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UNIVERSITY OF CALIFORNIA RIVERSIDE

Development of Room Temperature Excitonic Lasing From ZnO and MgZnO Thin Film Based Metal-Semiconductor-Metal Devices

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Electrical Engineering

by

Mohammad Zahir Uddin Suja

December 2016

Dissertation Committee: Dr. Jianlin Liu, Chairperson Dr. Roger Lake Dr. Elaine Haberer

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Committee Chairperson

University of California, Riverside

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ABSTRACT OF THE DISSERTATION

Development of Room Temperature Excitonic Lasing From ZnO and MgZnO Thin Film Based Metal-Semiconductor-Metal Devices

by

Mohammad Zahir Uddin Suja

Doctor of Philosophy, Graduate Program in Electrical Engineering University of California, Riverside, December 2016 Dr. Jianlin Liu, Chairperson

Room temperature excitonic lasing is demonstrated and developed by utilizing metal-semiconductor-metal devices based on ZnO and MgZnO materials. At first, Cudoped p-type ZnO films are grown on c-sapphire substrates by plasma-assisted molecular beam epitaxy. Photoluminescence (PL) experiments reveal a shallow acceptor state at 0.15 eV above the valence band edge. Hall effect results indicate that a growth condition window is found for the formation of p-type ZnO thin films and the best conductivity is achieved with a high hole concentration of 1.54×10^{18} cm⁻³, a low resistivity of 0.6 Ω cm and a moderate mobility of 6.65 cm² V⁻¹ s⁻¹ at room temperature. Metal oxide semiconductor (MOS) capacitor devices have been fabricated on the Cu-doped ZnO films and the characteristics of capacitance-voltage measurements demonstrate that the Cudoped ZnO thin films under proper growth conditions are p-type. Seebeck measurements on these Cu-doped ZnO samples lead to positive Seebeck coefficients and further confirm the p-type conductivity. Other measurements such as XRD, XPS, Raman and absorption are also performed to elucidate the structural and optical characteristics of the Cu-doped ptype ZnO films. The p-type conductivity is explained to originate from Cu substitution of Zn with a valency of +1 state. However, all p-type samples are converted to n-type over time, which is mostly due to the carrier compensation from extrinsic defects of ZnO.

To overcome the stability issue of p-type ZnO film, alternate devices other than pn junction has been developed. Electrically driven plasmon-exciton coupled random lasing is demonstrated by incorporating Ag nanoparticles on Cu-doped ZnO metalsemiconductor-metal (MSM) devices. Both photoluminescence and electroluminescence studies show that emission efficiencies have been enhanced significantly due to coupling between ZnO excitons and Ag surface plasmons. With the incorporation of Ag nanoparticles on ZnO MSM structures, internal quantum efficiency up to 6 times is demonstrated. Threshold current for lasing is decreased by as much as 30% while the output power is increased up to 350% at an injection current of 40 mA. A numerical simulation study reveals that hole carriers are generated in the ZnO MSM devices from impact ionization processes for subsequent plasmon-exciton coupled lasing. Our results suggest that plasmon-enhanced ZnO MSM random lasers can become a competitive candidate of efficient ultraviolet light sources.

Semiconductor lasers in the deep ultraviolet (UV) range have numerous potential applications ranging from water purification and medical diagnosis to high-density data

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storage and flexible displays. Nevertheless, very little success was achieved in the realization of electrically driven deep UV semiconductor lasers to date. In this thesis, we report the fabrication and characterization of deep UV MgZnO semiconductor lasers. These lasers are operated with continuous current mode at room temperature and the shortest wavelength reaches 284 nm. The wide bandgap MgZnO thin films with various Mg mole fractions were grown on *c*-sapphire substrate using radio-frequency plasma assisted molecular beam epitaxy. Metal-semiconductor-metal (MSM) random laser devices were fabricated using lithography and metallization processes. Besides the demonstration of scalable emission wavelength, very low threshold current densities of 29~33 A/cm² are achieved. Numerical modeling reveals that impact ionization process is responsible for the generation of hole carriers in the MgZnO MSM devices. The interaction of electrons and holes leads to radiative excitonic recombination and subsequent coherent random lasing.

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Chapter 1

Introduction

1.1. Introduction

Zinc oxide (ZnO), a II–VI semiconductor, has attracted a great deal of interest over the past decades, especially in its application to optoelectronics [1]. Apart from the huge potential in the optoelectronics [2], ZnO holds a piezoelectric property [3], ferromagnetic properties with potential for spintronics devices [4-6]. ZnO is also a biocompatible and bio-safe material [7-9]. It has a wide direct bandgap of 3.37 eV with high exciton binding energy of 60 meV. It grows preferentially in the hexagonal wurtzite-type crystal structure. It has advantages relative to GaN because of its bulk availability, single-crystalline form and its relatively larger exciton binding energy (~60 meV, compared to ~25 meV for GaN) [10-29]. Recent improvements in the quality and control of conductivity in bulk and epitaxial ZnO have amplified interest in the use of this material for ultraviolet light emitters and transparent electronics [10-23]. As a wide bandgap semiconductor, ZnO is a candidate host for solid state blue to UV optoelectronics, including laser development. This has important applications in high density data storage systems, solid-state lighting, secure communications and bio-detection [30]. Although research work on ZnO in the thin film form started during the 1930s [31], the interest faded away during the 1980s. The main reason was the fact that it is difficult to dope the material with both n- and p-type polarities, and particularly p-type. The possibility to dope with n- and p-type polarities is a prerequisite for optoelectronic applications. The early research on ZnO is reviewed in different papers, e.g. [32, 33]. Many efforts to grow ZnO thin films on other p-type substrates have been a focus for some time as a route to overcome the difficulty of p-type doped ZnO. Nevertheless, the lattice mismatch between different substrates and ZnO hinders the possibility of defect free growth of ZnO thin film heterostructures. Even very close lattice structure materials like 4H p-SiC and p-GaN used as substrates have not achieved acceptable device quality for the overgrown n-ZnO films. Limited success using ZnO thin films on p-type semiconductor substrates has been reported for LEDs and lasers; some recent reports can be found in [12, 34]. The bandgap of ZnO can be tuned via divalent substitution on the cation site. Cd substitution leads to a reduction in the bandgap to ~ 3.0 eV [35]. Substituting Mg on the Zn site in epitaxial films can increase the bandgap to approximately 4.0 eV while still maintaining the wurtzite structure. The bandgap can be increased to even higher for mixed-phase MgZnO film. In the thesis, we focus on designing and optimizing alternative device structures other than p-n junction for higher output efficiency. We also demonstrate deep UV random lasers in MgZnO film based solid-state devices.

1.2. Organization of the dissertation

The dissertation is arranged as follows. In chapter 1, the motivation to work with ZnO based optoelectronic devices has been included in this chapter. In chapter 2, the growth procedure of ZnO and MgZnO thin films have been presented. Different characterization of the thin films has been introduced to determine the properties. In chapter 3, p-type doping of ZnO thin films have been investigated. Copper (Cu) has been used as the p-type

dopant. The doping results and film characteristics are discussed in details. In chapter 4, electrically driven plasmon-exciton coupled random lasers have been demonstrated in ZnO metal-semiconductor-metal devices. Different characterization methods and a numerical study have been utilized to confirm the performance and operation of the device. In chapter 5, deep UV laser has been demonstrated in MgZnO thin film based metal-semiconductor-metal device and lasing mechanism has been discussed in details. Finally, chapter 6 serves as an overall conclusion section of this dissertation work.

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Chapter 2

ZnO and MgZnO thin film growth

2.1 MBE system for thin film deposition

ZnO thin film can be grown by MBE, pulsed laser deposition (PLD), chemical vapor deposition (CVD), sputtering, and other deposition methods [1-10]. We are using radio-frequency (RF) plasma assisted MBE system from SVTA for the thin film deposition. MBE is an ultra-high vacuum (UHV) (~10E-10 Torr) epitaxial growth system. This provides several advantages over other deposition techniques, such as, highest purity growth, precise control of thickness and composition, flexibility of dopant sources, capability of in-situ growing of multiple layers structures etc.

Figure 2.1 and 2.2 show the schematic and image of MBE system. After cleaning the substrate, it is transferred in loadlock of the MBE. Then, the loadlock chamber is pumped down and later the substrate is transferred into the main growth chamber. We use high purity (6N) metal pellets, such as, zinc (Zn), magnesium (Mg) in the evaporation cells and highly pure oxygen gas through rf plasma source. The base pressure in the main chamber is usually maintained at $\sim 10^{-10}$ torr.

2.2 ZnO thin film growth

ZnO has stable wurtzite crystal structure. Among the commercially available substrates, we choose *c*-plane sapphire substrate considering the lattice mismatch (\sim 18%), cost and other factors (Table 2.1). Even though SiC and SCAM substrates has very little lattice mismatch with ZnO, however these are very costly and commercially not available,

respectively. To reduce the stress from lattice mismatch with *c*-plane sapphire substrate, different low temperature buffer layers, such as MgO, GaN, ZnO have been introduced [11-13]. We have used two-step buffer layer grown at lower temperature, to reduce the structural defects and as a nucleation layer. Figure 2.3 shows different steps of epitaxial film growth procedure. Initially, the substrate is pre-annealed, followed by lower temperature buffer layer growth. After that, the epitaxial layer is grown at elevated temperature. Finally, post annealing is done to activate the dopant, as needed.

2.3 MgZnO thin film growth

MgZnO is an important material in ZnO based alloy, as it can be employed as active layer for deep ultra-violet emission and in heterostructure devices as blocking or cladding layer [14]. ZnO can be alloyed with MgO (cubic, 7.7 eV) to increase the bandgap while maintaining the wurtzite crystal structure. Figure 2.4 shows a growth steps for MgZnO film growth. In MgZnO growth, one step buffer layer is employed which is accompanied by an annealing process. While doing epitaxial growth, Mg cell temperature (Mg flux) can be increased to incorporate more Mg in the film. Table 2.2 shows a series of samples grown at different Mg cell temperature. As the Mg cell temperature increases, more Mg can be incorporated in the MgZnO alloy yielding an increase in the bandgap. Figure 2.5 shows the room temperature (RT) absorption spectra of Mg_xZn_{1-x}O samples grown with different Mg cell temperatures. With increasing Mg flux, the bandgap tends to increase, however phase mixing starts to occur with increasing Mg as the crystal structure becomes thermodynamically unstable. Figure 2.6 shows the XRD spectra of MgZnO samples 1-7. For all samples except the sample 7, wurtzite hexagonal MgZnO 0002 peak is evident. With increasing Mg content in the film, the cubic MgZnO $10\overline{1}1$ peak start to appear from sample 3. For sample 7, the MgZnO film shows only the cubic phase. The broadening of FWHM with the concentration implies the change in crystallographic characteristics of the films.

2.4 Characterization systems

After the thin film growth, we need to characterize the film to find its properties. We use different structural, electrical and optical characterizations systems. For structural characterizations, scanning electron microscope (SEM) is used to know the surface morphology, X-ray diffraction (XRD) system is utilized to find the crystal orientation. For crystal quality, reflection high energy electron diffraction (RHEED) is used.

For electrical characterization, we use both Hall bar and Van der pauw system with 0.6 T and 1 T magnetic field, respectively. These measurements give the carrier type, concentration, mobility and resistivity of the film. A home-built seebeck measurement system is also used to confirm the carrier type of the film.

To perform the photoluminescence (PL) measurement, a He-Cd laser (325 nm) is used. The PL system has the capability of carrying out measurements even at 10 K temperature. Figure 2.3 and 2.4 show the schematic and image of PL system setup, respectively. PL spectroscopy is very important for optical properties of the film, because it indicates significant characteristics of the film, such as band gap, dopant type, optical emission quality etc. We are also using absorption spectroscopy, which gives band gap information along with phase uniformity of the film.

2.5 Conclusion

In this chapter, we discuss about the experimental setup for the deposition technique of ZnO and MgZnO thin film. We have utilized molecular beam epitaxy (MBE) system from SVT Associates (SVTA) for our II-VI thin film growth. An undoped ZnO thin film growth procedures is discussed. The various material and device characterization techniques have also been introduced to characterize structural, optical, electrical, and luminescence properties of the film and fabricated devices.

Figures



Figure. 2.1. Schematic of MBE system.



Figure. 2.2. SVTA MBE system of quantum structures laboratory (QSL, UCR).



Figure 2.3. Growth steps of ZnO epitaxial film.



Figure 2.4. Growth steps of MgZnO epitaxial film.



Figure 2.5. Absorption spectra of $Mg_xZn_{1-x}O$ samples grown with different Mg cell temperature.



Figure 2.6. XRD spectra of $Mg_xZn_{1-x}O$ samples grown with different Mg cell temperature.

Tables

	c-Sapphire	Si (111)	H-SiC (0001)	SCAM
Lattice mismatch	18%	(>30%)	3.5%	0.09%
Difference of TEC	34%	56%	~1%	~22%
Thermal Conductivity	0.5	1.5	4	0.062
$(W \text{ cm}^{-1} \circ C^{-1})$				

 Table 2.1. Comparison of ZnO with different substrates.

 Table 2.2. Growth condition for MgZnO film.

Samples	Heater (°C)	Zn Cell (°C)	Mg Cell (°C)	O2 Flux (sccm)	Growth Time (Hrs)
Sample 1	350	300	417	2.5	4
Sample 2	350	300	420	2.5	4
Sample 3	350	300	423	2.5	4
Sample 4	350	300	425	2.5	4
Sample 5	350	300	427	2.5	4
Sample 6	350	300	430	2.5	4
Sample 7	350	300	435	2.5	4

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Chapter 3

Realization of Cu-doped p-type ZnO thin films by molecular beam epitaxy

3.1 Introduction

Having a wide band gap of 3.37 eV at room temperature, zinc oxide (ZnO) has been recognized as a promising material for near UV optoelectronic devices ever since it demonstrated its p-type conductivity.¹⁻⁹ In addition, the large exciton binding energy (60 meV) of ZnO at room temperature (RT) generates the interesting possibility to utilize excitonic effects in RT optoelectronic devices.^{10,11} However, the major challenge for the fabrication of robust and long-lasting optoelectronic devices lies in achieving high-quality and highly stable p-type ZnO.

Many research groups have been working over the decades to search stable and reproducible p-type ZnO. P-type doping in ZnO may be possible by substituting either group IA elements (Li, Na, and K) for Zn sites or group V elements (N, P, As and Sb) for O sites.¹² Group IA elements tend to occupy the interstitial sites rather than substitutional sites, due to their smaller ionic radii than that of Zn, which makes it difficult in producing p-type materials.¹³ On the other hand, even though there are many reports on successful p-doping using group V elements,^{3,14-19} the reproducibility and reliability of these results are still under constant debate,²⁰ as the origin of p-type may not be from direct substitution of these group V elements on the O sites, but from defect complexes.²¹ Because of the
limitations of group IA and V elements, recently several groups have focused on group IB elements (Cu, Ag and Au), especially Ag, for p-type doping.²²⁻²⁷ From the first-principles calculations of doping effects with group IB elements, the formation energies are very low on the substitutional sites than the interstitial sites under oxygen-rich growth conditions, which suppress the formation of major hole-killer defects, such as oxygen vacancies and Zn interstitials.²⁸ Thereby, the group IB elements could act as an acceptor in ZnO, if incorporated on substitutional Zn sites.²⁹ Fan et al. suggested that Ag can exist both on substitutional Zn sites (Ag_{Zn}) and in the interstitial sites (Ag_i).³⁰ On the other hand, there have been very few reports regarding Cu-doping of epitaxial ZnO. Mollwo et al. reported the existence of an energy level of the Cu^{2+} atoms located 0.19 eV below the conduction band edge for Cu/In co-doped ZnO.³¹ Later, Kanai also reported that Cu²⁺ level is located at 0.17 eV below the bottom of the conduction band as Cu atom substitutes at the Zn site.³² Recently, Xu et al. reported that Cu doping introduces an acceptor (Cu⁺) level in ZnO at 0.45 eV above the valence band.³³ One can conclude from these reports that Cu may assume a valency of either +1 or +2 depending on its chemical environment, for example in the compounds Cu₂O and CuO, respectively. However, whether and how Cu doping can lead to p-type ZnO remains unclear.

In this chapter, we report on molecular beam epitaxial (MBE) growth and characterization of Cu-doped ZnO thin films. Photoluminescence (PL), Hall effect, Seebeck effect, capacitance-voltage, etc. were used to assess the films. A growth window of Cu doping to achieve p-type ZnO thin films is demonstrated. Shallow acceptors with an

activation energy of 0.15 eV are proved. Strong p-type conductivity with room-temperature hole concentration exceeding 1×10^{18} cm⁻³ is demonstrated.

3.2 Experimental section

3.2.1 Cu-doped ZnO thin film growth

Cu-doped ZnO thin films were grown on c-sapphire substrates using an SVTA radio frequency (RF) plasma assisted MBE system. Radical Knudsen effusion cells filled with elemental Zn (6N), Mg (6N) and Cu (6N) metals were used as Zn, Mg and Cu sources. Zn, Mg and Cu fluxes were controlled by the effusion cell temperatures. O_2 (6N) gas was fed through the RF plasma generator used as the oxygen source, and oxygen flow rate was precisely tuned by a mass flow controller. The substrates were cleaned in an aqua regia $(HNO_3: HCl = 1:3)$ solution at 150 °C for 20 min before DI water rinsing and blown dry by nitrogen. These substrates were then immediately transferred to the MBE chamber. During the growth, several steps were followed. In step I, the substrate was annealed in vacuum at 800 °C for 15 min to create an atomically smooth substrate surface. In step II, an MgO/MgZnO/ZnO low-temperature buffer layer was grown at 450 °C for 5 min with an estimated total thickness of 2-3 nm. In step III, another low-temperature ZnO buffer layer was grown at 500 °C for 10 min. During the growth of buffer layers, Zn and Mg cell temperature were kept at 320 °C and 470 °C respectively. Oxygen flow rate was 3 sccm with 400 W plasma power. The buffer layers minimize the lattice mismatch between Cudoped ZnO and c-sapphire substrate. In step IV, the Cu-doped ZnO films were grown at 600 °C on top of the buffer layer for 3 hours with Zn cell temperature and O_2 flow rate at $340 \ ^{\circ}C$ and 2 sccm, respectively. Cu effusion cell temperature was adjusted from $610 \ ^{\circ}C$

to 590 °C with an interval of 5 °C for Sample A through E, as summarized in Table 3.1. In step V, an in-situ annealing was performed at 650 °C for 20 min with 1 sccm of O_2 flow to activate the Cu dopants. The total thickness of the films was about 400 nm.

3.2.2 Structural, optical, electrical and Seebeck Characterization

The thickness of the films were measured using a Dektak 8 surface profilometer. Xray diffraction measurement was performed using a Bruker D8 Advance x-ray diffractometer. A Horiba LabRam Raman spectroscopy system was used to investigate Raman spectrum of the Cu-doped ZnO samples. Absorption spectrum was measured by a Varian Cary 500 double beam scanning UV/Vis/NIR spectrophotometer. PL study was carried out using a home-built PL system with a Janis cryostat, a 325 nm He-Cd laser for the excitation source, and a photomultiplier tube. Room-temperature Hall effect measurement was done in a variable magnetic field up to 6000 gauss. For Hall measurement system, a Keithley 6220 current source and a Keithley 2182 volt meter were used with minimum current capability of 0.1 pA, up to 105 V compliance, and voltage capability of 1 nV, respectively. Au/Ni (100 nm/10 nm) was deposited for Hall bar geometry sample as the metal contacts and also annealed properly using RTA process. A home-built heater and heat sink system, together with a Keithley 2401 digital multimeter, were used to measure the voltage and temperature for Seebeck measurements.

3.2.3 MOS device fabrication and characterization

A square geometry (200 μ m×200 μ m) MOS capacitor device was fabricated using standard photolithography process. An aluminum oxide (Al₂O₃) layer of 30 nm was deposited on the Cu-doped ZnO films by Atomic Layer Deposition (ALD) process. Au

(200 nm) was deposited on both Al_2O_3 and Cu-doped ZnO films as the contacts for metal and semiconductor by electron beam evaporation process. The capacitance was measured using an Agilent 4284A LCR meter.

3.3 Results and discussion

Table 3.1 summarizes the growth conditions of Cu-doped ZnO samples. All five samples adopted the same growth temperature of 500 °C, Zn cell temperature of 340 °C, oxygen flow rate at 2 sccm, and growth time of 3 hours. The only variable parameter is the Cu effusion cell temperature. The electrical properties of the films are summarized in Table 3.2 with the date measured. Sample A, which was grown at a Cu cell temperature of 610 °C, shows n-type conductivity with a carrier concentration of 7.5×10^{17} cm⁻³ and a mobility of 11.7 cm² V⁻¹ s⁻¹. With a Cu cell temperature of 605 °C (Sample B), the film exhibits ptype behavior with a hole concentration of 3.18×10^{17} cm⁻³ and a mobility of 4.3 cm² V⁻¹ s⁻ ¹. By decreasing the Cu cell temperature to 600 °C (Sample C), the carrier concentration increases to 1.54×10^{18} cm⁻³ while the mobility also increases to 6.65 cm² V⁻¹ s⁻¹. Further decrease of the Cu cell temperature to 595 °C (Sample D) leads to the decrease of hole carrier concentration to 1.63×10^{17} cm⁻³ with a slightly lower mobility of 6.6 cm² V⁻¹ s⁻¹. As the Cu cell temperature reaches 590 °C (Sample E), the film behaves as n-type. Therefore, an approximate p-type ZnO growth window is identified with the Cu effusion cell temperature between 595-605 °C. Sample C' represents the Sample C that turns into n-type after 5 months. Since all p-type samples converted into n-type after about 5 months, only the electrical property data of the representative Sample C' is included in Table 3.2 to avoid redundancy.

3.3.1 Structural and optical Characterizations

Figure 3.1(a) shows an XRD spectrum of Cu-doped ZnO film (Sample C). The spectrum exhibits diffraction peaks for ZnO (0002) and Al_2O_3 (0006). The absence of other ZnO directions indicates that the ZnO film is single-crystalline in nature. Moreover, no diffraction signal originated from Cu and its compounds are observed within the detection level. Figure 3.1(b) shows a Cu 2p core level XPS spectrum of Cu-doped ZnO film (Sample C) with an inset indicating peaks relative to Zn and O. The incorporation of Cu dopant is determined by two prominent peaks at 932.4 eV and 952 eV corresponding to Cu 2p_{3/2} and Cu $2p_{1/2}$ spin-orbit splitting, respectively. This result indicates that the incorporated Cu exists in the form of copper (I) oxide (Cu⁺) in our Cu-doped ZnO film. Since copper (II) oxide (Cu^{2+}) has hole states in the Cu 3d band (Cu 3d⁹ configuration), strong satellite peaks are commonly found between 940 eV and 945 eV due to electron shakeup.³⁴ Whereas the 3d band of copper (I) oxide (Cu⁺) is filled (Cu 3d¹⁰), and the 4s band is unoccupied, thus no satellites are expected which is in accordance with our result. The XPS spectrum of Sample C' is shown in Figure 3.1 (c). All peaks corresponding to Zn, O, and Cu elements resemble their original peaks in Figure 3.1(b), suggesting that the change of the conductivity originates from extrinsic factors as discussed later. Figure 3.1(d) shows Raman spectrum of Cu-doped ZnO film (Sample C). According to group theory, the following fundamental optical modes should exist in a wurtzite ZnO: E_2 (low) at 101 cm⁻¹, E_2 (high) at 437 cm⁻¹, A₁ (TO) at 380 cm⁻¹, A₁ (LO) at 574 cm⁻¹, E₁ (TO) at 407 cm⁻¹ and E_1 (LO) at 583 cm⁻¹. The low frequency E_2 mode is associated with the vibration of the heavy Zn sublattice, while the high frequency E₂ mode involves only the oxygen atoms.³⁵⁻

³⁷ From the Raman spectrum of Cu-doped ZnO film, a strong Raman shift signal appears at 437 cm⁻¹ due to the E₂ (high) mode of ZnO along with weak peaks at 378 and 574 cm⁻¹, which correspond to A₁ (TO) and A₁ (LO) modes of ZnO, respectively. The peak at 417 cm⁻¹ is attributed to the optical phonon mode of the c-sapphire substrate. As seen from the inset, there is no signal corresponding to copper oxide or other copper compounds in the Raman spectrum, which is consistent with the XRD results that no secondary phases are present in the Cu-doped ZnO film. Figure 3.1(e) shows the derived spectrum of α^2 versus photon energy (hu) of Sample C at room temperature, where α is the absorption coefficient. By utilizing the Tauc's plot, a direct band gap of 3.28 eV (378 nm) is obtained by taking the intercept of the extrapolation to the zero absorption. The excitonic resonance peak in the spectrum shows good optical quality and the single slope absorption edge ensures no significant phase mixing in the film.

3.3.2 Photoluminescence experiments

Figure 3.2(a) shows room-temperature PL spectra of Samples A-D. The near band edge (NBE) emission at about 3.27 eV (380 nm) and a weak broad green emission (GE) centered at about 2.25 eV (550 nm) can be observed from the Cu-doped p-type ZnO films (Samples B-D). For Cu-doped ZnO film outside the p-type growth window (Sample A), the GE center shifts towards shorter wavelength (~2.30 eV). The NBE emission results from exciton related recombination.^{38,39} The green emission might originate from intrinsic defects and/or Cu dopants. The origin of GE in undoped ZnO has been investigated extensively and explained by different types of electron transitions such as from oxygen vacancy (V_O) donor level to the valence band (D–h), from V_O to deep Zn vacancy (V_{Zn})

acceptor level (DAP), from the conduction band to the V_{Zn} acceptor level (*e*–*A*), and between two states of V_0 (intracenter).⁴⁰ In the case of Cu-doped ZnO, Gruzintsev et al. reported that visible emission observed at around 2.27 eV corresponds to DAP transitions from V_0 to Cu_{Zn} levels of Cu⁺:3d¹⁰.⁴¹ Since our Cu-doped p-type ZnO thin films (Samples B-D) were grown in O-rich condition and annealed in O-plasma environment, oxygen interstitial (O_i) and V_{Zn} should have dominant concentration.⁴² Therefore, the GE peak of 2.25 eV is more probably due to the transition between O_i level and conduction band.

Figure 3.2(b) shows temperature-dependent PL spectra of Sample C measured from 14K to 300K. Similar temperature-dependent PL spectra of other p-type samples (Sample B and D) are shown in Figure 3.2(c) and (d). For Cu-doped p-type ZnO films (Samples B-D), the NBE emissions associated with acceptor bound exciton ($A^{\circ}X$) are observed at 3.350-3.353 eV. With an increase of the temperature from 14 to 80 K, emissions of 3.285 and 3.209 eV observed at 14 K show blue shifts, which are typical characteristics of FA and DAP transitions.⁴³ Over the whole temperature range, 3.285 eV emission-line progressively merges into 3.209 eV emission-line, showing the feature of the thermal ionization of donors.⁴⁴ Therefore, these two emissions at 3.285 and 3.209 eV are identified as FA and DAP transitions, respectively. The acceptor activation energy E_A can be calculated from the Equation (1).^{15,43}

$$E_A = E_{gap} - E_{FA} + k_B T/2 \tag{1}$$

where the temperature-dependent transitions E_{FA} is approximately 3.285 eV at 14 K and the intrinsic band gap E_{gap} is about 3.43 eV at 14 K.^[44] Therefore, the value of E_A is calculated to be 0.15 eV. Figure 3.2(e) shows the integrated intensity of the $A^{\circ}X$ emission of Sample C as a function of temperature. The temperature dependence of the integrated PL intensity can be described by the Equation (2).⁴⁵

$$I(T) = I_0 / [1 + C \exp\left(-\frac{E_b^{A^0 X}}{kT}\right)]$$
(2)

where $E_b^{A^0 X}$ is the binding energy of the acceptor and free exciton, *C* is a fitting parameter, and I_0 is the integrated PL intensity at zero temperature, which is approximately the same as at *T*=14 K. From the fitting to Equation (2), $E_b^{A^0 X} = 17 \text{ meV}$ is obtained. If an Haynes factor $\frac{E_b^{A^0 X}}{E_A} \approx 0.1$ is used,⁴⁶ acceptor binding energy E_A is estimated to be 0.17 eV. This result is in close agreement with the value estimated above from spectroscopic data using Equation (1). On the other hand, if we assume that the acceptor activation energy is 0.15 eV, the Haynes factor for Cu-doped ZnO is estimated to be about 0.113, which is comparable with the value for Sb-doped ZnO.⁴⁶

Figure 3.2(f) shows temperature-dependent PL spectra of Sample C after it converts to n-type over time (denoted as Sample C'). The spectra have noticeably changed. A broad emission is observed at 3.294 eV at 14 K and redshifts with the increase of temperature for Sample C'. This suggests that the spectra are now dominated by donor-bound exciton emissions. Since the sample was stored in the ambient air, hydrogen-related impurities may absorb and diffuse into the ZnO, which contribute to a great deal of donors. These donors eventually compensate Cu-induced holes, leading to the conversion of the conductivity type.

3.3.3 Electrical characterization: Hall experiments and MOS device fabrication

Figure 3.3 shows Hall resistance as a function of magnetic field at room temperature for the samples. Positive increase in Hall resistance with applied magnetic field is observed in Samples B-D, demonstrating p-type conductivity of these samples. Sample C has the most positive slope, which supports its higher carrier concentration value compared with others. The negative sloped lines for Sample A and C' represent n-type conductivity of these samples.

MOS devices were fabricated to further study the p-type behavior of Cu-doped ZnO samples. The inset of Figure 3.4 shows the device structure, consisting of a metal gate (Au, 200 nm), Al₂O₃ (30 nm) and Cu-doped ZnO film (400 nm) on c-sapphire substrate. Capacitance-voltage (C-V) curves were measured at 300 K with a frequency of 100 kHz. For Samples B-D, by increasing the gate voltage from negative to positive values, the p-type Cu-doped ZnO film can accumulate holes (accumulation mode), then deplete holes (depletion mode), and finally fill with electrons on top of the Cu-doped ZnO film (inversion mode). In contrast, for Sample A, by decreasing the gate voltage from positive to negative values, the n-type film can accumulate electrons (accumulation mode), then deplete electrons (depletion mode), and finally fill with holes on top of the Cu-doped ZnO film (inversion mode). These trends of C-V curves further demonstrate the p-type conductivity of Cu-doped ZnO films.

3.3.4 Seebeck characterization

Figure 3.5 shows Seebeck effect measurement result of the samples. The decrease in voltage with the increase in temperature difference confirms the n-type conductivity of Sample A. Positive increase in voltage with the increase in temperature difference is evident for Samples B-D, which confirms their p-type conductivity. The most positive slope is observed in Sample C, which indicates its higher carrier concentration than other p-type samples (Sample B and D).

3.3.5 Discussion

Finally we brief discuss about the origin of the Cu-doped p-type ZnO. Owing to similar ionic radii between Cu and Zn, and low formation energy of group IB elements to occupy substitutional Zn site, Cu mostly substitutes Zn atom in Cu-doped ZnO films.²⁸ Due to proper O-rich conditions, these Cu atoms appear as a valency of +1 state, as revealed by XPS results. These Cu⁺ ions create a shallow acceptor level at 0.15 eV above the valence band indicated from PL studies, which is responsible for p-type conductivity in our Cu-doped ZnO films within a Cu effusion cell temperature window. Since the Cu-doped ZnO films were grown in O- rich conditions, the density of intrinsic donors has been minimized. Nevertheless, there are still some extrinsic donors originated from hydrogen-related complexes and other possible alien impurities during the growth, therefore the Cu cell temperature is needed to be raised to a point where Cu⁺ concentration is high enough to compensate these inadvertent donors to result in p-type conductivity. The dopant compensation can be clearly inferred from DAP emissions in PL studies. As the Cu cell

temperature exceeds the upper bound of the p-type film growth window, ZnO becomes ntype. This behavior may be explained by the nature of Cu doping in ZnO film. Since Cu⁺ and Cu²⁺ atoms can co-exist in ZnO and as more Cu atoms are incorporated into ZnO at a higher Cu cell temperature, Cu²⁺ atoms may outnumber Cu⁺ atoms. These excess Cu²⁺ atoms have a tendency to form deep donor levels, resulting in the disappearance of p-type conductivity.^{31, 32, 34}

3.4 Conclusion

Cu-doped p-type ZnO thin films were grown by MBE with an incorporation of proper number of Cu atoms and comprehensively characterized by a combination of Hall effect, Seebeck effect and C-V for the first time. A range of p-type conductivity was observed in the Cu-doped ZnO films with the strongest p-type behavior to exhibit a hole concentration of 1.54×10^{18} cm⁻³, a resistivity of 0.6 Ω cm and a mobility of 6.65 cm² V⁻¹ s⁻¹ at room temperature. PL studies revealed a shallow acceptor energy level of 0.15 eV above the valence band. The p-type behavior was found to originate from cationic substitution at the Zn site with Cu⁺ state. Although the stability of Cu-doped p-type ZnO films remains an issue, our experimental results indicate that Cu could be an excellent candidate for p-type ZnO fabrication.

Tables

Table 3.1 Growth condition for Samples A-E. A growth window of p-type Cu-doped

Samples	Heater	Zn Cell	Cu Cell	O ₂ Flux	Growth
	Temperature	Temperature	Temperature	(sccm)	Duration
	(°C)	(°C)	(°C)		(Hours)
Sample A	500	340	610	2	3
Sample B	500	340	605	2	3
Sample C	500	340	600	2	3
Sample D	500	340	595	2	3
Sample E	500	340	590	2	3

ZnO films (Samples B-D) is identified.

Table 3.2 The results of RT Hall measurements of Cu-doped ZnO films. Sample C'

represents the Sample C measured after 5 months.

Samples	Date Measured	Carrier Concentration (cm ⁻³)	Mobility (cm ² V ⁻¹ s ⁻¹)	Resistivity (Ω cm)	Electrical Types
Sample A	05/05/2014	8.3×10 ¹⁷	12.481	0.603	n-type
Sample B	05/07/2014	3.18×10 ¹⁷	4.3	0.59	p-type
Sample C	05/09/2014	1.54×10 ¹⁸	6.65	0.61	p-type
Sample D	05/10/2014	1.22×10 ¹⁷	0.59	87.5	p-type
Sample C'	10/20/2014	1.4×10^{17}	9.5	0.57	n-type

Figures





Figure 3.1. (a) XRD spectrum of p-type Cu-doped ZnO (Sample C), (b) Cu 2p core-level XPS spectrum of Sample C (inset showing XPS spectrum for Zn 2p and O 1s), (c) Cu 2p core-level XPS spectrum of Sample C' (inset showing XPS spectrum for Zn 2p and O 1s). (d) Raman spectrum of Cu-doped ZnO (Sample C), and inset is Raman spectrum showing no Cu-rich secondary phases, and (e) square of absorption coefficient (α^2) at room temperature of Sample C.







Figure 3.2. (a) Room-temperature PL of Cu-doped ZnO samples (Samples A-D), (b)-(d) temperature-dependent PL of p-type Cu:ZnO Sample C, Sample B, Sample D, respectively, (e) the integrated intensity of the A^oX emission as a function of temperature for Sample C. The triangles represent the experimental data, and the solid line is the fitting to Equation 2, (f) temperature-dependent PL of Sample C'.



Figure 3.3. RT Hall resistance as a function of applied magnetic field of various Cu-doped ZnO films. Inset shows one of the fabricated sample used for Hall effect measurement.



Figure 3.4. C-V characteristics of fabricated MOS capacitor (inset) devices utilizing Cudoped ZnO (Samples A-D) as the semiconductor layer, Al₂O₃ as the oxide layer and Au as the metal layer.



Figure 3.5. Variation in voltage with temperature difference for various Cu-doped ZnO samples (Samples A-D).

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Chapter 4

Electrically driven plasmon-exciton coupled random lasing in ZnO metal-semiconductor-metal devices

4.1 Introduction

Zinc oxide (ZnO) has been considered as one of the potential candidates for achieving ultraviolet (UV) lasers at room temperature (RT) due to a direct wide bandgap of 3.37 eV and a high exciton binding energy of 60 meV through several approaches such as, Fabry-Perot, random, and whispering-gallery mode in a variety of nanostructure systems.¹⁻⁸ Random lasing phenomenon occurs by forming random optical path through scattering in the grain boundaries of the random media, which results in random excitation of lasing modes in comparison with defined lasing modes in conventional lasers.⁹ Recently, random lasers have attracted a great deal of interest thanks to its simple device structures and potential applications in various fields, in particular, speckle-free imaging and water purification.¹⁰⁻¹⁵ Although ZnO-based random lasers have been demonstrated in ZnO films and nanostructures in both optical and electrical excitation,^{3,4,16-30} the relatively high threshold current and low output power have remained as major issues that hinder the further development of this technology into practical products.

To address these issues, p-n junctions together with double heterostructures and quantum confined structures would have been a natural direction to pursue.^{31,32}

Nevertheless, it is now known that although p-type conductivity can be realized in ZnO, its reliability still remains poor. Therefore, it is important to develop alternative device structures other than p-n junctions. Recently, surface plasmons (SP) have gained intensive attention due to their unique properties and applications in enhancing the emission efficiency of light emitting materials, including InGaN/GaN quantum wells, Si quantum dots (QD), CdSe QDs, and ZnO films.³³⁻⁴⁰ However, SP-enhanced electroluminescence (EL) of ZnO-based light emitting diodes (LEDs) and laser diodes has been rarely reported to date.³⁷⁻⁴⁰ In this chapter, we report SP-enhanced metal-semiconductor-metal (MSM) ZnO random lasers for the first time. The MSM devices were fabricated by using goldnickel (Au/Ni) and gold-titanium (Au/Ti) Schottky contacts onto copper (Cu)-doped ZnO thin films grown by radio-frequency (RF) plasma-assisted molecular beam epitaxy (MBE). The hole generation for lasing has been found to mainly originate from impact ionization processes using a ZnO MSM device model. Silver (Ag) nanoparticles (NPs) with different densities were incorporated on the surface of ZnO MSM devices to investigate the plasmonic enhancement. The plasmonic enhancement has been explained in terms of reduced threshold current, and enhanced internal quantum efficiency and output power, which originate from the efficient coupling between SPs in Ag NPs and excitons in ZnO.

4.2 Methods

4.2.1 Cu-doped ZnO thin film growth

Cu-doped ZnO thin film was grown on *c*-sapphire substrate in a SVTA (SVT Associates, Inc.) RF plasma-assisted MBE system. Knudsen effusion cells filled with high-

purity elemental Zn (6N), Mg (6N), and Cu (6N) were used as Zn, Mg and Cu sources, and O₂ (6N) gas was fed through a RF plasma generator as the O source. The substrate was cleaned in an aqua regia (HNO₃:HCl = 1:3) solution at 150 °C for 40 minutes, rinsed in deionized (DI) water, blown dry using a nitrogen gun, transferred to the MBE system, and annealed in vacuum at 800 °C for 15 minutes to produce an atomically clean surface. A low-temperature MgO/ZnO (~3 nm/8 nm) buffer layer was grown at a substrate temperature of 450 °C, an Mg cell temperature of 450 °C, a Zn cell temperature of 320 °C, and an O₂ flow rate of 2 sccm with a plasma power of 400 W. Then a thick ZnO (~400 nm) buffer layer was deposited for 3 hours at a substrate temperature of 400 °C, a Zn cell temperature of 320 °C, and an O_2 flow rate of 1.75 sccm, respectively. Next, while all the growth conditions were kept the same as that for the ZnO buffer, the shutter of a Cu effusion cell at a temperature of 750 °C was opened and the growth lasted for 2 hours, leading to a Cu-doped ZnO layer of ~280 nm. Finally, the film was in situ annealed at 700 $^{\circ}$ C for 20 minutes under O₂ environment with an O₂ flow rate of 2.5 sccm. The total thickness of the film is about 700 nm. The as grown film is designated as Sample 1.

4.2.2 Ag NPs incorporation

Ag NPs incorporation was carried out using two different ways and total three samples were prepared. For Sample 2, commercially purchased Ag colloids (20 nm, Ted Pella, Inc.) were spin-coated (1500 rpm for 15 s) on the surface of the ZnO:Cu film and then annealed at 150 °C for 2 minutes. This process was repeated 5 times to increase the density of Ag NPs. For Sample 3 and 4, Ag NPs were self-assembled by e-beam evaporation of Ag with a thickness of 1 Å (Sample 3) and 2 Å (Sample 4) on the ZnO:Cu film at a rate of 0.1 Å/s in a Temescal BJD 1800 e-beam evaporator, followed by a rapid thermal annealing (RTA) at 500 °C for 60 s.

4.2.3 Structural, optical and electrical characterizations

The thickness of the film was measured by a Veeco systems Dektak 8 surface profilometer. A Bruker D8 Advance X-ray diffractometer was used to perform X-ray diffraction (XRD) measurement. X-ray photoelectron spectroscopy (XPS) characterization was carried out by using a Kratos Axis Ultra DLD XPS system equipped with an Al Ka monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. Scanning electron microscope (SEM) images were captured by a Philips XL-30 SEM machine. SEM images were taken using an acceleration voltage of 10 KV and a secondary electron detector. Photoluminescence (PL) measurements were carried out using a home-built PL system consisting of a Kimmon Koha 325-nm He-Cd laser excitation source, an Oriel monochromator, a photomultiplier detector, a lock-in amplifier, a chopper and a Janis cryostat with a Cryo-con 22 temperature controller. A Varian Cary 500 double-beam scanning ultraviolet/visible/near-infrared (UV/vis/NIR) spectrophotometer was used for absorption measurements. For Hall effect measurements, a Keithley 6220 current source and a Keithley 2182 voltmeter were used with minimum current capability of 0.1 pA with up to 105 V compliance and voltage capability of 1 nV, respectively. Au/Ti (100 nm/10 nm) was deposited by e-beam evaporation for Hall bar geometry sample as metal contact and followed by a RTA annealing.

4.2.4 MSM random laser device fabrication and characterization

MSM random laser devices were fabricated using standard photolithography process. The outer circular ring contact area has an outer and inner diameter of 450 μ m and 400 μ m, respectively. The inner crossbar contact has an inner circle of diameter 100 μ m with four elongated cross rectangular section (100 μ m × 20 μ m). Au/Ni (150 nm/20 nm) and Au/Ti (150 nm/20 nm) were deposited by e-beam evaporation on the ZnO:Cu layer as inner crossbar and outer circular contact metals for the M(Au/Ni)-S(ZnO:Cu)-M(Au/Ti) structure, respectively. The current-voltage (I-V) characteristics were measured using an Agilent 4155C semiconductor parameter analyzer. MSM random laser devices were packaged on TO5 cans for electroluminescence (EL) measurements. EL spectra were collected using the same home-built system as PL. An external HP E3630A dc power supply was used to inject current to the devices. Output power of the devices was measured using a Thorlabs PM100 optical power meter.

4.2.5 MSM random laser device simulation

A 3D semiconductor model has been simulated to understand the electrostatic properties of Cu-doped ZnO MSM device using Finite Element (FE) analysis simulation tool, COMSOL.⁴¹ A 700-nm *c*-grown ZnO layer serves as the core of the model, with an assumption of no surface trap states and defect sites. The ZnO layer is assumed to have an electron carrier concentration of 9×10^{15} cm⁻³, which is selected to be in line with the experimental results. The bulk *c*-sapphire (Al₂O₃) substrate was effectively modeled as an insulating boundary. The Au/Ni and Au/Ti form two Schottky barriers with ZnO because

of the difference in their electron affinities.⁴² Since the Schottky barrier height is small (0.3~0.5 V), the device turn-on is rather fast, which is also consistent with observed experimental I-V curve. We used Fermi-Dirac statistics to describe the behavior of both majority (electron) and minority (hole) carriers. The electron mobility is $30 \text{ cm}^2/\text{V} \cdot \text{s}$, whereas the hole mobility is assumed to be very low (0.1~1 cm²/V·s).⁴³ An iterative non-linear solver is adopted to solve the coupled drift-diffusion, carrier continuity, Poisson, and thermionic emission equations in COMSOL.

To understand the origin of electroluminescence, we have simulated the hole concentration in a 2D ZnO channel using impact ionization model, as implemented in ATLAS.⁴⁴ The conventional drift-diffusion model cannot capture the non-local effect such as kinetic energy gain by electrons from high electric field, as well as energy lost to the lattice due to electron-lattice collision.⁴⁵ Hence, rather than relying on the local electric field, the carrier energy distribution (*i.e.*, carrier temperature) is used to calculate an effective non-local field, which describes the impact ionization process more accurately.⁴⁶ The carrier temperature is determined from the linearized Boltzmann transport equation, assuming a Maxwellian shape to the distribution of hot carriers.⁴⁷ The hot electrons subsequently cause impact ionization in the space-charge region of the reverse-biased junction. The electric field (E_{eff}) dependence of the impact generation coefficient is described by $\alpha_{ZnO} = A \exp \left[-\left(\frac{B}{E_{eff}}\right)\right]$,^{48,49} where $A = 7 \times 10^5 \ cm^{-1}$, $B = 5 \times 10^6 \ V/cm$ are the extracted material parameters calculated from the ionization rate reported for ZnO.⁵⁰

The saturation velocity for electrons in ZnO is taken as $\sim 3 \times 10^7$ cm/s,⁵¹ and the relaxation time is assumed to be 1.5 ps.⁵²

4.3 Results and discussion

4.3.1 Structural characterizations

Figure 4.1(a) shows an XRD spectrum of the Cu-doped ZnO film (Sample 1). The spectrum exhibits diffraction peaks of ZnO (0002) at ~34.4° and Al₂O₃ (0006) at ~41.6°, indicating that ZnO has grown preferentially along *c*-direction of the wurtzite lattice structure. Figure 4.1(b) shows XPS spectrum of as grown Cu-doped ZnO film, showing Zn 2p and O 1s core level spectra. In the range of Zn 2p orbital peak, two distinct peaks at binding energies of 1021 eV and 1044 eV corresponding to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively can be observed. The binding energy difference between these two states is around 23 eV, which lies within the standard reference value of ZnO.⁵³ The O 1s peak is centered at 529.8 eV, which is attributed to O^{2–} ions on the wurtzite structure of the hexagonal Zn²⁺ ion array, surrounded by Zn atoms.⁵⁴ Inset of Figure 4.1(b) shows the high resolution Cu 2p core level spectrum displaying peaks at 933.2 eV and 953 eV corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. This result indicates that Cu dopant exists in the form of copper (I) oxide (Cu⁺¹) in the film.⁵⁵

Figure 4.2(a) shows an SEM image of the ZnO:Cu film (Sample 1). The film possesses grains and air gaps, which facilitate the formation of random lasing cavities in the active layer. This morphology originates from a low-quality buffer layer and a relatively lowtemperature growth of active layer on a lattice mismatched sapphire substrate. Inset shows a cross-sectional SEM image of the sample, indicating that the film is continuous and relatively uniform. Figure 4.2(b) shows an SEM image of the ZnO:Cu film with spincoated Ag NPs (Sample 2). The size of the Ag NPs is 25~35 nm and the density is ~ 4.8×10^9 cm⁻². Figure 4.2(c) and (d) show SEM images of Sample 3 and 4, respectively. These selfassembled Ag NPs were formed by e-beam evaporation and subsequent annealing (Methods section). The size and density of Ag NPs in Sample 3 are 15~25 nm and ~ 1.6×10^{10} cm⁻², respectively, while the size and density of Ag NPs in Sample 4 are 35~45 nm and ~ 1.8×10^{10} cm⁻², respectively.

4.3.2 Optical characterizations

Figure 4.3(a) shows RT PL spectra of the four samples. The near band edge (NBE) emission peaks at 380 nm are observed for all samples and PL enhancement is evident after Ag NPs are incorporated on ZnO:Cu films. Compared with the sample without Ag NPs (Sample 1), the NBE peak enhancement ratio is about 4 for Sample 2, and increases to 5 for Sample 3 as the density of Ag NPs increases. The enhancement ratio is 2 for Sample 4 as both the size and density of Ag NPs reach the highest values compared to other samples. A slightly enhanced green emission peak is observed at around 500 nm for Sample 2, which can be attributed to some defects induced by the colloids of commercially purchased Ag NPs. Inset of Figure 4.3(a) shows NBE PL enhancement ratio with respect to the density of Ag NPs. The non-monotonous trend suggests that the plasmon coupling efficiency reflected in the enhancement ratio clearly correlates the density of Ag NPs.

Figure 4.3(b) shows absorption spectra of the samples. All spectra exhibit strong absorption in the spectrum region below 380 nm, and are almost transparent over 390 nm. The samples with incorporated Ag NPs show an absorption enhancement around 400 nm due to the excitation of localized surface plasmon modes in the Ag NPs. The absorption spectrum of Ag colloidal NPs exhibits an absorption band centered at 400 nm (Figure 4.3(c)), which can be attributed to the surface plasmon resonance (SPR) absorption of Ag NPs. Since the absorption band of Ag NPs overlaps with the ZnO NBE emission spectrum, the emission from the ZnO MSM devices can be enhanced resonantly by the surface plasmons of Ag NPs.³⁹

4.3.3 Electrical characterizations

Electrical properties of the Cu-doped ZnO films with and without Ag NPs are summarized in Figure 4.4(a) and Table 4.1. Figure 4.4(a) shows Hall resistance as a function of magnetic field at room temperature for all samples. The negative sloped lines represent the n-type conductivity of the samples. As seen from Table 4.1, all samples show a carrier concentration in the range of $1\sim 4\times 10^{15}$ cm⁻³, mobility of $17\sim 32$ cm² V⁻¹ s⁻¹ and resistivity of 80~140 Ω -cm. Since Cu is a p-type dopant for ZnO,⁵⁵ the incorporation of Cu atoms in the present ZnO film was not enough to make it p-type, nevertheless, these acceptors still heavily compensate unintentional donors, leading to the observed relative low electron carrier concentration and mobility. This low electron carrier concentration is desired for facilitating the formation of Schottky junctions instead of Ohmic junctions for lasing.⁵⁶ Figure 4.4(b) shows a schematic of ZnO MSM random laser devices with and without Ag NPs. As-deposited Au/Ni and Au/Ti serve as two contacts of the MSM device. I-V characteristics are shown in both linear and semi-log scale (inset) in Figure 4.4(c) for ZnO MSM devices with and without Ag NPs. The almost symmetric behavior of these I-V curves under forward (positive voltage on Au/Ni contact) and reverse biases indicates typical characteristic of MSM device.^{57,58} The similarity in the electrical properties and I-V curves indicate that the incorporation of discrete Ag NPs does not alter the electrical properties. This implies that the optical emission enhancement is triggered due to plasmonic effect rather than any change in carrier modification.

4.3.4 Lasing characteristics

Figure 4.5(a) shows EL spectra of ZnO:Cu MSM device without Ag NPs (Sample 1). The spectra were recorded from the top surface of Sample 1 at different dc injection currents under positive biases applied on the Au/Ni contact with respect to Au/Ti contact at room temperature. The same procedure was used to collect emission spectra for other samples. At lower injection currents less than 28 mA, a broad spontaneous emission peak is observed at around 380 nm, which can be attributed to the NBE emission of ZnO. As the injection current increases to about 31 mA, narrow peaks with a full width at half maximum (FWHM) of around 1.5~2 nm become visible at around 380 nm. Multiple narrow peaks emerge randomly between 370 nm and 400 nm with stronger intensity as the injection current increases further. The inset of Figure 4.5(a) shows the integrated emission intensity and output power as a function of injection current. The integrated emission intensity is an integral of the area under the emission spectra representing an output from all emission

wavelengths. The output power was obtained by real time measurement at the strongest lasing mode near 380 nm. As seen from the graph, an output power of about 40 nW is detected at an injection current of 40 mA. Both data show similar trend, deducing a threshold current of about 30 mA.

Figure 4.5(b)-(d) show EL spectra of Ag NPs incorporated ZnO:Cu MSM random laser devices (Samples 2-4). For Sample 2, a broad spontaneous emission is centered around 388 nm at an injection current of 18 mA. With higher injection currents, stimulated emission peaks with a FWHM of about 0.5 nm become superimposed on the broad spontaneous emission peak. Inset of Figure 4.5(b) shows integrated emission intensity and measured output power as a function of injection current of the device. The threshold current decreases to 20 mA (a 30% decrease compared to that of Sample 1) while the output power increases to 150 nW at the same injection current of 40 mA after incorporating Ag NPs on the ZnO:Cu MSM device (Sample 2). For Sample 3, a broad spontaneous emission peak is visible around 390 nm at an injection current of 16 mA. As the injection current increases, more and more stimulated emission peaks with a FWHM of about 0.3~0.5 nm emerging on top of the spontaneous emission peak. The threshold current is also about 20 mA for Sample 3 while the power increases to 180 nW (the increase is 350% compared to that of Sample 1) at an injection current of 40 mA as shown in the inset of Figure 4.5(c). Having the highest density of Ag NPs among these samples, Sample 4 shows similar broad spontaneous emission peak centered around 390 nm at lower injection currents and stimulated emissions (a FWHM of 0.3~0.5 nm) superimpose on the spontaneous emission at higher injection currents. The threshold current of about 26 mA is evident for Sample 4
and an output power of 80 nW was recorded at an injection current of 40 mA as depicted in the inset of Figure 4.5(d). Further comparison of EL spectra of samples with and without Ag NPs leads to the fact that both spontaneous and stimulated emissions are enhanced due to plasmonic effect.

4.3.5 Discussion

Finally, we discuss the mechanism of plasmon-exciton coupled lasing behavior from Ag-NP-coated ZnO:Cu MSM random laser devices. Although the majority carriers (electrons) control the transport in the ZnO MSM devices, the experimental observation of luminescence indicates the presence of minority carriers (holes). We can roughly estimate a lower bound number of electron-hole pairs necessary for radiative recombination at a particular lasing wavelength by the equation, $P_{out} = \frac{n}{t} \times hv$, where, hv is the photon energy. For ZnO:Cu MSM random laser device (Sample 1), the measured output power, $P_{out} = 40 \ nW$ at ~15 V [Figure 4.5(a) inset]. So the number of holes per second (n/t) responsible for recombination is in the range of ~7×10¹⁰ cm⁻³/s. Considering the photons from both stimulated and spontaneous emissions at other wavelengths and also additional non-radiative recombination, the total hole supply rate could be much higher than this rough estimation.

To understand how the holes are generated in these ZnO MSM devices, first, finite element simulation tool COMSOL Multiphysics was used to simulate electrical statistics of these devices (see Methods section for details). Figure 4.6(a) and (b) show band diagrams of an MSM device with a 50-mm ZnO channel terminated by Au/Ni and Au/Ti metal contacts in thermal equilibrium and under a positive bias of 15 V, respectively. Under applied positive bias on the Au/Ni contact, almost all the potential drops in the depletion region of Au/Ti/ZnO Schottky junction, resulting in a localized high field region. The electron can accelerate in the field region and gain energy to create electron-hole pairs (EHP) by impact ionization. Then, a non-local impact ionization model in an Atlas simulation tool was used to simulate the hole generation and steady state excess hole concentration (see Methods section for details). Figure 4.6(c) shows hole concentration as a function of position between Au/Ni and Au/Ti contacts. The generation of holes are confined only at the space charge region near the reverse-biased Schottky junction (outer Au/Ti contact in this case). As the applied bias increases, the hole generation increases. The highest steady-state excess hole concentration reaches $10^8 \sim 10^9$ cm⁻³ at a bias of ~15 V. Due to a high exciton binding energy of 60 meV in ZnO, the excess holes will have ample probabilities to instantaneously interact with electrons to form excitons, which can recombine radiatively to generate excitonic emission.⁵⁹ The generated photons scatter randomly at the grain boundaries with air gaps in the thin film to form the close-loop cavities for random lasing.³²

The Ag NPs are essentially nanoscale antennas that can radiate electromagnetic energy. Since the exciton energies in ZnO:Cu are similar to the electron oscillation energy of localized surface plasmon modes in Ag, the exciton energies can be coupled to the SP modes of Ag NPs due to the direct contact of these NPs with ZnO. These exciton-plasmon modes can be extracted as light in an alternative emission path rather than usual photon emission path from the surface of the ZnO:Cu layer.³⁷ The internal quantum efficiency (η_{int}) of light emission can be described as

$$\eta_{int} = \frac{R_{rad}}{R_{rad} + R_{non}},$$

where R_{rad} and R_{non} are the radiative and non-radiative recombination rates of electronhole pairs (EHPs) in ZnO, respectively. The internal quantum efficiency (η'_{int}) of the ZnO with exciton-SP coupling can be described as

$$\eta_{int}' = \frac{R_{rad} + C_{ext}' R_{LSP}}{R_{rad} + R_{non} + R_{LSP}},$$

where C'_{ext} is the probability of photon extraction from the generated SP's energy and R_{LSP} is the exciton-SP coupling rate.³⁵ The exciton-SP coupling rate is much faster than the radiative and non-radiative rates,³⁷ leading to enhanced internal quantum efficiency (η'_{int}). Figure 4.7 shows Arrhenius plots of the integrated PL intensities from ZnO:Cu films with and without Ag NPs. Temperature-dependent PL spectra of these samples are shown in Figure 4.8. Assuming $\eta_{int} \approx 100\%$ at 13 K for all samples, η_{int} can be estimated as 0.36% from the plot for ZnO:Cu without Ag NPs at room temperature.⁶⁰ After the incorporation of Ag NPs, the internal quantum efficiency increases 4.58 times ($\eta'_{int} = 1.65\%$) for Sample 2, 5.83 times ($\eta'_{int} = 2.1\%$) for Sample 3, and 2.02 times ($\eta'_{int} = 0.73\%$) for Sample 4, respectively. The enhanced internal quantum efficiencies can be construed as the increased spontaneous recombination rates as a result of the exciton-SP coupling, which further enhances the light emission efficiency.

4.4 Conclusion

Plasmon-enhanced ZnO MSM random laser devices were fabricated and studied. After the incorporation of Ag NPs on ZnO:Cu MSM devices, the efficient coupling of Ag SPs and ZnO excitons leads to the decrease of lasing threshold current by 30% and the increase of the output power by 350%. In addition, an increase of internal quantum efficiency by six times was observed. A numerical simulation of the ZnO MSM devices suggests that the supply of holes for lasing is originated from impact ionization process under relatively high voltages. This unique technique of employing surface plasmons to couple with excitons could lead to a new era of high-efficient optoelectronic devices.

Tables

Table 4.1. The results of RT Hall effect measurements of Cu-doped ZnO films with	out
and with Ag NPs.	

Sample	Carrier Concentration	Mobility (cm ² V ⁻	Resistivity (Ω	Electrical
	(cm ⁻³)	¹ s ⁻¹)	cm)	Types
1	3.393×10 ¹⁵	21.4863	85.7279	n-type
2	1.600×10 ¹⁵	32.4178	120.484	n-type
3	2.297×10 ¹⁵	19.427	140.066	n-type
4	2.794×10 ¹⁵	17.445	128.213	n-type

Figures



Figure 4.1. (a) XRD spectrum of Cu-doped ZnO thin film, (b) Zn 2p and O 1s core level XPS spectra, inset showing Cu 2p core level XPS spectrum.



Figure 4.2. (a) SEM image of Cu-doped ZnO thin film (Sample 1), inset shows cross sectional view SEM image of the film, (b) SEM image of Sample 2, (c) SEM image of Sample 3, (d) SEM image of Sample 4.





Figure 4.3. (a) RT photoluminescence spectra of ZnO films without (Sample 1) and with (Samples 2-4) Ag NPs, (b) Absorption spectra of ZnO films without (Sample 1) and with (Samples 2-4) Ag NPs, (c) Absorption spectra of commercial Ag NPs. Inset shows the Ag colloids in aqueous solutions.



Figure 4.4. (a) RT Hall resistance as a function of applied magnetic field of ZnO:Cu samples with and without Ag NPs. Inset shows one of the fabricated samples used for Hall effect measurements. (b) Schematic of MSM random laser devices with (right) and without (bottom) Ag NPs, (c) I-V characteristics in linear scale of MSM devices (Samples 1-4), inset shows the semi-log scale.





Figure 4.5. RT electroluminescence spectra from (a) Sample 1, (b) Sample 2, (c) Sample 3, and (d) Sample 4, under different injection current. Inset shows integrated intensity and output power as a function of injection current.



Figure 4.6. Band diagram of ZnO along A-A' section direction for (a) V = 0 V and (b) V = 15 V. The inset shows a closer view in the SC region and explains the impact ionization process by hot electrons, (c) Hole concentration along A-A' section, calculated from non-local impact ionization model.



Figure 4.7. Arrhenius plots of the integrated PL intensities of ZnO:Cu film without (Sample 1) and with Ag NPs (Samples 2-4).





Figure 4.8. Temperature-dependent PL spectra of ZnO:Cu samples without (Sample 1) and with (Sample 2-4) Ag NPs.

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Chapter 5

Electrically driven deep ultraviolet MgZnO lasers at room temperature

5.1 Introduction

Efficient laser devices operating in the deep UV region have a wide range of applications, which include fluorescence detection, water sterilization and purification, high-density data storage, medical diagnosis, and chemical and biological agent sensing¹⁻ ⁶. Owing to high efficiency, scalable size, and low power consumption, semiconductor lasers have advantages over traditional inefficient frequency converted solid-state lasers or excimer UV lasers that require the use of hazardous materials². UV spectral bands are commonly categorized into UV-AI (400~340 nm), UV-AII (340~315 nm), UV-B (315~280 nm), and UV-C (280~100 nm)^{7,8}. Over the last few decades, tremendous success was achieved on the development of electrically injected semiconductor laser diodes operating in the UV-AI band using GaN and ZnO based materials and their heterostructures⁹⁻²⁵. In contrast, very little has been succeeded on electrically pumped laser diodes in the UV-AII and shorter bands. The only available reports to date include AlGaN based quantum well lasers having lasing peaks at ~336 nm²⁶, MgZnO based metalinsulator-semiconductor (MIS) laser with lasing peaks at ~330 nm²⁷, and AlGaN nanowire random lasers operating in the UV-AII and UV-C bands at low temperature and operating in the UV-B band at room temperature²⁸⁻³⁰. Among all these lasers, only one has reached the shortest emission wavelength of 289 nm³⁰. Various issues associated with wide bandgap AlGaN materials including ineffective p-type doping and large effective masses of both electrons and holes have contributed to the severe gap in deep UV laser development³⁰.

Owing to the direct bandgap (3.37 eV) and high exciton binding energy (60 meV), ZnO has been studied extensively to realize low-threshold excitonic laser devices at room temperature^{15-25,31-49}. Wurtzite MgZnO ternary alloy is a direct, wider bandgap semiconductor that can lead to functional deep UV optoelectronic devices. Nevertheless, reliable p-type doping of ZnO and MgZnO has been extremely difficult. Thus a great deal of effort has been spent on the realization of lasers by circumventing the need for p-ZnO or p-MgZnO, including heterojunctions^{50,51}, Schottky diodes²⁴, and metal-semiconductormetal junctions²³. In this chapter, we report plasma-assisted molecular beam epitaxial (MBE) growth and characterization of MgZnO thin films on *c*-sapphire substrate. The polycrystalline MgZnO thin films possess high-density randomly distributed columns with air gaps between them, which act as random laser medium. Metal-semiconductor-metal (MSM) devices have been fabricated by depositing Au/Ti and Au/Ni Schottky contacts onto MgZnO films. We assessed several possible mechanisms and reached a finding that holes are generated near the space charge region of the reverse-biased metal-semiconductor junction during the operation of MgZnO MSM devices using a non-local impact ionization model in device simulation. A two-dimensional (2D) frequency domain mode analysis was performed to depict random lasing mode generation in the multiple grain structures. With

this study, we have demonstrated electrically injected MgZnO based random lasers operating in the UV-B and UV-AII bands, pushing the shortest wavelength ever reported for any electrically injected semiconductor lasers operating at room temperature down to 284 nm.

5.2 Results and discussion

The details regarding growth conditions of MgZnO thin films (Samples 1~4) are summarized in the Methods section. Figure 5.1 shows EDX spectra of the MgZnO samples, displaying peaks corresponding to O, Zn, and Mg. From the EDX spectra, the Mg composition *x* in Mg_xZn_{1-x}O can be calculated as 0.25, 0.3, 0.4 and 0.45 for Samples 1~4, respectively. Thus, the Mg concentration increases monotonously with the Mg effusion cell temperature. The inset in Figure 5.1 shows SEM images of the samples. The presence of multiple grains and air gaps in the films is evident. The grain sizes are in the range of 250~300 nm for Sample 1, 200~220 nm for Sample 2 and 130-160 nm for Samples 3 and 4. This kind of morphology originates from the low-temperature growth of the active layers on a large lattice mismatched sapphire substrate and facilitates the formation of random laser cavities in the MgZnO active layers.

Figure 5.2(a) shows XRD spectra of Samples 1~4, respectively. The spectra exhibit diffraction peaks of MgZnO (0002) peaks and Al₂O₃ (0006) for all samples. The XRD data indicates that MgZnO films have grown in highly *c*-axis oriented hexagonal wurtzite lattice structure on *c*-sapphire substrates. Along with MgZnO (0002) peak, Samples 3 and 4 show MgZnO ($10\overline{11}$) diffraction peak indicating the inclusion of cubic rocksalt structure into

the hexagonal wurtzite structure. For all samples, the MgZnO (0002) peak positions have shifted to higher angle from 34.55° to 34.72° proportionally to the Mg contents in the films. The shift is owing to the decrease in the lattice constant in the c-axis growth direction as a result of the substitution of Zn²⁺ ions (0.6 Å) by smaller sized Mg²⁺ ions (0.57 Å) in the host lattice^{52,53}. The *c*-axis lattice constant for MgZnO (0002) can be calculated by using the relation $c = 2d = \lambda/sin\theta$, where d is the plane spacing along the *c*-axis, θ is the diffraction angle, and $\lambda = 1.54$ Å is the wavelength of X-rays⁵⁴. The lattice constant shows a decreasing trend from 5.1859 Å to 5.1613 Å with the increase of Mg content (Table 5.1). The broadening of FWHM with the concentration implies the change in crystallographic characteristics of the films.

Figure 5.2(b) shows room temperature absorption spectra of the Mg_xZn_{1-x}O thin films with various Mg concentrations (x=0.25, 0.3, 0.4 and 0.45). The single slope absorption edges ensure no significant phase mixing in the MgZnO films. The spectra reveal that with the increase of Mg content, the band edge of MgZnO shifts to shorter wavelength (blue shift). Typically, pure ZnO film has a band edge at ~ 380 nm⁵⁵. For Sample 1, the MgZnO band edge is ~330 nm at 25% Mg concentration. The band edge shifts to ~320 nm for Sample 2 at 30% Mg concentration, and reaches a value of ~295 nm and ~280 nm at 40% (Sample 3) and 45% (Sample 4) Mg mole fraction, respectively. Evident increase of absorption coefficient near the absorption edge can be observed from all samples. High exciton binding energy (~60 meV) of ZnO and alloys play important role in the observation of these near-band-edge exciton absorption peaks in the absorption spectra at room temperature. The existence of excitons in the films at room temperature justifies the

excitonic lasing in our devices as is shown later. For evaluating the bandgap of MgZnO, we have employed the derived spectrum of α^2 versus photon energy (hv) at room temperature, where α is the absorption coefficient (Figure 5.2 (c)). The bandgap energy, E_g of the films can be calculated by utilizing Tauc's plot assuming $\alpha^2 \propto (hv - E_g)$ relationship^{31,56,57}. The inset of Figure 5.2(b) shows the variation of Mg_xZn_{1-x}O bandgap as a function of Mg concentration *x*. The bandgap widens in the range from 3.8 eV to 4.42 eV by introducing Mg content *x* from 25% to 45% in the Mg_xZn_{1-x}O film. These bandgap engineering results are in good accordance with the experimental observation of Ohtomo et al³¹.

The electrical properties of the MgZnO films characterized by Hall effect measurement are summarized in Table 5.2. These samples exhibit n-type conductivity with high resistivity ($\sim 10^2 \Omega$ -cm) and carrier concentration in the range of $\sim 10^{15}$ cm⁻³. MgZnO MSM random laser devices have been fabricated and packaged using standard photolithography, contact metallization and wire-bonding techniques (see Methods). The bottom right inset of Figure 5.3(a) shows a schematic of the fabricated devices. Au/Ni and Au/Ti metals act as the center crossbar and outer circular contact, respectively. The current-voltage characteristics are shown in Figure 5.3(a). The top inset shows semi-log I-V of the MSM devices. Typical I-V characteristics of the MSM device, namely, two Schottky diodes placed back-to-back, are evident from the nearly symmetric saturation current behavior under both forward (designated as positive voltage on Au/Ni contact) and reverse biases^{58,59}. The monotonous decrease in current with increasing Mg concentrations suggests that MgZnO thin films with wider bandgaps are more resistive. Figure 5.3(b) shows capacitance-voltage (C-V) characteristics of Samples 1~4. The C-V curves depict usual behavior of an MSM device, namely, the capacitance of the devices decreases as the amplitude of both positive and negative voltages increases, which is mainly due to the increase of the space charge region width of the reverse-biased Schottky diode in the loop.

Figure 5.4(a)-(c) shows PC spectra under zero and forward (positive voltage on the Au/Ni contact) biases for the MgZnO samples 2 - 4. Under forward biases, the photocurrent response increases as the photo-generated carriers are swept and collected under the applied electric field. The spectra show a peak at around 325 nm, 300 nm and 280 nm as the carriers are generated within the Mg_{0.3}Zn_{0.7}O, Mg_{0.4}Zn_{0.6}O and Mg_{0.45}Zn_{0.55}O layer, respectively. Long tail response is observed on the lower energy side of the spectra, which is due to carrier generation from the intraband states within the film. This enhanced photocurrent response is a result of more efficient collection of electrons and holes from the MgZnO film at higher voltages.

The lasing characteristics of MgZnO thin films were investigated by injecting continuous (dc) currents into the MSM devices (positive bias on center Au/Ni contact). All lasing spectra were collected from the top surfaces of the laser devices at room temperature. Figure 5.5(a)-(d) show EL spectra of Samples 1~4, respectively. All devices exhibit spontaneous emission at smaller injection currents, and stimulated emission superposing on spontaneous emission at higher injection currents. These sharp lasing modes with a full width at half maximum (FWHM) of 0.5~0.7 nm are associated with the formation of close-loop random laser cavities in these MgZnO thin films. The center lasing modes are clearly observed at 335, 325, 300, and 284 nm for Samples 1~4, respectively. To the best of our

knowledge, the 284-nm emission is the shortest wavelength ever reported from any semiconductor laser device under electrical injection at room temperature.

Figure 5.5(e)–(h) show the integrated EL spectral intensity and output power as a function of the injection current for the four devices, respectively. The output power was measured at the wavelength of the center emission in each device. The threshold behavior of the emission intensity and output power can be observed in all four plots. The threshold current is estimated to be ~37, 40, 40, and 43 mA for Samples 1~4, respectively. Considering the same device area of 1.26×10^{-3} cm² for all devices, the threshold current densities of 29~33 A/cm² are among the lowest threshold of lasers ever reported^{26,29,30}. The output power is found to be about 40, 30, 20, and 15 nW at the same injection current of 50 mA for Samples 1~4, respectively. Small output power suggest that the lasing is in excitonic emission region. Furthermore, the smaller output power in the samples with higher Mg content indicates that it is more difficult to generate electron-hole pairs in the wider bandgap semiconductors.

The lasing action was demonstrated by applying positive bias not only at the center crossbar contact (Au/Ni) as shown in Fig. 4 but also at the outer circular ring contact (Au/Ti) (Fig. 5.6(b)). Since the MSM device consists of back-to-back connected metal-semiconductor Schottky junctions, the occurrence of lasing emission under both voltage polarities suggests that these junctions are central element responsible for the lasing action. It should be noted that the EL spectra of Sample 2 in Fig. 5.6 were measured three months after the first measurement. Although the intensity slightly decreases, obvious lasing emission can still be detected from the device under injection currents similar to original

injection levels [Figure 5.5(b)], suggesting reasonable reliability due to the fact that the devices were not passivated. Figure 5.6(a) shows the EL spectra when positive bias is applied on the Au/Ni contact. A broad spontaneous emission at around 325 nm can be observed under an injection current of 36 mA. After the current is increased to 45 mA, some sharp peaks begin to appear on the broad emission band. Further increase of the injection current to 60 mA leads to more sharp lasing peaks. The FWHM of these sharp peaks is about 0.6 nm and the peak in the center of the band is at ~325 nm. Figure 5.6(b) shows EL spectra of Sample 2 when the positive bias is applied on the Au/Ti contact. The EL spectra displays sharp lasing peaks centered around 325 nm with a FWHM of around 0.7 nm as the injection current is higher than 48 mA, which is corresponding to the formation of random laser cavity in the Mg_{0.3}Zn_{0.7}O film.

The observation of luminescence indicates the presence of radiative recombination of excitons. The number of excitons going through radiative recombination can be inferred from the output power of the emission: $P_{out} = \frac{n}{t} \times hv$, where, hv is the photon energy. For example, since the measured output power for MgZnO MSM random laser device (Sample 4) is, $P_{out} = 23 nW$ at ~25 V [Figure 5.4(h)], the number of excitons or roughly the number of holes per second (n/t) accountable for recombination is ~3×10¹⁰ cm⁻³/s. The total hole supply rate could be much higher than this crude estimation, considering the photons from both stimulated and spontaneous emissions at other wavelengths and also additional non-radiative recombination. Thus, it is necessary to elucidate the origin of the generation of holes in the unipolar MSM devices.

The generation of the excess holes in the present MgZnO MSM devices assuming a positive voltage on the center Au/Ni contact could originate from several processes: hole leakage current from the forward-biased Au/Ni/MgZnO Schottky junction, trap-assisted band-to-band tunneling, and impact ionization near the reverse-biased Au/Ti/MgZnO Schottky junction. The 3D potential profile of the simulated device geometry shows that almost all the potential drops in the space charge region near the reverse-biased junction which is shown in Figure 5.7. Figure 5.8(a) and (b) show the band diagram along a narrow Mg_{0.45}Zn_{0.55}O channel region (~50 mm) between the inner Au/Ni contact fin and the outer Au/Ti circular contact (Sample 4) at equilibrium (0 V) and high bias (25 V) condition, respectively. Due to an uneven potential distribution across this channel as shown in Figure 5.7, most of the band to the right of the forward-biased Au/Ni/MgZnO junction is almost flat and a high field region occurs near the Au/Ti/MgZnO junction. Thus, hole leakage through thermionic emission at the forward-biased Au/Ni/MgZnO junction is negligible. Several authors have explained the origin of luminescence in ZnO devices by impact ionization process⁶⁰⁻⁶², which could be the dominant factor in the present case as well. When the injected electrons from the Au/Ti contact enter the high-field space charge region, the carriers accumulate high energy before getting scattered by optical phonons. The scattering length scale depends on the carrier saturation velocity and relaxation time. For ZnO, the reported hot electron energy relaxation time (τ) varies between 30 fs to 1.8 ps, depending on the growth condition, defects and doping in ZnO⁶³. In our MgZnO devices, we assume $\tau = 1.5$ ps, which results in a scattering length of ~300 nm. The electrons gain excess energy over the distance and eventually excite excess electron-hole

pairs by impact ionization. Figure 5.8(c) shows the estimated hole concentration from the non-local impact ionization model. The holes are mostly generated within the space charge region near the outer contact. The hole generation increases with applied bias. At a bias of 25 V, the highest steady-state excess hole concentration reaches 10^{10} ~ 10^{11} cm⁻³. This number is much smaller than the Mott density of 10^{17} cm⁻³ or so in ZnO⁶⁴, which further suggests that the present lasing is excitonic-like rather than electron-hole plasma type. The resulting excitons, formed by the interaction of these hole carriers and abundant electrons flowing in the devices, paves the way to excitonic emission⁶⁵.

The MgZnO films consisting of grains and air gaps act as highly scattered media to create a closed-loop cavity by multiple-scattering of photons as a result of excitonic recombination, which is a requirement of the realization of "coherent" random lasing⁶⁶. Multiphysics COMSOL simulation was carried out to investigate possible random lasing modes in the present devices (see Methods). Figure 5.8(d) shows the simulated electric field distribution of a typical confined mode in the MgZnO random cavity under an operating wavelength of 280 nm (Sample 4). Multiple modes exist in the same cavity and the results are simulated and shown for all samples in Figure 5.9. From the optical properties of MgZnO material, mode effective index was set to be around 2, and the simulation results for the default six modes have a deviation to the reference mode index within 0.015%. Figures 5.9(a)–(d) show the simulated electric field distribution of six random confined modes under operating wavelength from 335 nm to 280 nm for the four MgZnO MSM devices (Samples 1~4), respectively. The Mg composition in the MgZnO film is varied from 25% for Sample 1, 30% for Sample 2, 40% for Sample 3 and 45% for

Sample 4 according to the experimental values. The dimension of the device area is chosen to be $8 \times 8 \ \mu m^2$. Several possible modes found in different regions of the film provide some correlated evidences for the multiple emission peaks detected in the EL measurements. Multiple possible modes found in the different regions of the same cavity provide some correlated evidences for the formation of light closed loops and in turn, generation of random emission peaks detected in the EL measurements.

5.3 Methods

5.3.1 MgZnO thin film growth

MgZnO thin films were grown on one-inch diameter *c*-sapphire substrates by SVT associates (SVTA) molecular beam epitaxy (MBE) system equipped with a radio frequency (RF) plasma assisted oxygen source. High-purity elemental Zn (6N) and Mg (6N) were evaporated by using Knudsen effusion cells and the Zn and Mg fluxes were controlled by the effusion cell temperature. High-purity O_2 (6N) gas flow controlled by a mass flow controller was directed to the RF plasma source to generate active oxygen radicals. Prior to the growth, the sapphire substrate was cleaned in aqua regia (HCl:HNO₃) solution at a temperature of 150 °C for 40 minutes, rinsed in de-ionized (DI) water, blown dry by nitrogen gas and transferred immediately to the MBE chamber. To achieve an atomically clean surface, the substrate was annealed in vacuum at 800 °C for 15 minutes. The growth procedure followed several steps. First, a MgO/ZnO buffer layer was deposited on the substrate temperature of 450 °C for 5 minutes for all samples. The MgO/ZnO thickness in the buffer layer is varied from ~4.5/10.5, ~5/10, ~5.5/9.5, and ~6 nm/9 nm for Samples 1~4. The equivalent mole fraction of each element in the buffers was designed to

be equal to that in the MgZnO active layers grown on top. During the buffer layer growth, the effusion cell temperature for Mg and Zn was kept at 450 °C and 305 °C, respectively, while O_2 was introduced through the RF plasma tube at a flow rate of 1.5 sccm for all samples. The RF plasma power of 400 W was used during this step and MgZnO growth periods for all samples. In the next step, the samples were annealed at 650 °C for 5 minutes under ambient O_2 with an O_2 flow rate of 2.5 sccm. The active MgZnO layers were deposited at a substrate temperature of 350 °C, a Zn cell temperature of 300 °C and an O_2 flow rate of 2.5 sccm. The Mg cell temperature was varied from 417, 420, 425, to 427 °C for Samples 1~4, respectively. The growth duration for the MgZnO active layers was 4 hours for all samples. At the final step, the samples were annealed *in-situ* at 700 °C for 20 minutes under ambient O_2 with an O_2 flow rate of 2.5 sccm. All samples yield a total thickness of ~650 nm.

5.3.2 Structural and optical characterization

The thickness of the films was measured by a Veeco Dektek 8 profilometer system. X-ray diffraction (XRD) spectra were measured using a Bruker D8 Advance X-ray diffractometer. Scanning electron microscope (SEM) images were taken using a Philips XL-30 SEM machine. The SEM is equipped with an Energy Dispersive X-ray Spectrometer, which is utilized to measure energy dispersive X-ray (EDX) spectra. The experiments were performed using an electron beam with an acceleration voltage of 10 KV and a secondary electron detector. Room temperature absorption measurements were carried out by a Varian Cary 500 double-beam scanning ultraviolet/visible/near-infrared (UV/vis/NIR) spectrophotometer.

5.3.3 Device fabrication

For Hall effect measurement, Au/Ti (100 nm/10 nm) contacts were deposited on a Hall bar geometry sample by e-beam evaporation method and annealed at 400 °C for 1 minute by rapid thermal annealing process. MSM laser devices were fabricated by standard microfabrication process. The contacts comprise of an inner crossbar geometry with a circular ring (100 μ m diameter) having four extended fins (100 μ m × 20 μ m) and an outer circular ring (outer diameter of 450 μ m, inner diameter of 400 μ m). Au/Ni (150 nm/20 nm) and Au/Ti (150 nm/20 nm) metals deposited by e-beam evaporation method were served as inner and outer contacts, respectively. The schematic of the devices is shown in the inset of Fig. 3(a). Finally, the fabricated devices were wire-bonded on TO5 cans by using a Hybond 572A Wedge wire bonder and subsequently attached to a heat sink for electroluminescence (EL) measurements.

5.3.4 Device characterization

Hall effect measurement was carried out by a Keithley 6220 current source with a minimum current capability of 0.1 pA and up to 105 V compliance, and a Keithley 2182 voltage source with voltage capability of 1 nV. I-V characteristics were measured using an Agilent 4155C semiconductor parameter analyzer. C-V characteristics were measured using an Agilent 4284A LCR meter. EL spectra were collected from the top surface of the wire-bonded device using an Oriel monochromator, a photomultiplier detector, and a lock-in amplifier. Currents were injected to the device using an external HP E3630A dc power supply. A heat sink was attached to the back side of the devices to control the temperature
during the EL characterization. A Thorlabs PM100 optical power meter was used to measure the output power from the devices.

5.3.5 Device simulation

MgZnO MSM devices are simulated using both finite element simulation tool COMSOL Multiphysics⁶⁷ and TCAD simulator Atlas⁶⁸. The MgZnO channel is assumed to have an electron carrier concentration of 9 \times 10¹⁵ cm⁻³ to be consistent with the experimental results. The effect of surface trap states and grain boundary defects are ignored in band structure calculation. The bulk *c*-sapphire (Al₂O₃) substrate below the channel is modeled as an insulating boundary condition. Au/Ni/MgZnO and Au/Ti/MgZnO metal-semiconductor contacts are modeled as two Schottky diodes due to the difference of their work functions and electron affinity of MgZnO²³. The electron mobility is $38 \text{ cm}^2/\text{V} \cdot \text{s}$, whereas the hole mobility is negligible⁶⁹. The COMSOL model uses Fermi-Dirac statistics for both majority (electron) and minority (hole) carriers and resort to an iterative non-linear solver to numerically solve the coupled drift-diffusion, carrier continuity, Poisson, and thermionic emission equations. However, non-local effects, such as impact ionization and hot electron effects, which rely on thermal energy exchange between the electron (hole) and lattice, warrants us to go beyond the traditional semiconductor model⁷⁰. We use energy balance transport equations, as implemented in Atlas, which calculates carrier temperature from linearized Boltzmann transport equation, assuming a Maxwellian shape to the distribution of hot carriers⁷¹. Subsequently, calculated carrier temperature distribution is used as an effective non-local field (Eeff) that describes the impact ionization model precisely.⁷² The electric field dependence of the impact generation coefficient in MgZnO

is yet absent in literature. Hence, we take the impact generation coefficient of ZnO as a reasonable approximation for MgZnO: $\alpha_{MgZnO} = A \exp\left[-\left(\frac{B}{E_{eff}}\right)\right]$, where $A = 7 \times 10^5 \ cm^{-1}$, $B = 5 \times 10^6 \ V/cm$ are the calculated parameters of wide-gap ZnO⁷³. The saturation velocity for electron in MgZnO sample is ~2×10⁷ cm/s⁷⁴ and the relaxation time is assumed to be 1.5 ps⁶³.

Frequency domain mode analysis under radio frequency (RF) module of COMSOL Multiphysics 5.2 were used to simulate the electrical field distribution in the MgZnO thin films with columnar structures. Given that the grain size and emission wavelength are smaller than the film thickness, a 2D simulation was adopted to investigate the in-plane lasing modes behavior only. Randomly shaped and distributed hexagonal grains with lateral sizes of 200~400 nm and a filling factor of approximate 90% were generated. The morphology is closely in line with that of the devices studied here. The simulation area is chosen as $8 \times 8 \ \mu m^2$ although similar results can be obtained with larger dimensions, which require much prolonged computer simulation time.

5.4 Conclusion

In summary, we have demonstrated room temperature electrically driven deep UV random lasers in the wavelength range down to 284 nm for the first time based on MBE grown MgZnO MSM device structures. The hole generation in the MgZnO MSM devices is explained by impact ionization process through a comprehensive device modeling. Under the present conditions of operation of the devices, the number of excess holes is far less than Mott density, suggesting that the lasing is not in the region of electron-hole plasma. The excitons, formed through the interaction between these excess holes and electrons, can recombine radiatively, and with an assistance of a mode analysis, the resultant light is found to undergo multiple scattering and form closed-loop random cavities inside the multiple grain MgZnO structures, leading to extremely low threshold excitonic lasing. This work suggests an effective way in the development of deep UV semiconductor lasers at room temperature.

Tables

Samples (composition)	2θ (degree)	<i>c</i> (Å)	FWHM (degree)
Sample 1 (Mg _{0.25} Zn _{0.75} O)	34.55	5.1859	0.15
Sample 2 (Mg _{0.3} Zn _{0.7} O)	34.62	5.1757	0.23
Sample 3 (Mg _{0.4} Zn _{0.6} O)	34.68	5.1671	0.26
Sample 4 (Mg _{0.45} Zn _{0.55} O)	34.72	5.1613	0.27

Table 5.1. XRD data of Mg_xZn_{1-x}O Samples 1~4.

Table 5.2. Results of R	T Hall effect measurement	s of MgZnO Samples 1~4
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Samples	Carrier Concentration	Mobility (cm ² V ⁻¹	Resistivity	Types
	(cm^{-3})	s ⁻¹)	$(\Omega \cdot cm)$	
Sample	4.34×10^{15}	21.56	66.7	n-type
1				
Sample	1.28×10^{15}	73.18	66.7	n-type
2				
Sample	2.79×10^{15}	17.44	128.2	n-type
3				
Sample	3.64×10^{15}	38.44	44.14	n-type
4				

Figures



Figure 5.1. EDX spectra of (a) Sample 1 ($Mg_{0.25}Zn_{0.75}O$), (b) Sample 2 ($Mg_{0.3}Zn_{0.7}O$), (c) Sample 3 ($Mg_{0.4}Zn_{0.6}O$), and (d) Sample 4 ($Mg_{0.45}Zn_{0.55}O$). Inset shows SEM images and tables summarizing the elemental compositions of the samples.





Figure 5.2. (a) XRD spectra of MgZnO thin films (Samples 1-4) showing wurtzite and cubic MgZnO phases. (b) Room-temperature absorption spectra of MgZnO thin films (Samples 1-4), inset shows the variation of bandgap with Mg content in the film. (c) Square of absorption coefficient (α^2) at room temperature of Samples 1~4.



Figure 5.3. (a) I-V characteristics of Samples 1-4. Top left inset displays semi-log plot of I-V data. Bottom right inset shows a schematic of MSM device. (b) C-V characteristics of MgZnO MSM devices (Samples 1-4).



Figure 5.4. (a) - (c) Photocurrent spectra under different biases (positive voltage on Au/Ni contact) from the MgZnO samples 2-4, respectively.



Figure 5.5. (a) - (d) RT electroluminescence spectra of Samples 1-4 under different injection current. (e) - (h) Integrated intensity and output power as a function of injection current for Samples 1-4.



Figure 5.6. RT electroluminescence spectra of MgZnO Sample 2 under different injection current measured after 3 months, when (a) positive bias is applied on the Au/Ni contact, and (b) positive bias is applied on the Au/Ti contact.



Figure 5.7. (a) electrostatic potential distribution over the simulated device structure, for V = 25V, 0V and -25V. The color scheme indicates the potential difference (ΔV) with respect to the lowest potential on the geometry. (b)-(c) are the 2D cross-section along X-Z and near the reverse biased Ti/Au and Ni/Au metal contacts, respectively. The color profile shows the sharp potential variation in MgZnO around the Schottky junctions.



Figure 5.8. Band diagram of MgZnO along A-A' section direction for (a) V = 0 V and (b) V = 25 V. CBM and VBM in (a) stands for conduction band minimum and valance band maximum, respectively. The inset in (b) shows the impact ionization process by hot electrons in the high field region, (c) Hole concentration along A-A' section from non-local impact ionization model, (d) The intensity of electric field distribution along c-axis corresponding to one possible lasing mode for Mg_{0.45}Zn_{0.55}O film (Sample 4).



Figure 5.9. Mode analysis results of MgZnO samples with Mg composition of (a) 25%, (b) 30%, (c) 40% and (d) 45%. The operating wavelengths are 335 nm, 325 nm, 300 nm and 280 nm, respectively.

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Chapter 6

Conclusion

ZnO is one of the important material of the last few decades for its potential on optoelectronics. In this thesis work, ZnO and MgZnO were developed for optoelectronic device application by utilizing RF plasma-assisted molecular beam epitaxy. To overcome the bottleneck problem for ZnO, we have worked on the problem of p-type doping. Here, we used copper (Cu) as p-type dopant. A range of p-type conductivity was observed in the Cu-doped ZnO films with the strongest p-type behavior to exhibit a hole concentration of 1.54×10^{18} cm⁻³, a resistivity of 0.6 Ω cm and a mobility of 6.65 cm² V⁻¹ s⁻¹ at room temperature. PL studies exposed a shallow acceptor energy level of 0.15 eV above the valence band. The p-type behavior was found to originate from cationic substitution at the Zn site with Cu⁺ state. However, we found that the p-type of the film converted to n-type over time due to the intrinsic nature of ZnO based material.

To overcome the issue with p-type, we have utilized other type of solid-state device, such as metal-semiconductor-metal (MSM) devices. We fabricated Cu doped ZnO MSM devices for random laser application. We incorporated Ag nanoparticles to enhance the emission efficiency from the ZnO MSM devices. An increase in internal quantum efficiency was observed. The lasing threshold was decreased where the output power was increased after the incorporation of Ag nanoparticles. We have done numerical simulation to understand the mechanism of exciton lasing from the MSM device. Impact ionization has played a major role to generate holes in the MSM device. The generated holes combine with electrons to form excitons which in turn generate excitonic emission.

ZnO based alloy MgZnO is another important material due to its ability to yield a wider bandgap. We have grown MgZnO materials having bandgaps as wide as 4.42 eV. We fabricated MSM devices based on MgZnO thin films. We have achieved random lasing in the unprecedented wavelength range of ~284 nm. Several material and device characterizations have been done to establish the lasing behavior from the devices. Besides the demonstration of scalable emission wavelength, very low threshold current densities of 29~33 A/cm² were achieved. A thorough numerical simulation was also carried out to describe the excitonic lasing behavior. Non-local impact ionization model gives hole concentration number that complies with our experimental values. The number of excess holes was far less than Mott density, suggesting that the lasing is not in the region of electron-hole plasma. The excitons, formed through the interaction between these excess holes and electrons, can recombine radiatively, and with an assistance of a mode analysis, the resultant light is found to undergo multiple scattering and form closed-loop random cavities inside the multiple grain MgZnO structures, leading to extremely low threshold excitonic lasing.