Doped ZnO Thin Films: Fabrication, Characterizations and Performance Analysis as Ultraviolet Photodetectors

Ph.D. Thesis

by

Pankaj Sharma



DISCIPLINE OF ELECTRICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE

Doped ZnO Thin Films: Fabrication, Characterizations and Performance Analysis as Ultraviolet Photodetectors

A Thesis

Submitted in partial fulfillment of the requirements for the award of the degree **of**

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by

Pankaj Sharma



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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Doped ZnO Thin Films: Fabrication, Characterizations and Performance Analysis as Ultraviolet Photodetectors,** in the partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** and submitted in the **Discipline of Electrical Engineering, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from **January, 2014** to **August, 2017** under the supervision of **Dr. Shaibal Mukherjee, Associate Professor, Electrical Engineering**.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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Signature of Thesis Supervisor with date Dr. SHAIBAL MUKHERJEE

PANKAJ SHARMA has successfully given his/her Ph.D. Oral Examination held on ------

Signature(s) of Thesis Supervisor(s) Date: Convener, DPGC Date:

 Signature of PSPC Member #1 Signature of PSPC Member #2 Signature of External Examiner

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 Date:

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Pankaj Sharma

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Dedicated to the loving memory of my mother (Late. Mrs. Dhanpati Devi) and the source of joy in my life My loving daughter, Myra

LIST OF PUBLICATIONS

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- 1. Pankaj Sharma, Ritesh Bhardwaj, Rohit Singh, Shailendra Kumar, and Shaibal Mukherjee, *Investigation of formation mechanism of Li-P dualacceptor doped p-type ZnO*, Applied Physics Letters 111, 091604 (2017).
- 2. Pankaj Sharma, Aaryashree, Vivek Garg and Shaibal Mukherjee, Optoelectronic properties of phosphorus doped p-type ZnO films grown by dual ion beam sputtering, Journal of Applied Physics 121, 225306 (2017).
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- Pankaj Sharma, Ritesh Bhardwaj, Amitesh Kumar, Rohit Singh, and Shaibal Mukherjee, *Fabrication of low resistive and stable Li-P co-doped p-type ZnO by dual ion beam sputtering*, 3rd International Conference on Smart Materials and Structures, Orlando, Florida, USA, March 20-22, 2017.
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- **3.** Pankaj Sharma, Rohit Singh, Ritesh Bhardwaj, and Shaibal Mukherjee, *Self-powered high photoresponse UV photodetector based on dual ion beam sputtered Ga-doped ZnO*, Nanotech France 2016 and Joint International Conferences and Exhibition, Paris, France, June 1-3, 2016.

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- 5. Vishnu Awasthi, Sushil K. Pandey, Pankaj Sharma, Shailendra Kumar, C. Mukherjee, and Shaibal Mukherjee, *Characterizations of DIBS grown Ga-doped MgZnO thin films for solar cell application*, Photonics 2014: 12th International Conference on Fiber Optics and Photonics, IIT Kharagpur, India, December 13-16, 2014.

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ACRONYMS

DIBS	Dual Ion Beam Sputtering
DPC	Deposition Chamber
eV	electron Volt
EQE	External Quantum Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width at Half Maximum
GaN	Gallium Nitride
GZO	Gallium doped Zinc Oxide
IQE	Internal Quantum Efficiency
I-V	Current- Voltage
IPCE	Incident Photon Conversion Efficiency
LED	Light Emitting Diode
LLC	Load Lock Chamber
LPZO	Lithium Phosphorus codoped Zinc Oxide
PL	Photoluminescence
PDs	Photodetectors
PVD	Physical Vapor Deposition
PZO	Phosphorus doped Zinc Oxide
SE	Spectroscopic Ellipsometry
SEM	Scanning Electron Microscopy
ТСО	Transparent Conducting Oxide
UHV	Ultra High Vacuum
UV	Ultraviolet
WBG	Wide Band Gap
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
ZnO	Zinc Oxide

NOMENCLATURE

а, с	Lattice constant
E ₀	Dielectric constant
Zn _i	Zinc interstitials
O_{v}	Oxygen vacancies
V_{Zn}	Zinc vacancies
<i>O</i> _{<i>i</i>}	Oxygen interstitials
λ	Wavelength
E_g	Energy gap
μ_n	Electron mobility
μ_p	Hole mobility
ρ	Resistivity
α	Absorption coefficient
$ heta_B$	Bragg diffraction angle
mbar	millibar
hυ	Photon energy
V_H	Hall Voltage

ABSTRACT

Doped ZnO Thin Films: Fabrication, Characterizations and Performance Analysis as Ultraviolet Photodetectors

by

Pankaj Sharma

Hybrid Nanodevice Research Group, Discipline of Electrical Engineering

Indian Institute of Technology, Indore

Supervisor: Dr. Shaibal Mukherjee

ZnO has emerged as the subject of research for many optoelectronic applications in recent years, because it is nontoxic, abundant, chemically stable, and biocompatible. Due to its direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, it has been explored by many researchers for devices like light emitting diode, photodetectors, lasers, solar cells etc. Moreover, as compared to other semiconductor materials such as GaN, SiC, and AlN, ZnO offers several fundamental advantages such as high breakdown strength, high temperature operation, and transparency in the visible region.

In this work, the growth and characterization of doped ZnO based thin films by dual ion beam sputtering system was performed for the realization of high performance ZnO based ultraviolet photodetectors. The material study in this work focused on optimal deposition conditions of ZnO thin films with single dopant as gallium (Ga) and phosphorus (P) and codoping with lithium and phosphorus (Li-P) both. The structural, morphological, optical and electrical properties of these thin films has been studied by various characterizations. After the material optimizations the ultraviolet photodetectors were fabricated and spectral responses were analyzed while correlating with the properties of the thin films.

Ga doped ZnO (GZO) thin films were grown on *n*-Si (100) substrates at different growth temperature ranging from 200 to 600 °C. Various material characterizations including Hall measurement, X-Ray diffraction, spectroscopic ellipsometry, secondary ion mass spectroscopy were performed to investigate the films properties. Finally, the ultraviolet photodetectors were fabricated by depositing 50-nm thick Au interdigitated contacts on GZO films by magnetron sputtering at room temperature using the shadow masking techniques. Extremely good crystalline quality films were fabricated as indicated by XRD patterns of GZO. The Hall measurement data exhibited *n*-type conduction for all GZO films. A minimum resistivity of $5.3 \times 10^{-4} \Omega$ -cm along with a highest electron concentration of 12×10^{20} cm⁻³, was obtained.

The absorption spectra depicted that the GZO films have a strong absorption to photons with wavelength shorter than 370 nm. The spectral response of the photodetectors was measured in unbiased (zero bias) mode as well as applying a small positive bias voltage, 1V, from 300 to 500 nm, at room temperature. It was observed that the device grown at 300 °C has the highest responsivity of 58 mAW⁻¹ at zero bias. The response peak was centered on 325 nm and a cut-off wavelength around 370 nm corresponding to the band gap energy of GZO films. The external quantum efficiency (EQE) was observed to increase on application of external bias exhibiting the photoconductive gain. While the EQE at zero bias was measured to be ~22.5%, it reached to 48% at 1 V bias with an average photocurrent of 23 mA.

Phosphorus doped ZnO (PZO) thin films were fabricated on *n*-type Si (100) substrates and a detailed investigation of electrical and optical properties of PZO films was carried out. Post-deposition annealing of PZO films was carried out in N₂ ambient at 800 °C for 20 minutes to activate the acceptor dopants. The XRD pattern of PZO films shows that all the films were identified to be preferentially *c*-axis (002) oriented. XRD data analysis, concluded that P³⁺ replacing Zn²⁺ site was dominant mechanism resulting in the formation of PZO films were *p*-type with a room

temperature hole concentration of 8.6×10^{19} cm⁻³ and resistivity and mobility of 0.066 Ω cm and 1.08 cm²/Vs, respectively, for annealed PZO films grown at 500 °C. XPS analysis suggested the substitution of P atoms on Zn sites (P_{Zn}) along with formation of a fewer Po defects. The optical properties were investigated by spectroscopic ellipsometry in the photon energy range of 1.2 - 6.4 eV at different angles of incidence (65°, 70°, and 75°) at room temperature. Optical constants were obtained using a parameterized Psemi-M0 oscillator model. ε_1 peak at band edge shows a shift towards higher energy for the annealed PZO with an increase in amplitude of ε_1 with annealing corresponding to the increase in hole concentration and larger crystallite size. The line shape analysis of complex dielectric function resulted in a distinct red shift in the energy position of E_0 CP with an increase in hole concentration. Room temperature photoluminescence (PL) spectra of PZO films showed a strong ultraviolet emission corresponding to near bandgap energy.

Lithium and phosphorus codoped ZnO (LPZO) thin films were fabricated on *n*type Si (100) substrates and subsequent annealing at high temperature followed by a systematic investigation of photoresponse characteristics of Li-P codoped *p*-ZnO/ *n*-Si heterojunction photodetectors. XRD investigation suggested a preferentially *c*-axis oriented LPZO film growth with a substitution of Li and P atoms on Zn sites under the oxygen rich ambient resulting in the formation of Li_{Zn} and P_{Zn} defects. Hall effect measurement predicted a *p*-type behavior with a highest hole concentration of 2.31×10^{20} cm⁻³ for films grown at 300 °C. The resistivity was found to be 0.016 Ω .cm with a Hall mobility of 2.8 cm²/V.s for the film.

The current-voltage (I-V) characteristics of fabricated *p*-LPZO/ *n*-Si heterojunctions confirmed the rectifying behavior originated from the *p*-LPZO/*n*-Si junction. The elemental analysis carried out using XPS, confirmed the substitution of Li at Zn site forming the Li_{Zn}-O bonds in LPZO films creating the acceptor states. Also, phosphorus was found to be present in two different states. The photoresponse characteristics of the *p*-ZnO/*n*-Si heterojunction photodetector

were investigated at room temperature at different applied bias in wavelength range 300 to 500 nm. At zero applied bias, a low photoresponse was observed, and the peak responsivity was determined to be about 1.8 mA/W for 500 °C grown device. A peak photoresponsivity of 2.6 A/W at -6 V bias was measured for 500 °C grown devices corresponding to an EQE of order of ~ 10^3 %. The specific detectivity (D^*) of the device at -6 V was determined to be 2.32 × 10¹⁰ cm Hz^{1/2} W⁻¹.

Chapter 1

Introduction

1.1 Background

On planet Earth, Sun is the most important natural source of ultraviolet (UV) radiations. Although the UV spectrum constitutes less than 10% of the total energy output by the sun, overexposure to UV radiations may lead to skin cancer and premature aging [1]. Therefore, the detection of UV radiations presents a challenge to design UV photodetectors (PDs) capable of detecting even weaker UV rays. Furthermore, UV PDs have found potential applications in wide range of civil and military applications such as optical communications, astronomical studies, missile plume detection, flame detection, chemical and biological analysis, etc. [2]. Currently, most of the commercially available UV PDs are dominated by UV enhanced Silicon (Si) based devices, however, since the energy band gap of Si is only 1.1eV, the Si-based photodetectors are sensitive to visible and infrared radiation, therefore, the responsivity in the UV region is still low. Moreover, external filters are essentially needed to block the long-wavelength response to achieve UV detection. Therefore, such UV detectors often suffer from low responsivity, low speed or bulky volume, which is incompatible with the demands of modern UV PDs.

To overcome these disadvantages, wide bandgap materials (WBG) such as diamond, SiC, GaN, ZnO etc. have been explored as an alternate candidate to be used in UV photodetection applications [3]. The technological advancements in fabrication of these semiconductors have progressed substantially in the last two decades. Therefore, a large number of solid-state UV PDs have been fabricated and reported, which exhibit motivational results for future UV detection devices. Compared with traditional UV PDs, the WBG UV PDs have the advantage of improved performance, and they do not need complicated and bulky external

electrical power supplies or filters. Among these WBG semiconductors, the research activities focused on ZnO material system and its emerging applications in various fields of optics and optoelectronics have attracted much attention due to its advantageous material properties such as wide band gap, large exciton binding energy, and radiation hardness etc. [1,3].

1.2 ZnO as semiconductor

Zinc oxide (ZnO) is a group II-VI binary semiconductor material with excellent material properties. It has a direct and wide band gap of 3.37 eV, large exciton binding energy of 60 meV at room temperature, high electron mobility, high thermal conductivity, good transparency and ease of growing in the nanoscale range [3]. These unique properties make the ZnO material suitable for wide range of uses in optoelectronics, transparent electronics, lasing and sensing applications. ZnO prefers to form the crystal in stable hexagonal wurtzite structure at room temperature and normal atmospheric pressure. A schematic diagram of ZnO crystal is shown in figure 1.1.



Figure.1.1 Hexagonal wurtzite structure of ZnO. Zn atoms are shown with large light spheres and O atoms as dark small spheres.

In the wurtzite crystal structure of ZnO, each Zn cation is surrounded by four oxygen anions at the corners of a tetrahedron, and vice versa. In other words, the crystal structure of ZnO is composed of alternating planes of Zn^{2+} and O^{2-} ions stacking along the c-axis. The lattice constant of the ZnO hexagonal unit cell is

a=3.250 Å and c=5.206 Å [4]. Another important property of ZnO is its tunability of band gap. ZnO can be alloyed with MgO and CdO to modulate the bandgap suitable for the applications ranging from deep UV to visible and infrared.

Doping in ZnO is achieved by introducing a foreign atom into the ZnO host crystal. In general, the as grown ZnO shows the *n*-type conduction which is believed to originate due to the presence of native point defects such as zinc interstitials and oxygen vacancies [5]. The *n*-type conductivity can be further enhanced using the group III elements such as Al, Ga and In, which acts as extrinsic donors for ZnO material by substitution on Zn site. High electron concentration and high quality *n*-type ZnO films have been reported successfully grown by using pulsed laser deposition (PLD), molecular beam epitaxy (MBE), magnetron sputtering and metal organic chemical vapour deposition (MOCVD) [6,7]. Highly conductive and transparent *n*-type ZnO films have been used as a potential candidate to replace indium tin oxide (ITO) for displays, LEDs, and solar cells.

Even though the *n*-type doping is relatively easier in ZnO but, the *p*-type conduction in ZnO films is considerably difficult. There are several possible mechanisms to explain the difficulties of achieving *p*-type conduction in ZnO [8]. First, the acceptor dopants have low solubility in ZnO material to limit the accessible hole concentration. Secondly, the *p*-type conduction in ZnO is limited due to the self-compensation mechanisms such as the formation of deep defect centers. The *p*-type doping in ZnO is possible with substituting pentavalent impurity atoms such as N, P, As and Sb on an oxygen site or monovalent impurity atoms such as Li, Na, and K on a Zn site [9]. Although the *p*-type conduction has been realized by doping with N, As, P, Li and Li-N [10-13], reliable *p*-type behavior is still the key issue that hinders the development of all ZnO based electronics and optoelectronic devices.

1.3 Literature review

In the fast-expanding field of nanotechnology, a lot of research efforts have been put into the fabrication of ZnO based high performance UV PDs. This has been encouraged by both scientific advancements and extending critical applications in optical communications and military warfare. Semiconductor UV PDs exhibit many advantages such as the ideal spectral selectivity with wide direct bandgaps from the deep UV to the infrared region, high breakdown field, high thermal stability, radiation hardness, and high responsivity. The important performance parameters of semiconductor photodetectors are [1,14]

• Responsivity: Responsivity of a photodetector is defined as the ratio of output photocurrent per unit of incident optical power. It is expressed in amperes/watt (A/W).

$$R_{\lambda} = (I_{light} - I_{Dark}) / P_{light}$$
(1.1)

 Quantum Efficiency (η): Quantum efficiency of a photodetector is defined as the ratio of the number of photogenerated charge carriers (electronhole pairs) to the number of incident photons. Mathematically,

$$\eta = R_{\lambda}(hc/q\lambda) \tag{1.2}$$

where λ is the radiation wavelength, *h* is the Planck constant, *c* is the speed of light and q is the electron charge.

- Response time: The response time of a photodetector is characterized by the decay time, τ_d and rise time, τ_r . The decay time (rise time) is defined as the time in which the output photocurrent drops from 90% to 10% (or increases from 10% to 90%) of its maximum value when the device is illuminated with rectangular light pulses.
- Detectivity (D^{*}) and noise equivalent power (NEP): The NEP of a photodetector is the optical input power for which the signal-to-noise ratio is equal to unity. The detectivity characterizes the ability of a photodetector to detect a weak photo signal. It is the reciprocal of NEP value. If *I_{dark}* is the dark current then D^{*} can be calculated as

$$D^* = \frac{R_\lambda}{\sqrt{2qI_{dark}}} \tag{1.3}$$

Generally, the semiconductor UV PDs can be broadly classified into different categories as (i) metal semiconductor metal (MSM), (ii) p-n or p-i-n junction based and (iii) Avalanche photodetector. In literature, a number of growth techniques have been deployed to grow materials for ZnO UV PDs such as PLD, MOCVD, radio-frequency (rf) magnetron sputtering, and MBE etc. As discussed above, generally, group III elements such as Al and Ga have been used for n-type doping in ZnO and group I and group V dopants such as Li, N, Sb etc. for p-type doping in ZnO. In this work, a detailed literature survey of ZnO based MSM structured and p-n heterojunction UV PDs was performed.

Recently, Jiang *et. al.* [15] have reported an MSM structured ultraviolet PD fabricated by pulse laser deposition (PLD) using amorphous InGaZnO film at room temperature. The photodetector was reported to show a peak responsivity of 4mA/W at zero bias. Similarly, Chen *et. al.* [16] have demonstrated a self-powered photodetector based on the MSM structure. The peak responsivity of the molecular beam epitaxy (MBE) grown ZnO self-powered UV PDs was as high as 20 mA/W. In addition to this, Bai *et. al.* [17] have also reported a peak photoresponsivity of 1.8 mA/W from the MSM UV PD fabricated based on selectively grown ZnO nanowire array.

Huang *et. al.* [18] have reported a peak UV photoresponse of 0.8 A/W at -1 V from the PD fabricated using nitrogen doped *p*-ZnO nanorods/*n*- Si heterojunction. On the other hand, Luo *et. al.* [19] have reported a photoresponsivity of 0.07A/W under a 20V reverse bias from a heterojunction photodiode based on *n*-type ZnO/*p*-Si. Similarly, Jeong *et. al.* [20] have fabricated an *n*-type ZnO/*p*-Si structure UV PD using rf magnetron sputtering with a peak photoresponse of 0.5A/W under the applied reverse bias of 30 V.

1.4 Objective of the present work

The advancement of fabrication techniques and ease in the processing and characterization of novel materials have led to the research and development of devices with improved performance. Specifically, in the domain of optoelectronics, where the light-matter interaction is involved, the research has become more interesting. The motivation for this work is to explore the potential of developing high-performance ZnO thin films based semiconductor UV PDs with low-cost investments that could replace the photomultiplier tubes (PMTs) that are currently used for commercial applications. A clear understanding of various factors affecting the structural, electrical, morphological and optical properties, is essential for fabrication of high-quality optoelectronic devices. Therefore, the ultimate objective of this research work is to fabricate and analyze the performance of UV PDs using doped ZnO thin films. The growth of high crystalline-quality materials is carried out by dual ion beam sputtering (DIBS) system. Steps involved in order to achieve the above objectives are as follows:

- Fabrication and growth optimization of Ga-doped ZnO (GZO) thin films with performance analysis of photodetectors based on metal-semiconductor-metal (MSM) configuration.
- Growth optimization and characterizations of phosphorus (P)-doped ZnO (PZO) thin films in order to investigate the effect of temperature and oxygen partial pressure on *p*-type conduction in ZnO along with structural, optical and morphological properties.
- Fabrication and growth optimization of high quality lithium and phosphorus (Li-P) dual acceptor-doped ZnO thin films (LPZO) followed by the performance investigation of *p*-ZnO/*n*-Si heterojunction photodetector.

1.5Organization of the Thesis

The research work in this thesis has focused on the fabrication and characterizations of the doped ZnO thin films along with the analysis of the photoresponse of these thin films based photodetector devices. Therefore, the thesis has been organized systematically as follows

Chapter 1 provides a background and motivation for the current work, a brief literature review and an outline of this thesis.

Chapter 2 introduces the growth technique used for doped ZnO thin films deposition and various characterizations methods which have been employed to study structural, electrical, elemental, morphological properties and UV photoresponse of our fabricated PDs.

Chapter 3 presents the detailed optimization of GZO thin films with varying growth temperature (T_g) in 200-600 °C and fabrication of GZO based MSM UV PDs. The performance of zero bias operating PDs has been investigated.

Chapter 4 describes the growth of *p*-type PZO thin films with optimization of growth ambient and subsequent annealing. The optoelectronics properties along with structural, morphological and elemental properties were studied.

Chapter 5 demonstrates the realization of the *p*-type LPZO thin films and then analyses the performance investigation of p-LPZO / n-Si heterojunction based ultraviolet photodetector devices.

Chapter 6 draws conclusions from the thesis and proposes the scope for future work.

1.6 References

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Chapter 2

Fabrication and Characterization Techniques

In this chapter, the experimental setup used for the fabrication of thin films and devices and the characterization technique used to determine their properties are briefly explained. The doped ZnO thin films were grown by dual ion beam sputtering (DIBS) system. Various characterization techniques were employed to study the structural, optical, electrical, elemental, and morphological properties of thin films. The crystal structure of the films was characterized by X-Ray diffraction (XRD) system. Electrical properties of films were investigated by Four Probe Hall measurement system and Keithley 2612 source meter. The optical properties of films were determined by variable angle variable wavelength spectroscopic ellipsometry (SE) measurement system and photoluminescence (PL) measurement system. The surface morphology of the fabricated films was studied by Field Emission Scanning Electron Microscopy (FESEM) systems. The elemental properties and chemical bonding states of the films were analyzed using X-Ray Photoelectron Spectroscopy (XPS) system. Finally, the photoresponse of the fabricated devices were measured by incident photon conversion efficiency (IPCE) measurement system.

2.1 Growth Equipment

The ZnO thin films and the photodetector device investigated in this research work were fabricated using the DIBS system, explained briefly in the following section.

2.1.1 Dual Ion Beam Sputtering (DIBS) System

Elettrorava make DIBS system, is a specifically designed, compact, clean room compatible, and versatile state-of-the-art system. DIBS is a very effective physical

vapour deposition technique for the preparation of epitaxial films under moderate vacuum, or ultrahigh vacuum conditions [1-3]. This is a relatively simple and versatile technique commonly used for thin-film deposition of high crystalline quality. The main components of this system are

- (i) Deposition chamber (DPC),
- (ii) Load lock chamber (LLC),
- (iii) Ion sources,
- (iv) Robotic arm,
- (v) Vacuum pumps and vacuum gauges,
- (vi) Heater assembly, water chiller and parameter controlling unit

Figure 2.1 shows an actual image of DIBS system. The system consists of two chambers. First is main deposition chamber (DPC), and the other one is a load lock chamber (LLC).



Figure.2.1 Actual image of dual ion beam sputtering system

The actual growth is executed in DPC while the LLC is used for loading the sample. Both the chambers are separated by a gate valve. The vacuum is maintained in both DPC and LLC by two separate turbomolecular pumps. Vacuum gauges are employed to measure the vacuum level in the deposition and

load lock chamber. The background pressure inside the DPC and LLC are maintained at 10⁻⁸ mbar and 10⁻⁹ mbar respectively. The chambers are made up of stainless steel as it is non-corrodible, non-magnetic, easy to weld and clean, highly malleable and have good out gassing characteristics [4]. The substrate holder is attached to the heater assembly for maintaining the desired temperature ranging from room temperature to 1000 °C during the growth as well as annealing processes. The water chiller is employed to remove heat from the deposition chamber, target assembly and vacuum pumps. DIBS system growth parameters i.e. growth temperature, gas pressure, gas composition and RF power are controlled by parameter controlling unit of DIBS system [3-5]. In order to load the sample: first, the pressure of LLC is released and then the sample is kept in LLC, which is finally loaded in the main deposition chamber by an automatic computer-controlled robotic arm. The DIBS system's schematic diagram is shown in figure 2.2. This DPC chamber consists of two separate ion sources.

(i) Primary ion source or main deposition source



(ii) Secondary ion source or assist source

Figure 2.2 Schematic diagram of dual ion beam sputtering system

The function of main ion source is to sputter materials from a target. Four targets can be mounted in a rotating target assembly inside the chamber and the desired target can be chosen at the time of deposition. The secondary ion source i.e. the assist ion source which is exposed to substrate, is employed to pre-clean the substrate surface before film deposition and to hinder island formation and remove weak dangling bonds during the actual sputtering process [1,2]. The angle between the primary ion source and the sputtering target is fixed at 45° off normal while the angle between the assist ion source and the substrate is maintained at 60°. Another important unique features of the DIBS system are high-quality growth with reduced surface roughness, increased growth uniformity on a larger substrate area and in-situ substrate pre-cleaning before growth.



Figure 2.1 Schematic diagram of primary ion beam source

In DIBS system, Kauffman Robinson ion sources are employed to generate Ar^+ ion beam. Ar^+ ion beam is spatially mono-energetic and well confined [1-3]. Essentially, an ion beam source is a plasma source fitted with a set of grids enabling a stream of ions to be extracted. The primary ion source has three main parts: discharge chamber, grids and neutralizer. When the Ar gas is exposed to an RF field, it results in the production of Ar^+ gas in the discharge chamber. The gas is fed into a quartz or alumina chamber with an RF powered coil around it. The RF field excites free electrons until they have enough energy to break gas atoms
into ions and electrons. The gas is thus ionized and plasma is established. The various voltages applied on grids pull out the Ar^+ ions in the form of a beam from discharge chamber. Primary source contains three-grids to eject the ions and to reduce the beam spreading. The neutralizer (hollow cathode electron source) is used in primary source assembly to neutralize the positive ion beam [2]. The schematic diagram of primary ion source is shown in figure 2.3.



Figure 2.2 Schematic diagram of assist ion source

The assist ion source mainly contains end-Hall 400 ion source module and hallow-cathode neutralizer assembly. This source has three varieties of power supplies (1) Keeper power supply (2) Emission power supply (3) Discharge power supply. The keeper and emission power supplies are employed for hollow cathode neutralizer. Discharge power supply offers voltage and current to end-Hall 400 ion source module. The assist ion source possesses much higher ion-current capabilities at even low ion energies (e.g. 200 eV and less) enabling suitable etching rates [4]. Moreover, cost-effectiveness, broad ion-beam coverage, and greater reliability are the expected rewards of assist ion source. Figure 2.4 shows the schematic diagram of Assist ion source. The Discharge Power Supply offers voltage and current to the anode of the end-Hall 400 ion source module and generates the positive Ar^+ ion beam. In order to ignite the hollow cathode and keeping the cathode hot enough for thermionic emission of electrons, the Keeper

Power Supply delivers voltage and current to the hollow cathode neutralizer [3,4]. The Emission Power Supply provides a negative voltage to the hollow cathode after it is ignited by the Keeper Power Supply and controls the electron beam emitted from the hollow cathode neutralizer to neutralize the positive ion beam of end-Hall 400 ion source.

2.2 Characterization techniques

The various characterization performed on the thin films and devices in this research work are illustrated briefly in following sections.

2.2.1 X-ray Diffraction

X-ray diffraction is one of the widely used nondestructive experimental techniques to acquire a wide variety of information such as lattice parameters, preferred orientation of the crystal, phase composition, grain sizes, lattice strain, residual stress etc.[6,7]. A collimated X-rays beam incidents on a sample and is diffracted by the crystalline phases in the sample follows the Bragg's law such that:

$$n\lambda = 2d\,\sin\theta\tag{2.1}$$

where λ is the wavelength of the incident X-ray beam, *d* is the inter-plane separation of lattice between atomic planes in the crystalline phase, θ is the angle between atomic planes and the incident X-rays beam and *n* is an integer that represents the interference order.



Figure 2.3 Schematic diagram of X-Ray diffraction

The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ . This diffraction pattern is used to identify the sample crystalline properties [7]. The basic principle of X-Ray diffraction is shown in figure 2.5. The arrangement of atoms in a pure solid in a regular periodic pattern is called 'lattice'. The inter-atomic distance and interaction of atoms of each crystalline lattice are unique hence each of them possess a unique XRD pattern which helps to identify its crystal structure. The XRD patterns of the diffracted beam not only include the information of peak position and intensity but also offers several information of the crystal structure of the samples under consideration.

In this research work, the crystal structure of the thin films was examined by a Bruker D8 Advance X-rays diffractometer equipped with a copper target (CuK α) to generate the incident X-rays of wavelength $\lambda = 0.154178$ nm for the diffraction measurement in Bragg Brentano configuration [7]. The actual image of this XRD system is shown in the figure. 2.6.



Figure 2.4 Photograph of Bruker D8 Advance X-ray diffractometer

2.2.2 Hall Measurement

The electrical behavior of the thin films was characterized by Hall Effect measurements using the Van der Pauw configuration [8]. The Hall Effect offers a relatively simple and straightforward way for measuring the electrical parameters such as carriers (electrons and holes) concentration, electrical resistivity and the mobility of carriers in semiconducting thin films. The Hall Effect is based on the principle that when the magnetic field is applied perpendicular to the charge carriers flow then the Lorenz's force act on charge carriers in the perpendicular both magnetic field as well as the charge carrier flow. The Hall Effect geometry is shown in figure 2.7.



Figure 2.75 Hall Effect geometry

In order to determine carrier concentration first, the Hall voltage (V_H) was measured by applying both a magnetic field perpendicular to the sample and a current through the sample. The combination of the current flow (I) and the magnetic field (B) causes a transverse current. The resulting potential (V_H) is measured across the device. In figure 2.7, a constant current 'I' is flowing along the 'x'-axis from left to right while the magnetic field applied in 'z' direction which is perpendicular to the current flow. The direction current 'I' is in the direction hole flow or in the opposite direction of the electron flow. In either case, the magnetic Lorentz force $B.(v \times q)$ causes the carriers to drift toward the negative 'y'-axis and accumulate on the side of the sample to produce an electrical surface charge. As a result, a potential drop across the sample called Hall voltage (V_H) is formed. Using this Hall voltage, carrier concentration is calculated [9,10]. Figure 2.8 shows the photographic image of four probe Hall measurement system. In order to calculate the electrical behavior, both the sample thickness (d) and its resistivity (ρ) need to be measured.



Figure 2.8 Photograph of Four Probe Hall measurement system

The electrical resistivity (ρ) is calculated by measuring current-voltage characteristics in eight Van der Pauw configuration. The carrier mobility (μ) of carrier in the material depends on free-carrier concentration (n) and electrical resistivity (ρ) of material as in equation [10]:

$$\mu = \frac{1}{qn\rho} \tag{2.2}$$

where q = Electron charge (C/cm²), n = Carrier concentration (cm⁻³) and $\mu =$ Carrier mobility (cm²/Vs). In this work, the electrical properties i.e. resistivity, carrier concentration and mobility of doped ZnO based thin films were measured using Four Probe Hall measurement setup in Van der Pauw geometry using Keithley source meter (model 2612A) with a magnetic field of 0.5 Tesla.

2.2.3 Field Emission Scanning Electron Microscopy

Field emission scanning electron microscope (FE-SEM) is commonly used for analyzing morphological properties of the samples under observation. FE-SEM is considered as a very powerful microscopic technique which provides 100000 times magnified image of the sample [11]. The FE-SEM mainly involves four components: (a) an electron source known as an electron gun, (b) an electron condenser lens which controls the size of the electron beam, (c) XY defection coils to move the electron beam in a controlled fashion, and (d) the electron detectors. All components are fixed in a chamber and this whole chamber is kept under ultra-high vacuum conditions. In FE-SEM system, a different type of electron source called Field Emission Gun is used for very high magnification. In this system, the source is not heated by the current; instead, an electric field is used to obtain the electrons from the source, which is a very sharp tungsten crystal or zirconium oxide. Here, the electrons have energy in the range of 1-40 KeV [11]. A ZEISS Supra55 FE-SEM system was used to observe the surface morphologies of the doped ZnO thin films. Figure 2.9 shows the actual image of this FE-SEM system



Figure 2.6 Photograph of field emission scanning electron microscope

When the electron beam falls on the sample, it interacts with the atoms and the electron is slowed down due to strong elastic scattering. The atoms absorb the energy and get ionized. Some of the electrons from the sample atoms are released. These are called 'secondary electrons'. They usually have lower energy (< 50 eV) compared to the primary electrons from the electron gun. When the electron beam falls on the surface of the sample, the electrons are scattered and the beam diameter increases. Hence, in the beginning, it spreads like a cone and the area below the surface also is probed. The beam energy decreases as it goes deeper inside the sample. The number of secondary electrons produced also decreases. Besides, the electrons from the surface easily escape and arrive at the detector. The electrons from the bottom (trough) may be captured by other atoms before they escape to the surface. Hence only fewer secondary electrons from the trough

come to the detector. Overall, the secondary electrons at the detector are essentially produced at the top of the surface. These secondary electrons are used to present the morphology and topography of the sample. The detector of instrument counts the number of e-interactions and display on the screen whose intensity is determined by this number, producing the FE-SEM image [11-12].

2.2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is very well known spectroscopic technique. XPS offers various information about the sample under consideration such as the identification of the elements present in the film, elemental composition, oxidation states, and chemical state of each element. Because of its versatility, it is also called Electron Spectroscopy for Chemical Analysis (ESCA). This technique is based on the principle of photoelectric effect [13,14]. The basic principle of the method is when photons of high energy incident on the surface of a sample under observation then interact with an electron present in any of the orbitals of the element. The electron is ejected out with certain kinetic energy. This kinetic energy is measured by the detector. The binding energy is then calculated by subtracting the kinetic energy of the electron and work function from the energy of incident photon. The spectrum is obtained by electron counting rate as a function of binding energy. The binding energy of each electron of an element is unique. The binding energy of an atom can be evaluated by the following equation.

$$E_{b} = \hbar\omega - E_{kin} - \varphi_{s} \qquad (2.3)$$

where E_{kin} is kinetic energy of the emitted electron, $\hbar\omega$ the energy of the x-ray photon and φ_s the spectrometer work function. In the XPS spectrum, the binding energy of electron present in the innermost orbital of an element obviously appears at higher binding energy than an electron which is present in the outer orbital. Binding energies of 1s orbitals increase with atomic number. The variation of the kinetic energies of the ejected electrons identifies the elements present and chemical states of the elements [13,14]. Electrons are emitted from the core levels of the elements in the material and collected by a detector which can be used to determine the binding energies of the individual core levels on the surface. The number of electrons with a particular energy is counted and this data can then be deconvoluted to fit reference peaks for the individual elements. The exact chemical nature of the materials can then be determined from both the binding energy positions of the peaks and from the integrated area under the curves, which gives information regarding the quantity of the material present.

XPS utilizing a PHOIBOS 100 analyzer with Al K_{α} radiation source (1486.6 eV) as shown in figure 2.10 was used for elemental analysis of doped ZnO thin films in this research work. Before carrying out XPS measurements, each film was etched using 1 KeV Ar⁺ ions beam in order to remove the contaminated surface layer of thin films.



Figure 2.7 Photograph of X-ray photoelectron spectroscopy system

The main components of XPS system are X-ray Source, Sample Holder, Analyzer, Detector and Signal Processor [13,14]. A common X-ray source is an X-ray tube with both Al or Mg target and a suitable filter. In sample holder, a sample of a piece of metal is mounted close to the source in the chamber, which is evacuated to 10^{-9} torr to avoid contamination by oxygen and water vapors. Hemispheric analyzers are used to distinguish electrons of different energies by applying electrostatic and magnetic fields.

2.2.5 Spectroscopic Ellipsometry

Spectroscopic Ellipsometry (SE) is an important tool to analyze the optical properties of different thin film materials since it possesses exceptional benefits in comparison to other techniques [15]. Being a non-destructive and sensitive technique, it is commonly used to determine film thickness and optical constants. However, it is also used to characterize composition, crystallinity, roughness, doping concentration, and other material properties associated with a change in optical response [15,16]. In this technique, these two independent quantities ψ and Δ denoted a change in amplitude and phase of polarization respectively, are measured consequently and hence the real and imaginary part of the complex dielectric function can be obtained directly. Thereafter a suitable model allows the precise extraction of the optical constants with precise values of for these parameters Ψ and Δ can be related to the complex reflectance ratio ρ given by the equation below [29-31].

$$\rho = \frac{r_p}{r_s} = \tan \psi \, e^{i\Delta} \tag{2.4}$$

where r_p and r_s are referred as the complex reflection coefficients for the *p*- and *s*polarized electromagnetic waves, respectively, tan (Ψ) is the ratio of the amplitude reflection coefficients, and Δ is the phase difference between *s*- and *p*polarized waves $\Delta = \delta_p - \delta_s$. The spectra of these ellipsometric parameters ψ and Δ depends on opto-electronic properties of the material under observation. The primary components of ellipsometry system are a light source, polarization generator, sample, polarization analyzer, and detector [15,16]. The polarization generator and analyzer consist of optical components that manipulate the polarization: polarizers, compensators, and phase modulators.

In this work, optical properties and thickness of thin films were measured by M-2000D J. A. Woollam Variable Angle Variable Wavelength Spectroscopic Ellipsometer. In this system, the measurement can be performed at different angles for the wavelength range of 200-1000 nm. The photographic image of

Variable Angle Variable Wavelength Spectroscopic Ellipsometer is shown in figure 2.11. The SE measurement data analysis was performed using a three-layer optical model consisting of an Si substrate, doped ZnO layer, and a top roughness layer [16]. Theoretical spectra by fitting the parameters with the PSemi-M0 oscillator model is in good agreement with experimental spectra with a low value of mean square error (MSE). PSemi-M0 model is utilized to model the complex dielectric function which is occurring due to excitonic transitions for a crystalline semiconductor such as ZnO. PSemi-M0 model is based on the inter-band transition at the energy-band critical points and, the real and imaginary parts of the dielectric function are related each other by Kramers–Kronig dispersion relations, which is essential for a many-parameter determination from measured data. Moreover, this model is also suitable to illustrate transparent semiconducting materials with absorption in the wide wavelength range.



Figure 2.81 Photograph of spectroscopic ellipsometry system

2.2.6 Photoluminescence

Photoluminescence (PL) is the optical emission obtained by photon excitation and is commonly observed with III-V semiconductor materials. This type of analysis allows non-destructive characterization of semiconductors [17]. A light source (usually laser) possess the photon energy larger than the band-gap energy of the semiconductor under observation producing the electron-hole pairs within the semiconductor. The produced electron-hole pairs can be recombined via either radiative or non-radiative recombinations. The light emitted from radiative recombination is detected by a detector which gives the photon count as a function of wavelength. The information of the energy band structure of semiconductor and defect levels could be obtained from the analysis of PL spectra [17]. The peak emission in PL spectra correspond to transitions of electrons from conduction band minimum to valance band maximum and related to the band gap of the material. The image of PL spectroscopy experimental set-up is demonstrated in Figure 2.12.



Figure 2.9 Photograph of Photoluminescence Measurement Setup

In this research work, the luminescent properties of doped ZnO based films were measured by using Dong Woo Optron PL set-up, affixed with a 20 mW continuous wave (CW) He-Cd laser (excitation wavelength = 325 nm, TEM₀₀ mode), monochromator, chopper, lock-in amplifier, and a photomultiplier tube (PMT) detector. All measurements were performed in a completely dark room.

2.2.7 Incident Photon Conversion Efficiency

The spectral response of a photodetector device provides information on the physics at play at the device. The quantum efficiency (QE), also referred to as

Incident Photon to Charge Carrier Efficiency (IPCE) - indicates the ratio of the number of photons incident on a solar cell to the number of generated charge carriers. In order to understand the conversion efficiency as a function of the wavelength of light impingent on the cell, the QE/IPCE measurement is critical for materials research and device design [18]. This measurement is performed by shining a monochromatic probe beam onto the sample and recording the photocurrent generated as a function of wavelength. The beam power of the probe is first characterized, using a detector of known responsivity. Subsequent measurement of the photocurrent generated by the device under test as a function of wavelength allows for the determination of spectral responsivity. In this work, the fabricated photodetector devices were characterized using Bentham PVE300 IPCE system. The actual image of IPCE measurement set-up is shown in figure 2.13.



Figure 2.103 Photograph of IPCE measurement setup

The unique features of IPCE system are as below [18]

- (i) Optimized tunable light source based on xenon-quartz tungsten halogen dual source and a single monochromator.
- (ii) A wide range of operation (300-2500nm).
- (iii) Reflective optics beam delivery to sample plane.

- (iv) A range of sample mounts and detection electronics to suit all device types and architectures.
- (v) Windows control software provides full automation via USB.
- (vi) Direct determination of device spectral response (AW⁻¹).
- (vii) Direct determination of device external quantum efficiency (EQE %)
- (viii) Direct determination of total reflectance, R, and transmittance, T.

2.3 References

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Chapter 3

Gallium doped ZnO MSM Photodetector

3.1 Introduction

In recent times, the research on ZnO based ultraviolet (UV) photodetectors (PDs) have gained interest due to its unique properties such as direct wide band gap of 3.37 eV, large exciton binding energy of 60 meV, high radiation hardness and hence they find applications in air quality monitoring, flame detection and defense applications such as UV communications and missile warning systems [1, 2]. ZnO films for UV PDs have been deposited by various techniques such as magnetron sputtering [3], molecular beam epitaxy [4], and pulse laser deposition [5]. Moreover, various studies based on Ga-doped ZnO (GZO) thin films for UV PDs have been reported [6-9]. However, there are no reports on a detailed study of GZO based UV PD fabricated by dual ion beam sputtering deposition (DIBSD) [10, 11] system. Different PD structures such as photoconductive, Schottky, metal semiconductor metal (MSM), *p-n* and *p-i-n* junction based on ZnO material have been reported. However, MSM structure is preferred over others for UV PD applications because of its attractive advantages such as fabrication simplicity, single active layer requirement, and high gain [12].

Since almost all kind of photodetectors require external supply for their operation, it is highly desired to have PDs based on self-powered mechanism. These PDs are critical in terms of energy saving point of view and are preferred for long-term monitoring of air-pollution and wastewater. However, the reports on unbiased photoresponse of ZnO based MSM photodetectors are still rare. Instead, recently, Bai *et. al* and Ni *et. al* have reported similar results, for ZnO based heterostructure [13, 14]. In this work, we discuss the phenomenon of zero bias photoresponse of GZO thin film PD, grown by DIBSD system, by investigating

the electron transport mechanism through Au/GZO interface. In our GZO based photodetector, the internal quantum efficiency (IQE) at zero bias was as high as 37% with ultraviolet to visible rejection ratio of more than five orders.

3.2 Experimental details

GZO films, with a thickness of ~350 nm, employed as an active layer photodetector was grown on Si (100) by DIBSD using 3 at. % GZO ceramic target. Other relevant growth details are mentioned elsewhere [15]. The deposition was carried out in Ar ambient (5 sccm) at varying substrate temperatures from 200 to 600 °C (samples S2 to S6). Finally, the UV PDs (D2 to D6) were fabricated by depositing 50 nm thick Au interdigitated contacts on GZO films by magnetron sputtering at room temperature. The mobility and carrier concentrations were measured by four-probe Hall measurement technique in van der paw geometry. X-Ray diffraction (XRD) of films was carried out using a Rigaku X-Ray diffractometer with Cu K alpha radiation ($\lambda = 1.54$ Å). Currentvoltage (I-V) measurements were performed using Keithley 2612 sourcemeter and Everbeing cryogenic probe station. The thickness and the optical constants of the films were determined by J. A. Woollam spectroscopic ellipsometer. Hiden Secondary ion mass spectroscopy (SIMS) workstation with oxygen ion gun of energy up to 5 KeV was used to verify the presence of Ga in GZO film. The spectral responses and the quantum efficiency of the fabricated devices were characterized with Bentham photovoltaic characterization system consisting of 150 W Xe lamp, chopper, monochromator, and a lock-in amplifier.

3.3 Results and discussion

3.3.1 Electrical and structural properties of GZO films

XRD of GZO films deposited at various growth temperatures (T_g) are shown in figure 3.1(a). It can be clearly observed that all GZO films have a preferred *c*-axis orientation perpendicular to the substrate. No metallic Zn or Ga or any of Ga oxide characteristic peaks were observed in XRD pattern suggesting that Ga atoms have substituted Zn atoms effectively without changing the original hexagonal structure of ZnO [16]. The position of (002) peak and its corresponding full-width at half-maximum (FWHM) and grain size, as estimated by Scherer's formula [17] are populated in table-3.1.



Figure 3.1 (a) XRD patterns of GZO films grown at different T_g , (b) carrier concentration, mobility, and resistivity of GZO films, (c) SIMS profile of as grown GZO S3 film.

Sample	Growth Temp.	Peak Position 20	FWHM	Grain Size
(Device)	(°C)	(Degree)	(Degree)	(nm)
S2 (D2)	200	34.05	0.32	27.1
S3 (D3)	300	34.3	0.2	43.4
S4 (D4)	400	34.25	0.36	24.1
S5 (D5)	500	34.32	0.3	28.9
S6 (D6)	600	34.27	0.68	12.7

Table 3.1 XRD Peak position, FWHM, grain size of GZO films.

The angular position of (002) peaks is much closer to that of ZnO powder peak (34.34°) indicating stress-free film deposition. As represented in figure 3.1(a), as T_g was increased from 200 to 300 °C, intensity of (002) peak increased on account of increase in the dopant atomic energy that allowed the dopants to move from interstitial and/or grain boundary regions into the Zn lattice sites, resulting in an increase in the crystallinity along with higher carrier concentration [16]. However, the (002) peak intensity declined with further increase in T_g beyond 300 °C, indicating a reduced crystalline quality with higher T_g (400-600 °C) [18]. The FWHM of (002) diffraction peak is the smallest at $T_g = 300$ °C, indicating the largest grain size and highest crystalline quality. Moreover, the grain size increases with the increase in T_g from 200 to 300 °C, whereas it reduces with further increase in T_g .

The Hall measurement exhibited *n*-type conduction for all GZO films. This *n*-type conduction is due to Ga incorporation into GZO where Ga will occupy Zn sites and be ionized into Ga⁺³. This process supplies one free electron to the conduction band for each Ga atom added. Figure 3.1(b) shows the carrier concentration, mobility, and resistivity of GZO films as a function of T_g . The electrical resistivity of GZO film decreased marginally when Tg reached 300 °C and afterward the resistivity increased sharply with higher Tg. A minimum resistivity value of $5.3 \times 10^{-4} \Omega$ -cm is obtained at 300 °C. Similarly, the carrier concentration demonstrated an enhancement [19] up to 300 °C and then reduced gradually with further increase in T_g. The trend of variation of electrical resistivity and carrier concentration was guided by the crystallinity of GZO films, as depicted in figure 3.1(a) [19]. However, the carrier mobility exhibited an initial increase with increasing T_g from 200 to 400 °C and then decreased sharply at 500 °C. This decay in mobility, with a carrier concentration of $\sim 10^{20}$ cm⁻³, may have been caused by ionized impurity scattering [20]. As it is well known that mobility in heavily doped ZnO is controlled by various factors such as dislocations, grain boundary scattering, ionized impurity scattering, and carrier concentration etc. [20], a sharp increase in mobility at 600 °C may be correlated to lesser scattering

effect with comparatively low electron concentration at 600 $^{\circ}$ C [21]. The depth profile of the main elements in an as-grown GZO film (S3) is shown in figure 3.1(c). It is evident that Ga has been clearly detected, and its concentration profile is quite flat throughout the film depth.



Figure 3.2: (a) Schematic structure of MSM photodetector. (b) Optical absorption spectra of GZO film grown at $T_g = 300$ °C. Inset shows a plot of $(\alpha hv)^2$ vs. hv of all GZO films. (c) Normalized photoresponse of all fabricated devices. (d)

Spectral responsivity of device D3 at zero bias and 1V bias. (e) The timedependent photoresponse of GZO photodetector at 1V bias. (f) The responsivity decay of PD w.r.t time.

3.3.2 Photoresponse measurement of MSM PDs

Shadow masking technique was deployed to fabricate MSM-type device structure using a metal interdigitated mask. The electrode fingers were 5 mm long, 100 μ m wide and the spacing between two adjacent fingers were 200 μ m. The schematic diagram of the fabricated device is shown in figure 3.2(a). Figure 3.2(b) shows the absorption spectra of sample S3 that clearly depicts that the layer has a strong absorption to photons with a wavelength shorter than 370 nm, while it is almost transparent to those with a wavelength longer than 400 nm. The spectral response measurements of PD, as shown in figure 3.2(c), were carried out from 300 to 500 nm.

The photoresponsivity was measured in unbiased (zero bias) mode as well as applying a small positive bias voltage, 1V at room temperature. It is observed that the device D3 has the highest responsivity of 58 mAW⁻¹ at zero bias, which is ~15 times and 3 times larger than that reported in ref [8] and ref [22], respectively. The response peak is centered on 325 nm and a cut-off wavelength around 370 nm corresponding to the band gap energy of GZO films. Table-3.2 compares the various reports on zero bias photoresponse from available literature [8, 22, 23]. Responsivity (R_i) of the photodetector can be expressed as $R_i =$ $\eta g(q\lambda/hc)$ [9], where λ is wavelength, q is electronic charge, h is the Plank's constant, c is light velocity in free-space, η is EQE, and g is the gain. An increase in the quantum efficiency was observed on application of external bias exhibiting the photoconductive gain. Table-3.3 shows the values of absorption edge wavelength, as calculated using the inset of figure 3.2(b), and peak photoresponse wavelength, as evaluated from figure 3.2(c), of all GZO samples and zero bias EQE and IQE of corresponding devices. It is clear that the trend of variation of photoresponse peak wavelength is governed by that of absorption peak wavelength.

Structure	Deposition Technique	Peak Responsivity	Ref.	
MSM	Plasma assisted PLD	4 m	[8]	
(Au - IGZO - Au)	I lasilla assisted-I LD	4 IIIA W		
MSM	Plasma assisted_MRF	$20 \text{ m} \text{ A} \text{ W}^{-1}$	[22]	
(Au - ZnO - Au)	T lasina assisted-wide	20 1117 1		
MSM	RF magnetron sputtering	1.82 m	[23]	
(Al - ZnO NW - Pt)	KI [*] magnetron sputtering	1.02 IIIA VV	[23]	
MSM	Dual ion beam sputtering	58 m Λ W ⁻¹	This work	
(Au - ZnO - Au)	Duar fon beam sputtering	50 IIIA W	THIS WOLK	

Table 3.2 Comparative analysis of zero bias photoresponse from MSM-based UV PD in literature

Table 3.3 The absorption edge wavelength and peak of photoresponsewavelength, zero bias EQE, and IQE of GZO based UV PDs

Sample	Absorption	Peak Photoresponse	EQE	IQE
(Device)	Edge (nm)	Wavelength (nm)	(%)	(%)
S2 (D2)	356	355	6.11	10.18
S3 (D3)	325	325	22.5	37.41
S4 (D4)	340	365	3.21	5.35
S5 (D5)	351	355	1.01	1.68
S6 (D6)	363	375	0.99	1.65

Figure 3.2(d) shows the spectral response of device D3 at zero and 1V bias, respectively. Device IQE was determined by normalizing the EQE as IQE = EQE/(1-R) [24], where R is the measured reflectance of the GZO layer. While the EQE at zero bias was measured to be ~22.5%, it reached to 48% at 1 V bias with an average photocurrent of 23 mA. A significantly higher value of IQE at zero bias was calculated to be 37.4%. On further increase in applied bias, the photocurrent reaches saturation and the measurement was limited by instrument capability. Moreover, photosensitivity measurements of the GZO PDs were performed by turning the continuous UV illumination at 325 nm ON and OFF at an applied bias of 1 V. Figure 3.2(e) shows the photocurrent rise and decay as a function of time at an applied bias of 1 V. The device was kept in dark for 12 hours to stabilize and then exposed to UV radiation for 25 s. The rise time is

defined as the time needed to reach 90% from 10% of the maximum photocurrent while the fall time is the time needed to reach 10% from 90% of the maximum photocurrent [6]. From figure 3.2(e), the values of rise time of 806 ms and fall time of 54 s were obtained for the GZO UV photodetector. The photosensitivity (S) can be expressed as $S = (I_{light} - I_{dark}) / I_{dark}$ [11], where I_{light} and I_{dark} are the light and dark current with and without UV illumination, respectively. The values of photosensitivity and on/off ratio (I_{light} / I_{dark}) for device D3 were calculated to be 0.076 and 1.076, respectively. In order to assess the feasibility of using the MSM PD for practical applications, the responsivity measurement at zero bias voltage is conducted, as demonstrated in figure 3.2(f), for different intervals: (a) first 7 days, (b) 14 days, (c) 30 days, and (d) 60 days after device fabrication. It should be noted that the device was kept in normal ambient condition without having any passivation layer on top of it during the photo stability measurement.

3.3.3 Electron transport mechanism

In order to get a better understanding of the carrier transport phenomenon at the Au/GZO interface, one must recognize which transport process plays a dominant role in our MSM PD. Various models have been proposed to explain the excess leakage current through Au/GZO Schottky barrier but in general, the total current constitutes of both thermionic emission and tunneling component. Assuming that thermionic emission is predominant, the reverse saturation current of a diode with tunneling is given as [25],

$$I = I_s e^{(V_r/E')} \tag{3.1}$$

where I_s is saturation current, V_r is applied reverse bias, and E' is the characteristic energy related to tunneling probability with E_{00} as the tunneling parameter given as

$$E_{00} = (q\hbar/2)(N_D/m^*\varepsilon_s)^{1/2}$$
(3.2)

where \hbar is reduced Plank's constant, N_D is donor density, m^* is effective mass of electron, ε_s is relative dielectric constant of semiconductor. If $kT \gg qE_{00}$, thermionic emission prevails over tunneling otherwise tunneling plays the

dominant part when $kT < qE_{00}$. In our case, we have obtained a reasonable fit with the measured values as $m^* = 0.39m_0$, $\varepsilon_s = 8.12$ [26], and N_D of the order of 10^{20} cm⁻³, from Hall results. By fitting the above parameters in equation (2), the minimum value of E_{00} was calculated to be 74 meV for D5 and maximum value was found to be 374 meV for D3, which is almost 14 times higher than the thermal energy (25 meV), to conclude that tunneling is the predominant mechanism responsible for the conduction in all the samples. The maximum value of E_{00} for D3 is justified from the fact that the grain size of S3 is the largest, as observed in table-3.1, indicating a large surface area to volume ratio and hence increased mobility [20] and improved crystal quality resulting in enhanced photoresponsivity [7].





Figure 3.3: Semilogarithmic I-V plots for (a) Au1/ZnO/In (b) Au2/ZnO/In, with varying temperature and in dark condition. (c) I-V plots of both Au contacts in dark at 80 and 300K. (d) Energy band diagram at zero bias voltage.

In order to investigate the high photoresponse at zero applied bias, a model based on thin surface barrier [27] with asymmetric electrodes [28, 29] is assumed. It is well known that surface barrier lowering occurs at the metalsemiconductor interface [25, 30] due to the presence to donor defect states, resulting in a reduction of Schottky barrier width such that the electron can easily tunnel across the junction, as confirmed by above calculation. To establish the dissimilar characteristic of identically deposited Au electrodes on GZO films, I-V measurements for both forward and reverse bias voltages were performed in a temperature ranging from 80 to 300 K. Indium contact was realized on top of GZO surface to form a perfect ohmic contact. Figure 3.3(a) shows the temperature dependent ln(I)-V curves for Au1/GZO/In while figure 3.3(b) displays the temperature dependent ln(I)-V curves for Au2/GZO/In, where Au1 and Au2 are two Au contacts on GZO films, respectively. It is clearly observed that the current for Au1/GZO/In is temperature independent confirming the tunneling of carriers, whereas current increases for Au2/GZO/In contacts demonstrating a relatively weaker Schottky behaviour. Moreover, figure 3.3(c) depicts I-V characteristics of both Au contacts at 80 and 300 K illustrating the clear inhomogeneity in the identically deposited electrodes.

The asymmetrical behavior of Au electrodes may have been originated from the dissimilar accumulation of surface/donor defect states at the interface of Au/GZO junction [31]. The variation in the generation of such interface defect

states might have been resulted due to dissimilar surface damage triggered by sputtering of Au electrodes on GZO films. Based on the experimental results and analysis, the energy band diagram for GZO-based MSM PD in zero biased conditions is shown in figure 3.3(d). Under the UV illumination, the photogenerated electrons tend to move towards the GZO while the photogenerated holes move towards the metal contacts. The interface states may be ionized by the accumulation of these hot carriers, modifying the local potential, which has been displayed by the band bending at the interface of figure 3.3(d). In order to verify the assumed hypothesis, the Schottky barrier heights for two Au contacts is calculated using the equation $I = AA^*T^2 \exp(-q\Phi_B / K_B T)$ where I is the current through the Schottky barrier, A is the contact area, A^* is Richardson's coefficient, T is absolute temperature, and $q\Phi_h$ is the barrier height [32]. The values of $q\Phi_b$, as measured from the forward biased region in figure 3.3(c) at room temperature, show very little difference for Au1/GZO/In (0.342 eV) and Au2/GZO/In (0.345 eV). However, in the reverse bias region this difference is comparatively larger with 0.344 eV for Au1/GZO/In and 0.352 eV for Au2/GZO/In. Liu et. al [32] have reported similar observations in ZnO film with electron concentration of order of 1×10^{17} cm⁻³, due to trapping of carriers in the presence of trap states. In this case, GZO films having an electron concentration $\geq 10^{20}$ cm⁻³ the phenomenon is attributed to the ionization of interface states [33] on exposure to UV light. This ionization of interface states in highly conducting films enhances the free electron charge in conduction band and the thereby shifting the quasi Fermi level to higher energies [34] resulting in lowering of barrier height and enhanced carrier tunneling. There can be two-fold explanations behind higher zero bias photoresponse from our MSM-based UV PD as compared to others in literature, as shown in table-3.2: (1) good crystalline quality of GZO film deposited by DIBSD system, (2) high electron concentration of the order of 10^{21} cm⁻³ and a very low electrical resistivity allow a significantly larger amount of photocurrent to pass between the electrodes under the exposure of UV illumination. The physical transport of electrons dominated by tunneling

under the effect of asymmetric Schottky barrier enables the device to operate at zero bias voltage.

3.4 Conclusions

In conclusion, highly conductive GZO film based UV photodetectors were fabricated by dual ion beam sputtering. Peak photoresponse of 58 mA/W at room temperature was observed at zero bias with a cut-off wavelength of 325 nm. The value of EQE at zero bias was ~22.5% and it reached to 48% at 1 V bias with an average photocurrent of 23 mA. A significantly higher value of IQE at zero bias was calculated to be 37.4%. The dissimilar characteristics of identically deposited electrodes due to process induced interface states were confirmed by temperature dependent I-V measurements. Tunneling of carrier across Au/GZO interface was observed due to high electron concentration and ionization of interface states.

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Chapter 4

Optoelectronic properties of P-doped *p***-type ZnO**

4.1 Introduction

As discussed in the previous chapter, the research activities focused on ZnO and its emerging applications in various fields of optics and optoelectronics have gained momentum due to its advantageous material properties such as wide bandgap, large exciton binding energy, and radiation hardness etc. [1,2]. To realize these applications, the necessity is to have high-quality p-type ZnO films and their properties thoroughly investigated. Various research groups have put in considerable efforts for successful realizations of p-type ZnO by using group I and group V dopants such as Li [3-5], N [6,7], Sb [8] etc. Among these reports, the *p*-type conduction in phosphorus doped ZnO (PZO) has been reported by using pulsed laser deposition (PLD) [9-11], metal organic chemical vapor deposition (MOCVD) [12,13], RF magnetron sputtering [14-17], molecular beam epitaxy (MBE) [18], and ion-implantation [19] etc. However, the high resistivity, low carrier concentration and stability of the *p*-type behavior still remained a concern. Despite the several reports on the electrical and optical properties of phosphorus doped ZnO, the information on the doping effects of phosphorus on the dielectric function and optical constants of ZnO is still rare. Since, the optical constants play an important role in optical communication and designing of the optical waveguides and devices, as they are closely related to the electronic polarizability of ions and the local field inside materials [20], therefore, it is important to investigate the complex dielectric function of p-type ZnO considering the doping effects to make it useful in devices such as solar cells, light emitting diodes, lasers and photodetectors etc.

Spectroscopic Ellipsometry (SE) has been proved as a meaningful tool to analyze complex growth processes and layer structures and is capable of determining optoelectronic properties using reliable analytical models. Compared to other optical characterization techniques, SE analysis has distinct advantages [21], as it is a nondestructive technique that is very sensitive to ultrathin films and surfaces. Secondly, in this approach, two separate angular quantities (ψ and Δ) are measured simultaneously and hence the real and imaginary part of the complex dielectric function can be obtained directly. Moreover, the SE data can be analyzed using Kramers-Kronig consistent dispersion equations that enforce the physical relationship between the real and imaginary parts of the optical constants. Various reports have carried out spectroscopic ellipsometric studies of Al [20, 22], and Ga [23,24] doped *n*-type ZnO, however, a detailed spectroscopic ellipsometric study of P doped p-type ZnO grown by dual ion beam sputtering (DIBS), has not been investigated. Therefore, in this chapter, a reproducible method of fabrication of low resistive, stable and high hole concentration p-type ZnO by dual ion beam sputtering and a detailed investigation of electrical and optical properties of PZO films is presented.

4.2 Experimental details

PZO films were grown on sapphire and *n*-type Si (100) (resistivity 0.001 Ω -cm) substrates by DIBS [25] using P (5 at. %) doped ZnO ceramic targets. PZO deposition was carried out in oxygen-rich ambient in order to reduce the oxygen vacancy formation during deposition, with the Argon to Oxygen ratios of 2:4 while maintaining a deposition pressure of 3 × 10⁻⁴ mbar inside the deposition chamber. The deposition of PZO films was carried out at a substrate temperature (*T_g*) ranging from 300 to 500 °C. For simplicity, a notation of D3, D4, and D5, has been used for 300, 400 and 500 °C grown films, respectively. Post-deposition annealing of PZO films was carried out in N₂ ambient at 800 °C for 20 minutes to activate the acceptor dopants.

Structural and electrical properties were investigated by X-ray diffraction (XRD) [Rigaku X-Ray diffractometer with Cu-K α radiation ($\lambda = 1.54$ Å)] and Hall measurement in Van der Pauw configuration, respectively. The morphology of the samples was characterized by field-emission scanning electron microscopy (FESEM) using (Carl Zeiss Supra5) instrument. Current voltage (I-V) measurements were done using Keithley 2612A sourcemeter and Everbeing probe station for the samples deposited on low resistive n-Si. Secondary ion mass spectroscopy (SIMS) was performed on annealed PZO films using Hiden workstation equipped with oxygen ion gun of energy up to 5 KeV, to examine the incorporation of phosphorus dopants. The elemental analysis of PZO films was investigated by X-ray photoelectron spectroscopy (XPS) utilizing a PHOIBOS 100 analyzer with an Al K α radiation (1486.6 eV) as an excitation source. The films' thickness and optical constants were determined by spectroscopic ellipsometry [M-2000D J. A. Woollam rotating compensator spectroscopic ellipsometer]. The ellipsometric spectra were measured in the photon energy range of 1.2 - 6.4 eV at different angles of incidence (65°, 70°, and 75°) at room temperature. Room temperature photoluminescence (PL) measurements were carried out using a 20 mW continuous wave He-Cd laser having an excitation wavelength of 325 nm.

4.3 Results and discussion



4.3.1 Electrical and structural properties of PZO films



Figure 4.1 (a) XRD patterns for as-grown and annealed PZO films, (b) SIMS depth profile of annealed p-type PZO films grown at different temperatures. (c) I-V characteristics of p-PZO/n-Si heterojunction with PZO grown at 500 °C. The inset shows the linear I-V curves of In-n-Si and In-p-PZO contacts along with schematic diagram of p-PZO/n-Si structure.

Figure 4.1(a) shows the XRD pattern of PZO films grown on Sapphire, as a function of deposition temperature T_g . The crystal structures of all the films, asgrown as well as annealed films, were identified to be preferentially *c*-axis (002) oriented [26]. No other peaks corresponding to the presence of either elemental P or its oxide (P_2O_5) were identified in the XRD measurements. The diffraction peak intensity of (002) peak of PZO was observed to increase upon annealing along with a reduction in full-width at half-maximum (FWHM) [27], which signifies an improvement of crystalline structure, whereas the peak position shifted towards lower angle side for annealed films as compared to the as grown films. The crystallite size (D) of PZO films was calculated using Scherer's formula as, $D = (0.94 \lambda)/(B \cos \theta)$, where λ is incident wavelength, B is the FWHM, and θ is the Bragg diffraction angle. The crystallite size was observed to increase after annealing due to coalescence of smaller crystallites to form larger crystallites as previously reported [28]. The FESEM images of all the as-grown and annealed films are shown in figure 4.2 (a)-(f). The improvement in crystallinity and increment in the crystalline size can be easily observed for films grown at 500 °C, where the difference in crystallite size is significant as observed from XRD data in table 4.1.



Figure 4.2 FESEM images of as-grown PZO films (a) $300 \ ^{\circ}C$ (b) $400 \ ^{\circ}C$ (c) $500 \ ^{\circ}C$ and annealed PZO films (d) $300 \ ^{\circ}C$ (e) $400 \ ^{\circ}C$ (f) $500 \ ^{\circ}C$.

Table 4.1 summarizes the structural parameters e.g. full-width half-maximum (FWHM) of (002) diffraction peak, *c*-axis lattice constant and calculated crystallite size of *as-grown* and annealed PZO films. The (002) peak position of PZO was observed to shift towards higher angle side with an increase in T_g , whereas the calculated *c*-lattice parameter of the PZO films was found to decrease. It can be explained by considering the ionic radii of different elements in the tetrahedral coordination. Since the ionic radii of P³⁺ (0.058 nm) are much lesser than that of O²⁻ (0.138 nm) [17,29], the c-axis lattice constant would significantly decrease if P³⁺ substituted the O²⁻ site but this was not observed as shown in table 4.1.

Tg	Sample	Peak	FWHM (Deg.)	Crystallite	<i>c</i> -axis
	description	(2 0)	± 0.005	size (nm)	constant (Å)
300°C	as-grown	34.36	0.18	48.26 ± 1.53	5.21
	annealed	34.35	0.17	51.11 ± 1.52	5.22
400°C	as-grown	34.43	0.19	45.79 ± 1.41	5.20
	annealed	34.40	0.17	51.12 ± 1.48	5.21
500°C	as-grown	34.49	0.21	42.46 ± 1.72	5.19
	annealed	34.45	0.16	54.32 ± 1.69	5.20

Table 4.1 FWHM, crystallite size, (002) diffraction peak position and c-axis lattice constant of PZO films.

Since the radii of P^{3+} is smaller than that of Zn^{2+} (0.074 nm), it is expected to replace Zn^{2+} resulting in the shifting of diffraction peak to a larger angle [27]. Therefore, it was expected that P^{3+} replacing Zn^{2+} site was dominant mechanism resulting in the formation of P_{Zn} defects which acts as a donor but prefer to form $P_{Zn}-2V_{Zn}$ acceptor complex under optimum O-rich growth conditions [30,31]. The SIMS depth profiling of the annealed PZO films was performed in order to verify the incorporation of phosphorus in ZnO films and to determine the effect of deposition temperature on dopant concentration. Figure 4.1(b) shows the depth profile of the elements in the annealed PZO films. It was observed that the incorporation of phosphorus in the PZO films was almost uniform with respect to the thickness of the film confirming the good quality of deposited PZO films. An increase in phosphorus concentration was observed with increase in growth temperature, eventually resulting in higher hole concentration.

Dof	Denosition Mathad	Dopant	Hole Concentration	Mobility	Resistivity
Kel.	Deposition Method		(cm ⁻³)	(cm ² /Vs)	(\Omegacm)
[3]	Sol-gel spin coating	Li	$5.89 imes10^{17}$	0.2379	44.59
[4]	Pulsed DC sputtering	Li	$3 imes 10^{18}$	2.6	0.56
[5]	DC Magnetron sputtering	Li	$1.44 imes 10^{17}$	2.65	16.4
[6]	Plasma-assisted MBE	N	$2.21 imes 10^{16}$	1.33	202.14
[7]	Atomic layer deposition	N	$1 imes 10^{15}$	0.4	0.5
[9]	Pulse Laser Deposition	Р	$9 imes 10^{16}$	2	~10 ²
[12]	MOCVD	Р	$1.61 imes 10^{18}$	0.838	4.46
[14]	RF Magnetron sputtering	Р	$5 imes 10^{18}$	2	2
[10] Pulsa Lasar Daposition		D	5×10^{14} 1.5 $\times 10^{17}$	2.38 -	17 330
[10]	Fuise Laser Deposition	Г	5 × 10 - 1.5 × 10	38.3	17-330
[13]	MOCVD	Р	1.84×10^{18}	0.227	14.9
[15]	RF Magnetron sputtering	Р	$2.7 imes 10^{16} - 2.2 imes 10^{17}$	4 – 13	10.4 - 19.3
[17]	RF Magnetron sputtering	Р	$3.81 imes10^{16}$	2.82	64.2
[18]	Plasma-assisted MBE	Р	$6.0 imes 10^{18}$	1.5	
[29]	RF sputtering	Р	$9.2 \times 10^{15} - 4.2 \times 10^{16}$		20-51
[11]	Pulse Laser Deposition	Р	3.31×10^{15}	0.53	3.56×10^{3}
[52]	RF Magnetron sputtering	Р	$3.32 \times 10^{17} - 1.75 \times 10^{19}$	2.3	0.11 - 3.97
[8]	Dual Ion beam sputtering	Sb	$5.53 imes10^{16}$	8.84	12.7

Table 4.2 List of p-type ZnO reports and their electrical performance parameters in literature.
The *as-grown* PZO films were identified to be highly resistive hence the Hall measurement could not be performed on these samples. Therefore, the postdeposition annealing of the samples was carried out at 800 °C in N₂ ambient for 20 minutes to activate the acceptor dopants. After the annealing process, the Hall measurement revealed that all of the films were converted to *p*-type. The highest room temperature hole concentration was calculated to be 8.6×10^{19} cm⁻³ with resistivity and mobility of 0.066 Ω cm and 1.08 cm²/Vs, respectively, for annealed D5 films. The increase in hole concentration of D5 films over low temperature grown films could be correlated to the increased phosphorus content [29] as observed in the SIMS spectra in figure 4.1(b). These values of hole concentration are highest ever reported till date for phosphorus doped *p*-type ZnO with such a low resistivity. Table 4.2 presents a comprehensive list of *p*-type doped ZnO with a various dopant, and their electrical performance parameters reported in the literature.

To further confirm the *p*-type conduction in PZO, the I-V measurement of *p*-PZO/*n*-Si structure was performed. Figure. 4.1(c) shows the room temperature I-V characteristics of D5 film, in which a clear rectifying behaviour was observed confirming the *p*-type electrical conduction in PZO. Indium electrodes were deposited and annealed at 250 °C to obtain good ohmic contacts with PZO and *n*-Si. The schematic of *p*-PZO/*n*-Si device is illustrated as an inset of figure 4.1(c) along with the linear I-V plots of In-*n*-Si and In-*p*-PZO contacts indicating that all the electrodes exhibited good ohmic contact formation. The turn-on voltage for heterojunction with PZO films appears around 1.6 V - 1.8 V under forward bias, whereas the forward to reverse bias current ratio for *p*-PZO/*n*-Si junction at ±3 V was ~45 and ~31 for D3 and D5 PZO films, respectively. It is well known that P behaves as an amphoteric dopant in ZnO [2], with acceptor formation when it substitutes for O site (Po) and triple donor when it replaces Zn site (Pzn). However, since the formation energy of Pzn-2Vzn defect complex is much lower than Po in O-rich conditions [30], therefore the *p*-type behavior is expected due to

the formation of P_{Zn} -2 V_{Zn} acceptor complex at high temperature annealing [17], in agreement with the XRD results.

	Carrier Concentration /		Mobility		Resistivity	
T_{g}	type (cm ⁻³)		(cm ² /Vs)		(Ωcm)	
	(just after)	(after 1 year)	(just after)	(after 1 year)	(just after)	(after 1 year)
300 °C	8.94 x 10 ¹⁸	$4.32 \ge 10^{18}$	17.2	21.12	0.014	0.016
	<i>p</i> -type	<i>p</i> -type			01011	0.010
400 °C	6.10×10^{19}	1.41×10^{19}	7 57	11.5	0.013	0.014
	<i>p</i> -type	<i>p</i> -type	1.51	11.5	0.015	0.011
500 °C	8.62×10^{19}	3.77×10^{19}	1.08	2 /1	0.066	0.068
	<i>p</i> -type	<i>p</i> -type	1.00	2.41	0.000	0.008

Table 4.3 Electrical parameters of p-type PZO grown by dual ion beam sputtering

Since, the stability of p-type behavior in doped ZnO films remains a great concern, because many groups have reported the re-conversion of p-type films to n-type, over a period of time. Therefore, the Hall measurements were performed again on PZO samples after a year of sample fabrication and the data is populated in table 4.3. The films were observed to retain p-type behavior with a similar order of hole concentration as on the day of fabrication. Hence, it could be concluded that the DIBS provide a reliable and reproducible method to fabricate high quality and stable p-type PZO films.

4.3.2 Elemental analysis

In order to understand the chemical bond formation in *p*-type PZO, XPS analysis was performed. Figure 4.3(a) shows the binding energy spectra of P 2p core levels for 300 °C grown films. The experimentally obtained XPS spectra were fitted with Gaussian curves with peaks located at 127.9 eV and 132.5 eV. It has been reported in the literature that the binding energy of P 2p in P-O-P and P-O-Zn bonds lies between 133.2 and 133.8 eV, [32] therefore, the binding energy of 132.5 eV can be assigned to the P-O bonds indicating the substitution of P atoms on Zn sites (P_{Zn}). Furthermore, a shoulder peak with weak intensity was also observed at a binding energy of 127.9 eV. This peak was believed to be originated from the P-Zn bonds corresponding to the binding energy of 128.3 eV in Zn₃P₂

and 129.8 eV in ZnP₂ [33] implying that a fewer P₀ defects were also formed. The presence of two different binding energy peaks in a single XPS spectra of P 2p indicated the existence of two states of P, as earlier reported for P-doped ZnO [18,34]. Since it has been reported theoretically that the formation of $P_{Zn} - 2V_{Zn}$ complex defect is preferred to P₀ defect in oxygen rich ambient due to lower ionization energy [30], therefore the p-type behaviour of PZO films was dominated by the $P_{Zn} - 2V_{Zn}$ defects. The ratio of the area under curves for P_{Zn} and P₀ defects (P_{Zn}/P_0) was approximately 5.04, indicating that the formation of $P_{Zn}-2V_{Zn}$ complex was favored over P₀ defects.



Figure 4.3 Core-level XPS spectra of (a) P 2p (b) O 1s for 300 °C grown PZO film.

Figure 4.3(b) shows the binding energy spectra for O 1s core level. It was observed that O 1s peak could be deconvoluted in three distinct Gaussian curves centered at binding energies of 530.7, 531.9 and 533.2 eV, indicating distinct states of oxygen in PZO films. The peaks at a low binding energy of 530.7 eV and with the maximum intensity were correlated to the Zn-O bonds in the wurtzite lattice structure [31]. The binding energy peaks at 531.9 eV were ascribed to O^{2^-} ions in the oxygen-deficient regions within the matrix of phosphorus doped ZnO indicating substitution of a few dopant P atoms on O lattice sites [35] and the shoulder peaks at 533.2 eV were ascribed to the adsorbed oxygen on the surface.

4.3.3 Spectroscopic ellipsometry analysis

Figure 4.4(a) and (b) shows the experimentally measured and fitted curves of ellipsometric parameters, Psi (ψ) and Delta (Δ), respectively, measured at 70° incidence angle for PZO films. The fitting of the experimental data with theoretical models was obtained using completeEase software supplied by J.A. Woollam Co. Inc., which uses a standard, iterative, and non-linear regression algorithm namely the Lavenberg-Marquardt method to automatically minimize the mean square error (MSE) by adjusting the fit parameters such as thickness, roughness and optical function parameters in PZO films. The goodness of data fit is quantified by MSE values given by [21]

$$MSE = \sqrt{\frac{1}{3n-m} \sum_{i=1}^{n} [(N_{Ei} - N_{Gi})^2 + (C_{Ei} - C_{Gi})^2 + (S_{Ei} - S_{Gi})^2]} \times 1000 \quad (4.1)$$

where *n* is the number of wavelengths, *m* is the number of fit parameters and N = $\cos(2\psi)$, $C = \sin(2\psi)\cos(\Delta)$, $S = \sin(2\psi)\sin(\Delta)$, Ei and Gi subscript refer to the measured and calculated values respectively. The SE data were fitted to a three-layer model including air/surface roughness, bulk ZnO film and Si, where the surface roughness was modeled using a 50% air and 50% ZnO, Bruggeman effective approximation [36]. The film thickness was measured by fitting the spectra below ~3 eV by Cauchy model and then the complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$ across the spectral range from 1.2 to 6.4 eV was extracted using a parameterized semiconductor oscillator (Psemi-M0) model [37]. In principle, the Psemi-M0 model is similar to Kim and Garland's model which can describe a semiconductor's dielectric function and higher order derivatives above, below, and through the fundamental direct gap and uses Gaussian broadening for complete transparency ($\varepsilon_2 = 0$) below the bandgap energy [38]. The advantage in using this model is its Kramers-Kronig consistency and it is much more flexible to fit any type of excitonic lineshape based on a sum of contributions from one or more oscillators and is applicable to a wide range of materials. The basic underlying equation for dielectric function for this model can be given as [39]

$$\widetilde{\varepsilon}(E) = 1 + i \int_0^\infty W(E') \widetilde{\Phi}(E, E') dE'$$
(4.2)

where *E* is the photon energy and *E'* is a dummy integration variable. The joint density of states is included in unbroadened absorption spectrum W(E'), and $\tilde{\Phi}$ is the broadening function given as



$$\widetilde{\Phi}(E,E') = \int_0^\infty e^{i\left(E-E'+i\gamma(s)\right)s} ds - \int_0^\infty e^{i\left(E+E'+i\gamma(s)\right)s} ds$$
(4.3)

Figure 4.4 (a) ψ and (b) Δ curves for p-type PZO films, (c) ε_1 and (d) ε_2 spectra of all PZO films determined by Psemi-M0 oscillator model fitting.

Table 4.4 Extracted SE model parameters of p-type PZO films

Model Parameters	$(T_g = 300 \ ^{o}C)$	$(T_g = 400 \ ^{o}C)$	$(T_g = 500 \ ^{o}C)$	
MSE	9.8	10.7	12.4	
Thickness (nm)	246.4 ± 0.19	250.4 ± 0.19	236.4 ± 0.29	
Roughness (nm)	3.5 ± 0.10	3.2 ± 0.11	9.2 ± 0.17	
\mathcal{E}_{∞}	1.37 ± 0.21	1.41 ± 0.24	1.52 ± 0.30	

A1	4.43 ± 0.23	3.52 ± 0.13	2.63 ± 0.14
Γ1	0.13 ± 0.003	0.11 ± 0.003	0.08 ± 0.002
Eo1	3.43 ± 0.012	3.39 ± 0.007	3.34 ± 0.004

The detailed derivation and mathematical descriptions of the Psemi-M0 and others Gaussian models are beyond the scope of this work and can be found elsewhere [39,40]. The oscillation patterns, as observed in figure 4.4(a) and (b), below ~3.3 eV, were interference fringes due to the reflection at PZO/Si interface. A good agreement obtained between the experimental and theoretical spectra by the low values of MSE suggested the accuracy of the model for the determination of the thickness, roughness and optical function parameters in PZO films. The extracted parameters for *p*-type PZO films are summarized in table 4.4. As observed from tables 4.3 and 4.4, the values of various model-fitting parameters such as amplitude (A1), oscillator energy (Eo1) and broadening parameter (Γ 1) were seen to decline with an increase in hole concentration. However, the value of high-frequency dielectric constant (ε_{∞}) was observed to increase from 1.37 to 1.52 with the corresponding enhancement in hole concentration. The fitted values of ε_{∞} matches well with the previous reported values by Postava *et. al.* [41] and Gilliot *et. al.* [42] using similar model dielectric functions.

From the fitted ellipsometric data, the real (ε_1) and imaginary (ε_2) parts of complex dielectric function were extracted and shown in figure 4.4(c) and (d), respectively. As observed in the spectra of figure 4.4(c), a peak value of ε_1 was obtained at the Γ point of Brillouin zone corresponding to E₀ critical point (CP) [43]. ε_1 peak at band edge shows a shift towards higher energy for the annealed PZO with respect to their *as-grown* counterpart samples, but this shift is more prominent for D3 films. Also an increase in amplitude of ε_1 with annealing was observed which could be correlated to the increase in hole concentration and larger crystallite size, at higher T_g . For all PZO samples, ε_2 was observed to be zero below the absorption onset, while above the absorption onset, it rises more sharply for annealed PZO films as compared to *as-grown* ones with a blueshift in peak energy. Moreover, an increase in the value of ε_2 in the range of 3.5-4 eV was observed in annealed PZO films as compared to its corresponding unannealed counterparts. This increase is more prominent for annealed D5 film as compared to the other two films, mostly due to the improvement in the values of crystallite size [1] and FWHM as seen in table 4.1. It is well-known that the presence of excitons near the band edge significantly influences the dielectric function of the material [44]. The formation of these excitons are attributed to the splitting of valence band into three bands due to crystal field and spin-orbit splitting in wurtzite ZnO, resulting in three interband transitions referred as A, B, and C [45].

In modeling of the dielectric function of PZO films, we have used a single Psemi-M0 oscillator to describe these contributions from the interband transitions as well as discrete and continuum exciton transitions together with the effects due to exciton-phonon complexes. From the figure 4.4(c), the narrowing of ε_1 was observed after annealing which was more prominent for films grown at higher T_g , therefore, it could be inferred that the excitonic lifetime and stability improved upon annealing [36]. The analysis for change in the shape of ε_2 as a function of T_g and subsequent annealing was done by line shape fitting of different contributions adding to the imaginary part of the dielectric function. The fitting procedure is similar to earlier works on GaN [46] and AlN [43] and based on theory for hydrogenic excitons [47]. The contributions of discrete exciton states with exciton binding energy E_B^X and the energy band gap E_g towards ε_2 , can be expressed as [48]

$$\varepsilon_2^X = \frac{C^X}{(\hbar\omega)^2} \sum_n \frac{1}{\gamma n^3} \exp\left(-\frac{(\hbar\omega - E_n)^2}{\gamma^2}\right)$$
(4.4)

where $E_n = E_g - E_B^X/n^2$, *n* being the exciton state and γ is broadening parameter, \hbar is the reduced Plank's constant, C^X is a proportionality constant and defines the intensity of transitions. Figure 4.5(a)-(d) shows the line shape fitted ε_2 curves for all PZO films. To explain the experimental observations, we have considered the contribution from A and B excitons and exciton-phonon complexes similar to what Neumann *et. al.* [49] have considered for modelling the dielectric function of MgZnO alloys. Exciton continuum is considered along with the assumption that all excitonic transitions are broadened by Gaussian distribution.



Figure 4.5 Line shape fitting of ε_2 [(a), (c), (e)] for as-grown PZO films and [(b), (d), (f)] for annealed PZO films

In the fitted curves, dark bubbles represent the experimental data and blue dashed lines indicate the excitonic contributions from A and B valance bands while pink dashed lines indicate exciton-phonon contributions. The green dashed line represents the exciton continuum while the red solid line is the sum of all contributions. Individual excitonic resonance due to A and B exciton could not be resolved, rather a relatively broader excitonic doublet peak observed at room temperature. The presence of such pronounced excitonic features in the observed dielectric function at E_0 critical point even at room temperature confirms the improvement in the crystalline quality of *p*-type PZO films upon annealing. In order to obtain the energy of CP and compare the excitonic peaks, a line shape analysis was done by fitting the second order derivative spectra of the complex dielectric function with respect to photon energy [50]. Figure 4.6(a) shows the $d^2\varepsilon_2 / dE^2$ spectra for annealed PZO films numerically calculated based on standard analytic CP expression

$$\frac{d^{2}\varepsilon}{d\omega^{2}} = n(n-1)Ae^{i\emptyset}(\hbar\omega - E + i\Gamma)^{n-2} \qquad n \neq 0$$
$$= Ae^{i\emptyset}(\hbar\omega - E + i\Gamma)^{2} \qquad n = 0 \qquad (4.5)$$

where, the exponent *n* has the values $-1, -\frac{1}{2}, 0, \frac{1}{2}$ for excitonic, one, two, and three dimensional CPs, respectively. The E_0 critical point in the band edge spectral region, best represented by n = -1 excitonic line shape, can be easily observed for PZO films. The energy positions of such an excitonic transitions were determined by taking the zero crossing of the second order derivative spectra of the imaginary part of complex dielectric function [51]. The values of CP energy of 3.39, 3.36 and 3.34 eV were obtained for annealed D3, D4 and D5 PZO films, respectively. A clear red shift was observed in the energy positions of the E_0 CP with an increase in hole concentration.

4.3.4 Photoluminescence

The room temperature photoluminescence (PL) spectra of *as-grown* and annealed PZO films are illustrated in figure 4.6(b). All PZO samples showed a strong ultraviolet emission corresponding to near bandgap energy. It is well known that

bound excitonic transition can be easily quantified at low temperatures while the free exciton transition becomes more prominent at higher ambient temperature [52].



Figure 4.6 (a) Second derivative spectra of fitted ε_2 of p-type PZO films, (b) Room temperature photoluminescence spectra of as-grown and annealed PZO films.

The PL peak at 386 nm (~3.212 eV) for D5, 381.4 nm (~3.251 eV) for D4 and 379.1 nm (~3.270 eV) for D3 films has been referred to the recombination of a free electron to acceptor (FA) for PZO [29]. A broad, weak red emission centered at ~635 nm (~1.95 eV) was observed for *as-grown* PZO deposited at 400 °C. The occurrence of such a red emission from PZO has been rarely reported in the literature and indicates the absence of oxygen vacancy levels [53]. Moreover, after annealing, the NBE PL intensity improved and the weak deep level defects giving out red emission were suppressed indicating that the crystalline property of PZO was improved after annealing [14].

4.4 Conclusion

In this study, we report the fabrication of stable and low resistive phosphorus doped *p*-type ZnO thin films, grown by DIBS system. Room temperature *Hall measurements* revealed a high hole concentration of 8.62×10^{19} cm⁻³ for annealed PZO films grown at 500 °C with a forward to reverse bias current ratio for *p*-PZO/*n*-Si junction at ±3 V was ~31. Spectroscopic ellipsometry data analysis was performed to determine the complex dielectric function in the energy range

(1.2 - 6.4 eV) at room temperature. The optical constants were obtained using a parameterized Psemi-M0 oscillator model. The line shape analysis of complex dielectric function resulted in a distinct red shift in the energy position of E_0 CP with an increase in hole concentration. Moreover, upon annealing, the NBE PL intensity improved and the weak deep level defects giving out red emission were suppressed confirming an improvement in PZO crystalline property after annealing. These results provide important information for the fabrication of highly conductive *p*-type ZnO for application in high performance optoelectronic devices.

4.5 References

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Chapter 5

Performance study of Li-P co-doped *p*-ZnO/*n*-Si Heterojunction Photodetector

5.1 Introduction

In the previous chapters, it has been discussed that due to its large direct energy band gap and the high absorption coefficient in the ultraviolet spectrum range, ZnO has been considered as a promising candidate for application in UV photodetectors (PDs), light emitting diodes (LEDs) and lasers. Moreover, ZnO based UV PDs provide superior performance metrics and are cheaper alternatives as compared to other wide bandgap semiconductors like SiC, GaN, and diamond etc. [1-3]. Typically, the photodetector structures can be classified as photoconductor, Schottky diode, metal semiconductor metal (MSM), p-n junction, and avalanche photodiode. Among these, p-n junctions type PD provides an advantage of simple structure, high responsivity, fast response time and selfpowered operation mechanism due to photovoltaic effect. However, the fabrication of such devices still poses problems with the unavailability of stable ptype ZnO. Till date, a limited number of ZnO homojunction photodiodes [4-6] have been reported along with numerous ZnO based heterojunction UV PDs based on different p-type material such as Si [7-9], GaN [2,10], NiO [11,12], CuO [13], CuI [14], CuSCN [15]. Various research groups have put in considerable efforts for successful realizations of *p*-type ZnO by monodoping approach using group I and group V dopants such as Li [16-18], P [19-20], N [21-11] and Sb [23-24] etc. Besides these monodoping studies, others have proposed dual acceptor doping processes with different acceptor dopant combinations involving Li-N [25-31], N-P [32-34], N-As [35], As-Sb [36] for p-type conduction in ZnO materials. Table 5.1 presents an analytical comparison of electrical properties of various dual acceptor doped ZnO reports in the literature for *p*-type conduction using different deposition techniques. Unfortunately, the high resistivity, low carrier concentration and reliability of *p*-type behavior still remain a concern. Recently Oder. *et. al* [37] have studied Li-P codoped ZnO which initially revealed *p*-type behavior but later converted to *n*-type. Therefore, the formation mechanism of *p*-type ZnO incorporating both Li and P as dual-acceptors is unclear yet. To the best of our knowledge, there have been no reports of low resistive and stable *p*-type ZnO fabrication by dual acceptor doping with Li and P. Therefore, in this work, we first present a reproducible method of growth of stable, low resistive and high hole concentration *p*-type ZnO films co-doped with Li-P and later in the paper, we discuss the high-quantum efficiency photoresponse characteristics of *p*-ZnO/*n*-Si heterojunction photodetector.

Dual acceptor	Deposition method	Hole concentration (cm ⁻³)	Mobility (cm²/V.s)	Resistivity (Ω.cm)	Ref.
Li-N	Pulsed laser deposition	8.92×10^{18}	0.75	0.93	[25]
Li-N	RF-magnetron sputtering	3.07×10^{16}	1.74	1.19×10^{2}	[26]
Li-N	Plasma-assisted MBE	8.22×10^{16}	1.36	60	[27]
Li-N	Successive ionic layer adsorption and reaction (SILAR)	8.02×10^{18}	0.75	1.04	[29]
N-P	Ultrasonic spray pyrolysis	5.3×10^{17}	0.94	12.5	[32]
N-P	RF magnetron sputtering	1.16×10^{18}	1.35	3.98	[34]
As-Sb	Plasma-assisted MBE	1×10^{16}	20	-	[36]
Li-P	Magnetron sputtering	2.31×10^{15}	0.5	-	[37]

Table 5.1 Comparative analysis of electrical properties of dual acceptor doped ZnO

5.2 Experimental details

5.2.1 Material growth and device fabrication

Li-P doped ZnO (LPZO) films (~ 250 nm) were deposited on sapphire substrates by dual ion beam sputtering (DIBS) system using a high-purity (99.99%) ceramic LPZO target. Prior to the growth process, the substrates were ultrasonically cleaned in dilute hydrofluoric acid (5%), trichloroethylene, acetone, isopropanol, and deionized water sequentially for 10 minutes each, in order to remove the dust particles, organic impurities, and other contaminants. The substrates were then purged with 5N-pure nitrogen gas. Before the deposition process, the deposition chamber was evacuated to a base pressure of 4.7×10^{-7} mbar and then the substrates were pre-baked at 700 °C to improve the adhesion of LPZO films on the substrates. The oxygen rich growth ambient was maintained during the deposition process with a 99.999% pure mixture of Ar: O₂ = 2:3 with working pressure of 2.3×10^{-4} mbar. The ion beam power of deposition source was kept at 14 W. The depositions were performed at varying substrate temperatures (T_g) ranging from 100 to 500 °C. Post-deposition annealing was carried out at 800 °C in N₂ ambient for 20 minutes to activate the acceptor dopants.

p-n heterojunction photodiodes were fabricated by DIBS in the similar way as discussed above by depositing *p*-type LPZO films on an *n*-type Si (100) wafer at 300 °C (device D3) and 500 °C (device D5). The DIBS growth temperature was selected based on the electrical properties of LPZO films. Depositing Indium on both *p*-type LPZO films and *n*-type Si formed the contact electrodes.

5.2.2. Thin films and device characterizations

Structural properties of films were investigated by X-ray diffraction method (XRD) using Bruker D8 Advance X-ray diffractometer with Cu-K α radiation (λ = 1.54Å). Surface morphology was characterized by employing ZEISS Supra55 field emission scanning electron microscopy (FE-SEM). The electrical properties were determined by Hall measurement in the Van der Pauw configuration at room

temperature in magnetic fields of 5000 G and a current of 30 μ A. Current-voltage characteristics were determined using Everbeing probe station and Keithley 2612A sourcemeter. Chemical bonding states of Li and P in *p*-type LPZO films were examined by X-ray photoelectron spectroscopy (XPS) utilizing a PHOIBOS 100 analyzer with an Al K α radiation (1486.6 eV) as an excitation source. The film thickness and the optical absorption spectra were determined by spectroscopic ellipsometry (M-2000D J. A. Woollam spectroscopic ellipsometer). The spectral response and the external quantum efficiency (EQE) of the *p*-ZnO/*n*-Si heterojunction devices were characterized with Bentham photovoltaic characterization system consisting of 150 W Xe lamp, chopper, monochromator, and a lock-in amplifier.

5.3 Results and discussion

5.3.1 Structural and morphological properties of LPZO films

XRD patterns of films are shown in figure 5.1(a). As observed, the crystal structure of all the films was identified to be preferentially *c*-axis (002) oriented. No other secondary phases were observed in the XRD patterns. As the growth temperature (T_g) increased from 100 to 300 °C, the intensity of (002) peak increased consistently indicating an enhancement of (002) crystal orientation. However, a further increase in T_g upto 500 °C resulted in the reduction of (002) peak intensity. As observed in figure 5.1(b), the full width at half maximum (FWHM) of (002) plane of LPZO films decreased almost linearly confirming the improvement in crystalline quality. The improvement in crystallinity can be correlated to the migration of dopant atoms from interstitial sites or other lattice points to Zn lattice sites [38]. The microstructural parameters such as crystallite size and *c*-axis lattice constants were calculated based on the XRD data for all LPZO films and listed in Table 5.2.

The position of (002) peak was observed to shift towards higher angular position while a decrease in *c*-axis lattice constant for LPZO films was observed with increase in T_g from 100 to 500 °C. This phenomenon can be explained by considering the ionic radius of Li, P, Zn and O in the tetrahedral coordination.

T (0 C)	c (A °)	Peak, 20	FWHM	Crystallite size
Ig (°C)	± 0.002	(degree)	(degree) ± 0.05	(nm)
100	5.196	34.46	0.30	28.92 ± 0.5
200	5.195	34.48	0.26	33.08 ± 0.9
300	5.190	34.51	0.24	34.30 ± 1.1
400	5.193	34.51	0.20	42.24 ± 1.6
500	5.184	34.55	0.14	58.99 ± 2.5

Table 5.2 Microstructure parameters of p-type LPZO films grown at different temperatures

Since the ionic radius of Li^{1+} (0.060 nm) is smaller than that of Zn^{2+} (0.074 nm), Li atoms were expected to replace Zn sites under the oxygen rich ambient resulting in the formation of Li_{Zn} defects [17, 39-40]. On the other hand, as the ionic radii of P^{3+} (0.058 nm) is smaller than that of O^{2-} (0.138 nm), a significant decrease in *c*-axis parameter was expected if P substituted O site in ZnO lattice, however, this was not observed in our case. Furthermore, since the ionic radius of P^{3+} is lower than that of Zn^{2+} , therefore, if P occupied Zn site, it also should cause a small shift of (002) peak in higher Bragg angular position [41], as observed in table 5.2. Hence it was deduced that P was also doped in ZnO lattice by replacing Zn atoms forming P_{Zn} defects. Figures 5.1(c) and 5.1(d) show FE-SEM images of films grown at 300 and 500 °C, respectively. It was observed that the films grown at 300 °C have the best morphology with a smooth surface that composed of dense grains and uniform dimensions. This film had a good thickness uniformity, no visible pores, and defects over the film, whereas the film grown at 500 °C showed the formation of microcracks due to coalescence of smaller crystallites together to form larger crystallites at higher temperatures [42].



Figure 5.1 (a) XRD patterns of all the LPZO films grown at different temperatures, (b) FWHM and crystallite size variation as a function of growth temperature, and FE-SEM images of LPZO films grown at (c) 300 °C and (d) 500 °C.

5.3.2 Electrical properties and heterojunction device

The electrical properties of the LPZO films were determined by the Hall effect measurement system immediately after the thermal activation of dopants by post-

deposition annealing. All the annealed LPZO films clearly depicted p-type behavior at room temperature, as illustrated in table 5.3. The highest hole concentration was calculated to be 2.31×10^{20} cm⁻³ for LPZO films grown at 300 °C. The resistivity was found to be 0.016 Ω .cm with a Hall mobility of 2.8 cm^2/V s for the film. This value of hole concentration is the highest ever reported results till date for dual acceptor doped ZnO as evident from tables 5.1 and 5.3. In order to ascertain the reliability of *p*-type doping in LPZO, all films were kept in air ambient. After a span of 90 days, the Hall measurements were carried out again to examine the stability and reliability of *p*-type conduction with time. The measurement results, as in table 5.4, show that the films retained their *p*-type behavior even after 90 days of storage with almost the similar hole concentration as obtained during initial measurements. For dual acceptor doped p-type ZnO reports, the maximum hole concentration remained of the order of $\sim 10^{16}$ cm⁻³ for Li-N [27], ~10¹⁷ cm⁻³ for Li-N [31], ~10¹⁸ cm⁻³ for N-P [34] and ~10¹⁵ cm⁻³ for Li-P [37]. Therefore, our results clearly indicate that the *p*-type LZPO films grown by DIBS are significantly of superior quality and widely applicable for highperformance electronic and opto-electronic applications.

T (QC)	Carrier concentration /	Mobility	Resistivity	
$\operatorname{Ig}(\mathbf{C})$	conduction type (cm ⁻³)	(cm ² /V.s)	(Ω.cm)	
100	$\frac{1.18\times10^{19}}{p\text{-type}}$	4.43	0.119	
200	$\begin{array}{c} 2.20\times10^{20}\\ p\text{-type} \end{array}$	1.49	0.018	
300	2.31×10^{20} <i>p</i> -type	1.67	0.016	
400	$\frac{1.25 \times 10^{20}}{p\text{-type}}$	2.61	0.018	
500	7.42×10^{18} <i>p</i> -type	2.68	0.313	

Table 5.3 Electrical properties of LPZO films just after thermal annealing.

Т _g (°С)	100	200	300	400	500
Carrier					
concentration /	$1.38 imes 10^{19}$	$3.13 imes 10^{20}$	2.55×10^{20}	$5.06 imes 10^{19}$	$1.33 imes 10^{18}$
conduction type	<i>p</i> -type	<i>p</i> -type	<i>p</i> -type	<i>p</i> -type	<i>p</i> -type
(cm ⁻³)					

Table 5.4 Carrier concentration of LPZO films after 90 days.

Theoretically, for Li-doped ZnO (LZO), Li atom substitutes for Zn lattice site to form Li_{2n} defects that possess shallower acceptor level [18]. However, the *p*-type behavior of LZO is usually unstable due to the formation of donor complexes, such as interstitial Li (Li_i) and Li_{Zn}-Li_i complex [16]. Similarly, for p-type conduction using only phosphorus dopant in ZnO, P atoms incorporate into ZnO by either forming P_0 (P atom substitutes for O lattice site) defects, which are deep acceptor or by creating P_{Zn} defects (P atom substitutes for Zn lattice site), which act as donor, however, prefer to form acceptor type P_{Zn}-2V_{Zn} complex under Orich growth conditions [20]. As O-rich growth conditions were deployed in this study, thus it would suppress the formation of P_0 defects and promote the generation of antisite P_{Zn} donors and Li_{Zn} acceptor defects [17,20], as observed in XRD analysis. Therefore, high hole concentration in LPZO films was realized due to the formation of shallow acceptor levels with the formation of both Lizn and Pzn-2Vzn defects. For LPZO film grown at 500 °C, a relatively lesser hole concentration was determined as compared to other films grown at lower Tg. It can be inferred that the reduction in hole concentration at 500 °C may be associated with the formation of defect clusters as observed in FE-SEM images.

In order to further verify the *p*-type conduction in LPZO films, the current-voltage (I-V) characteristics of fabricated *p*-LPZO/ *n*-Si heterojunctions were investigated. Figure 5.2(a) shows the schematic diagram of fabricated *p*-LPZO/ *n*-Si heterojunctions. Figure 5.2(b) shows the room temperature I-V characteristics for heterojunction devices in which apparent rectification behavior was observed. The inset of figure 5.2(a) shows I-V plots of In-In contacts on both of *n*-Si and *p*-

LPZO, in which the linear curves indicated that all the electrodes exhibited good ohmic contact formation, implying that the rectifying behavior originated from the *p*-LPZO/*n*-Si junction instead of any Schottky contacts. The values of turn-on voltage of +1.65 and +1.90 V were determined for devices D3 and D5, respectively. Moreover, the forward to reverse bias current ratio (I_F/I_R) at \pm 3 V was ~76 and 170 for devices D3 and D5, respectively. These values of current ratio are better than the earlier reported values for *p*-ZnO/*n*-Si heterojunctions [43-44].



Figure 5.2 (a) Schematic diagram of fabricated p-LPZO/n-Si heterojunctions. Inset shows I-V curves displaying ohmic contact formation with Indium on n-Si and p-LPZO. (b) I-V curves for p-n heterojunctions on a linear scale. Inset shows I-V curves for p-n heterojunctions on a semi-logarithmic scale.

The traditional thermionic emission model was assumed to analyze the electrical parameters of the fabricated p-n junction. According to this model, the current across the junction is given by equation (1) [43],

$$I = I_0 \left[\exp \frac{qV}{\eta KT} - 1 \right]$$
(5.1)

where I_0 is the reverse saturation current, q is the electron charge, V is the forward bias voltage, K is the Boltzmann constant, η is the ideality factor, and T is the absolute temperature. I_0 can be expressed as equation (2),

$$I_0 = AA^*T^2 exp\left(\frac{-qV_{bi}}{\kappa T}\right)$$
(5.2)

where *A* is the junction area, A^* is the effective Richardson constant (for ZnO the theoretical value of A^* is 32 A cm⁻².K⁻²)[43], and V_{bi} is the built-in potential at zero bias. The experimentally obtained I_0 was determined from the *y*-axis intercept of linear portion of $\ln(I)$ -V plot and η was obtained from the slope of forward bias (for qV > 3KT), as shown in the inset of figure 5.2(b). The values of I_0 and η were calculated to be 59 × 10⁻⁶ A and 3.58 for device D3 and 17 × 10⁻⁶ A and 4.44 for device D5, respectively. Since for an ideal *p*-*n* junction, the ideality factor should be 1, therefore the deviation of η values from the ideal value indicated the presence of interface states, which provide multiple current pathways at *p*-*n* junction interface. The built-in potential was calculated to be 0.60 and 0.65 V for devices D3 and D5, respectively.

5.3.3 Chemical bonding analysis of Li-P in *p*-LPZO

To understand the chemical bonding states of Li and P in *p*-type LPZO films, XPS analysis was performed. Prior to performing XPS measurements, each LPZO film was etched using 1 KeV Ar⁺ ions beam for 5 minutes in order to remove the contaminated surface layer. The XPS spectra for D3 and D5 LPZO films are shown in figure 5.3. The experimentally obtained spectra were deconvoluted with nearly Gaussian curves using standard XPS peakfit software with a Shirley background. Li 1s peaks, as shown in figure 5.3(a)-(b), were deconvoluted into two components with peaks centered at 53.6 and 55.2 eV for D3 and 54.3 and 56.1 eV for D5, respectively. The higher binding energy peak centered at 55.2 and

56.1 eV were assigned to Li_{Zn} -O bonds in LPZO films, while the lower binding energy curves were ascribed to Li interstitial (Li_i) defects [17,40]. Since, the areas under these deconvoluted curves indicate the relative concentrations of Li at interstitial (Li_i) and substitutional (Li_{Zn}) sites, it can be concluded that the Li_i defect density was higher in D5 as compared to that in D3, hence resulting in the decline of (002) XRD peak, as observed in figure 5.1(a), and reduction in hole concentration as measured by Hall analysis.

Figure 5.3(c)-(d) show the binding energy spectra of P 2p and Zn 3s core levels for D3 and D5 films, respectively. The experimentally obtained broad peak was deconvoluted into two sub-peaks by Gaussian fitting, corresponding to P 2p (and Zn 3s) located at 137.9 eV (140.7 eV) and 137.5 eV (139.9 eV) for D3 and D5 films, respectively. Theoretically, it has been reported that the formation of P_{Zn} -2V_{Zn} complex defect is preferred to P_O defect in oxygen rich ambient due to lower ionization energy [20], the peaks at 137.9 eV and 137.5 eV were assigned to the P-O bonds as they matched closely to the binding energy of P 2p in LiPON films [45] and LiPF₆ films [46], and hence indicating the substitution of P atoms on Zn sites. Furthermore, a shoulder peak with weak intensity was also observed at binding energy of 128.8 eV in D3 and 128.9 eV in D5 films. These peaks were believed to be originated from the P-Zn bonds corresponding to the binding energy of 128.3 eV in Zn₃P₂ and 129.8 eV in ZnP₂ [47] implying that a fewer P₀ defects were also formed. The presence of two different binding energy peaks in a single XPS spectra of P 2p indicated the existence of two states of P, as earlier reported for P-doped ZnO [48-49]. The ratio of the area under the curve for P_{Zn} and P_O defects (P_{Zn}/P_O) was 2.02 and 1.25 for D3 and D5, respectively, indicating that the formation of P_{Zn} - $2V_{Zn}$ complex was favored over P_0 defects in both films. Moreover, the decrease in the ratio also supported the decline in p-type conduction as observed above in electrical properties.

O 1s binding energy spectra for D3 and D5 grown films are shown in figure 5.3(e)-(f). These were deconvoluted to generate four distinct Gaussian curves centered at binding energies of 529.3, 531.3, 532.1, 533.5 eV for D3 and 529.0,



531.0, 531.8 and 533.5 eV for D5 films, respectively indicating four distinct states of oxygen in LPZO films.

Figure 5.3 Core-level XPS spectra of (a) Li 1s (c) P 2p (e) O 1s of 300 °C grown films, (b) Li 1s (d) P 2p (f) O 1s of 500 °C grown films.

The peaks at a low binding energy of 529.3 and 529.0 eV could be ascribed to the Li_{Zn} -O bonds as it matched closely to the O 1s state in Li_2O [50] whereas the maximum intensity peaks at 531.3 and 531.0 eV were related to the Zn-O bonds in the wurtzite lattice structure [40]. The binding energy peaks at 532.1 and 531.8 eV were ascribed to O^{2-} ions in the oxygen-deficient regions within the matrix of phosphorus-doped ZnO indicating substitution of dopant P atoms on O lattice sites [51] and the shoulder peaks at 533.5 and 532.9 eV were ascribed to the adsorbed oxygen on the surface. It was observed that the ratio of the area under the adsorbed oxygen peaks almost doubled for D5 as compared to that for D3 indicating an increase in the presence of surface states confirming the observation made by XRD and FE-SEM analysis.

5.3.4 Photoresponse and quantum efficiency of heterojunction photodetector

The optical absorption spectra of D3 and D5 films were determined by spectroscopic ellipsometry at room temperature as shown in Figure 5.4 (a). The optical band gap was determined by observing the intersection of linear extrapolation of absorption spectra with $(\alpha hv)^2 = 0$, where α is the absorption coefficient and hv is the photon energy. The values of optical band gap energy for D3 and D5 were found to be 3.32 and 3.34 eV, respectively. A clear red shift in the optical band gap of *p*-type LPZO films was observed with increase in hole concentration, as previously reported by Hu *et al.* [52]. The photoresponse characteristics of the *p*-ZnO/*n*-Si heterojunction photodetector were investigated at room temperature at 0 to -6 V. Figure 5.4(b) shows the schematic of incident photon conversion efficiency (IPCE) measurement system and the measurement was calibrated using a silicon photodiode in wavelength range 300 to 600 nm. The responsivity (R_{λ}) of the fabricated devices was calculated using equation (3)[53-54]

$$R_{\lambda} = (I_{light} - I_{Dark}) / P_{light}$$
(5.3)

where I_{light} is the current of the device under UV illumination and P_{light} is the light power intensity. At zero applied bias, a low photoresponse was observed, and the peak responsivity was determined to be about 1.5 mA/W for device D3

and 1.8 mA/W for device D5. The low responsivity was due to the flow of minority carriers dominating the photocurrent and the interface defects leading to carrier recombination. At -1 V, the peak responsivity reached 10 mA/W and 15 mA/W for D3 and D5, respectively, with a peak response at ~325 nm and cutoff at ~370 nm corresponding to the absorption edge of ZnO, as shown in figure 5.4(c)-(d). The peak photoresponse was observed to increase with the increase in reverse bias voltage. The external quantum efficiency (η) of the fabricated UV photodetector was determined from the measured spectral response using equation (4)[38]

$$\eta = (R_{\lambda}/G) \times (hc/q\lambda) \tag{5.4}$$

where G is the gain, *h* is the Planck's constant, *c* is the speed of light in vacuum, and λ is the wavelength of incident light. The peak photoresponsivity of D3 at -6 V bias was measured to be 0.32 A/W corresponding to an EQE of ~130% considering the unity gain, while the peak photoresponsivity of D5 was measured to be 2.6 A/W corresponding to an EQE of order of ~10³%. Furthermore, the UV to visible rejection ratio (ratio of responsivity measured at 325 nm to that at 450 nm) of the heterojunction devices was 6.66 and 21.88 for D3 and D5, respectively. The internal quantum efficiency (IQE) of the devices was determined by normalizing the EQE as IQE = EQE/(1 - R)[38] where *R* is the measured reflectance at near normal incidence of the LPZO films. The IQE values were calculated to be ~150% and ~ 1150% for device D3 and D5, respectively. The observed photoresponse of our devices is better than the reported values in literature for ZnO/Si based heterojunction photodetector, as presented in table 5.5. Considering the dark current as the major source of noise, the specific detectivity (D^*) of the devices is given by equation (5)[12]

$$D^* = \frac{R_\lambda}{\sqrt{2qI_{dark}}} \tag{5.5}$$

where I_{dark} is the dark current at the same value of reverse bias used to determine R_{λ} . Figure 5.4(e) shows the EQE and detectivity variation for these heterojunction devices as a function of applied reverse bias voltages The values of D^* at -6 V was determined to be 2.08×10^9 cm Hz^{1/2} W⁻¹ and 2.32×10^{10} cm Hz^{1/2} W⁻¹ for devices D3 and D5, respectively.



Figure 5.4 (a) Optical absorption spectra of p-type LPZO films for devices D3 and D5; (b) schematic diagram displaying IPCE measurement system; photoresponse spectra of heterojunction devices (c) D3 and (d) D5 at different reverse bias voltages; (e) EQE and detectivity variation of heterojunction PDs as a function of applied reverse bias.

ZnO PD	Responsivity	UV/Visible	EQE	Ref
structure		ratio	(%)	
<i>n-</i> ZnO/ <i>p-</i> Si	0.5 A/W at -3 V			[7]
<i>p</i> -ZnO/ <i>n</i> -Si	0.8 A/W at -1 V			[8]
<i>n-</i> ZnO/ <i>p-</i> Si	0.07 A/W at -20 V			[9]
<i>p</i> - ZnO/ <i>n</i> -Si	2.6 A/W at -6 V	~22	~10 ³	This work

Table 5.5 Performance metrics of ZnO/ Si based heterojunction photodiodes reported in literature

The time-dependent photoresponse of the heterojunction PD was measured at -3 V by turning on and off a 325 nm light source on the device. Due to the limitation of the manual switching for the on-off state of UV light source, the accurate response and recovery time could not be obtained. Figure 5.5(a) shows the photocurrent rise and decay as a function of time. The rise time is defined as the time needed to reach 90% from 10% of the maximum photocurrent while the fall time is the time needed to reach 10% from 90% of the maximum photocurrent. From figure 5.5(a), the average values of the rise time of 1.7 s and fall time of 11 s were obtained for D5 PD. Figure 5.5(b) shows the dark current and photocurrent spectra of heterojunction devices illuminated with incident light of 325 nm as a function of applied bias. The photo-response mechanism of the heterojunction PDs leading to the high efficiency was investigated by understanding the carrier transport mechanism across p-ZnO/n-Si junction in terms of the energy band diagram based on Anderson's model [44]. Figure 5.5(c) and (d) show the band diagram at zero and reverse bias, respectively. The measured band gap value for LPZO was $E_{gZnO} = 3.34$ eV, the electron affinity value was considered as $\chi_{ZnO} =$ 4.35 eV, whereas, for Si, the band gap at room temperature and electron affinity were considered as $E_{gSi} = 1.12$ eV and $\chi_{Si} = 4.05$ eV [43-44]. At equilibrium condition, the model showed a small conduction-band offset of 0.3 eV and a large valence-band offset of 2.52 eV. Therefore, the photogenerated holes get trapped in the potential well formed at the valence band junction resulting in lesser photocurrent at zero bias. It is important to note that prior to the spectral response

measurement, the devices were kept in dark ambient for 48 hours in order to eliminate any stray current component. Under the dark conditions, the atmospheric oxygen got adsorbed on LPZO surface and converted to O_2^- as shown by equation (6)[55]



Figure 5.5 (a) Time-dependent photoresponse of device D5; (b) dark current and photocurrent spectra under illumination of 325 nm light; energy band diagram of heterojunction device D5 (c) at zero bias (d) reverse bias under UV illumination.

When the junction was UV illuminated, the incident photons generated electronhole pairs in the space charge region that were separated due to the built-in potential. When an external reverse bias was applied, the photogenerated electrons moved towards the cathode (Si side) while the photogenerated holes moved towards the anode (LPZO side). The photogenerated electron got easily drifted towards n-Si whereas the photogenerated holes got stuck in the potential well and in the interface trap states, as shown in figure 5.5(d). Due to the applied reverse bias, the photogenerated holes tunneled across the junction though these trap states resulting in the enhanced photocurrent. When these holes reached LPZO surface, they effectively oxidize the adsorbed oxygen on the surface resulting in the desorption of oxygen and leaving behind the trapped electrons free to increase the conductivity ultimately resulting in the higher photoresponse [12, 56-58]. For devices D3 and D5, the performance variation can be attributed to the photogenerated carrier transport process in *p*-*n* junction interface and in *p*-type films. The hole concentration in *p*-type LPZO for device D5 was ~7 × 10¹⁸ cm⁻³ and for device, D3 was ~2 × 10²⁰ cm⁻³ and electron concentration in *n*-Si was ~ 6 × 10¹⁹. The width of space charge region on *p*-side was calculated using equation (7)[9]

$$W = \sqrt{\frac{2\varepsilon_p \varepsilon_n N_d (V_{bi} - V_a)}{q N_a (\varepsilon_p N_a + \varepsilon_n N_d)}} \tag{7}$$

where the ε_p and ε_n were the relative dielectric constants for *p*-type and *n*-type semiconductors, N_a and N_d were acceptor and donor concentrations, respectively. V_{bi} was built-in potential at zero bias and V_a was applied bias voltage. At bias of -6 V, the depletion region width on *p*-side was calculated to be 28.8 nm for D5 and 2.83 nm for D3. Therefore, the depletion width on *p*-side for device D5 was ~10 times to that of device D3 at a fixed bias voltage indicating the presence of broader space charge region on *p*-side for device D5 and hence resulting in the formation of large number of photogenerated electron hole pairs under the UV illumination and consequently leading to higher internal gain. Also, since the density of adsorbed oxygen on surface was double for D5 than that for D3, as observed in XPS investigation, therefore this resulted in enhanced photoresponsivity in D5. Besides, another probable reason for larger photoresponse from D5 device could be due to the larger crystallite size of D5 film as compared to that of D3 film, as observed in the XRD investigation [59].

5.4 Conclusions

In conclusion, the fabrication of DIBS deposited p-n heterojunction UV photodetector based on dual-acceptor doped p-type ZnO / n-type Si was performed. Li and P elements were used as the p-type doping agents to produce

low resistive and stable *p*-type conduction in ZnO. The *p*-type conduction was achieved by thermal annealing at 800 °C for 20 minutes in N₂ ambient. The lowest resistivity was calculated to be 0.016 Ω .cm with a hole concentration and Hall mobility of 2.31×10^{20} cm⁻³ and 1.6 cm²/V.s, respectively. The *p*-ZnO/ *n*-Si heterojunction diodes depicted a clear rectification behavior with a rectification ratio up to 170. The photodiodes exhibited excellent UV photoresponse with a peak observed around ~325 nm and cutoff wavelength around 370 nm. The maximum responsivity of the fabricated photodiodes was measured to be 2.6 A/W with an external quantum efficiency of the order of ~10³ % at -6 V.

5.5 References

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Chapter 6

Conclusions and Scope of Future Work

In this research work, the optimization of fabrication of ZnO thin films with different dopant was performed using the state of art DIBS system. After the growth, the thin films were characterized for structural, electrical, optical, morphological and elemental properties. The optimization of growth parameters included a variation of deposition temperature and gaseous ambient in the DIBS system. Efforts were put to establish the correlations among different properties by employing XRD, AFM, FESEM, XPS, SE, and Hall measurements techniques. It was observed that the thin films properties were highly dependent on the growth parameters and the high-quality films can be successfully obtained at even low temperature by DIBS system. Moreover, after investigating the material properties, the spectral response of photodetector devices based on these doped films were analyzed.

6.1 Conclusions

The main outcomes of this thesis are summarized as follows:

(i) GZO based UV PDs were fabricated in MSM configuration. GZO films, employed as an active layer of photodetectors, were grown on Si (100) substrate by DIBS at varying temperatures from 200 to 600 °C. The UV PDs were fabricated by depositing 50-nm thick Au interdigitated contacts on GZO films by magnetron sputtering at room temperature. The spectral responses and the quantum efficiency of the fabricated devices were characterized. XRD of GZO films showed that all GZO films have a preferred *c*-axis orientation perpendicular to the substrate and angular position of (002) peaks. The best crystalline quality of thin films was observed at 300 °C. The Hall measurement data exhibited *n*-type conduction for all GZO films due to the incorporation of Ga into GZO. A minimum resistivity of $5.3 \times 10^{-4} \Omega$ -cm along with the highest electron concentration of 12×10^{20} cm⁻³, was obtained at 300 °C. The absorption spectra measured by spectroscopic ellipsometry clearly depicted that the films have a strong absorption to photons with a wavelength shorter than 370 nm, while it is almost transparent to those with a wavelength longer than 400 nm.

The spectral response measurements of MSM UV PDs were carried out from 300 to 500 nm. The device grown at 300 °C showed the highest responsivity of 58 mAW⁻¹ at zero bias. The response peak was centered on 325 nm and a cut-off wavelength around 370 nm corresponding to the band gap energy of GZO films. The external quantum efficiency (EQE) was observed to increase on the application of external bias exhibiting the photoconductive gain. While the EQE at zero bias was measured to be ~22.5%, it reached to 48% at 1 V bias with an average photocurrent of 23 mA. Low-temperature current-voltage (I-V) measurements for both forward and reverse bias voltages performed in the temperature range from 80 to 300 K indicated the dissimilar characteristic of identically deposited Au electrodes on GZO films. Based on the experimental results and analysis, the high responsivity was attributed to the tunneling of carriers across the dissimilar junctions. The physical transport of electrons dominated by tunneling under the effect of asymmetric Schottky barrier enables the device to operate at zero bias.

(ii) Stable and high hole concentration *p*-type PZO films were fabricated by DIBS system along with detailed investigation of electrical and optical properties. Post-deposition annealing of as-grown PZO films was carried out in N₂ ambient at 800 °C for 20 minutes to activate the acceptor dopants. The XRD pattern of PZO films shows that all the films, *as*-grown as well as annealed films, were identified to be preferentially *c*-axis (002) oriented. XRD data analysis, concluded that that P^{3+} replacing Zn^{2+} site was dominant mechanism resulting in the formation of P_{Zn} defects which acts as a donor but prefer to form P_{Zn} -2V_{Zn} acceptor complex under optimum O-rich growth conditions. The Hall measurements established that the annealed PZO films were *p*-type with a room temperature hole concentration of 8.6×10^{19} cm⁻³ and resistivity and mobility of 0.066 Ω cm and 1.08 cm²/Vs, respectively, for annealed PZO films grown at 500 °C. XPS analysis suggested the substitution of P atoms on Zn sites (P_{Zn}) along with the formation of a fewer P_O defects.

The optical properties of *p*-type PZO films were investigated by spectroscopic ellipsometry in the photon energy range of 1.2 - 6.4 eV at different angles of incidence at room temperature. Optical constants were obtained using a parameterized Psemi-M0 oscillator model. From the fitted ellipsometric data, the real (ε_1) and imaginary (ε_2) parts of complex dielectric function were extracted. ε_1 peak at band edge shows a shift towards higher energy for the annealed PZO with an increase in amplitude of ε_1 with annealing corresponding to the increase in hole concentration and larger crystallite size, at higher T_g . The critical point (CP) energy determination was done by fitting the second order derivative spectra of the complex dielectric function with respect to photon energy. The line shape analysis of complex dielectric function resulted in a distinct red shift in the energy position of E_0 CP with an increase in hole concentration. Room temperature photoluminescence (PL) spectra of PZO films showed a strong ultraviolet emission corresponding to near bandgap energy. These results provide important information for the fabrication of highly conductive ptype ZnO for application in high performance optoelectronic devices.

(iii) The fabrication and characterizations of LPZO films were performed followed by a systematic investigation of photoresponse characteristics of Li-P codoped p-ZnO/ n-Si heterojunction photodetectors. XRD investigation suggested a preferentially oriented LPZO film growth with a substitution of Li and P atoms on Zn sites under the oxygen-rich ambient resulting in the formation of Li_{Zn} and P_{Zn} defects. The electrical properties of the LPZO films determined by the Hall effect measurement predicted a p-type behavior at room temperature. The highest hole concentration was calculated to be 2.31×10^{20} cm⁻³ for LPZO films grown at 300 °C. The resistivity was found to be 0.016 Ω .cm with a Hall mobility of 2.8 cm²/V.s for the film. The current-voltage (I-V) characteristics of fabricated p-LPZO/ *n*-Si heterojunctions confirmed the rectifying behavior originated from the p-LPZO/n-Si junction. The turn-on voltage of +1.90 V was determined for devices grown at 500 °C with a forward to reverse bias current ratio (I_F/I_R) at \pm 3 V of 170. The elemental study confirmed the substitution of Li at Zn site forming the Li_{Zn}-O bonds in LPZO films creating the acceptor states. Also, phosphorus was found to be present in two different states. The substitution of P atoms on Zn sites (PZn) was identified, consequently forming the P_{Zn} - $2V_{Zn}$ acceptor complex due to lower ionization energy. Similarly, a fewer Po defects (P atoms on O sites) were also identified, however the, ratio of area under curve for P_{Zn} - 2V_{Zn} was almost double than that for P_0 defects indicating that the formation of P_{Zn} - $2V_{Zn}$ complex was favored over Po defects.

The optical absorption spectra of LPZO films were determined by spectroscopic ellipsometry at room temperature. The photoresponse characteristics of the *p*-ZnO/*n*-Si heterojunction photodetector were investigated at room temperature at different applied bias in the wavelength range 300 to 500 nm. At zero applied bias, a low photoresponse was observed, and the peak responsivity was determined to be about 1.8 mA/W for 500 °C grown device. The peak photoresponsivity at -6 V bias was measured to be 2.6 A/W for 500 °C grown devices corresponding to an EQE of the order of ~10³%. Furthermore, the UV to visible rejection ratio (ratio

of responsivity measured at 325 nm to that at 450 nm) of the heterojunction device was 21.8. The specific detectivity of the device at -6 V was determined to be 2.32×10^{10} cm Hz^{1/2} W⁻¹.

6.2 Scope of future work

Although, the effect of doping and process parameters on the growth of ZnO thin films were studied in this work, in order to realize the cost-effective and reliable fabrication of UV photodetector devices, however, the scope of improvement in performance always remains there. Therefore, the proposed areas where future work can be focused are as below

- Device performance enhancement of heterojunction and homojunction UV photodetector devices with noise consideration.
- (ii) Fabrication and performance study of ZnO based avalanche photodetector.
- (iii) Feasibility study and fabrication of ZnO based UV photodetector focal plane array.