasing pump area as the pump intensity reduces for a fixed pump power.⁸² Since the medium is disordered, the frequencies of the lasing peaks may also differ when the excitation region is changed.⁷³

c) Angle dependence: The output emission from random laser is non-directional since scattering occurs in all directions. For 300 nm thick ZnO film deposited on sapphire substrates, the number of modes recorded varies with the detection angle

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from the edge of the samples and a shift in peak wavelength has been observed.⁹⁴ However for emission from the sample surface, it is found that the peak wavelength, linewidth, intensity and the number of modes are independent of the observation angles. It is proposed that scattering of light occurs from the surface in all directions such that there are not many changes observed from the emission spectra. However from the edge, scattering of light from the surface may be detected as well when the observation angle increases, thus resulting in changes in the emission.⁹⁴ This phenomenon has also been observed in powder.⁴⁰

d) Sample size: The lasing threshold generally reduces for increasing sample size with an inverse relationship ($P_{th} \propto A^{-x}$ where A is the area of the sample). It has been proposed that this is due to the higher probability of having optimum configurations of high quality cavities rather than formation of larger cavities. This implies that by having a special arrangement of particles, a large sample size is not necessary.⁹⁵ Moreover, a bigger sample volume will also provide a larger number of saturated lasing modes.⁸²

e) Scatterer size: As mentioned in section 2.2.2, the size of the scatterer (i.e., affecting the size parameter) is important in determining the degree of scattering. Experimentally for ZnO spheres, with diameter d ranging from 85 to 617 nm, and cold-pressed into pellets, lasing threshold reduces with an increase in the size of the spheres. However for 85 nm sphere, only ASE was observed.⁸⁸ Also, I_t reduces with larger spheres. Both I_t and the lasing threshold will reach a saturation point after a certain size parameter (i.e., nd/λ where n is the refractive index).

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2.3.1 Measurements of Coherent Random Lasing Properties

In a disordered medium, random scattering of light results in emission in all directions. Hence, there is debate as to whether the emission is coherent and directional. Thus, attempts are made to show that the emissions from random lasing samples are indeed coherent. Some ways to do so are as listed:

a) Photon statistics: this method counts the number of photons arriving at the detector. This is done by recording the input emission spectrum versus time using a CCD camera for a small wavelength range of ~ 6.7 nm. The data obtained is then fitted either with a Bose-Einstein distribution function for incoherent emission or Poisson function for coherent emission for single mode operation.^{81, 97} Such experiments have been carried out for ZnO nanoclusters,⁹⁸ and π -conjugated polymer film.⁹⁹ Both groups have confirmed that the narrow emission lines are indeed coherent radiation. Studies have also shown that for coherent random lasers, though multi-peaks appear, the photon statistics show that it behaves like a sum of almost independent single mode lasers, which indicates the presence of many independent random cavities in the medium.¹⁰⁰

b) Fourier transform: If the emission peaks are coherent, that will imply that there is a feedback in the system. One way to determine the presence of feedback is to apply Fourier transform (FT) to the emission spectrum. The units of the emission spectrum need to be in wavenumber ($1/\text{length}$) so that unit in FT is in length. The expected FT for a FP resonator will consist of equally spaced harmonics with decreasing amplitude and the actual separation is nL/π where n is the index of refraction and L is the mirror separation. For a ring resonator, the mirror separation is replaced by half a circumference and the resulting FT harmonics appear at

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multiples of $nD/2$ where D is the ring diameter. In random lasers, it is observed that ring cavities are formed and thus ring resonator configuration is used to determine the cavity length of the random laser.¹⁰¹

2.4 The Development of Random Lasers

Early works on random lasers are based on laser dye solutions with the incorporation of particles as scatterers for the fundamental study on the properties of random lasers.^{72,102} However, particles may sediment or agglomerate in the solution over time. As such, solid-state medium are preferred for more practical applications since they are easier to control. Hence more quantitative studies have also been made on nanocomposite films, which either consists of laser dye and scatterers,^{79,82,100} or active scatterers in passive medium.¹⁰³ From the fundamental studies on random lasers' properties, it is undeniable that random lasers suffer from high lasing threshold, multimode operation and non-directional emission due to weak confinement of light. As such, researchers have also examined ways to improve the efficiency of random lasers.

One method is to incorporate waveguide designs for better directional emission and confinement of light.^{88,104} By depositing a layer of ~200 nm thick MgO film on a ZnO thin-film ridge waveguide laser, the directionality of the transverse beam profile has shown great improvement. This is because MgO has a lower refractive index (~1.67) than ZnO (~2.1) and serves as a cladding layer of better light confinement. Hence this reduces scattering loss, increases the number of lasing modes, reduces the lasing threshold and improves the lasing efficiency.¹⁰⁴ Efforts have also been made to increase the feedback by placing a mirror near the sample edge^{105,106} or coated the facets with metal.¹⁰⁴ Experiments show that the

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lasing threshold is reduced to half if the mirror is not more than 800 μm from the sample edge.¹⁰⁵ This is attributed to the possibility that the mirror reflects the scattered light and reinjects them to the film. This leads to an increase in optical gain which gives rise to higher output intensity and more lasing modes.¹⁰⁴⁻¹⁰⁶ This effect is stronger if the mirror is moved closer to the film.¹⁰⁵ It is also suggested that external feedback allows control of lasing frequencies and thus achieve single mode lasing.⁷⁴

Single mode operation is important in laser applications. However, it is a common phenomenon that random lasers operate in multimode operation. Theoretical studies have shown that by having localized gain (i.e., pumping the sample locally at certain spots since the modes are spatially localized) or altering the pumping rate just above threshold, it is possible to achieve single mode operation.⁷³ On the other hand, by integrating disordered gain medium with traditional laser designs to form random DFBs^{107,108} and micro random lasers¹⁰⁹ or by inducing a grating design in the random lasers,¹¹⁰ improvements in the lasing characteristics are achieved. Researchers have also investigated the effect of temperature,^{20,111,112} and electric field¹¹³ on the random laser properties.

Instead of using optical pump source to excite these random media, continuous-wave random lasing (i.e., narrowing of spectrum with the existence of lasing threshold) has also been demonstrated in δ -alumina nanopowders doped with Ce^{3+} , Pr^{3+} or Nd^{3+} when pumped with electron-beam current.¹¹⁴⁻¹¹⁶ More recently, electron pumping of ZnO nanoparticles has also been reported.⁴⁴ These show that it is possible to attain random lasing using other sources of excitations.

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2.5 Applications of Random Lasers

The theoretical studies on random lasers have brought in new insights on the physics of wave transport and localization.⁹⁷ The study on the interaction between lasing modes has contributed to the understanding of the chaotic theory. A clearer picture on the light scattering mechanisms in random lasers has also increased the understanding of galaxy masers and stellar lasers.⁹⁷

Researchers have also proposed possible applications in research fields such as laser, military and medical. In the laser field, forming random medium provides an alternative way to produce laser emission especially in the short wavelength range where effective mirrors are not available easily.^{97,117} This is particularly useful in the development of ZnO based lasers since the fabrication cost is low and is suitable for all kinds of substrates as mentioned in section 1.1.1.

For proposed military applications, Balachandran *et al* have tried to add TiO₂ scatterers and laser dyes in textile resins and draw them into fibres. It was proposed that the presence of random laser action in the fibres allows the integration of codes into textiles. By using different dyes and scatterers in military uniform, friend or foe can be identified.¹¹⁸ Similar methods can also be used for implementing photonic codes for anticounterfeiting or for emergency applications.¹¹⁹

Random lasers have also found possible applications in the medical field. The experimental results show that both healthy and cancerous tissues soaked in Rhodamine 6G laser dye exhibits coherent random lasing and the cancerous one shows more lasing peaks. Also, the average PFT (power Fourier transform) of the random laser spectra reveals that the random resonator for healthy and cancerous

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tissues from the same organ is different. This may be one possible technique for diagnostic imaging.¹²⁰

2.6 Concluding Remarks

To date, the fundamentals and properties of random lasers are already well studied. Random lasing has been used to account for the lasing mechanisms in various disordered films, nanocomposite films, powders and nanostructures. However, random lasers suffer from high loss and multimode operations. Therefore, researchers are now moving further to improve the efficiencies of random lasers. The coupling of random laser cavities to traditional waveguide designs is believed to be one possible way to reduce loss and improve light confinement to build a more efficient random laser system.

Another possible direction for random laser research is to excite these disordered media electrically for more useful applications such as displays, or light emitting devices. Although electrically pumped lasing has been obtained from rare-earth-metal-doped dielectric nanophosphors and Nd-doped δ -alumina nanopowders,¹¹⁴⁻¹¹⁶ the operating voltage (in the range of kVs) is still too high. Hence, more works are still required in achieving electrically pumped random lasers.

Chapter 3: Fabrication and Characterization Techniques

3. Fabrication and Characterization Techniques

In this thesis, we are concerned with the fabrication and characterization of nanocrystals semiconductor lasers in the form of nano-composite and disordered films. Both the sol-gel and filtered cathodic vacuum arc (FCVA) techniques are used, respectively, to provide flexibility in the design of random laser structures. The reasons for using these techniques and the related informations are highlighted in the following sub-sections of the first part of this chapter. In the second part, the characterization techniques used for measuring the properties of the random laser emission are also presented. The description on the set-up and the experimental procedures will also be mentioned in this section.

3.1 Fabrication Techniques

3.1.1 Sol-gel Technique

The sol-gel technique is a wet chemical synthesis method for making ceramic and glass materials in various forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials.¹²¹⁻¹²³ This method also provides flexibility in preparing nano-composite films, which are one of our subjects of concern for the study of random lasers. Depending on the type of precursors used, inorganic, organic and hybrid films can be fabricated. For this thesis, both inorganic and hybrid films have been prepared and the fundamentals of these processes are briefly covered in the next few sub-sections.

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3.1.1.1 Inorganic Film

A sol is a dispersion of solid particles (few hundred nm) in a liquid and a gel is a solid network containing liquid components. The starting materials used in the preparation of the sol are usually metal alkoxides. In this thesis, we are interested in silica films and the commonly used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethylorthosilicate (TEOS). In here, we will describe the chemical process taking place using TEOS (i.e., the precursor used for this thesis).

Generally two types of reactions take place during the aging process of the sol. They are namely (a) hydrolysis and (b) condensation (i.e., water and alcohol). Hydrolysis and condensation take place concurrently when metal alkoxides are mixed with water and alcohol. In some cases, some acid is added to speed up the hydrolysis process. As the metal alkoxides are insoluble in water, alcohol is essentially required for mixing them with water. The basic reactions for SiO_2 are given below:

The molecular formula for TEOS is Si(OR)_4 and $\equiv$ represents three OR bonds. OR denotes the alkoxyl group and OH represents the hydroxyl group. As seen from equation (1), the hydrolysis process produces the silanol (Si-OH) group and gives off alcohol. The silanol groups formed either react with other silanol groups to form water (i.e., water condensation in equation (2)) or react with the alkoxide group to produce alcohol (i.e., alcohol condensation in equation (3)). From the

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above equations, both condensations produce the siloxane (Si-O-Si) group. After aging the sol for some time for the reactions to take place, the sol solution is then spin-coated onto the substrates, which then forms a gel. Annealing at high temperature is often required to remove the remaining organic components.

3.1.1.2 Hybrid Film

Inorganic films have to be formed at high temperature ($>600\text{ }^{\circ}\text{C}$), which is detrimental in some fabrication processes that involve multi-layers film deposition. On the other hand, hybrid films (inorganic-organic composite film) can be processed at temperature below $200\text{ }^{\circ}\text{C}$ and form thick layers without cracks. Hybrid films are well-known to possess much better properties such as thermal, mechanical, electrical and magnetic as compared to pure organic materials and have often been used to replace organic films.¹²⁴ In this thesis, (i.e., in chapter 7 on electrically pumped random lasers), hybrid films were used to replace the inorganic films as the annealing process may have adverse effect on the device performance and organic films for better and stable film properties.

Organic group is made up of a simple alkyl chain and may contain functional group such as amine, epoxy or methacrylate group.¹²⁵ A more popular choice of preparing hybrid film is to form UV patternable films whereby both thermal (at low temperature) and UV polymerization processes can be undertaken. In this thesis, such hybrid films were prepared. The organic precursor used contains a methacrylate group, which is essentially an ester of methacrylic acid that has an unsaturated monomer (i.e., carbon-carbon, $\text{C}=\text{C}$, double bonds), allowing it to be polymerized during the UV curing process. The sol will also contain at least one photosensitive organic material, known as the photoinitiator, to

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speed up the photopolymerization process.¹²⁶ The preparation process is similar to that of the inorganic case where aging is required for the organic and inorganic precursors to hydrolyze and spin-coating technique is used to deposit the sol onto the substrates. The substrates are then pre-baked to remove the solvent so that the mask for patterning will not stick onto the substrate. Then they are exposed to UV radiation for polymerization process to occur. During this process, the photoinitiator will absorb the UV light, give off free radicals to react with the methacrylate group and initiate the free radical radiation. Postbaking is also done to fully hard-bake the pattern. The temperature used is often below 200 °C.

3.1.2 Filtered Cathodic Vacuum Arc Technique

The Filtered Cathodic Vacuum Arc (FCVA) coating system was first developed in Russia and was intensely studied in NTU in 1993 to fabricate ta-C films. Currently, the FCVA technique has been extended to develop both carbon and metal oxide materials. It can be regarded as a physical vapor deposition method as the working principles are related to arcings at low pressures (i.e., 1×10^{-6} Torr)¹²⁷ and the coating species are pure ions that have tunable energy.¹²⁸

The FCVA technique has been proven to offer (1) high deposition rate (2) low temperature deposition and (3) good quality films. Moreover, various characterization works on the fabrication of ZnO (using 99.99% purity Zn target) and ZnO:Al films (99.99% purity Zn target doped with 1, 2, 3, 5 and 7% Al content) have shown good electrical characteristics. In addition, both types of films exhibit strong UV emission with low defect-related luminescence.^{129 - 131} Furthermore, the post-growth annealing technique forms irregular grains and voids in the FCVA grown ZnO films. These grains (i.e., scatterers) and voids provide

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large refractive index contrast, which facilitate strong scattering and form closed loop cavities. This supports coherent random laser action and the size of the scatterers can be controlled via the annealing temperature and time. The ease in forming such disordered films paves new ways to study and design more efficient random laser structures.^{38,104} It has also been demonstrated recently that the quality of FCVA grown ZnO and ZnO:Al films are good enough to be used in the fabrication of light-emitting diodes. This is reflected by the presence of strong UV emission and relatively much weaker green emission with low turn-on voltage of ~ 3.8 V.⁶¹ Therefore the FCVA technique has been undertaken in this thesis for the fabrication of ZnO random lasers and LEDs.

3.1.2.1 Description of the FCVA System

Figure 3.1 shows the design of the FCVA system. It consists of an anode/cathodic design and the target is located at the cathode. When biased, the act of striking the trigger onto the target produces cathodic arc spots and plasma discharge is formed.

Figure 3.1: Schematic of FCVA system

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For our process when using Zn and Zn:Al targets, the current of the arc source is ~60 A and the voltage of the plasma is ~18-20 V. The plasma beam consists of macroparticles and neutral atoms and is transported up through a bend to the substrate. The bend consists of filtering coils (⊗) which are connected to power supply. This forms a cross magnetic and electric field to filter out the undesired macroparticles and neutral atoms. For better filtering efficiency and plasma throughput, our system is equipped with an off-plane double bend.¹³² A focusing coil is also placed at the output of the filtering coil to direct the plasma from the filter bend to the substrate. For deposition of metal oxide films, an oxygen gas inlet is placed near the focusing coil for the plasma to react with the oxygen.¹³³ The oxygen flow rate is controlled using a gas flow controller and the substrate holder is attached to a heater so that heating of substrate is possible for better film quality.

3.2 Characterization Techniques

In this thesis, photoluminescence (PL), field profiles, and electroluminescence (EL), have been carried out to characterize the samples. The setups are described in the next few sub-sections.

3.2.1 Photoluminescence Setup

The optical pump source is a tripled-frequency pulsed operated Nd:YAG laser (6 ns, 10 Hz). The emission wavelength at 1064 nm is filtered at the separator as shown in figure 3.2 and the emission at 532 nm is filtered by a filter lens such that the pumping wavelength is 355 nm. The attenuator is used for varying the input pump power and the photomultiplier tube (PMT) is for signal detection. The

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Figure 3.2: Experimental setup for optical testing

signal is sent to a lock-in amplifier where the lock-in frequency is provided by a home-made frequency detector attached near the laser source and the readings are recorded using a Labview program. A cylindrical lens is also used to focus the pump source to a pump stripe on the sample and a polarizer is placed between the sample and the objective lens for polarization measurements.

3.2.2 Field Profiles Setup

The near and far field profile setups are shown in figure 3.3. The excitation of the sample is similar to that described in the PL section. For the far field profile, an objective lens is placed in the focal point for the CCD camera to capture the beam. As for the near field setup, two objective lens are used to magnify the images. The near field profile gives a clearer view on the order of the TEM modes while the far field profile shows the divergence of the emission beam. In general, if the waveguide of the lasing samples are properly designed, the transverse mode

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Figure 3.3: Experimental setup for near and far field profiles

will only consist of the fundamental TEM_{00} mode. Also for good lasing samples, the far field profile will show directional emission with small scattering, as captured by a CCD camera. For both setups, a polarizer may be placed at the output of the emission to measure the field profiles for different polarizations.

3.2.3 Electroluminescence Setup

An in-house pulsed circuit is built to convert the input direct-current signal from the power supply to pulsed source. The function generator provides the lock-in frequency for the lock-in amplifier and controls the input frequency and pulse width of the biasing voltage. The pulse signal supply is then connected to the sample and emission is collected by an objective lens focused to a monochromator. Light output is then amplified by a PMT and transmitted to the lock-in amplifier. Just like the PL setup, the intensity readings are collected by a Labview program.

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Figure 3.8: Electroluminescence Setup

4. Optically Pumped Nano-composite Random Lasers

4.1 Introduction

This thesis is devoted to the design, fabrication, testing and analysis of nanocrystal semiconductor lasers based on ZnO material using both optical and electrical pump techniques. We shall first look at optically pumped powder based nano-composite random lasers. In particular, we shall only concentrate on film-based structures instead of colloidal solutions since the latter is not suitable for practical applications due to higher probability of agglomeration and sedimentation problems in solutions.

Lasing peaks from ZnO powder electrophoresis-deposited on ITO coated glass substrates have already been observed.⁴⁰ However this method will only form thick films with much difficulty in controlling the concentration of the powder. This is impractical if such random medium are to be used in devices as the powder film can be scratched off easily. A more practical approach is to fabricate nano-composite film since it provides better processability and control over the concentration. Moreover nano-composite films have been employed in both organic and inorganic light emitting diodes,¹³⁴⁻¹³⁶ and this forms one possible future development of ZnO light emitting devices.

Nano-composites are made up of two or more different domains of materials, in nanometers range, and are usually used for optical applications.¹³⁵ One way to form nano-composite structure is adding semiconductor nanoparticles or nanocrystals (i.e., of size smaller than the Bohr radius of the electrons and holes of the semiconductor) into materials such as glass, ceramics or polymers to study their enhanced optical properties.¹³⁵ Usually, these nano-composites can be processed into fibers or films. In this thesis, only nano-composite films will be

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considered. They can be of organic, inorganic or hybrid type, depending on the nature of the materials and requirement of applications. In this case, both the particles' size and the type of matrix have to be carefully selected to avoid optical scattering, which is detrimental to the performance of the system.

On the other hand, this kind of optical scattering is extremely important in the design of nano-composite random lasers. The nanoparticles embedded in the material may just act as scatterers or have dual roles as scatterers and optical gain media. Examples include scatterers such as silica spheres,⁷⁹ TiO₂ powder,^{82,137} liquid crystals^{110,113,138} in laser dye or polymer matrix, and active media such as ZnO powder in inert polymer matrix such as epoxy or polydimethylsiloxane (PDMS),¹⁰³ or in surfactant.¹³⁹ Films can be formed by spin coating,¹³⁹ cell casting^{82,119} or dip coating.¹³⁷ Table 4.1 summarizes some of the nano-composite random lasers according to the type of matrix and particles.

Table 4.1: Summary of nanocomposite random lasers

Particles	Size (nm)	Matrix	Type of random laser	Ref
Silica balls ($n \sim 1.46$)	300	Rhodamine 6G laser dye (30 μm film on glass)	Coherent	79
TiO ₂ ($n \sim 2.4$)	400	PMMA ($n \sim 1.49$) + rhodamine 640 perchlorate dye (150 μm polymer sheet)	Coherent	82
ZnO powder ($n \sim 2.1$)	125 ± 25	PDMS ($n \sim 1.45$) /epoxy ($n \sim 1.43$ -1.62) (cured in a mold)	Incoherent	103
TiO ₂ ($n \sim 2.4$)	20	MEH-PPV ($n \sim 1.6$ -1.9) on glass substrate	Incoherent	137
ZnO powder ($n \sim 2.1$)	100 (250-300 after anneal)	Surfactant (Trinitron-X100) (1-3 μm film glass substrate)	Incoherent	139

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Two common similarities in obtaining coherent random laser action from nano-composite lasers lie in large particle size used (>100 nm) and rather thick nanocomposite films (>30 μm). Similarly, for coherent random lasing from ZnO powder film, the thickness of the film ranges from 6-15 μm .⁴⁰ This means that the lack of a proper waveguide may lead to non-directional emission and multi-mode transverse confinement of light. It will also be difficult to obtain electrically pumped devices using such thick nano-composite films. Moreover, only gain narrowing is obtained from ZnO based nano-composite random lasers.

Therefore, more work has to be done to find a better method to form the nano-composite film. This method should provide ease in controlling the (i) thickness of the film, (ii) concentration of powder and more importantly, (iii) able to form high quality random media for coherent feedback. To satisfy these requirements, the sol-gel technique is selected. Coherent random lasing has been successfully achieved through two different waveguide structures with the use of active and passive metal-oxide powders. Directional and polarized emissions are demonstrated from both structures. The results obtained showed the superiority of the sol-gel technique over other methods in obtaining high quality random media from the nano-composite films. In the following sections, we shall see how and why this technique is able to lead to coherent random lasing.

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4.2 Random Lasing from ZnO-SiO₂ Nano-composite Waveguide

4.2.1 Design Consideration

The construction of ZnO based nano-composite waveguide random lasers involves the design of (i) the nanocomposite film and (ii) the buffer or cladding layers. The gist lies in obtaining large degree of light scattering in the nanocomposite film. From chapter 2.2.2, we know that this depends on both the refractive index contrast between the particles and the medium they are embedded in, and the size of the particles. ZnO particles may be synthesized by chemical methods. However, it requires much work in optimizing the size and quality. On the contrary, commercialized high quality ZnO powder can be purchased at low cost. Moreover, the commercially available powder (ZnO Puratonic, Alfa Aesar) has a size of ~120 nm, which is similar to that used in realizing coherent random lasing.⁴⁰ Therefore they are employed in the experiment.

As the refractive index of ZnO is ~2.1, the material on which ZnO powder should be embedded in should have much lower refractive index for (i) better confinement and guiding of light and (ii) higher degree of scattering. One possible choice is silica matrix since silicon dioxide (i) has a small refractive index of ~1.45, (ii) is transparent to UV light and (iii) can be easily processed using the sol-gel technique. Moreover, similar nano-composite films fabricated using the sol-gel technique have demonstrated high UV PL.^{140, 141} However those films do not demonstrate random lasing due to the small particle size of ZnO.

The schematic of the proposed ZnO-SiO₂ nano-composite waveguide laser is shown in figure 4.1. A SiO₂ buffer layer (of refractive index ~1.45) is inserted between the nano-composite film (of effective refractive index, n , varying between 1.5 and 1.9, depending on the concentration of ZnO powder) and Si substrate so

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Figure 4.1: Schematic of a ZnO-SiO₂ composite waveguide laser

that transverse optical confinement can be achieved in the nano-composite film with minimal absorption loss. Hence, light will travel in a direction parallel to the surface of the nano-composite films (i.e., 2-D light confinement). According to chapter 2.1, the designed thickness of the nano-composite film is estimated to be ~200 to 600 nm, depending on n for single mode transverse confinement of light.

4.2.2 Fabrication Process

In the preparation of SiO₂/Si substrates, the Si substrate was first ultrasonic cleaned in acetone and followed by 2-propanol bath. The substrate was then washed under DI water and blown dry using nitrogen gun. After cleaning, the Si substrate was annealed in open air in a furnace for at least 10 hours (hrs) at 1100 °C to form a thick layer of ~600 nm SiO₂ buffer layer. The SiO₂/Si substrate was then cleaved into 6 samples of sizes 2×2 cm².

Before the fabrication of the ZnO-SiO₂ nano-composite film, there is a need to optimize the thickness of the SiO₂ film without any ZnO powder. TEOS was used as the precursor for SiO₂ and 2-propanol (or IPA) as the solvent. TEOS

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was first mixed with IPA before the addition of water and nitric acid. The sol was then stirred for 24 hrs before spun-coated on the pre-cleaned SiO₂/Si substrates (2×2 cm²) at a spin speed of 3500 rpm for 30 secs. After then, the samples were annealed at 950 °C in open air for 5 min.

In general, the molar ratio of TEOS:IPA:H₂O affects the viscosity and hence the thickness of the film.¹⁴² For simplicity, the ratio of TEOS:H₂O is kept constant at 1:4 by assuming that each OR group of TEOS is replaced by the OH group of H₂O and the ratio of TEOS:IPA varies from 1:1 to 1:30. A summary of the experimental results is shown in table 4.2. The variation of spin speed and time may cause the thickness to change (in the range of 10s of nm), which is smaller as compared to the variation of IPA added. As the addition of powder may increase the thickness of the film, the molar ratio of TEOS:IPA:H₂O was optimized at 1:10:4.

To incorporate the ZnO powder into silica matrix, 6 bottles of sol (i.e., TEOS:IPA:H₂O = 1:10:4) were prepared and left to stir for 4 hrs before the addition of ZnO powder. The molar ratio of ZnO:SiO₂ was varied from 1:5 to 1:30. The sol was then aged for another 20 hrs before spun-coated on the SiO₂/Si substrates. The spinning and annealing conditions are the same as mentioned above. It is observed that ZnO clusters are formed on the SiO₂ surface with parallel-stripe pattern, as evident in the scanning electron microscope (SEM) (JEOL JSM-5910 LV) images shown in figure 4.2. In general, the stripe spacing increases with higher molar ratio. The parallel-stripe pattern is formed during spin coating of the sol on the SiO₂/Si substrate due to outward radial force of the sol acting on the surface of the substrate.^{143,144}

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Table 4.2: Variation of film thickness with IPA concentration

TEOS:IPA:H ₂ O	Thickness (nm)		TEOS:IPA:H ₂ O	Thickness (nm)
1:1:4	700-850		1:20:4	85-110
1:5:4	350-450		1:30:4	60-90
1:10:4	170-200		-	-

Figure 4.2: SEM images of the surface of samples with molar ratio of ZnO:SiO₂ at (a) 1:5 and (b) 1:20.

4.2.3 Results and Discussion

The room temperature (R.T.) optical characteristics of ZnO–SiO₂ composite waveguide lasers were studied under optical excitation by a frequency-tripled Nd:YAG laser (355 nm) at pulsed operation (6 ns, 10 Hz). Optical pump was achieved using a cylindrical lens to focus a pump stripe of length ~0.5 cm and width ~400 μm at an angle, θ , to the parallel-stripe pattern of ZnO clusters to realize random laser action with coherent feedback.

Figures 4.3a and b show the burnt mark made by the laser pump source when excitation intensity is increased to ~3 MW/cm² under coherent random lasing condition. The possible mechanism of 2-D light confinement inside the nano-composite films under optical excitations is shown in figures 4.3c and d.

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Figure 4.3: Macroscopic pictures of the surface of the ZnO–SiO₂ composite films with molar ratio of (a) 1:5 and (b) 1:20 taken at $\times 5$ magnifications. Schematic of the formation of one possible closed loop path of light inside the nanocomposite films with molar ratio (c) 1:5 and (d) 1:20 under optical excitation. θ is the angle between the parallel-stripe pattern of the ZnO clusters and the pump stripe.

The ZnO clusters act as scatterers with gain to scatter the light to form a closed loop path along the pump stripe. The light emitted from the edge of the samples was then collected by an objective lens coupled to a monochromator. It is noted that for small θ , light is propagating almost parallel to the stripe patterns of the ZnO clusters so that long travel-distance of light is required before being amplified and scattered to other clusters. Hence, the amplification is insufficient to overcome the loss of the random cavities and lasing is difficult to be sustained. For large θ , although more scattering and amplification will occur, light will also have a higher chance to escape to the unpumped region rather than emit from the edge

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and weak output intensities are detected instead. As such, a compromise has to be made to achieve a balance between the gain and loss of the closed loop paths to form lasing peaks.

A series of test on the effect of angle light made on the stripe pattern on the emission spectra has been carried out for the sample with molar ratio 1:5 and 1:20 (ZnO:SiO₂). It is found that at small angles $\sim 5^\circ$ and at large angles greater than $\sim 50^\circ$, very weak spectra are detected. A typical spectrum obtained at an angle of $\sim 30^\circ$ under high excitation intensity of 2.13 MW/cm^2 is shown in figure 4.4. Only ASE occurs due to light escaping to the unpumped region and thus closed loop paths are unable to form. From figures 4.3a and b, it is found that the angle for coherent random lasing to occur is around 10° . Thus it is concluded that $\theta \sim 10^\circ$ is an optimum value to achieve maximum output intensity and this value of θ is used in the following measurements for all the samples.

Figure 4.5 shows the light-light (L-L) curve and emission spectra for the sample with molar ratio 1:5 (ZnO:SiO₂). At pump intensities below threshold, a single-broad spontaneous emission spectrum with a full width at half maximum

Figure 4.4: Spectrum 1:5 sample when light is at an angle of $\sim 30^\circ$ to the stripes

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(FWHM) of ~ 10 nm is observed. Increase in pump intensity above threshold results in sharp peaks (lasing modes) emerging from the emission spectra, indicating the formation of closed loop paths of light. However, further increase in pump intensity does not excite more sharp peaks. Instead, narrowing of emission spectra occurs and the FWHM of the emission spectrum reduces to ~ 2.5 nm at an excitation intensity of ~ 2.2 MW/cm². The narrowing of emission spectrum, which limits the number of excited sharp peaks, is due to intense amplification of light arisen from the high density of active scatterers (i.e., narrow stripe spacing of ZnO clusters). As shown in figure 4.5, four sharp peaks, having spectral separation and linewidth of ~ 0.7 nm and ~ 0.6 nm respectively, are distinct from the emission spectrum at high pump intensities. The wider linewidth as compared to *ref.* 88 could be attributed to the weaker disorder due to the stripe patterns that leads to overlapping modes.⁹⁶

Figure 4.5: (a) Light-light curve and (b) emission spectra of the sample with molar ratio 1:5 versus pumped excitation intensities. The insets of (a) are the near and far field profiles for the TE mode at excitation intensity of ~ 1 MW/cm².

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The corresponding near and far fields are inserted in figure 4.5a at the excitation intensity of $\sim 1 \text{ MW/cm}^2$. It is noted that the light emission from the edge is TE dominant due to the strong transverse and lateral confinement of light (i.e., bright single-spot emission). The strong transverse (lateral) confinement of light is due to the SiO_2 dielectric matrix and the SiO_2 buffer layer (scattering of light between the stripe patterns since closed loop paths are formed). As such, the field profile looks almost circular. Similar behaviors of the emission spectra and field profiles have been observed for samples with molar ratio 1:10 and 1:15.

Figure 4.6a shows the emission spectra of the sample with molar ratio 1:20. At low pump intensities, a single-broad emission spectrum with a FWHM of $\sim 12 \text{ nm}$ is observed. When the excitation intensity exceeds a threshold, sharp peaks at around 387 nm with linewidth less than $\sim 0.6 \text{ nm}$ emerged from the emission spectrum. Further increase in pump intensity increases the number of sharp peaks and the FWHM of the entire spectrum is reduced to $\sim 5 \text{ nm}$.

Figure 4.6: Emission spectra of samples with molar ratio (a) 1:20 with pump intensities and (b) 1:30. The excitation conditions are the same as figure 4.5.

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The wider spectrum width (as compared with figure 4.5) is attributed to the wider parallel-stripe spacing of ZnO clusters as the corresponding density of active scatterers is reduced, leading to a weaker gain narrowing effect. Sharp peaks are also observed from the emission spectra of the sample with even higher molar ratio (1:30) under high pump intensities, see figure 4.6b. This implies that closed loop paths of light can still be formed inside the sample with low concentration of ZnO clusters, but at the expense of high pump threshold. The polarization and field profiles observed from these samples are similar to that given in figure 4.5 and are not repeated here.

The variations of threshold pump and number of peaks (at pump intensity of $\sim 2.2 \text{ MW/cm}^2$) versus molar ratio are plotted in figure 4.7. As molar ratio increases, the reduction in optical gain and the increase in scattering loss lead to an increase in the threshold pump. However they do not hold a linear relationship. Instead, the threshold pump exhibits a step change with the variation of molar ratio. From molar ratio 1:5 to 1:10 (1:25 to 1:30), the change in scattering loss and optical gain is small. Thus the threshold does not increase a lot. However, a step increase in threshold (by $> 40\%$) is observed when the molar ratio is increased from 1:10 to 1:15 and from 1:20 to 1:25. This implies that the optical gain is reduced more rapidly than the increase in scattering loss since a higher amount of gain is required to compensate for the scattering loss.

Furthermore, it is shown that the number of sharp peaks is maximized at molar ratio 1:20 but minimized at both lower and higher molar ratios. At higher molar ratio (i.e., 1:30), the wider spacing (i.e., longer scattering mean-free path, hence higher scattering loss) between the parallel-stripes of ZnO clusters and the low concentration of ZnO clusters (i.e., lesser optical gain) imply a lower

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Figure 4.7: Plots of (a) threshold pump intensity and (b) number of sharp peaks (lasing modes) versus molar ratio of the ZnO–SiO₂ composite waveguide lasers.

possibility of sustaining closed loop paths and thus lesser modes are observed. At lower molar ratio 1:5, the narrowing of emission spectra and gain competition may account for the decrease in the number of lasing peaks. At molar ratio of 1:20, these effects are lower, thus the number of lasing peaks is maximized.

From the above experiment, it is noted that incoherent random lasing is not observed in all the samples. In order to verify that coherent random lasing is due to the proposed configuration of the composite waveguide, a layer of ZnO powder mixed with water was sprayed on quartz substrate to form a film with concentration of ZnO powder similar to that given in figure 4.5a. It can be shown that only incoherent random lasing is supported in the randomly distributed ZnO powder film of $\sim 1 \mu\text{m}$ (after dried) under optical excitation. This proves that our claim that stripes of ZnO clusters are needed to form coherent random lasing is justified.

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4.3 Random Lasing from Metal-oxide Nano-composite Waveguide

4.3.1 Design Consideration

In the above described waveguide laser, ZnO clusters have a dual role as a gain medium and scatterer. This is probably why the lasing trend differs from the case where the variation of passive particle density in laser dye solution can result in different types of random laser action.⁷² The study of the influence of passive particles on the random lasing behavior in solid-state medium is important as well since this is a more desirable solution for the realization of practical random cavities. Using similar idea as above, the fabrication of the nano-composite layer can be modified to contain only passive particles for ease of controlling the scattering effect via the concentration. In addition, the amount of optical gain can be fixed by simply depositing a layer of active ZnO film on top of the nanocomposite film. In this case, the nano-composite film acts as a scattering layer for the ZnO film.

The schematic of the proposed random laser is shown in figure 4.8. It consists of a SiO₂ buffer layer (refractive index ~ 1.46), a guiding layer composed of clusters of metal-oxide powder embedded in dielectric SiO₂ matrix and a ZnO active layer film (refractive index ~ 2.1). The selection of metal-oxide powder to form the composite structure requires the i) effective refractive index, n , of the metal-oxide-SiO₂ composite film to be lower than that of ZnO film, ii) high contrast of refractive index between metal-oxide powder and SiO₂ matrix and iii) low optical absorption of the metal-oxide powder at the lasing wavelength. Hence, MgO and ZrO₂ powders (Aldrich Chemical) of refractive index (diameter) ~ 1.67 (~ 120 nm) and ~ 2.0 (~ 100 nm), respectively, are chosen.

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Figure 4.8: Schematic of a mirrorless ZnO thin-film waveguide laser, consisting of a metal-oxide-SiO₂ composite guiding layer and a ZnO thin-film active layer.

4.3.2 Fabrication Process

As outlined in section 4.2.2, several $2 \times 2 \text{ cm}^2$ SiO₂/Si substrates were first prepared. Then, a $\sim 300 \text{ nm}$ thick metal-oxide-SiO₂ composite film was deposited on the SiO₂ buffer layer by sol-gel technique to form the guiding layer.¹⁴⁵ The molar ratio of metal-oxide:SiO₂ and TEOS:IPA:H₂O were allowed to vary. Depending on the ratio, nano-composite films with and without stripe patterns could be fabricated. Finally, a $\sim 150 \text{ nm}$ thick ZnO thin film was deposited on the MgO (ZrO₂)-SiO₂ composite by the FCVA technique.¹³¹ This thickness was selected to optimize the optical gain and scattering inside the active and guiding layers, respectively. The substrate temperature and oxygen partial pressure were set to 230°C and $2 \times 10^{-4} \text{ Torr}$ respectively. Since the size of the samples and thickness of active layer were kept the same, it can be assumed that the amount of gain for all samples is the same and the only varying parameter was the MgO (ZrO₂) scatterers.

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4.3.3 Construction of Nano-composite Film with Randomly Distributed Powder

For the fabrication of MgO-SiO₂ nano-composite film with randomly distributed particles, the molar ratio of MgO:SiO₂ and TEOS:IPA:H₂O were set to 1:1 and 1:30:4 respectively. The field emission SEM (FE-SEM, JSM-6340F) image of the surface morphology and cross-sectional view are shown in figure 4.9. Some cracking of the film is observed due to the high concentration of powder embedded in the SiO₂ matrix. In addition, the surface is corrugated due to the presence of clusters, which consists of small MgO powder. The maximum height of the clusters is ~500 nm and on average, the thickness of the nano-composite film can be estimated to be ~300 nm.

4.3.3.1 Results

The optical characteristics of the disordered samples were studied at R.T. by focusing a pump stripe of length ~0.5 cm and width ~0.05 cm on the films. Emission is collected from the edge of the samples. Figure 4.10 shows the corresponding L-L curve and emission spectra. It is observed that at pump

Figure 4.9 (a) Surface morphology and (b) cross-sectional view of sample with MgO powder (molar ratio 1:5)

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Figure 4.10: (a) Light-light curve and (b) emission spectra of sample with 1:1 molar ratio of MgO:SiO₂ in 1:30:4 TEOS concentration. The inset is the emission far field profile at pump intensity of $\sim 1.5 \text{ MW/cm}^2$.

intensity of 0.1 MW/cm^2 , the emission spectrum has a FWHM of $\sim 12 \text{ nm}$ with peak at $\sim 386 \text{ nm}$. A sudden narrowing of emission spectrum occurs at $\sim 0.48 \text{ MW/cm}^2$ (i.e., the threshold). The far-field profile at 1.5 MW/cm^2 is also shown in the inset of figure 4.10a. It is noted that the emission shows non-axial radiation and is less polarization dependent.

The experiment is repeated by fabricating the sample with less scatterers at molar ratio of 1:5 (MgO:SiO₂). It is observed that the FWHM at $\sim 0.22 \text{ MW/cm}^2$ is $\sim 12 \text{ nm}$. Narrowing of emission spectrum to $\sim 4 \text{ nm}$ with a slight red shift of $\sim 1 \text{ nm}$ occurs only when the excitation intensity increases to $\sim 1.15 \text{ MW/cm}^2$. Sample with molar ratio of 1:10 is also fabricated and it is found that the pump threshold and FWHM are increased significantly. Table 4.3 summarizes the corresponding experimental conditions and results of the samples. The random distribution of MgO clusters inside the SiO₂ matrix will only sustain incoherent random lasing

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Table 4.3: Summary of experimental results for MgO samples without stripe pattern

Powder type, x	TEOS: IPA: H ₂ O	Molar ratio (x :SiO ₂)	Pump threshold (MW/cm ²)
MgO	1:30:4	1:1	0.48
		1:5	1.15
		1:10	2.3

(i.e., narrowing of emission spectra) in ZnO films as it does not satisfy the conditions of coherent random lasing. In the case of a better scatterer, ZrO₂ (i.e., large refractive index contrast between ZrO₂ and SiO₂ matrix), it is also found that only incoherent random lasing is exhibited from the samples with random distribution of ZrO₂ clusters for the same molar ratio as that of MgO powder.

4.3.4 Construction of Nano-composite Film with Patterned Powder

Coherent random lasing may be excited in ZnO films if stripe pattern of the metal-oxide clusters is formed inside the SiO₂ matrix.¹⁴⁵ Literature studies show that the formation of striations (radial outflow of line pattern) is due to the evaporation of solvent during spin-coating and Marangoni effect and therefore depends on the 1) mixture of sol, 2) spin speed and 3) viscosity.^{143,144} Generally, a more viscous sol will result in wider stripe spacing.¹⁴³ Thus, an attempt to form the stripe pattern via the variation of viscosity was carried out by keeping the molar ratio of MgO:SiO₂ constant at 1:5 (as too much metal-oxide powder in SiO₂ matrix will result in cracking of films and too little would reduce the scattering strength) while the concentration of TEOS:IPA:H₂O was prepared at 1:20:4, 1:10:4 and

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1:5:4. It was found that stripes of MgO clusters are formed at 1:10:4 and 1:5:4, but not at 1:20:4 TEOS concentration at a spin speed of 3500 rpm for 30 seconds.

4.3.4.1 Results and Discussion

Figure 4.11 shows the L-L curve and emission spectra of the samples with stripe pattern pumped under the same conditions as described in section 4.3.3.1. The inset in figure 4.11a shows the surface morphology of the MgO clusters in 1:10:4 TEOS concentration. It is observed that the stripe width of MgO clusters is ~ 8 to $11\ \mu\text{m}$ while the stripe spacing is $\sim 40\ \mu\text{m}$. For coherent lasing to occur, it is required that the pump stripe is set at an excitation angle θ ($= \sim 50^\circ$ to 55°) to the stripe pattern. At other angles, only ASE is obtained with intensity at least 4-5 times less than the lasing intensity. Due to the formation of closed loop paths

Figure 4.11: (a) Light-light curve and (b) emission spectra of sample with 1:5 molar ratio of MgO:SiO₂ in 1:10:4 TEOS concentration. The inset at the top of (a) shows the surface morphology and that at the bottom shows the emission of TE-dominant far field profile at pump intensity of $\sim 300\ \text{kW/cm}^2$.

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within the stripe pattern as shown in figure 4.12a,¹⁴⁵ low threshold of $\sim 85 \text{ kW/cm}^2$ is obtained. Sharp peaks of linewidth $\sim 0.4 \text{ nm}$ also emerged from the emission spectra. The increase in excitation intensity increases (redshifts) the number of sharp peaks (the emission spectra by $\sim 10 \text{ nm}$). The large redshift of emission spectra indicates a transition from excitonic to electron-hole-plasma radiative recombination due to better confinement and hence higher density of electron-hole pairs induced by the stripe pattern so that gain saturation is observed from the light-light curve.¹⁹ At higher pumping, more cavities (i.e., closed loop paths) of higher loss can be overcome such that more peaks emerge and overlap, resulting in some peaks to be unresolved. Since gain saturation regime has been reached, it is unlikely that the spectrum will transit to just a broad peak at even higher pumping.

On the other hand, the TE-dominant far-field profile of the lasing light exhibits a bright single-spot at $\sim 300 \text{ kW/cm}^2$, see the inset in figure 4.11a. This implies that strong lateral and transverse confinement of light occurs due to the presence of stripe pattern and ZnO waveguide structure, respectively. The stripe patterns of MgO clusters also provide strong suppression of TM polarization. For MgO clusters in TEOS concentration of 1:5:4, the corresponding stripe width (stripe spacing) is found to be $\sim 9\text{-}16 \text{ }\mu\text{m}$ ($\sim 56 \text{ }\mu\text{m}$). It is observed that the lasing characteristics are similar to that in figure 4.11 except the threshold increases to $\sim 1.2 \text{ MW/cm}^2$ and θ is also reduced to $\sim 14^\circ\text{--}18^\circ$. The experimental conditions and results for samples with stripe pattern are summarized in table 4.4.

It is observed that θ is related to the stripe width whereby a wider stripe (hence higher density of MgO clusters within each stripe) contributes to larger scattering angle, ϕ , and hence, the stripes have to tilt at a smaller θ from the pump stripe (since $\phi \approx 90^\circ - \theta$) for emission to be detected from the edge of the sample,

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see figure 4.12a. Generally, wider stripe spacing leads to less reflection of light between the stripes and reduces the chance for optical feedback. Moreover, the area of the pump stripe is the same. Hence less active regions are being excited so that the pump threshold is increased considerably. In addition, the higher scattering effect within each wider stripe (see figure 4.12) may result in higher chance of light escaping to the unpumped region, as compared to the thinner stripes. These account for the large increase in pump threshold for MgO clusters in 1:5:4 TEOS concentration as compared to that in 1:10:4. The lasing characteristics of stronger scatterers, $\text{ZrO}_2\text{-SiO}_2$ composite ZnO thin-film waveguide lasers, are also investigated. In this case, stripe pattern can be formed at TEOS concentration and $\text{ZrO}_2\text{:SiO}_2$ molar ratio of 1:30:4 and 1:5, respectively. The stripe width (stripe spacing) is $\sim 20\text{ }\mu\text{m}$ ($\sim 55\text{ }\mu\text{m}$) and θ is found to be $\sim 15^\circ\text{--}17^\circ$, which is quite similar to the MgO sample with molar ratio 1:5 in TEOS concentration 1:5:4.

Figure 4.13 shows the corresponding light-light curve and emission spectra. It is observed that the pump threshold occurs at $\sim 95\text{ kW/cm}^2$. The low pump threshold and better lasing spectra is due to the strong optical scattering of ZrO_2 clusters as compared to MgO clusters.

Table 4.4: Summary of experimental results for samples with stripe patterns

Powder type, x	TEOS: IPA: H_2O	Molar ratio ($x\text{:SiO}_2$)	Stripe width (μm)	Stripe spacing (μm)	Excitation angle, θ	Pump threshold (kW/cm^2)
MgO	1:10:4	1:5	$\sim 8\text{--}11$	~ 40	$\sim 50^\circ\text{--}55^\circ$	~ 85
	1:5:4	1:5	$\sim 9\text{--}16$	~ 56	$\sim 14^\circ\text{--}18^\circ$	~ 1200
ZrO_2	1:30:4	1:5	~ 20	~ 55	$\sim 15^\circ\text{--}17^\circ$	~ 95
	1:30:4	1:25	~ 15	~ 65	$\sim 20^\circ\text{--}25^\circ$	~ 1380

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Figure 4.12: Mechanism of how light travels within the stripes of MgO clusters (molar ratio 1:5). The TEOS concentration in the top (bottom) diagram is 1:10:4 (1:5:4). θ is the excitation angle of the pump stripe and ϕ is the scattering angle. It is noted that the pump stripe and detection of emission are always at right angle to each other as shown in the top left hand corner.

On the other hand, coherent random lasing can still be obtained in samples with lower molar number of ZrO_2 (and MgO) if stripe patterns are formed. For example, in the case where the molar ratio of $\text{ZrO}_2:\text{SiO}_2$ and TEOS concentration are equal to 1:25 and 1:30:4, respectively, the formation of stripe pattern can sustain coherent lasing. However, the number of sharp peaks (threshold) is reduced (increased to $\sim 1.38 \text{ MW/cm}^2$) due to the reduction of optical scattering. Hence, we have shown the importance of the formation of stripe pattern to achieve coherent lasing.

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Figure 4.13: a) Light-light curve and (b) emission spectra of sample with 1:5 molar ratio of $\text{ZrO}_2\text{:SiO}_2$ in 1:30:4 TEOS concentration.

4.4 Discussion on Striations

As discussed above, the formation of stripes of clusters is the key point in supporting coherent random lasing action in disordered gain medium. Therefore, it is important to understand how these stripes are formed and also the effect of the TEOS concentration on the stripe width and spacing during the sol-gel process based on literatures and experimental studies. The objective is to show that this technique is controllable. However, more detailed experiments are required to fully characterize these effects, which is beyond the scope of this thesis.

The method used for deposition of sol solution on substrates is the spin-coating technique. This process involves (i) depositing fluid on substrate, (ii) accelerating the substrate to the desired rotational speed, which creates a wavefront around the edges of the substrate, (iii) rotating the substrate at a constant speed for a certain period. This causes excess fluid to hurl off from the edge. This is the

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stage where viscous forces dominate and the process of spinning off fluid may result in edge effect (i.e., layer of thicker coating around the edges of the substrate). The degree of this effect depends on the surface tension, viscosity and rotation rate; and (iv) evaporating of some solvent from the surface after fluid stops to flow. This process determines the thickness of the film.^{147,146} From literatures, it has long been reported that the spin-coating technique will give rise to defects such as striations, comets and wafer edge effects.¹⁴⁷ These are also the common characteristics that can be found in the sol-gel films prepared for random lasing testing. In particular, the macroscopic view of the striation defects in sol-gel fabricated SiO_2 samples as shown in figure 4.14^{147, 148} resembles the surface morphology of TEOS solution (with powder) spin coated on Si substrates.

As for TEOS solution with powder, the stripes (radial spread from the centre) and circles (in the middle of sample) are replaced by the powder clusters. In fact, this kind of phenomena is common in spin-coating of colloidal suspensions.¹⁴⁹ Therefore, by knowing how striations are formed, this will aid in the understanding of how TEOS solution with powder can form radial spread of stripes of clusters.

Figure 4.14: Macroscopic view of striation defects obtained from sol-gel fabricated SiO_2 sample.

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During the preparation of the sol, a mixture of solvent, which includes TEOS, IPA, water and nitric acid, is used and each solvent has its own vapor pressure (related to the rate of evaporation) and surface tension (see table 4.5). It is believed that these two parameters will result in unbalanced capillary forces during the evaporation process of spin-coating,^{144,148} which then affects the width and spacing of the striations. It is noted that adding IPA in the sol will reduce its surface tension. During spin coating, IPA will evaporate at the fastest rate and leave behind a gel having a surface tension higher than the starting sol. Instability occurs and the top surface of the gel that has higher surface tension will pull the solution away from the adjacent region that has lower surface tension. This is known as the Marangoni effect and is affected by the change in surface tension with temperature, viscosity, gel thickness, difference in temperature between the top and bottom of the gel, and thermal diffusivity. Generally, the increase in the amount of IPA leads to more evaporation, and hence thinner films, see table 4.2.

On a separate experiment using TEOS concentration with IPA replaced by 2-methoxyethanol, only random distribution of metal-oxide powders (ZnO, MgO and ZrO₂) can be found in the nano-composite films. This is because the vapor pressure of water is higher than that of 2-methoxyethanol. Hence water will evaporate first and since it has a higher surface tension, the surface tension of remaining sol will be lower and the sol is stable.

Table 4.5: MSDS for solvents used in sol-gel solution

	TEOS	IPA	2-methoxyethanol	Water
Surface Tension (mN/m)	NA	24	33	72
Vapor Pressure @ 20 °C (mmHg)	2	33	6.17	17.54

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The viscosity of the sol affects the out-flow characteristics of fluid and the rate at which the striations are formed. This, together with the airflow condition in the spin-coater determines the amount of lateral traction of the gel. The evaporation of the solvent will increase the viscosity of the surface layer, which leads to a smaller Marangoni number and hence increase in stability and stripe spacing decrease.¹⁴³ In the above experiments, it is observed that a decrease in the amount of IPA (less evaporation as in the case of MgO molar ratio 1:5 in TEOS concentration 1:5:4 compared with TEOS concentration 1:10:4) will result in an increase in the stripe spacing ($\sim 56 \mu\text{m}$ compared with $\sim 40 \mu\text{m}$). Since the molar ratio of powder and size of the substrate are the same, the stripe width, which contains the powder will increase for a larger stripe spacing.

However it is noted here that the addition of powder will change the viscosity of the sol. In addition, different types of powder have different isoelectric point (IEP) as shown in table 4.6.¹⁵⁰ Coincidentally, it seems that materials with IEP less than 9 (i.e., ZnO and ZrO_2) seem to form striations easily at less viscous sol solution. Addition of SnO_2 powder (lower IEP) has also been shown experimentally to form striations in TEOS concentration of 1:30:4. Hence the stability of the powder in the sol may also affect the forming of stripes of clusters. Furthermore, it has also been reported that addition of ZnO powder affects the polymerization rate (hence material properties) of the sol.¹⁵¹ Thus other types of powder may also have this effect. However due to lack of proper equipment, it is difficult to measure the influence of the addition of different types of powder (i.e., size, IEP, pH, and concentration) on the properties of the sol, which eventually affects the formation of striations.

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Table 4.6: Isoelectric point of metal oxide powders¹⁵⁰

Powder type	ZnO	MgO	ZrO ₂	SnO ₂
IEP	9	12	4-6	4-5

4.5 Summary

In summary, R.T. random laser action with coherent feedback is realized in ZnO-SiO₂ and passive metal-oxide-SiO₂ nano-composite waveguide lasers prepared by the sol-gel technique. This process favors the formation of radial stripes of oxide clusters, which allows closed-loop paths of light to occur. These stripes act as high-quality random media and the proposed waveguide lasers provide 2-D confinement of light inside the nano-composite films.

The advantage of using the sol-gel technique is that these stripes of oxide clusters can be controlled via the viscosity of the TEOS solution and concentration of the powder. Furthermore, this technique allows coherent random lasing to occur even at low concentration of powder. Results show that the pump threshold of the random lasers are influenced by the concentration of powder, scattering effect of the nano-composite film (ie., type of powder in the film) and the stripe spacing. The effect of the particle density on the random lasing behavior of films is also found to be different to that of laser dye solution. In the latter, there is less stringent limitation on the amount of particles that can be added. As such a transition from incoherent to coherent random lasing can be observed with the increase of particle density.⁷² However for nano-composite film, too much particles may result in cracking of the film. In addition, the above ZnO-SiO₂ and metal-oxide-SiO₂ nano-composite waveguide lasers have shown that it is difficult to obtain coherent random lasing from thin films of randomly distributed particles.

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This probably accounts why some research groups can only achieve incoherent random lasing from their nano-composite films,^{103,137,139,152} unless the film is thick enough to support scattering in the transverse direction (i.e., 3-D scattering to lead to stronger scattering effect)

More importantly, it has been demonstrated that the lasing characteristics of random cavity lasers can be controlled and with the right choice of powder, the random lasers can exhibit low threshold and directional emission, which are compatible to that of FP lasers with cleaved facets. This will contribute to the future development of random lasers for practical applications.

5. Optically Pumped ZnO Disordered Film Waveguide Random Lasers

5.1 Introduction

In chapter 4, we have seen that radial stripes of powder clusters are critical in obtaining coherent random lasing emission from ZnO film and powder. Moreover, the stripe patterns provide lateral confinement of light such that directional circular beam profiles with minimal scattering are observed. On the other hand, coherent random lasing emission can be achieved easily by post-growth annealing of FCVA-deposited ZnO films. The nanograins formed during the thermal annealing process facilitate the formation of random cavities.³⁸ Nevertheless, the emission is non-directional and the modes are difficult to control. Therefore the two main objectives in improving the random lasing performance of ZnO disordered films are achieving (i) single mode operation and (ii) directional and coherent emission.

Currently, two techniques have been proposed to achieve single-mode operation in random media as described in chapter 2.4. Nevertheless, the requirement of small excitation and/or gain area and low pump rate will not allow high-power performance. On the other hand, most random lasers lack a good waveguide design, which is essential for the confinement and control of the propagation light such that directional emission can be achieved.¹⁵³ Recently, our group has demonstrated directional emission (i.e., low scattering loss and axial emission) from ZnO ridge waveguide structure with MgO capped layer.¹⁰⁴ It was proposed that the MgO layer acts as a cladding layer to trap the light scattered from the surface of the ZnO disordered film by total internal reflection since it has a refractive index ($n \sim 1.67$) lower than that of ZnO ($n \sim 2.1$). In addition, this

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method improves the pump threshold and emission efficiency. These imply that the use of small disordered gain medium with a proper waveguide design will reduce the modes and support higher power operation.

In this chapter, we report the lasing characteristics of the ZnO master oscillator power amplifier (MOPA) and rib waveguide designs to tackle the above problems. High-power reduced mode operation has been achieved by reducing the mode number using a small random medium and amplified it with a traveling wave amplifier in the MOPA design. On the other hand, significant mode reduction without much adverse effect on pump threshold has been observed from narrow rib waveguides. Strong directional TE-polarized emission has been observed from both waveguides. In addition, the polarization characteristics of the random media under the influence of optical rib waveguide are also investigated. This study is important because the presence of optical waveguide may alter the light scattering paths such that the polarization of the lasing emission does not only depend on the size and disordering of the random medium.^{88, 154} Therefore, if the designed polarization of the optical waveguide is different from that of the random medium, the corresponding lasing efficiency can be deteriorated. Rate equations analysis and Fourier transform studies are used to account for the polarization dependency random laser action under the influence of rib waveguide.

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5.2 ZnO Master Oscillator Power Amplifier (MOPA)

5.2.1 Design Consideration

1-D modeling of ZnO disordered thin film has been carried out by our group.¹⁵⁵ Using transfer matrix equations, the numerical solutions show (i) the number of lasing modes increases with higher pumping and saturates after a certain pump intensity, (ii) position of lasing modes depends on the configurations of ZnO grains and voids, (iii) pump intensity and pump length influence the photon density distributions, which in turn affects the number of lasing modes and (iv) the existence of spectral and spatial redistributions of lasing modes are due to localization and repulsion of the modes. The simulation results agree well with the 1-D calculation and experiments carried out by other research groups.^{83,94} In particular, for the simulation on various pump lengths, the results show that while lasing modes are greatly reduced when pump length reduces from 160 μm to 20 μm , the threshold pump intensity is only increased by 1.3 times.

This also means that if the size of the disordered medium is reduced, the lasing modes will be greatly reduced at the expense of slightly higher pump threshold. Thus high-power single mode emission may be realized by controlling the photon density distribution through selective excitation of the modes. The reduction in optical gain due to smaller gain medium size can be compensated if the lasing emission undergoes light amplification, which eventually leads to the master oscillator power amplifier (MOPA) design.

The proposed MOPA design as shown in figure 5.1 is made up of a short random cavity of length L_c and a uniform traveling wave amplifier (TWA) of length L_A ($=L_{A1}+L_{A2}$). As explained previously, the short random cavity will allow small number of lasing modes to exist in the device and the TWA will amplify the

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lasing emission. This is to ensure that high-power single-mode operation can be achieved. Numerical simulation has shown that the saturated mode number is less than 5 for random cavity of length $\sim 40 \mu\text{m}$. In addition, this length is easier to handle during the fabrication process. As such, the length of the random cavity is defined to be $40 \mu\text{m}$. As for L_A , the only requirement is that $L_{A1} + L_C$ should be smaller than the length of the pump stripe.

The random cavity can be easily achieved from post-growth annealing of our ZnO thin film fabricated by the FCVA technique.³⁸ Due to the growth in grain size and voids in the ZnO thin film during annealing, the formation of the lateral facets of the ZnO grains provide strong optical scattering and hence results in closed loop paths of light. On the other hand, the as-grown ZnO film fabricated by the FCVA technique is able to provide high optical gain.¹³¹ Thus, it can be used to form the TWA region to amplify the lasing peaks. Another thing to note is that in this design, transverse confinement of light is expected due to the presence of the

Figure 5.1: Schematic of the MOPA random laser design

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SiO₂ buffer layer. Based on previous calculations done by our group,¹⁵⁶ the thickness of the SiO₂ buffer layer is set to be ~400 nm as this thickness will allow high transverse coupling coefficient (>0.91) and low absorption loss ($<1.0 \text{ cm}^{-1}$).

5.2.2 Fabrication Process

The fabrication procedure for the proposed MOPA is shown in figure 5.2. The n-type (100) silicon substrate first underwent thermal dry oxidation to form a ~400 nm thick SiO₂ buffer layer. A ~180 nm thick ZnO thin film was then deposited by FCVA technique on the SiO₂ buffer layer as shown in figure 5.2a. During the deposition, the substrate temperature and oxygen partial pressure were set to 230 °C and 2×10^{-4} Torr, respectively. To form the random cavity, the ZnO thin film underwent post-growth annealing using standard Lindberg type furnace with quartz tube reactor at 900 °C for 2 hrs in open air as shown in figure 5.2b. A photoresist stripe, which has a width of 40 μm , was formed on the surface of the

Figure 5.2: Fabrication procedures of the ZnO MOPA

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Table 5.1: UV photolithography recipe

Photoresist	Intensity	Prebake	Exposure	Develop	Post bake
AZ 5214	5 mW/cm ²	90 °C, 2 min	20 sec	30 sec	120 °C, 5 min

annealed ZnO thin film by photolithography technique (Quintel Q2001 CT maskaligner), see figure 5.2c. The details of the photolithography process are shown in table 5.1.

The unmasked region of the annealed ZnO thin film was completely removed by wet etching using diluted HCl solution, see figure 5.2d. A ~220 nm thick ZnO film was then re-deposited on the sample by FCVA technique at the same deposition conditions as described above. It is noted here that the substrate temperature was set to 180 °C to prevent over-heating of the photoresist film. The photoresist film was then removed by dipping the sample in acetone for few hours. The end product of the fabrication is shown in figure 5.2e. For the sample to be tested, L_A and L_C were found to be ~0.2 cm and ~40 μm , respectively.

5.2.3 Results and Discussion

The optical characteristics of the ZnO film before and after annealing and the ZnO MOPA were studied at room temperature (R.T.) The optical pump was focused to a pump stripe of length 5 mm and width 8 μm on to the films. It is noted that the entire random cavity and TWA region are optically excited. Emission is collected from the edge of the films as shown in figure 5.1. Figure 5.3 shows the emission spectra for the as-grown and annealed ZnO thin films at excitation intensity of ~1.5 MW/cm². For the as-grown sample, a single-broad spontaneous emission spectrum with peak wavelength and FWHM of ~383 nm and ~15 nm,

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Figure 5.3: Emission spectra of the (a) annealed and (b) as-grown ZnO thin film at pump intensity of $\sim 1.5 \text{ MW/cm}^2$

respectively is observed. On the other hand, sharp peaks (i.e., lasing modes at $\sim 387 \text{ nm}$) with linewidth less than 0.4 nm emerged from the emission spectrum of the annealed ZnO sample. These indicate that our as-grown and annealed ZnO thin film exhibit ASE and coherent random lasing, respectively, as expected.^{38,131} It is expected that by reducing the width of the random cavity, the number of lasing modes appearing will reduce.

Figure 5.4 shows the light-light (L-L) curve and emission spectra of the MOPA. A kink at pump intensity of $\sim 1.3 \text{ MW/cm}^2$ is observed from the L-L curve. In addition, the spectral linewidth reduces from $\sim 13 \text{ nm}$ to $\sim 2 \text{ nm}$ as the input pump intensity increases above the kink. The presence of the kink accompanied by a narrowing of the spectral linewidth suggests the sample exhibits random lasing. It is also observed that the narrowing of the emission spectra ('C' and 'D') is caused by the merging of sharp peaks. It is noted that the peak wavelength of the emission spectra ($\sim 387 \text{ nm}$) is consistent with the peak emission wavelength of the random lasing spectrum as shown in figure 5.3. Hence, it is shown that the

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Figure 5.4: (a) Light-light curve and (b) corresponding emission spectra at various pump intensities for the ZnO MOPA

sharp peaks emitted from the short random cavity are under amplification as well as linewidth broadening inside the TWA. In addition, it is verified that the MOPA design can minimize the number of lasing modes. This is because the short random cavity only supports few sharp peaks as expected from the calculation.¹⁵⁵ The comparison between the spectra width given in figure 5.3a (~10 nm) and that given in curve 'A' (~2 nm) of figure 5.4b supports our claim. Furthermore, it is found that the facets of the MOPA laser are too rough (too low reflectivity) to sustain FP modes.¹³¹

In order to verify that the annealed ZnO thin film has been fully etched and the re-deposited ZnO thin film on the etched surface will not give rise to extra lasing peaks, a simple test is carried out to measure the spectrum of the re-deposited ZnO thin film. This is done by using a black plastic to cover the anneal

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ZnO stripe region. The spectrum obtained at $\sim 1.6 \text{ MW/cm}^2$ is shown in figure 5.5. It shows only a broad spectrum emission at $\sim 383 \text{ nm}$. Figure 5.6 shows the near and far fields of the TE mode of the ZnO MOPA. It is noted that the intensities of the TE mode and the unpolarised mode for the field profiles obtained are similar. However the TM mode profile ‘disappears’, implying that the TM mode of the output field profile has been strongly suppressed. Therefore this implies that the emission is TE dominant and light is confined in the lateral direction due to the waveguide structure.

Figure 5.5: Spectrum of re-deposited ZnO thin film on etched surface

Figure 5.6: TE field profile of ZnO MOPA laser

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5.3 ZnO Rib Waveguide Lasers

5.3.1 Waveguide Design

In a conventional FP laser, the cavity length determines the longitudinal modes and the thickness of the gain medium affects the transverse modes of the laser, which follows the theory of optical waveguide as described briefly in chapter 2.1. On the other hand, properties such as the number of lasing modes, cavity length and lasing threshold will change if the size of a random medium changes, see chapter 2.3. This may also affect the polarization characteristics of the random media. Therefore, ZnO rib waveguide random lasers, as illustrated in figure 5.7, are designed and fabricated for the study of the lasing characteristics. In this experiment, the width, w , of the ZnO random medium is allowed to vary while the length and thickness of the ZnO film are fixed. As such, any changes in the polarization characteristics will be a result of a change in the formation of random cavities due to the change in w . For transverse confinement of light, the ZnO film is grown on SiO_2/Si substrate.

Figure 5.7: Schematic of ZnO rib waveguide random laser with stripe of width w

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5.3.2 Fabrication Process

A ~ 400 nm thick SiO_2 buffer layer was first formed on (100) Si wafer by thermal dry oxidation. Then, a ~ 180 nm thick ZnO film was deposited on the buffer layer by the FCVA technique.¹⁰⁴ To form the random cavities, post-growth annealing of the ZnO film was carried out in a furnace in open air at 900°C for 2 hrs.¹⁰⁴ Subsequently, a line mask was made on the surface of the annealed ZnO film by photolithography technique using the recipe in table 5.1. The unmasked ZnO region was then etched to the SiO_2 buffer layer at an etching rate of ~ 4.5 nm/min by ion-beam sputtering method (Kaufman gridded ion source).¹⁰⁴ The recipe for ion beam etching is shown in table 5.2. A low ion-beam current and voltage were used to prevent hardening of the photoresist and surface damage to the unmasked region. Several ZnO rib waveguide random lasers with a fixed length (~ 0.1 cm) and width, w (~ 1.7 to $6.5\ \mu\text{m}$) were fabricated.

Table 5.2: Ion Beam Etching Recipe

Ion beam source	Accelerator	Ar Pressure	Etching rate
600 V 65 mA	300 V 4 mA	3×10^{-4} Torr	4.5 nm/min

5.3.3 Results and Discussion

The UV lasing characteristics of the samples were studied at R.T. A pump stripe of length ~ 0.2 cm and width $\sim 200\ \mu\text{m}$ was focused parallel to the stripe. Emission was collected from the edge of the sample as shown in figure 5.7. The polarized emission was also recorded by placing a polarizer before the detector.

In general, all the samples exhibit a broad spontaneous emission spectrum

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with emission peak at ~ 385 nm under optical excitation of intensity, $P < P_{th}$, where P_{th} is the pump threshold. For $P > P_{th}$, sharp lasing peaks start to emerge and the number of lasing peaks increases with the increase of P until saturation (i.e., $\sim 2 \times P_{th}$) is reached. Figure 5.8a shows the influence of w on the TE lasing spectra of the samples at $P = 2 \times P_{th}$. For the annealed ZnO film (without a rib waveguide), the emergence of many lasing peaks overlapped to form a broad spectrum. For the rib waveguide laser with $w \sim 6.5$ μm , the corresponding emission spectrum is similar to that of the annealed film except that the overall spectrum width is reduced from ~ 6.4 to ~ 4.1 nm. Further reduction of w does not change the spectrum width until w reaches ~ 3.0 μm . It is observed that the number of lasing peaks is significantly reduced and can be resolved spectrally to ~ 13 peaks. Figure 5.8b shows the TE spectra of sample with $w \sim 1.7$ μm . It is clearly observed that the emission spectrum is narrowed to ~ 1 nm. In addition, the total number of lasing peaks is ~ 6 at $2 \times P_{th}$ and the linewidth of each lasing peak is ~ 0.4 nm. The inset in figure 5.8b shows the near field profiles of the TE polarization at $2 \times P_{th}$ for w at 6.5 and 1.7 μm , respectively. At $w = 6.5$ μm (1.7 μm), three (one) transverse modes, which indicates strong confinement of light inside the rib waveguides, are (is) observed.

Figures 5.8c and 5.8d show the corresponding TM lasing spectra of the samples. The trend of the change in the emission spectra is similar to that of TE polarization. The inset of figure 5.8d compares the number of lasing peaks for both TE and TM polarizations versus w at $2 \times P_{th}$ (i.e., saturation pump intensity). It shows fewer lasing peaks for TM polarization, especially when w is small (< 3.6 μm). The near field profile of TM polarization is similar to that of TE polarization (except the emission intensity is much weaker) and is not repeated here.

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Figure 5.8: TE optical spectra of ZnO random lasers with (a) various w at $P = 2 \times P_{th}$, and (b) for $w \sim 1.7 \mu\text{m}$ at various P . Inset shows the near field profiles for $w = 6.5$ and $1.7 \mu\text{m}$ sample at $P = 2 \times P_{th}$. TM optical spectra of ZnO random lasers (a) with various w at $P = 2 \times P_{th}$, and (d) for $w \sim 1.7 \mu\text{m}$ at various P . Inset plots the number of TE and TM lasing peaks against w and area of stripe. Optical spectra of annealed ZnO thin film (i.e., without rib waveguide) are also shown in the figures for comparison.

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Figure 5.9 plots P_{th} for both TE and TM polarizations versus w . It is observed that P_{th} for both polarizations increases with the reduction of w and the increase in P_{th} for TM polarization is faster than that of TE polarization. The P_{th} of the annealed ZnO film for both polarizations is found to be $\sim 0.28 \text{ MW/cm}^2$. The variation of P_{th} for both polarizations with w can be approximated by $P_{th,TE(TM)} \sim A_{TE(TM)} + \chi_{TE(TM)}/w$ where $A_{TE(TM)}$ and $\chi_{TE(TM)}$ are two constants to be determined. As P_{th} of both polarizations is roughly inversely proportional to w , the rib waveguide lasers are considered to exhibit 2-D random laser action.⁸² It can be shown that $P_{th,TM}/P_{th,TE}$ increases (i.e., from 1 to ~ 1.23) with the decrease of w . This indicates that the cavity loss of TM polarization is always higher than that of TE polarization and thus results in higher pump threshold. Therefore, the relatively larger cavity loss of TM polarization reduces the probability of forming random

Figure 5.9: The 2 extrapolated curves (solid lines) show the relationship between the pump threshold P_{th} and the stripe width w . It is found that A_{TE} (A_{TM}) is 0.273 MW/cm^2 (0.26 MW/cm^2) and χ_{TE} (χ_{TM}) is 0.1195 MW/cm (0.273 MW/cm). The linear fit graph (dashed line) shows the ratio of slope efficiency η_{TE}/η_{TM} at different w .

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cavities so that fewer lasing peaks are observed from the spectra. Figure 5.9 also plots the ratio of slope efficiency between TE and TM polarizations, η_{TE}/η_{TM} , versus w . η_{TE}/η_{TM} increases (from ~ 1.4 to ~ 3.2) with the reduction of w (from 6.5 to 1.7 μm). This shows that TE polarization is dominant in rib waveguide random lasers especially with small w .

From the earlier experimental results, two phenomena, which are different from other random lasing media, are observed from our rib waveguide random lasers: i) The rib waveguide lasers are TE dominant while others mostly, reported to be TM dominant.^{88,154,157} ii) The number of lasing peaks from the rib waveguide lasers is less than that from the circular disk structure⁸² (i.e., for gain area of $\sim 2500 \mu\text{m}^2$, the saturated number of lasing peaks from the rib waveguide is ~ 14 while that from the disk structure is ~ 35).

The polarization characteristics of rib waveguide random lasers can be understood from the rate equations for population density, n , and photon number density, ϕ , as shown.¹⁵³

$$\frac{dn}{dt} = \frac{P}{h\nu d} - \frac{n}{\tau} - c_g \sigma n \phi, \quad (5a)$$

$$\frac{d\phi}{dt} = -\frac{\phi}{\tau_p} + c_g \Gamma \sigma n \phi, \quad (5b)$$

where $h\nu$ is the photon energy at pump wavelength, d is the thickness of active medium, τ is the carrier lifetime, c_g is the group velocity, σ is the emission cross section, Γ is the confinement factor and τ_p is the photon escape lifetime from the random medium. From equation (5), the slope efficiency, η ($\equiv \phi d h\nu / P$) of both polarizations can be expressed as $\eta = \Gamma \tau_p (1 - h\nu d / c_g \sigma \Gamma \tau \tau_p P)$. For large P , $\eta \sim \Gamma \tau_p$,

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$$\frac{\eta_{TE}}{\eta_{TM}} \approx \frac{\Gamma_{TE}}{\Gamma_{TM}} \frac{\tau_{p,TE}}{\tau_{p,TM}}. \quad (6)$$

From equation (6), the relationship between η_{TE}/η_{TM} and Γ_{TE}/Γ_{TM} indicates that the polarization of the random media is affected by the presence of optical waveguide. At threshold, $dn/dt = 0$, $d\phi/dt = 0$, $\phi \approx 0$. Hence, from equation (5), we can write $P_{th}/h\nu d = 1/c_g \tau_p \sigma \Gamma$ so that $\tau_{p,TE}/\tau_{p,TM} \sim P_{th,TM}/P_{th,TE}$ as $\Gamma_{TE}\sigma_{TE}/\Gamma_{TM}\sigma_{TM} \sim 1$ (i.e., from the slope of the lines in figure 9 of ref 156). Thus, $\tau_{p,TE}/\tau_{p,TM}$ is always greater than 1 and is increased with the reduction of w . From our effective index method calculation, it is found that Γ_{TE} (Γ_{TM}) is approximately equal to 0.791 (0.538) for rib waveguide with $w = 6.5 \mu\text{m}$ and is reduced to 0.764 (0.492) for $w = 1.7 \mu\text{m}$. Although the value of Γ_{TE}/Γ_{TM} is almost independent of w , it is noted that $\Gamma_{TE} > \Gamma_{TM}$ for all w . Hence, we can conclude that TE polarization is dominant inside the rib waveguide.

If a FP cavity is used to model the rib waveguide random lasers, the equivalent effective reflectivity, R , (i.e., proportional to the scattering strength) can be associated with τ_p by $\tau_p^{-1} \sim c_g L^{-1} \ln(1/R)$ where L is the path length of closed-loop paths inside the rib waveguide random laser.¹⁵³ Hence, the effective reflectivity for both polarizations can be related by

$$\frac{\tau_{p,TE}}{\tau_{p,TM}} = \frac{L_{TE} \ln(1/R_{TM})}{L_{TM} \ln(1/R_{TE})} > 1 \quad (7)$$

where L can be deduced from the fundamental harmonic of the Fourier transform (FT) of the corresponding lasing spectra.¹⁵⁸

Figure 5.10a shows the Fourier transform of the TE spectra for $w = 6.5$ and $1.7 \mu\text{m}$ at $P = 2 \times P_{th}$. The relationship between L and w for both polarizations at $P = 2 \times P_{th}$ is plotted in figure 5.10b. It is observed that L increases linearly with w .

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Figure 5.10: (a) Fourier transform of the TE lasing spectra of ZnO waveguide random lasers with $w = 6.5$ and $1.7 \mu\text{m}$. (b) The variation of path length, L , (i.e., obtained from the fundamental harmonic of the Fourier transformed spectra) for both TE and TM polarizations versus w .

This implies that the width of the rib waveguide (with fixed length of $\sim 0.1 \text{ cm}$) limits the light scattering closed-loop paths. This explains why the rib waveguide structure shows less lasing peaks than the disk structure for the same gain area. On the other hand, the value of $L_{\text{TE}}/L_{\text{TM}}$ is independent of w as shown in figure 5.10b. From figure 5.9, it is noted that the value of $\eta_{\text{TE}}/\eta_{\text{TM}}$ (and hence $\tau_{p,\text{TE}}/\tau_{p,\text{TM}}$ as given by equation (6)) increases with the reduction of w . Therefore from equation (7), it can be shown that the reduction of w increases the value of $R_{\text{TE}}/R_{\text{TM}}$ (since $L_{\text{TE}}/L_{\text{TM}} < 1$ for this range of w). As $0 < R_{\text{TM}} < R_{\text{TE}} \leq 1$, TE polarization experiences stronger optical feedback (i.e., large scattering strength) within the closed-loop

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paths than TM polarization. Therefore, the higher scattering strength of TE polarization inside the random media especially for small w also contributes to the dominant TE lasing emission. The weak optical feedback (i.e., weak scattering strength) of TM polarization may be due to the short column length of ZnO grains whereas the dominant TM polarization reported in refs. 88,154, and 157 is due to the infinite height (i.e., vertical direction) of the random media.

5.4 Summary

In conclusion, MOPA and rib waveguide lasers have successfully demonstrated reduced mode operation and directional edge emission. In the MOPA design, preliminary results have proven that 1) the lasing modes from the short random cavity can be amplified by the TWA of the MOPA laser and 2) the number of lasing modes is limited by the design of short random cavity. It is expected that the intensity of the lasing mode will increase with longer L_A . However L_{AI} should not be too long as the pump stripe has to excite both the TWA and the random cavity regions to achieve the desired output from our design. Also, a larger L_A may induce higher amplification of light such that broadening of the lasing emission may occur. Thus much work needs to be done to study the effect of L_A on the lasing properties of the lasing mode.

On the other hand, the polarization characteristics of ZnO rib waveguide random lasers were investigated. It is shown that ZnO rib waveguide random lasers with narrow stripe exhibit stronger TE lasing emission than the one without waveguide. Rate equation analysis has shown that the dominant TE polarization is attributed to the large Γ_{TE} and R_{TE} inside the random media due to the presence of rib waveguides. In addition, FT studies have shown that the width of the rib

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waveguide confines the closed-loop paths to smaller region and thus reduces the number of lasing peaks. Furthermore, the random cavities formed are linear since the cavity length increases linearly with the rib width. Hence, the experimental results agree well with the 1-D rate equation analysis.

The two waveguide designs have shown that it is possible to achieve low mode operation and yet achieve strong emission. They also show the importance of the waveguide structure in confining the emission such that in-plane scattering can be achieved. This proves random scattering can be controlled, which will be useful for future development of random lasers.

6. Disordered ZnO Film Based Light-Emitting Diodes

6.1 Introduction

ZnO based devices are more useful if they are operated electrically. Moreover, ZnO is a promising semiconductor material to fabricate high-efficiency UV LEDs. A summary on the ZnO based LEDs that have been fabricated and tested at room temperature (R.T.) is listed in table 1.3. It is observed that most LEDs are based on as-deposited ZnO films, nanowires and nanorods, except for ref. 65 where Zn films are oxidized at 550 °C in oxygen atmosphere to form *n*-ZnO films. So far, the effect of nanoparticles on the emission efficiency of ZnO LEDs has not been reported. On the other hand, nanoparticles play an important role in improving the performance of polymer-nano-composite LEDs. It is believed that the increase in reliability, current density and light output strongly depend on the device morphology.¹⁵⁹ In addition, nanoparticles can also act as scatterers to improve the light extraction from LEDs.¹⁶⁰ It is also reported that by nanotexturing the surface of the films, the external quantum efficiency can be improved by 30%.¹⁶¹ Therefore, if nanoparticles are introduced into ZnO based LEDs, the operation performance may be much improved. In the earlier sections, we have seen that ZnO nanoparticles can be in the form of powder or nanograins. We shall first investigate the effect of ZnO nanograins on the light emitting performance.

Nanograins (of size ~100 nm) can be formed inside ZnO film by thermal annealing technique. It has been reported that this technique can improve the UV emission of ZnO thin films.¹⁶²⁻¹⁶⁴ However, thermal annealing process may also introduce multiple energy levels in the ZnO bandgap so that the corresponding optical and electrical properties can be affected. Therefore, the influence of thermal annealing on the EL of ZnO based LEDs are studied in details.

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6.2 Design of Disordered LED

For this study, *p-i-n* heterojunction diodes were fabricated. Although the realization of reproducible and reliable *p*-type ZnO has been achieved,¹⁵ further improvement on the hole concentration of the *p*-type ZnO may be required to obtain high-quality ZnO homojunction LEDs. ZnO and GaN are similar in many aspects of their physical properties and *p*-type GaN is often used as the hole injection layer in ZnO-based heterostructure LEDs, see table 1.3. Therefore, it is necessary to further understand the radiative recombination mechanism at the interface of *n*-ZnO/*p*-GaN when thermal annealing technique is employed as a means to improve the extraction efficiency of the ZnO based heterojunction LEDs. The schematic of the heterojunction diode is shown in figure 6.1 and the fabrication details are explained in the section 6.3.

Figure 6.1: Schematic of the *n*-ZnO:Al/*i*-ZnO/*p*-GaN:Mg heterojunction LED on sapphire substrate.

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6.3 Fabrication Details

A ~ 130 nm thick intrinsic ZnO (*i*-ZnO) layer was deposited by the FCVA technique on a ~ 3 μm thick *p*-type GaN:Mg film grown on (0001) sapphire substrate (i.e., obtained from Technologies and Devices International, Inc).¹²⁹ During deposition, the oxygen partial pressure and substrate temperature were set to $\sim 5 \times 10^{-4}$ Torr and ~ 250 °C, respectively. The sample was then cleaved into 2 pieces (of size $\sim 1 \times 1$ cm²) and one of them was thermally annealed in open air at 900 °C for 2 hrs. It was reported that loosely packed ZnO grains were formed inside the annealed samples.¹⁶² Both as-deposited and annealed samples were then deposited with a layer of ~ 200 nm thick *n*-type ZnO:Al (3%) (i.e. 3 at.% of Al in the Zn:Al alloy target) film by FCVA technique with oxygen partial pressure and substrate temperature set to $\sim 5 \times 10^{-4}$ Torr and ~ 150 °C, respectively.⁶¹ Under the same deposition condition, another ~ 100 nm thick ZnO:Al (5%) layer was deposited onto the samples to form transparent contact. In order to realize ohmic contact on the *p*-type GaN:Mg layer, one-third of the samples were coated with photoresist and the exposed regions were then dipped into HCl to etch away the *i*-ZnO and *n*-ZnO:Al layers. A ~ 100 nm thick Ti layer was then deposited onto the *p*-type GaN:Mg layer by e-beam evaporation. A ~ 100 nm thick Ni was also e-beam evaporated to form the ohmic contact for ZnO:Al film.⁶¹

6.4 Construction of Contact Holder

The EL setup is shown in figure 3.5. To ease the testing of the diode, a Teflon sample holder is made. A square hole of 8×8 mm² is cut off from the centre of the holder. An Aluminium (Al) metal of size similar to the hole is cut for placing the sample on it. The sample attached to the Al metal is then supported

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Figure 6.2: Illustration of Sample Holder with Contacts.

using a transparent ITO (ZnO:Al (5%)) film coated on quartz for p (n)- electrode, in front (as shown in figure 6.2) and a spring at the back.

6.5 Results and Discussion

Electrical pulses (with repetition rate of 13 Hz and pulse width of 60 ms) were used to drive the LEDs so that self-heating effect (i.e., red-shift of emission spectrum) can be avoided. Light is then collected from the surface of the ZnO:Al (5%) transparent contact by an objective lens.

Figure 6.3 compares the electroluminescence (EL) spectra of the as-deposited and annealed LEDs. From figure 6.3a, a weak emission spectrum with peak wavelength and FWHM of ~ 387.4 and ~ 38 nm, respectively, is observed from the as-deposited LED at low bias. As the bias increases, the FWHM slightly reduces to ~ 32 nm and the corresponding peak wavelength slightly blue-shifts by ~ 2.4 nm. The increase in optical gain with the bias current leads to the narrowing of emission spectra. In addition, the slight blue-shift of peak wavelength is likely to be due to the influence of band filling effect.¹⁶⁵ In fact, the measured EL

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characteristics of the as-deposited LED are similar to that reported in the literatures.^{165,166}

On the other hand, the emission characteristics of the annealed LED are quite different to that of the as-deposited LED. From figure 6.3b, it is observed that the peak wavelength of the EL spectra blue-shifts from ~ 506 to ~ 413.8 nm and the corresponding FWHM reduces from ~ 80 to ~ 60 nm with the increase in bias. The blue-shift of the EL spectra can be explained by the on-set of radiative recombination at the blue and green emission bands. In figure 6.3b, the EL spectra (dashed lines) are fitted by two Gaussian curves (solid lines) with peak wavelength of ~ 435 and ~ 504 nm at low bias. We allowed a blue-shift (~ 20 nm for blue band and ~ 35 nm for green band) of these Gaussian curves with the increase in bias current. It is observed that all the EL spectra can be fitted well by the combination

Figure 6.3: EL spectra of the (a) as-deposited LED and (b) annealed LED with different bias current. The EL spectra for the annealed LED are fitted with two Gaussian curves. The original (curve-fitted) EL spectrum is given by the solid (dashed) line.

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of the two Gaussian curves. Hence, this indicates that the large blue-shift of the EL spectra is due to the competition between the green and blue bands with different intensities.

Figure 6.4 compares the current-voltage (I-V) and light-current (L-I) characteristics of the as-deposited and annealed LEDs. From the I-V curves given in figure 6.4a, it is observed that both devices exhibit rectifying diode like behavior but the annealed LED has better I-V response (i.e., larger breakdown reverse bias voltage). The inset of figure 6.4a shows the I-V characteristics of two as-deposited Ti contacts (with area of $1 \times 2 \text{ mm}^2$ and separation of 1.5 mm) on *p*-GaN:Mg layer. It is observed that the I-V curve of the as-deposited Ti/*p*-GaN:Mg contacts exhibit roughly ohmic behavior. Hence, we have proven that the rectifying diode-like I-V behavior is attributed to the formation of *p-n* junction between the *i*-ZnO and *p*-GaN:Mg layers. The corresponding L-I curves are plotted in figure 6.4b. The turn-on current of the as-deposited and annealed LEDs is found to be ~ 0.22 and ~ 0.08 mA, respectively. Furthermore, the emission efficiency (i.e., slope efficiency) of the annealed LED is 1.3 times better than that of the as-deposited LED. The plots of peak wavelength of the emission spectra for both as-deposited and annealed LEDs versus forward bias current are also shown in figure 6.4b. It is observed that the annealed LED has a drastic shift in peak wavelength from ~ 506 to ~ 420 nm for the increase in bias current to 0.4 mA. For bias current above 0.4 mA, the peak wavelength remains at ~ 410 nm. This indicates that the green (blue) band is dominant at bias current below (above) 0.4 mA.

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Figure 6.4: (a) *I-V* characteristics of the as-deposited and annealed LED. The inset in (a) shows the *I-V* characteristic for the Ti metal contact deposited on GaN:Mg/sapphire substrate. (b) Light intensity and peak wavelength versus bias current for both as-deposited and annealed LEDs.

Annealed ZnO heterostructure LED with the replacement of *p*-type GaN:Mg on sapphire substrate by a single-face polished *p*-type SiC (4H) (obtained from Cree, Inc) as the substrate was also fabricated. This is because *p*-type SiC contributes no PL and EL emission.⁶¹ Hence, the corresponding EL spectra will be mainly due to the radiative recombination from the annealed *i*-ZnO layer. Figure 6.5 shows the R.T. EL spectra of the *n*-ZnO:Al/*i*-ZnO/*p*-SiC heterostructure LED with the same thermal annealing treatment as mentioned before. At bias current of ~0.28 mA, a broad green band emerges from the EL spectrum with peak wavelength at ~501.4 nm. As current increases, the peak wavelength of the green band is slightly blue-shifted to ~496.4 nm and a weak UV emission with peak wavelength at ~383.9 nm also emerges from the EL spectrum. This agrees well with the PL spectrum of annealed ZnO films after thermal annealing.¹⁶² However, green emission tends to dominate in EL due to higher probability for electrons to be trapped at the defect states or grain boundaries. It is observed from the *I-V*

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Figure 6.5: EL spectra and I-V characteristic for the $n\text{-ZnO:Al}/i\text{-ZnO}/p\text{-SiC}$ heterostructure with thermal annealing treatment

curves that the turn-on voltage of the LED is $\sim 20\text{V}$, which is larger than that reported in $n\text{-ZnO}/p\text{-SiC}$ heterojunction LED (i.e., 3.8 V).⁶¹ In addition, the measured leakage current at reverse bias voltage of -35 V is less than $\sim 2\text{ }\mu\text{A}$. This is because the thermal annealing process at $900\text{ }^{\circ}\text{C}$ will start the oxidation process of SiC at atmospheric pressure and forms a thin SiO_2 layer between the interface of ZnO and SiC layers.¹⁶⁷ Hence, we believe that the green band emission from the ZnO/GaN heterostructure LED is from the annealed $i\text{-ZnO}$ layer while the blue band originates from the annealed $p\text{-type GaN:Mg}$ layer.

To understand the origin of the blue emission band, we studied the PL of the as-deposited and annealed GaN:Mg films under the excitation of a continuous wave He-Cd laser (325 nm). Figure 6.6 shows the PL spectrum of the annealed GaN:Mg film on sapphire substrate. A sharp peak at $\sim 362\text{ nm}$ is observed with a tail extending to $\sim 520\text{ nm}$. The curve can be fitted with two Gaussian curves at

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~363 and ~400 nm. The emission at ~363 nm is attributed to the near band edge emission of GaN whereas emission at ~400 nm is likely to be transition from the conduction band to the Mg acceptor level.^{45,68} As for the as-deposited one, the corresponding PL spectrum is similar except that the intensity is lower for both peaks. The inset in figure 6.6 also shows the PL spectrum of an *i*-ZnO layer deposited on GaN:Mg/sapphire. It is observed that the as-deposited *i*-ZnO layer exhibits an excitonic emission at ~387 nm. Hence, we can conclude that the EL emission from the annealed LED is due to the combination of radiative recombination from the *i*-ZnO (at ~500 nm) and *p*-GaN:Mg (at ~410 nm) layers. The EL emission of the as-deposited LED, however, is mainly due to the emission from the *i*-ZnO layer (at ~387 nm).

Figure 6.6: PL spectrum for an annealed GaN:Mg film on sapphire substrate. The PL spectrum is fitted with two Gaussian curves with peak wavelength at ~363 nm and ~413 nm. The inset shows the PL spectrum of an as-deposited *i*-ZnO film on GaN:Mg film/sapphire substrate.

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6.5.1 Carrier Transport Mechanism

To investigate the blue-shift of the emission spectrum of the annealed LED under forward bias, it is necessary to understand the carrier transport mechanism inside the junction diodes. The basic material properties of the various layers needed for constructing the band diagram are listed in table 6.1. Using the data, the energy band diagram before and upon contact for Ti/*p*-GaN/*i*-ZnO/*n*-ZnO:Al/*N*-ZnO:Al/Ni are shown in figure 6.7 and 6.8, respectively. As the exact value of the work function for ZnO:Al is unknown due to lack of proper equipment for testing, it can only be estimated from the literature to give a rough idea on what the energy band structure looks like.

Table 6.1: Material properties of the films for the construction of junction diodes

	<i>p</i> -GaN:Mg	ZnO	ZnO:Al	Al	Ti	Ni	<i>p</i> -SiC (4H)
Bandgap, E_g (eV)	3.4	3.37	No data	-	-	-	3.26
Electron affinity, χ (eV)	3.3 ref:168 or 4.2 ref:169	4.35 ref:170	No data	-	-	-	3.6 ref:171
Work function, ϕ (eV)	5.5 – 5.8 ref:168 or 6.7 ref:172	5.3 ref:173	3.7-4.4 ref:174 or 5.2 ref:175	4.28 ref:176	4.33 ref:176	5.1 ref:176	No data
High frequency dielectric constant, $\epsilon_{r,hf}$	5.2 ref:177	8.1 ref:178	No data	-	-	-	6.52 ref: 179
Static dielectric constant, ϵ_r	10.0 ref:177	4.0 ref:178	No data	-	-	-	9.66 Ref: 177
Concentration, (cm ⁻³)	10^{18}	10^{20} ref: 129	$>10^{20}$ ref: 130	-	-	-	10^{19} ref: 61
Mobility (cm ² /Vs)	1-10	12 ref: 129	>13 ref: 130	-	-	-	120 ref: 61

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Figure 6.7 Energy band diagram for Ti/p-GaN:Mg/i-ZnO/n-ZnO:Al/N-ZnO:Al/Ni heterojunction structure before Fermi level alignment

Figure 6.8: Energy band alignment at the (a) contacts and (b) p-i-n-N layers at the point of contact

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Based on the work function of the various materials, it is observed that the metal/semiconductor interface for both *p*- and *n*- type materials exhibit schottky contacts. Nevertheless, the I-V characteristics show that they form ohmic contacts. A possible mechanism for this is through tunneling since the barrier width, W , is small at both contacts. Generally, $W = \sqrt{\frac{2\epsilon_r\epsilon_o}{qN_{a,d}}(V_{bi} - V - \frac{kT}{q})}$, where V_{bi} is the built-in voltage, $N_{a,d}$ is the acceptor or donor concentration.¹⁸⁰

The depletion width extends into the intrinsic layer of the LED and hence excitonic radiative recombination tends to occur inside the *i*-ZnO layer.^{63,68} Moreover, barriers for electron injection to the *i*-ZnO layer are smaller as compared to the hole injection and are likely to be confined in the *i*-ZnO region. Similar transport mechanism is also observed in annealed LED except that radiative recombination at the defect/interface states dominates inside the *i*-ZnO layer. This is because thermal annealing process increases the number of defect levels at the grain boundaries/interfaces. The presence of the defect states (i.e., either donors and/or acceptors) will result in a change in the Fermi level. However the exact type of defects that exist in the film is hard to quantify as there are much controversy over the mechanism of the green band emission.¹⁸¹ Nevertheless, experimental study on the mechanism of defect emission carried out by Djuricic *et al* has revealed that for green band emission, the defects are mainly located at the surface.¹⁸¹ Hence, defect states may also occur at the *p*-GaIn:N:Mg/*i*-ZnO interface. Therefore, electrons confined in the *i*-ZnO region are likely to be trapped at the defect states and increases the probability of recombination at these states. At larger forward bias, the barrier at the *p*-GaIn:N:Mg/*i*-ZnO interface reduces and energetic electrons diffuse further into the *p*-GaIn:N:Mg layer so that radiative

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recombination at the acceptor states of the p -GaN:Mg layer occurs. As a result, there is a competition between the recombination processes at the p - and i - layers. Inevitably, this leads to a shift of the EL spectra with applied bias (i.e., as shown in figure 6.3b). Due to better optical properties of GaN:Mg film as compared to that of i -ZnO film, recombination process at the p -layer leads to higher emission intensity. These account for the enhancement (reduction) of output intensity (turn-on current) as observed in figure 6.4b. As for the device with p -SiC substrate, luminescence can only take place in the intrinsic layer since there is no radiative recombination from p -SiC substrate and hence large blue-shift of EL spectra is not observed.

6.6 EL Under Reverse Bias

EL has been reported under reverse biasing for p -GaN/ n -ZnO heterojunction diodes.^{45,64} Therefore, the polarity of the pulsed circuit to the contacts was interchanged to investigate if EL also occurs under reverse bias (RB) and if the RB EL differs for diodes with and without thermal annealing treatment. Figure 6.9a shows the EL spectra for the as-deposited LED. It is noted that two emission peaks at ~ 357 nm and ~ 406 nm are observed. The increase in RB current slightly red-shifts (blue-shifts) the UV (blue) emission peak by ~ 5 nm (~ 23 nm). On the other hand, for the annealed LED, an increase in RB current results in a blue shift of the peak wavelength by ~ 4 nm and a reduction of FWHM to ~ 64 nm.

Comparing the EL in figure 6.9 with the PL in figure 6.6, it is likely that radiative recombination occurs at the near band-edge and deep acceptor level at the p -region. As injection voltage increases, recombination starts to occur at the interface between the i -ZnO and p -GaN region for the as-deposited LED. This

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Figure 6.9: EL spectra of (a) as-deposited and (b) annealed LED under RB

accounts for the shift in emission from 406 nm to 383 nm as shown in figure 6.9a. As for the annealed LED, the thermal annealing process results in more transition levels (i.e., defect states) in the p - and i - regions. As such, radiative recombination mainly takes place at the acceptor levels. In fact, the measured EL characteristics of the as-deposited LED are similar to that reported in ref. 64. However this contradicts with that in ref. 45 where recombination first occurs in n -ZnO region at low reverse bias and then at p -GaN region at higher reverse bias.

In this case, tunneling at the p -GaN/ i -ZnO interface may not be the sole mechanism for the presence of RB current. The potential barrier at Ti/ p -GaN interface is smaller than that at Ni/ N -ZnO:Al interface (see figure 6.8a). Hence, it is easier for the minority electrons to tunnel to the p -GaN layer and recombine with the majority holes in the valence band and acceptor level. In addition, the large number of electrons in the valence band of p -GaN layer can also easily tunnel to the conduction band of i -ZnO layer, resulting in reverse current to occur.

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With higher RB voltage, recombination will also take place in the *i*-ZnO region. For annealed LED, the increase in surface states in *p*-GaN traps more carriers such that recombination only occurs at the *p*- region for the range of RB voltages tested.

As for the case where *p*-SiC(4H) substrate is used, the larger built-in voltage at the interface between *p*-SiC(4H) and *i*-ZnO results in a wider depletion width. This makes tunneling difficult and thus RB current is small.

6.7 Summary

The influence of thermal annealing (i.e., to form nanograins) on the EL characteristics of the *n*-ZnO:Al/*i*-ZnO/*p*-GaN:Mg heterojunction LEDs has been studied. It is demonstrated that a large blue shift of ~96 nm in the peak wavelength occurs under the control of applied voltage. We have verified that the tuning of emission spectrum is due to the combination of two emission spectra at blue (i.e., recombination between GaN conduction band and Mg acceptor level) and green (i.e., defect related green band emission from ZnO grain boundaries/interfaces) bands. Furthermore, we have shown that the emission efficiency (turn-on current) of the LEDs can be improved (reduced) by thermal annealing treatment. This is because the optical properties of the *i*-ZnO and *p*-GaN layers have been improved by thermal annealing. Light extraction from the surface is also enhanced due to the rougher surface as a result of thermal annealing process. In addition, EL can also be observed under RB and radiative recombination mainly occurs in the *p*-region.

7. ZnO Nano-composite Based Heterojunction Laser Diodes

7.1 Introduction

Chapter 6 shows that the technique of thermal annealing (i.e., increases surface roughness of the film) indeed increases light extraction. However, the increase in grain boundaries results in oxygen or zinc to diffuse more easily into the polycrystalline film. As such, vacancies can be formed easily and induce more recombination at the defect states (i.e., green emission band).¹⁶² On the other hand, thermal annealing will also cause the number of native acceptors in *p*-GaN film to increase and hence blue band emission increases.⁶⁵ This is detrimental to the UV performance of the LEDs.

It may be easier to obtain strong UV emission using ZnO powder. This is because the PL of ZnO powder shows stronger UV than green emission. The advantage of using ZnO powder in the design of LEDs is not just limited to enhancing light extraction. They can also be used as gain and/or scattering medium to induce random laser action.⁴⁰ However this property has not been explored in electrically pumped devices. The main reasons are the difficulty in injecting carriers into the nanoparticles and at the same time have high pumping efficiency and gain to sustain scattering effect. It is also difficult to realize high-quality random media as most reported nano-composite random media exhibit incoherent random lasing action, see table 4.1. In addition, the dispersion effect of the nanoparticles in the film^{159,182} and the size of the particles¹⁸³ do play a part in the performance of electrically pumped devices.

Although random lasing has also been observed from dielectric powders doped with rare-earth ions under electrical injections, they require bias voltage of few kilo-voltages.^{114,115} Therefore, it seems technically challenging to fabricate UV

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ZnO random laser diodes. Nevertheless, it is still highly desirable to achieve lasing from the ZnO random media under electrical excitation. This is because the use of random media can avoid the difficulty in cleaving smooth facets from the ZnO material to sustain lasing so that this will lead to low-cost and high-volume fabrication of UV laser diodes.³⁸

In chapter 4, effective UV random lasing from the patterned ZnO-SiO₂ nano-composite films under optical excitation has been demonstrated. This is because the appropriate patterning of ZnO clusters enhances the lasing characteristics (i.e., higher gain and lower loss) of the random media.¹⁴⁵ Furthermore, the sandwiching of nanoparticles between the electron and hole injection layers has shown to enhance the injection efficiency of carriers so that the nanoparticles can attain high optical gain under electrical excitation.^{184,185} Hence, if the patterned ZnO-SiO₂ nano-composite films can be used as the intrinsic layer of the ZnO-based heterostructural *p-i-n* junctions,⁶¹ UV random lasing action may be achieved.

In this chapter, the use of nano-composite intrinsic layer in a *p-i-n* heterojunction diode to form random lasing action will be investigated. Both surface emitting and edge emitting random lasers have been demonstrated by manipulating the injecting layers and concentration of the powder. The factors i.e., size and concentrations of powder affecting the random lasing behavior are also investigated.

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7.2 Surface Dominant UV Random Lasing from p -SiC(4H)/ i -ZnO-SiO₂ Nano-composite/ n -ZnO:Al Heterojunction Diode

7.2.1 Design Consideration

Figure 7.1 shows the schematic of the p -SiC(4H)/ i -ZnO-SiO₂ nano-composite/ n -ZnO:Al heterojunction diode structure. ZnO:Al (5%) film is used as an ohmic contact for ZnO:Al (1%) film. The few considerations to take into account in the preparation of the intrinsic layer include (i) the nano-composite film should support random lasing action, (ii) the fabrication process of the intrinsic layer should complement that of the whole diode, (iii) the ZnO powder may act as a resistor; therefore clustering of powder should be minimized, (iv) the ZnO powder should touch the n -ZnO:Al film and the p -SiC substrate, and (v) in regions without the powder, there should be an insulating film between the n -ZnO:Al film and p -SiC substrate but this layer should not be so thick to increase the series resistance.

Figure 7.1: Schematic of the p -SiC(4H)/ i -ZnO-SiO₂ nano-composite/ n -ZnO:Al heterojunction diode structure.

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The above considerations can be satisfied easily using the sol-gel technique to fabricate a thin layer of nano-composite film. However, as described in chapter 4, this technique requires high temperature annealing (950 °C, 5 min). Therefore, in here, hybrid nano-composite film prepared by the sol-gel technique is proposed to act as the intrinsic layer for the heterojunction diode.

7.2.2 Fabrication Process

Two sets of hybrid SiO₂ sols were prepared using Tetraethylorthosilicate (TEOS), 3-(Trimethoxysilyl) propylmethacrylate (MPS), IPA and water at a molar ratio of 0.75:0.25:50:4. This recipe was used so that the thickness of the SiO₂ matrix was ~60-100 nm. TEOS and MPS act as the precursor for the inorganic and organic SiO₂ film, respectively. 3% by weight of photoinitiator (hydroxyl methylpropiophenone) may be added to make it UV curable. But in this case, thermal processing was used to polymerize the film. ZnO powder was then added to the sol and stirred for 2 days. The molar ratio of ZnO:SiO₂ was set to 1:5. ZnO powder of size 100 nm (Aldrich) and 60 nm (Nanophase) were used for the preparation of the intrinsic layer. This was to enable the study on the effect of the size of the powder on the performance of the diode. The prepared sol was then spun-coated onto the single-side polished *p*-SiC(4H) substrate (5x5 mm², Cree, Inc) at a spin speed of 3500 rpm for 30 sec. The film was formed by heating the samples on a hotplate at 110 °C for 30 min.

A ~250 nm thick ZnO:Al (1%) and a ~50 nm thick ZnO:Al (5%) films were then deposited onto the samples by the FCVA technique. The substrate temperature and oxygen partial pressure were set to 150 °C and 5×10^{-4} Torr, respectively. Metal contacts were formed on the rough surface of the *p*-SiC

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substrate and ZnO:Al (5%) layer by depositing Al (25 nm)/Ti (150 nm) and Ni (100 nm) films, respectively using e-beam evaporation.

7.2.3 Results and Discussion

The sample holder used is similar to that in figure 6.2. But in this case, ZnO:Al (5%) film coated on quartz is used as the *n*- electrode while positive power supply is connected to the Al metal that supports the back of the *p*-SiC (4H) substrate using silver epoxy. The room temperature (R.T.) EL measurement setup of the diodes is shown in figure 7.1. The biasing voltage is a train of rectangular pulses with pulse width and repetition rate of 60 ms and 13.7 Hz, respectively. The emitted light from the surface of the *n*-layer was collected via an objective lens.

Figures 7.2a and b show a portion of the surface morphology of the diodes with 100 and 60 nm ZnO powder, respectively with the *n*-layer films on top of the powder. The insets of the figures show the radial outspread profile of the powder stripes on the spin-coated substrates. The region where emission is measured is also circled in the inset of the figures. It is observed that ZnO clusters with stripe pattern are formed across the intrinsic layer. In the centre region, only random distribution of ZnO clusters is observed. The diode with 60 nm ZnO powder tends to form wider and longer stripes of clusters with closer spacing than the one with 100 nm ZnO powder. This is because although the molar ratio of ZnO to SiO₂ is the same, 60 nm ZnO powder being smaller and hence lighter will have more particles in the sol. Moreover, smaller powder size tends to form clusters more easily than larger one. Figure 7.2c shows the cross-sectional SEM image of the diode with 60 nm ZnO powder. It is observed that the ZnO clusters, which cause

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Figure 7.2: Surface morphology of the diodes with (a) 100 nm and (b) 60nm ZnO powder taken from an optical microscope. The insets show the schematic of the surface for the whole diode and the circled part shows the region where the emission and surface morphology are obtained. (c) Cross-sectional SEM image for the diode with 60 nm ZnO powder.

the formation of corrugated surface of the diodes, are enclosed inside the SiO_2 matrix.

Figure 7.3a shows the EL spectra of the diode with 100 nm ZnO powder. A weak visible spectrum (i.e., with wavelength stretching from 400 to 550 nm), which is due to the defect state radiative recombination, is observed at low injection current. However, the emergence of UV emission with peak wavelength at ~ 383 nm suppresses the visible spectrum at large injection current. It is noted that strong UV emission (i.e., within detection range of $\sim 10^\circ$ from the normal of the sample plane) is only supported near the region as indicated in the inset of

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figure 7.2a where stripes of clusters are more distinct. In regions nearer to the centre, the random distribution of ZnO clusters result in large scattering loss and as such UV emission is weak and the intensity of defect-state radiative recombination is almost equally strong under high injection current of ~ 3 mA as shown in the inset of figure 7.3a. To the naked eye, both diodes appear green in the centre region and purplish-white in the outer regions under high injection current. This indicated that the patterned ZnO clusters forms high-quality random media so that UV emission is promoted under electrical excitation. At injection current of ~ 1.8 mA, sharp peaks with linewidth ~ 0.5 nm start to emerge from the emission spectrum and the excitation of sharp peaks is more prominent at higher injection current.

Figure 7.3b shows the EL spectra of the diode with 60 nm ZnO powder. Narrowing of the UV spectra is observed from the diode. The FWHM of the UV spectra reduces from 19 to 11 nm with an increase in injection current. The peak wavelength of the emission spectra, however, remains at ~ 383 nm for different values of injection current. Sharp peaks of linewidth ~ 0.5 nm also emerged from the emission spectra at high injection current. It is believed that the narrowing of emission spectra is due to incoherent random lasing action and this is favourable for the diode with denser and longer stripe pattern of ZnO clusters. The emergence of sharp peaks, which are attributed to coherent random lasing action, is due to the presence of stripe patterns to allow the formation of closed-loop random cavities.^{145,186} To verify that the sharp peaks correspond to the formation of closed-loop random cavities, FT is applied to analyze the EL spectra obtained at high injection current. The corresponding FT spectrum as shown in the inset of figure 7.3b exhibits periodic features, indicating the formation of closed loop paths.¹⁵⁸

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Figure 7.3: EL spectra for the p-i-n diode with (a) 100 nm and (b) 60 nm ZnO powder. Inset of (a) shows the EL emission obtained near the centre of the diode at injection current of ~3 mA. Fourier transform spectrum of the EL emission of the diode with 60 nm ZnO powder biased at 3.2 mA is shown in inset of figure 7.3b. (c) Possible mechanisms to achieve random laser action inside the diodes.

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The fundamental (shortest) cavity path formed is $\sim 6.2 \mu\text{m}$, which approximates to the spacing of the closest stripes. This value is smaller than the diode with 100 nm ZnO clusters ($\sim 7.5 \mu\text{m}$) since the stripes are more closely spaced. Higher harmonics indicating larger closed loop paths can also be formed inside the diodes.

Using the CBS experiment, the transport mean free path, l_t , of the medium (i.e., ZnO-SiO₂ layer) with 60 and 100 nm powders is estimated to be ~ 30 and $\sim 36 \mu\text{m}$, respectively. Since the medium with 60 nm powder has slightly closer stripes than that with 100 nm powder, it is expected that more scattering will take place between the stripes in the medium with 60 nm powder and hence the value of l_t for medium with 60 nm powder is smaller than that with 100 nm. The large l_t obtained also tallies with the weak disordering from both diodes. This implies that the condition of $kl \sim 1$ to obtain strong localization of light may not be necessary if there is a way to form high quality optical cavity in the media. Although it has been reported that sharp peaks can also be observed in samples with large kl as light can travel very long paths in the sample (i.e., not due to formation of closed loop paths), the study is only limited to 3-D samples and not for solid samples.⁹³ On the other hand, the formation of closed loop paths between the stripes of ZnO clusters is believed to be the key point for the cause of narrowing of EL spectra and emergence of lasing peaks. This is because it has been previously verified in chapter 4 that the stripes are important for the coherent feedback.¹⁸⁶

Figure 7.3c explains the formation of random laser action inside the intrinsic layer of the diodes. If stimulated recombination occurs inside the ZnO powder (i.e., as indicated in figure 7.1), light will emit in all directions. Some of it will travel in open-loop zig-zag paths to result in further amplification and get scattered by the ZnO clusters so that incoherent random lasing is obtained.

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Coherent random lasing is due to the closed-loop zig-zag paths of light. In addition, the lack of transverse confinement of light (i.e., the refractive indices of SiC substrate and n -ZnO:Al layer are higher than that of the ZnO-SiO₂ nano-composite layer) and corrugated surface favors surface emission of the diode but limits the formation of random cavities (i.e., only a few peaks can be excited).

Figure 7.4a plots the output intensity and FWHM of the emission spectra of the diodes versus injection current. The electrical characteristics of ZnO heterojunction LEDs reported before in ref. 61 are also plotted for comparison. It is observed that the diode with 60 nm ZnO powder has better electrical-to-optical conversion efficiency than that with 100 nm ZnO powder. It is also noted that the use of ZnO powder as the intrinsic layer can increase the emission efficiency as well as reduce the FWHM of the emission spectra of the heterojunction diodes. This improvement is expected as it has been reported previously that the use of nanoparticles as the scatterers can help to enhance the light extraction from the light emitting devices.¹⁵⁹

Figure 7.4 (a) L-I and (b) I-V characteristics of the diodes with 60 nm and 100 nm ZnO powder. The data for the p-n heterojunction ZnO LED given in ref 61 is also included for comparison. The change in FWHM of the UV spectra with injection current is also plotted in (a).

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Figure 7.4b shows the corresponding I-V characteristics of the diodes. It is observed that the diode with 100 nm ZnO powder has higher turn-on voltage than that with 60 nm ZnO powder. Also, the series resistance for diode with 100 nm ZnO powder is $\sim 6 \text{ k}\Omega$ and is ~ 1.7 times larger than that of the diode with 60 nm ZnO powder ($\sim 3.5 \text{ k}\Omega$). This implies that the ZnO clusters are electrically active since they provide conducting paths in the diode and act as radiative recombination centres, especially for the diode with the 60 nm ZnO powder (i.e., more clusters and therefore more conducting paths). Hence, a smaller powder size is preferred for better lasing spectra and better operating efficiency. As expected, the turn-on voltage and series resistance ($\sim 1.5 \text{ k}\Omega$) of the heterojunction diode from the literature⁶¹ is the lowest as the corresponding light emitting layer is *n*-doped.

The PL spectra of the diodes at R.T. were studied under optical excitation by a Nd:YAG laser (355 nm) operating at pulsed operation (6 ns, 10 Hz). Optical pump was achieved by using a cylindrical lens to focus a pump stripe of length ~ 5 mm and width $\sim 50 \text{ }\mu\text{m}$ in a direction parallel to the surface of *n*-ZnO:Al(1%). The emission was obtained from the surface of the quartz substrate via an objective lens. Figure 7.5a shows the PL spectra of the diode with 60 nm ZnO powder. At low excitation intensity, the FWHM and peak wavelength of the UV spectrum are ~ 17.4 and $\sim 383 \text{ nm}$, respectively. With higher excitation intensity, it is observed that the wavelength of the emission peak red-shifts to $\sim 386 \text{ nm}$ and the FWHM of the emission spectrum reduces by $\sim 13 \text{ nm}$. In addition, sharp peaks emerged from the emission spectra at high excitation intensity. For the diode with 100 nm ZnO powder, similar optical characteristics are also observed from the emission spectra.

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Figure 7.5 (a) PL for diode with 60 nm ZnO powder. The inset shows the PL for ZnO:Al (1%) film on p- SiC(4H) and for a layer of 60 nm ZnO powder deposited on glass. (b) Light-light curve for the diodes with 60 nm and 100 nm ZnO powder. The change in FWHM of the UV spectra with excitation intensity is also plotted for both diodes.

Figure 7.5b plots the output intensity and the FWHM of the emission spectra of the diodes versus excitation intensities. The threshold pump intensities of both diodes are roughly equal to 0.15 MW/cm^2 . However, the conversion efficiency of the diode with 60 nm ZnO powder is better than that with 100 nm ZnO powder. This is consistent with the L-I curves shown in figure 7.4a. Furthermore, the trend in narrowing of the emission spectra under the influence of optical excitation is similar to that of the electrical excitation as shown in figure 7.4a. Hence, both diodes exhibit random laser action under electrical and optical excitations. The enhancement in emission (i.e., larger narrowing of spectra and higher output emission) under both excitations for the diode with 60 nm ZnO powder imply that closer and longer stripes of clusters form better cavities. On the other hand, the peak wavelength of the diodes under electrical excitation is

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stationary at ~ 383 nm and that under optical excitation is red-shifted from ~ 383 to ~ 386 nm. The inset of figure 7.5a shows the PL spectra of 60 nm ZnO powder uniformly deposited on a glass substrate and of a ZnO:Al(1%) film deposited on a SiC substrate under optical excitation of ~ 0.4 MW/cm². No narrowing of FWHM is observed from the PL spectra. This is because narrowing of emission spectrum can only be obtained from patterned ZnO clusters.^{145,186} The peak wavelength of the 60 nm ZnO powder and the ZnO:Al(1%) film is found to be ~ 382.7 and ~ 385 nm, respectively. These indicated that the PL spectra of the diodes arise from the competition of the emission spectra of the ZnO-SiO₂ nano-composite layer and the ZnO:Al(1%) film. At low pump intensity, emission from the patterned ZnO clusters, which has better optical properties than ZnO:Al(1%) film, dominates the PL spectrum. At high pump intensity, emission from the ZnO:Al(1%) film (i.e., the top layer) contributes to the red-shift of the PL spectrum. In addition, the narrowing of the PL spectrum is due to the support of an incoherent random lasing action inside the patterned ZnO nano-composite layer. On the other hand, the EL peak coincides with the PL emission of the ZnO powder and this verifies that stimulated recombination takes place inside the electrically active ZnO clusters rather than at the ZnO:Al film.

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7.3 Directional Edge-Emitting UV Random Lasing from $p\text{-GaN:Mg}/i\text{-ZnO-SiO}_2$ nano-composite/ $n\text{-ZnO:Al}$ Heterojunction Diode

7.3.1 Random Laser Diode Design

The work described in chapter 7.1 shows that the use of high refractive indexed $p\text{-SiC}$ substrate causes most of the scattered emission to occur from the surface. If higher (lower) refractive indexed intrinsic (injection) layers were used, transverse confinement of light can be realized to sustain in-plane lasing inside the nano-composite film. In this proposed diode, the $p\text{-SiC}$ substrate is replaced by a GaN:Mg/sapphire substrate. In order to further improve the transverse confinement of light, a more heavily doped (i.e., lower refractive index) ZnO:Al film is used as the carrier injection layer. The schematic of the heterojunction diode is illustrated in figure 7.6.

Figure 7.6: Schematic of $p\text{-GaN}/i\text{-ZnO-SiO}_2$ nano-composite/ $n\text{-ZnO}$ heterojunction diode. The formation of the closed-loop random cavity is illustrated in the figure. The inset shows the cross-section SEM image of the diode with molar ratio 1:5.

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7.3.2 Fabrication Process

The preparation of the nano-composite film is similar to that described in section 7.2.2. In this experiment, only ZnO powder of size 60 nm (Nanophase) is prepared since it has been clearly shown that this size is preferred over the 100 nm ZnO powder for better lasing spectra and efficiency, see chapter 7.2. The molar ratio of ZnO:SiO₂ was varied from 1:1 to 1:10.¹⁴⁵ For this experiment, half of a 8×5 mm² *p*-GaN/sapphire substrate (Technologies & Devices International Inc) was coated with photoresist. Then the ZnO-SiO₂ sol was spun coated on to the substrate at a spin speed of 3500 rpm for 30 sec and then thermally polymerized to form a film by baking in a furnace for ~2 hrs at 110 °C. Radial spreading of stripes of ZnO clusters, which extend out from the centre to the edges of the sample, is formed inside the nano-composite film. After that, a ~200 nm thick ZnO:Al(3%) film followed by a ~100 nm thick ZnO:Al(5%) film were deposited using FCVA technique to form the *n*- layers.¹⁸⁷ Ti (100 nm) and Ni (100 nm) were then e-beam evaporated onto the *p*- and *n*- layers respectively. The cross-section SEM image of the heterojunction diode with molar ratio 1:5 (see the inset of figure 7.6) shows that the ZnO clusters are embedded within the SiO₂ matrix.

7.3.3 Results and Discussion

Figure 7.7a shows the EL spectra measured from the edge of the diode with molar ratio 1:5 (denoted as diode A). The diode was biased under electrical pulses (60 ms, 12.6 Hz) at R.T.. The corresponding I-V curve, which shows a rectifying behavior, is also plotted in the inset of figure 7.7a. It is observed from figure 7.7a that at injection current, $I < 4.3$ mA, a broad spontaneous emission spectrum at ~395 nm is recorded. As $I > 4.3$ mA, sharp peaks, with average linewidth of ~0.6

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nm, at ~ 386 nm start to emerge from the spectra and the number of sharp peaks increases with I . Radiative recombination is likely to occur inside the ZnO clusters and the excitation of random lasing action is due to the presence of ZnO patterned stripes inside the nano-composite layer, which facilitates the formation of closed-loop zig-zag paths (i.e., closed-loop random cavities; see figure 7.6).^{145,186,187} For $I > 8.5$ mA (i.e., high concentration of injected electrons), the lasing spectra blue-shifted to ~ 372 nm. This indicates that radiative recombination starts to take place at the interface between the p - and i - layers and eventually dominates the entire recombination process. The inset of figure 7.7a also shows the far-field emission taken from the edge of the diode at $I = 15.8$ mA. Several spots along the interface between GaN:Mg and ZnO:Al layers were observed. This shows that the formation of closed-loop random cavities within the ZnO-SiO₂ nano-composite layer is obtained and the emission observed from the edge of the diode is directional.

Figure 7.7b shows the EL spectra measured from the surface of diode A. Only broad spontaneous emission spectra with peak at ~ 386 nm are observed and no sign of gain narrowing or lasing peak is recorded with the increase of I . This is because the patterned stripes of ZnO clusters (which have stripe width and spacing of ~ 7 and ~ 16 μm , respectively, see the inset in figure 7.7b) are not dense enough to support scattering of lasing light to the surface. The L-I curves of diode A are also plotted in the inset of figure 7.7b. A kink at I equals to 4.3 mA (i.e., turn-on current, I_{to}) is observed in the L-I curve for the case of edge emission. It is noted that for $I < I_{to}$, both edge and surface emissions are of similar intensity.

When $I > I_{to}$, the intensity of edge emission increases exponentially and lasing peaks emerged from the emission spectra. However, the intensity of surface emission is suppressed at $I > I_{to}$. The above results show that the presence of lower

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Figure 7.7: EL spectra recorded from the (a) edge and (b) the surface of diode A. The inset of (a) shows the far-field profile of the diode. The I-V curves for diodes A and B are also plotted in the inset of (a). The surface morphology of diode A taken at $5\times$ optical magnifications and L-I curves for the surface and edge emissions are shown in the inset of (b).

refractive-indexed injection layers enhances the transverse confinement of in-plane scattered light inside the nano-composite layer so that lasing emission is observed from the edge of diode A. Similar results have been observed for diodes with higher molar ratios (i.e., lower concentration of ZnO powder) and are not repeated here. However, for diodes with lower molar ratio, a different phenomenon is observed.

The above measurements are repeated for another diode (denoted as diode B) with molar ratio 1:1 of the nano-composite layer. The I-V curve of diode B is also plotted in the inset of figure 7.7a for comparison.

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Figure 7.8: EL spectra recorded from the (a) edge and (b) the surface of diode B. The inset of (a) plots the L-I curves for the surface and edge emissions. The inset of (b) shows the surface morphology of diode B taken at $5\times$ optical magnifications.

Figure 7.8 shows the emission spectra measured from the edge and surface of diode B. Unlike diode A, the edge emission of diode B (see figure 7.8a) only exhibits weak and broad emission with peak at ~ 410 nm. However, sharp lasing peaks are observed from the surface of diode B (see figure 7.8b). The L-I curves of diode B are plotted in the inset of figure 7.8a. It is observed that surface emission is more intense than edge emission and sharp lasing peak appears at ~ 386 nm for $I > I_{to}$ (~ 4 mA). This is unexpected as the effective refractive index of the nano-composite layer is increased due to high concentration of ZnO clusters, which should lead to a better transverse confinement of light.

To investigate why edge lasing emission is only supported in diodes with less concentration of ZnO clusters, we study the surface morphology of the diodes

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(see inset of figures 7.7b & 7.8b). The ZnO clusters inside diode B are more closely packed (i.e., more corrugated film surface) than that in diode A, and the corresponding stripe width (spacing) is found to be ~ 3 (~ 11) μm wide. We also estimated the path length of closed-loop random cavities of both diodes A and B by Fourier transform. The fundamental path length of closed-loop random cavity of diode A (B) biased at $2 \times I_{to}$ is found to be ~ 6 (14) μm .¹⁸⁷ It is noted that edge lasing emission is not supported in diodes with spacing of patterned stripes smaller than the fundamental path length because the strong scattering effect will supersede the transverse optical confinement of the diode.¹⁶⁰

For further verification, the surfaces of diodes A and B were optically pumped by a tripled-frequency pulse operated Nd:YAG laser (355 nm, 6 ns, 10 Hz). The excitation light is collimated to a pump stripe of length ~ 5 mm and width ~ 50 μm at an angle of $\sim 15^\circ$ to the stripes of ZnO clusters.^{145,187} Emissions were then collected from the surface and edge of the diodes. Figure 7.9 shows the PL spectra obtained from the diodes at pump intensity of ~ 0.9 MW/cm^2 . It is observed that the intensity of edge emission from diode A (B) is stronger (weaker) than that of the surface emission. These emission characteristics of the diodes are consistent with that under electrical excitations.

On the other hand, sharp peaks (broad spectra) at peak wavelength of ~ 374 nm (~ 383 nm) were observed from the edge (surface) emission of both diodes under optical excitations. These indicated that the lasing peaks observed under electrical injection of carriers are from the nano-composite layer. The emission peak at ~ 374 nm is the result of re-absorption of ~ 362 nm light emitted from GaN layer by ZnO clusters. This is reasonable as the excitonic recombination of ZnO powder is at ~ 383 nm and the PL of *p*-GaN/sapphire consists of a strong near

Figure 7.9: PL spectra measured from the surface and edge of diodes A and B under optical excitation of $\sim 0.9 \text{ MW/cm}^2$.

band-edge emission at $\sim 362 \text{ nm}$ and a weak recombination due to transition of electrons in the conduction band to the deep Mg acceptor level at $\sim 400 \text{ nm}$.⁴⁵

To further examine the emission characteristics of the diodes, we measured the ratio of surface to edge emission intensities of the diodes with different molar ratios, see figure 7.10. The diodes were driven by electrical pulses at a constant biased current of $2 \times I_{t0}$. It is observed that edge emission is favored for diodes with molar number of SiO_2 , x , larger than 4.5 (i.e., low concentration of ZnO cluster). However, the reduction of x from 4.5 increases the scattering strength inside the nano-composite layer so that edge emission is suppressed. This is because the strong off-plane scattering of lasing light deteriorates the transverse confinement of light inside the diodes. On the other hand, I_{t0} decreases with the reduction of x

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Figure 7.10: Relationship of surface/edge emission intensity taken at $2 \times I_{to}$ and I_{to} with the molar ratio (ZnO:SiO₂) of the nano-composite layer.

(i.e., increase in the concentration of ZnO clusters). This is expected as the volume of active region is directly proportional to the concentration of ZnO clusters. Therefore, there is an optimum value of x (i.e., 5 in this study) to achieve directional emission from the edge of the diodes and maintain a reasonably low I_{to} value.

7.4 Summary

These results demonstrate the realization of electrically pumped UV random laser diodes. The narrowing of the emission spectra and the emergence of sharp peaks have confirmed the existence of random laser action inside the laser diodes. It is shown that the UV emission of the laser diodes originates from the ZnO-SiO₂ nano-composite layer and the use of ZnO powder can improve the

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electrical-to-optical conversion efficiency of the heterojunction diode. In addition, the patterned ZnO clusters in the SiO₂ matrix enhance the quality of random media so that random lasing action can be sustained.

The size of powder is found to influence the scattering effect of the nano-composite layer, which in turn affects the performance of the diodes. On the other hand, the use of relatively low refractive indexed carrier injection layers (i.e., cladding layers) and relatively high refractive indexed intrinsic layer with stripes of ZnO clusters (i.e., core layer) allows the transverse confinement of in-plane closed-loop random cavities. Hence, directional lasing emission can also be observed from the edge of the diodes. However highly concentrated ZnO clusters, intended to enhance the transverse confinement and optical gain, do not aid in the achievement of guided wave laser action in the intrinsic layer. It is believed that this study will aid in the future design and development of more practical UV random laser diodes.

8. Conclusions and Recommendations

8.1 Conclusions

Directional and coherent UV random laser action has been achieved from both optically and electrically pumped nano-composite random lasers. The use of sol-gel technique to fabricate the SiO_2 matrix involves the use of a mixture of chemicals, which favor the arrangement of radial outspread of stripes of powder clusters. Studies have shown that these stripes aid in the formation of closed loop paths of light for coherent feedback and are believed to be the primary cause for forming high quality random media. In optically pumped nano-composite random lasers, the effects of the concentration of powder and stripe spacing on the lasing behavior have been analyzed. For active nano-composite films containing ZnO powder, it is found that coherent random lasing can still be obtained from low concentration of ZnO powder but at the expense of high pump threshold. On the other hand for passive nano-composite films, the pump threshold depends on the type of powder (i.e., MgO or ZrO_2) and the stripes spacing. The stripes also provide lateral confinement of light such that the edge emission is directional.

In electrically pumped nano-composite random lasers, the size of the powder is found to affect the series resistance and lasing EL spectra. The turn-on voltage is slightly higher than some of the ZnO film based LEDs and this is attributed to the presence of SiO_2 insulating layer between the ZnO powder and the carrier injection layers. It has also been found that the design of the waveguide structure for transverse confinement of light is important for edge emission to be observed. It is further found that while higher concentration of powder leads to higher effective refractive index in the nano-composite layer, it also forms a rougher surface and facilitates surface emission. This finding is important for

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future development of random laser diodes using nano-composite films. The realization of the first ZnO random laser diode also implies that it is possible to obtain random lasing via electrical injections if the disordered medium is of high-optical-quality and if the carriers can be injected into the ZnO powder efficiently.

More in-depth studies on the optically pumped ZnO disordered film waveguide lasers have been carried out to investigate the effect of the sample area on the lasing behavior. The experiment on the ZnO MOPA shows that the short random medium limits the number of lasing modes and the traveling wave amplifier amplifies and broadens the lasing emission from the random medium. This method provides a more systematic way of achieving lesser longitudinal modes.

The study on various stripe widths reveals the width dependence of the number of lasing modes, pump threshold and polarization characteristics of ZnO rib waveguide random lasers. Fourier transform analysis of the lasing spectra has also shown that the cavity length of the TM polarization is longer than that of the TE polarization. In addition, the cavity length increases linearly with the rib width, indicating that the random cavities formed are linear and the experimental results agree well with the 1-D rate equation analysis. This implies that the optical waveguide theory can also be applied to random lasers for controlling the scattering from the random cavities.

The influence of thermal annealing on the performance of ZnO based LEDs has also been investigated. It is found that the process of thermal annealing improves the crystallinity of the film and the formation of nanograins to form a rough surface improves the light extraction from the surface of the diode. The increase in grain boundaries also favors the formation of vacancies and carriers are

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more easily trapped at the defect states. As such, defect-level emission tends to dominate the EL spectra after thermal annealing.

8.2 Recommendations

In the past 3 years, although directional emission and reduction of mode operation have been achieved through the various waveguide random lasers, single mode laser with linewidth < 1 nm has yet been achieved. In addition, a more thorough investigation on some of the works carried out in the past can be done to achieve higher performance from the random lasers. Furthermore, the realization of the first UV random laser diode implies that more efficient random laser diodes can be developed in near future. In the next few paragraphs, several possible ways to achieve single-mode lasing and higher efficient random laser diodes will be recommended.

The sol-gel technique has been proven to be a useful method for incorporating high-quality random cavities in the nano-composite films. Although electrically pumped random lasing has been observed from ZnO-SiO₂ nano-composite films, the use of a scattering layer in addition to an active ZnO gain medium in a heterojunction structure may further improve the lasing efficiency of the random laser diodes. A possible material to be used as a scatterer is SnO₂ powder. SnO₂ is a direct wide bandgap material ($E_g \sim 3\text{-}3.6$ eV) and has a refractive index of ~ 1.998 , which is slightly lower than that of ZnO. In the optical point of view, the incorporation of SnO₂ powder in SiO₂ matrix will form a nano-composite film of effective refractive index lower than that of ZnO film. This will form a guiding layer for the emission. Moreover, the large refractive index contrast between SnO₂ and SiO₂ will favor strong scattering effect to induce closed-loop

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paths in the ZnO film. The presence of gain in SnO₂ will also provide additional gain feedback to the ZnO emission. On the other hand from the electrical point of view, SnO₂ is a conducting material. Hence, it will also favor the flow of holes from the *p*-type substrate to the ZnO films and reduce the resistance and hence turn-on voltage of the diode, unlike the use of MgO or ZrO₂ which are insulators.

It will also be useful if metal oxide powders can be dispersed evenly in the SiO₂ matrix. This helps in improving the performance of the diode, as too many clusters will deteriorate the electrical characteristics. A well-dispersed metal oxide powder film may also act as a randomly distributed feedback layer for the emission from ZnO film. This method can help in controlling the mode operation of a random laser.

A more in-depth study on the cause of striations when powders are added to TEOS solution can also be carried out. An understanding of this will aid in controlling the formation of powder stripes. If powder can be well dispersed in the matrix and at the same time form stripes pattern, this will pave a new way to form periodic structures to facilitate single mode lasing. This is because it is very difficult to form small ($\sim\lambda/4$) patterned structures for UV emission using the traditional photolithography method.

The work on the MOPA can be investigated more thoroughly by testing the effect of the TWA on the lasing behavior. Having a TWA region may broaden the lasing peak while lowering the pump threshold. Hence, by having an optimum length of the TWA region, improved single mode emission with narrower FWHM may be achieved.

From the works, we have seen that a waveguide structure is useful in controlling and directing the propagation of light. Therefore, if such structure can

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be used on LEDs and laser diodes, the efficiency of the light emitting devices can be improved. For example, ridge waveguides or MOPA designs can be implemented on heterojunction structures as a means to enhance the performance. This will certainly benefit the future development of UV devices.

The ability to limit multiple-mode operation and eventually realize single mode lasing is one important future direction in the development of UV lasers. This requires careful design of the cavity to sustain only one mode lasing. At the UV range, alternative methods such as nanosphere lithography (i.e., employing colloidal spheres as nano masks) and alumina membranes (i.e., with pore sizes in the range of tens of nanometers acting as masks) can be employed to form periodic structures. Holographic patterning may also be one possible way to achieve regular patterns of sizes in few hundreds of nanometers. These structures may then act as gratings to provide feedback for a particular wavelength, hence allowing single mode lasing to be realized.

There is a need to seek alternative ways to obtain high-quality random media. The presence of SiO_2 matrix around the ZnO powder increases the resistance of the diodes. Therefore if direct injection of carriers into the random medium can be achieved, this will lower the turn-on current and voltage. From the literatures, we have seen that random lasing and microcavities can be obtained from ZnO nanostructures. Thus, the fabrication of such nanostructures in heterojunction structures may allow improved, sustained lasing.

From the above suggestions, it shows that more research can be carried out to achieve better performing UV light emitting devices. Furthermore, the acquired experience in realizing UV random laser diodes will aid in future design and development of other types of UV lasers.

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