SYNTHESIS AND STUDY OF CRYSTALLOGRAPHICALLY ORIENTED ZINC OXIDE (ZnO) NANOSTRUCTURES

Ph.D. Thesis

By ANKIT SONI



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020

SYNTHESIS AND STUDY OF CRYSTALLOGRAPHICALLY ORIENTED ZINC OXIDE (ZnO) NANOSTRUCTURES

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by ANKIT SONI



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **SYNTHESIS AND STUDY OF CRYSTALLOGRAPHICALLY ORIENTED ZINC OXIDE (ZnO) NANOSTRUCTURES** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from December 2014 to June 2020 under the supervision of Dr. Krushna R. Mavani, Professor, Discipline of Physics.

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.

Signature of the student with date (ANKIT SONI)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

3/3/2021

Signature of Thesis Supervisor with date (PROF. KRUSHNA R. MAVANI)

ANKIT SONI has successfully given his Ph.D. Oral Examination held on March 03, 2021 (Wednesday).

Signature of Chairperson (OEB) Date: 3/3/2021

Signature of PSPC Member #1 Date: 03/03/2021

Signature of Head of Discipline Date: 03/03/2021

Signature of External Examiner Date: 03 63 64

Date:

Signature(s) of Thesis Supervisor(s) Date: 3/3/2021

Signature of Convener, DPGC Date: 3rd March 2021

On behalf of Dr. Pankaj Sagdeo, Head of Physics, IIT Indore (as HOD Representative)

Sudip Chakraborty

ACKNOWLEDGEMENTS

You are what you believe in. You become that which you believe you can become"- The Bhagavad Gita Thank you, Lord Krishna, for your compassion.

This thesis would never come into existence without the supervision, assistance and support provided by the individuals mentioned below. I would like to extend my deepest gratitude to these people.

First and foremost, I would like to express my great appreciation to my Ph.D. thesis supervisor, Prof. Krushna R. Mavani, who has been an indispensable cornerstone of this thesis. I am forever grateful to become a part of her research group. Her meticulous and precise research attitude has certainly been infectious and has very much shaped my research work. Her constant input of time, patience, guidance and moral support has guided me through this wonderful journey. Even during the lockdown in the country due to the COVID-19 world pandemic, she also guided me from her home and was always open for the discussion on the phone. Her constructive criticism, innovative ideas and fruitful discussions adequately helped me in accomplishing my PhD successfully.

I would like to extend my sincere gratitude to my PSPC members Dr. Preeti A. Bhobe (Discipline of Physics) and Dr. Srivathsan Vasudevan (Discipline of Electrical Engineering), IIT Indore for their encouragement and valuable suggestions in improving my research work.

I sincerely wish to express my gratefulness to all the faculty members of the Discipline of Physics who have contributed in their own way.

I am extremely thankful to Prof. Dhanvir Singh Rana, IISER Bhopal, for permitting me to use his laboratory and experimental facilities. I thank all the group members of his laboratory for providing a healthy and friendly environment during my lab visits. I also thank Mr. Manoj Prajapat, staff, IISER Bhopal for helping in some XRD measurements.

I thank Sophisticated Instrumentation Centre (SIC), IIT Indore, specifically, Mr. Kinny Pandey and Mr. Nitin Upadhyay for their support. I also thank all the staff members of IIT Indore for providing all comfort and convenience. I also thank the health centre, IIT Indore especially Dr Shilpa Raut for her efforts and the medical guidance throughout my PhD study.

I acknowledge MHRD, New Delhi for providing the fellowship as a teaching assistant at IIT Indore. I also acknowledge SERB, New Delhi, for providing the international travel support to present a part of my research work at the international conference held at the University of California, Los Angeles, USA. I also thank the then head, Discipline of Physics, IIT Indore for providing financial support to attend some important national and international conferences during the Ph.D. tenure.

Our group members have given me great zeal and support during my Ph.D. tenure. I thank my senior fellows Dr. Fozia Aziz and Dr. Mahesh Chandra, for sharing the knowledge and helping me at the earlier stage of my Ph.D. work, I thank my comrades Mr. Harisankar, Mrs. Kavita Soni, Ms. Komal Mulchandani, Ms. Ekta Yadav, Ms. Reena Yadav, Ms. Komal Pathy, Mr. Shubham Kothari and Mr. Sourav Singh Tomar for providing a friendly and fulfilled environment in the lab. In particular, I want to thank Komal Mulchandani for her help and support during the experiments. I also thank Ekta Yadav for helping in Raman spectroscopy measurements and analysis. I highly appreciate Harisankar and Kavita for the fruitful scientific discussions that really helped me in writing the papers and this thesis.

I want to thank all my friends of IIT Indore, especially Dr. Vikas and Dr. Prateek for helping and encouraging me and my wife, Kavita all the time. I can not forget Dr. Shama and Dr. Amitesh, for their constant guidance regarding US Visa during the need. I express my special thanks to Nimai Sunder Das Prabhu (ISKCON, Ujjain) for teaching me valuable life lessons. At last, but by no means least, I would like to express my sincere gratitude to my parents (Mr. H. N. Soni and Mrs. Anjana Soni), elder brothers (Mr. Manish Soni and Mr. Mahesh Soni) and the whole family for their timely support. I can always feel their unconditional love and support, even on the other side of the earth. My mother is always being a source of inspiration and encouragement to me throughout my entire life. From the beginning itself, she has never compromised my studies for the rest.

I greatly appreciate and thank the support received from my in-laws; the words are not enough to express my indebtedness for them. I will never forget their guardianship and time what they have spent on my child. Only due to the inherent supportive nature of my son, I could focus on my Ph.D. work. I also thank my brother-in-law, Kapil Soni, who is always ready to help me in any situation.

I especially thank my beloved wife cum lab mate, Kavita Soni for her love and care, for the risk she took, the energy and endurance she invested to support me and her extraordinary understanding and patience. I learnt so many things from her, how to be happy and to keep others happy. I feel very fortunate that she is with me by 24x7. She made me comfortable for every situation and always stood with me at my even and odd time. She discussed ideas and prevented several wrong turns. With her by my side, thesis writing became less stressful.

Lastly, my heartfelt thanks to all those people also who have helped me directly or indirectly in my Ph.D. journey.

ANKIT SONI

Dedicated to the Lord (Krishna' and My Dear Son (Adyaan'

LIST OF PUBLICATIONS

A. Relevant to the Thesis (Peer-reviewed Journals):

- Ankit Soni, Komal Mulchandani, K. R. Mavani
 "UV activated visible-blind Ga:ZnO photodetectors using the GLAD technique: a comparative study in different gas atmospheres and temperatures" J. Mater. Chem. C, 8 (2020) 7837. (doi.org/10.1039/D0TC00990C). Impact factor: 7.059
- 2. Ankit Soni, Komal Mulchandani, K. R. Mavani

"Effects of substrates on the crystalline growth and UV photosensitivity of glancing angle deposited porous ZnO nanostructures" **Sensors and Actuators A: Physical 313 (2020) 112140**. (doi.org/10.1016/j.sna.2020.112140). **Impact factor: 2.904**

3. Ankit Soni and K. R. Mavani

"Controlling porosity and ultraviolet photoresponse of crystallographically oriented ZnO nanostructures grown by pulsed laser deposition" Scripta Materialia, 162 (2019) 24-27. (doi.org/10.1016/j.scriptamat.2018.10.026). Impact factor: 5.079

Ankit Soni, Komal Mulchandani, K. R. Mavani
 "Crystallographically oriented porous ZnO nanostructures with visible-blind photoresponse: Controlling the growth and optical properties" Materialia, 6 (2019) 100326. (doi.org/10.1016/j.mtla.2019.100326).

B. Other than Thesis:

- Ankit Soni, Reena Yadav, K. R. Mavani
 "Photo-induced electronic transition and effect of thickness on resistivity of Li-doped ZnO thin films" Mater. Res. Express 6 (2019) 106433. (doi.org/10.1088/2053-1591/ab3dd4). Impact factor: 1.929
- Ankit Soni, G. L. Prajapati, S. Prabhu, K. R. Mavani
 "Terahertz time-domain spectroscopic investigations on rare earth Gd-doped ZnO nanostructures grown by GLAD-assisted pulsed laser deposition" (under preparation).
- Komal Mulchandani, Ankit Soni, K. R. Mavani
 "Structure influenced rapid hydrogenation using metal-acid contacts on crystallographically oriented VO₂ thin films" Applied Surface Science 541 (2021) 148369. (doi.org/10.1016/j.apsusc.2020.148369). Impact factor: 6.182
- 4. Komal Mulchandani, Ankit Soni, Komal Pathy, K. R. Mavani
 "Structural transformation and tuning of electronic transitions by Wdoping in crystallographically oriented VO₂ thin films"
 Superlattices and Microstructures (accepted). Impact factor: 2.120
- Komal Mulchandani, Ankit Soni, Komal Pathy, K. R. Mavani
 "Rapid hydrogenation of VO₂ thin films using mild electric fields in ionic solution at room temperature" Materials Letters (under revision). Impact factor: 3.204

C. Conference Proceedings/ Poster (Oral) presentation:

- Ankit Soni, Komal Mulchandani, K. R. Mavani "Ultraviolet photoresponse of crystallographically oriented nanostructured thin films of ZnO grown by pulsed laser deposition" AIP Conference Proceedings 2100 (2019) 020077. (doi.org/10.1063/1.5098631).
 [Poster presentation and proceedings]
- Komal Mulchandani, Ankit Soni, K. R. Mavani "Effects of deposition temperature on growth and properties of pulsed laser deposited VO₂ thin films and nanostructures" AIP Conference Proceedings 2100 (2019) 020051. (doi.org/10.1063/1.5098605).
- Ankit Soni, Komal Mulchandani, K. R. Mavani "Deposition and optical properties of crystallographically oriented porous ZnO nanostructures" Advances in Functional Materials (AFM), International Conference-2019, University of California, Los Angeles, USA, 19-22 Aug. 2019. [ORAL presentation]
- Ankit Soni and K. R. Mavani "Synthesis and porosity control of crystallographically oriented ZnO nanostructures by pulsed laser deposition" International Conference on Functional Nanomaterials (ICFNM), IIT BHU, Varanasi, India, 22-25 Feb. 2019. [*BEST POSTER presentation award*]
- Ankit Soni and Krushna R. Mavani "Oxygen pressure dependent resistivity and nanostructure growth of ZnO by pulsed laser deposition method" International Conference on Laser Deposition (*i*COLD), IIT Madras, India, 20-22 Nov. 2019. [*Poster presentation*]

TABLE OF CONTENTS

LIST OF FIGURES	viii
LIST OF TABLES	xiv
ACRONYMS	XV
Title	Page
	No.
Chapter 1: Introduction	l
1.1 Nanostructures: A brief overview	2
1.1.1 Features of Nanostructures	3
1.2 Material	4
1.2.1 Zinc Oxide (ZnO): The material of choice	4
1.3 Overview of Properties of ZnO	
1.3.1 Crystal Structure	6
1.3.2 Vibrational Properties	7
1.3.3 Optical Properties	9
1.3.3.1 Band Structure	9
1.3.3.2 Photoluminescence	10
1.3.4 Other Properties	12
1.4 Doping in ZnO	12
1.5 Synthesis Mechanism and Techniques	13
1.5.1 Theory of Glancing Angle Deposition (GLAD)	16
1.5.1.1 Advanced GLAD Processes	18
1.6 Utility of ZnO	19
1.6.1 Ultraviolet Photodetectors	20
1.6.1.1 Mechanism and Working Principle of UV Photo-detection	21
1.7 Motivation and Objectives	23
1.8 Organization of the Thesis	25

Chapter 2: Experimental and Characterization Techniques	27
2.1 Substrate Preparation	28
2.2 Synthesis Methods	28
2.2.1 Synthesis of Bulk Targets	28
2.2.2 Synthesis of Nanostructures	29
2.2.2.1 Experimental Setup of Pulsed Laser Deposition (PLD)	29
2.2.2.2 Pre-deposition Treatment (Stage I: Substrate Seeding)	33
2.2.2.3 Glancing Angle Deposition (Stage II: Nanostructures	
Growth)	34
2.3 Characterization Techniques	36
2.3.1 Structural Characterization	36
2.3.1.1 X-ray Diffraction	36
2.3.1.2 Raman Spectroscopy	38
2.3.2 Surface Morphology and Porosity Analysis	40
2.3.2.1 Atomic Force Microscopy	41
2.3.2.2 Scanning Electron Microscopy	42
2.3.2.3 Porosity Analysis by ImageJ	44
2.3.3 Optical Characterization	45
2.3.3.1 Ultraviolet-Visible Spectroscopy	45
2.3.3.2 Photoluminescence Spectroscopy	47
2.3.4 Transient Ultraviolet Photo-detection Studies	49
2.3.4.1 Photodetector Fabrication	49
2.3.4.2 Photo-sensing Setup and Working Method	50
Chapter 3: Influence of Deposition Parameters on the Growth and	
Properties of ZnO Nanostructures	53
3.1 Introduction	54
PART-A	
3.2 Influence of Oxygen Partial Pressure	56
3.2.1 Experimental	56
3.2.2 Results and Discussion	57

3.2.2.1 Structural Analysis	57
3.2.2.2 Morphological Analysis	59
3.2.2.3 Optical Analysis	61
3.2.2.4 Transient Ultraviolet Photo-detection Studies	64
3.2.3 Summary	66
PART-B	
3.3 Influence of Deposition-angle (Seeding-angle)	67
3.3.1 Experimental	67
3.3.2 Results and Discussion	69
3.3.2.1 Structural Analysis	69
3.3.2.2 Morphological Analysis	73
3.3.2.3 Optical Analysis	75
3.3.2.4 Transient Ultraviolet Photo-detection Studies	79
3.3.3 Summary	81

Chapter 4: UV Photo-detection by ZnO and Ga-doped ZnO

Nanostructures: A Comparative Study Under Different Gas

Atmospheres and Temperatures	83
4.1 Introduction	85
4.2 Experimental	87
4.2.1 Bulk Zn _{1-x} Ga _x O (x=0.00, 0.02)	87
4.2.2 Nanostructure Synthesis	87
.3 Results and Discussion	
4.3.1 Structural Analysis	88
4.3.2 Morphological Analysis	92
4.3.3 Optical Analysis	93
4.4.4 Electrical and Photo-detection Studies	95
4.4.4.1 I-V Characteristics	96
4.4.4.2 Study of Visible-blindness	97
4.4.4.3 Photo-detection under Various Atmospheres	99

4.4.4 Photo-detection at Low-temperature	105
4.4.4.5 Role of Ga Doping in Improving the UV Photoresponse	107
4.4 Summary	108
Chapter 5: Fabrication of Ultraviolet Photodetectors of ZnO	
Nanostructures on Different Substrates	110
5.1 Introduction	111
5.2 Experimental	113
5.3 Results and Discussion	114
5.3.1 Structural Analysis	114
5.3.2 Morphological Analysis (by SEM and AFM)	118
5.3.3 Optical Analysis	121
5.3.4 Electrical and Photo-detection Studies	124
5.3.4.1 I-V Characteristics	124
5.3.4.2 Photo-detection under Ultraviolet and Visible Lights	125
5.4 Summary	130
Chapter 6: Conclusions and Future Prospects	131
6.1 Conclusions	132
6.2 Future Prospects	134
REFERENCES	135

LIST OF FIGURES

Figure No.	Figure caption	Page No.
1.1	Assembly of nanostructures showing different types of morphology.	3
1.2	Different crystal structures of ZnO: (a) cubic-rocksalt, (b) cubic zinc blende, (c) hexagonal wurtzite, (d) representing lattice parameters ' a (= b)' and ' c ' of hexagonal wurtzite	6
1.3	Optical phonon modes of wurtzite ZnO. Green and red spheres represent the oxygen and zinc atoms, respectively. Blue arrows represent the dominating displacement vectors. The vibrations of A_1 and B_1 modes are directed towards the <i>c</i> -axis whereas, the E_1 and E_2 modes have vibrations perpendicular to the <i>c</i> -axis.	8
1.4	Schematic representation for the (a) direct and (b) indirect band gap of semiconductors.	10
1.5	Typical photoluminescence spectra of bulk ZnO	11
1.6	Schematic representation for various energy levels of ZnO	11
1.7	Various synthesis techniques of nanostructures	15
1.8	Schematic of a basic GLAD apparatus, where ' α ' defines the angle between the axis of vapor flux and substrate' normal	16
1.9	Schematic view of GLAD growth: (a) vapor flux arrives at an angle ' α ' and produces a random distribution of nuclei on the substrate' surface, (b) nuclei grow and evolve shadows, (c) columnar growth with partial suppression of neighboring, (d) inclined columnar structures and growth restrictions for smaller columns.	17

1.10	Schematic representation for the lower flux capture to tilted substrates compared to the normally oriented substrate	18
1.11	ZnO nanostructures: (a) in the dark condition, (b) oxygen adsorption and formation of the depletion layer, and (c) during UV illumination process.	23
2.1	Schematic representation of the experimental setup of a pulsed laser deposition system.	31
2.2	Experimental setup of pulsed laser deposition system at a thin film laboratory, IIT Indore.	32
2.3	Photograph of the plasma plume generated from a ZnO target.	32
2.4	Schematic diagram of the experimental arrangement for the synthesis of nanostructures by GLAD-assisted PLD method.	33
2.5	Schematic diagram of the experimental setup for XRD measurement for the θ -2 θ scan.	37
2.6	Schematic representation of elastic and inelastic Raman scattering processes.	39
2.7	Schematic diagram of a micro Raman spectroscopy setup	40
2.8	Schematic representation of (a) atomic force microscope and (b) contact and non-contact modes of AFM.	42
2.9	Schematic diagram showing the interaction of electrons with an atom.	43
2.10	Schematic representation of a scanning electron microscope.	44
2.11	Evaluating the porosity value by processing the SEM image using ImageJ.	45
2.12	Schematic diagram of UV-Visible spectroscopy setup	46
2.13	Principle of photoluminescence spectroscopy	47

2.14	Schematic diagram of photoluminescence spectroscopy setup.	48
2.15	Schematic diagram of (a) fabricated photodetector and (b) photo-sensing experimental setup.	51
3.1	XRD patterns of ZnO nanostructures grown at different oxygen partial pressure.	58
3.2	Scanning electron micrographs with surface morphology (left panel) and cross-sectional view (right panel) of ZnO nanostructures grown at 7.5 Pa (a,b), 10.0 Pa (c,d), and 15.0 Pa (e,f).	59
3.3	UV-Visible spectra of ZnO nanostructures grown at different oxygen partial pressure. The inset shows a linear fit of the graph $(\alpha hv)^2$ versus (hv) for the optical band gap (E_g) calculation.	62
3.4	Photoluminescence spectra of ZnO nanostructures grown at different oxygen partial pressure.	63
3.5	Transient photoresponse characteristic curves of ZnO nanostructures grown at different oxygen partial pressure	65
3.6	Schematic representation of the seeding-angles for the first- stage of deposition.	68
3.7	XRD patterns of ZnO nanostructures grown at different seeding-angles.	69
3.8	Variation in crystallite size, FWHM of (002) peak, and intensity ratio of (002) and (100) peaks with changing seeding-angle.	71
3.9	Room-temperature Raman spectra of ZnO nanostructures grown at different seeding-angles. A Raman spectrum of the quartz substrate is also plotted for the comparison	72

3.10	Surface morphology (left panel) and cross-sectional view (right panel) of ZnO nanostructures grown at 0° (a,b), 30° (c,d), 45° (e,f), 60° (g,h), and 75° (i,j) seeding-angle	74
3.11	(a-e) UV-Visible spectra of ZnO nanostructures grown at different seeding-angles. The inset shows a linear fit of the graph $(\alpha hv)^2$ versus (hv) for the optical band gap (E_g) calculation. (f) Absorbance ratio in UV and visible wavelengths.	76
3.12	(a) Photoluminescence spectra of ZnO nanostructures grown at different seeding-angles. (b) The ratios of intensities for near-band emission to deep-level emission. (c) Normalized PL plot	78
3.13	Transient photoresponse characteristic curves of ZnO nanostructures grown at different seeding-angles.	80
4.1	XRD patterns of undoped and Ga-doped ZnO nanostructures.	89
4.2	Room-temperature Raman spectra of undoped and Ga-doped ZnO nanostructures. A Raman spectrum of the quartz substrate is also plotted for the comparison.	91
4.3	(a-d) Surface morphologies and the cross-sectional view of undoped ZnO and Ga-doped ZnO nanostructures. (e) EDX spectra image of Ga-doped ZnO nanostructures grown on a quartz substrate.	93
4.4	UV-Visible spectra of undoped ZnO (left) and Ga-doped ZnO (right) nanostructures. The inset shows a linear fit of the graph $(\alpha hv)^2$ versus (<i>hv</i>) for the optical band gap (Eg) calculation.	94
4.5	Photoluminescence spectra of undoped ZnO and Ga-doped ZnO nanostructures.	95
4.6	I-V characteristics of undoped ZnO and Ga-doped ZnO nanostructures.	97

4.7	Transient photoresponse characteristic curves of (a) undoped ZnO and (b) Ga-doped ZnO nanostructures under red, green and blue lights.	98
4.8	Comparison of photoresponse under blue and UV light for (a) undoped ZnO and (b) Ga-doped ZnO nanostructures	98
4.9	Room-temperature transient photoresponse characteristic curves of undoped ZnO and Ga-doped ZnO nanostructures under different atmospheric conditions. The gases are at ambient conditions. The increase in response upon Ga doping is denoted by a vertical arrow in the figure.	99
4.10	Schematic representation of the adsorption process under the different medium. The red color spheres represent adsorbates, bottom layer (green color) represents the quartz substrate, and the thick top layer (yellow color) represents the depletion width.	100
4.11	Transient photoresponse characteristic curves in the air at room temperature for undoped ZnO and Ga-doped ZnO nanostructures.	102
4.12	Temperature-dependent transient photoresponse characteristic curves of undoped ZnO and Ga-doped ZnO nanostructures. The inset shows a typical semiconducting behavior of ZnO in resistivity (ρ) versus temperature (T) curve.	106
4.13	Schematic representation for the principal mechanism of photoresponse for different grain size of nanostructures	108
5.1	XRD patterns of ZnO nanostructures grown on the quartz, MgO and Al ₂ O ₃ substrates.	115
5.2	(a) Enlarged view of ZnO (002) XRD peak, (b) Crystallite size and FWHM of (002) peak of ZnO nanostructures grown on different substrates.	116

5.3	Room-temperature Raman spectra of ZnO nanostructures deposited on different substrates. The letter 'S' represents the contribution from individual substrates.	117
5.4	SEM (top) and AFM (bottom) images of ZnO nanostructures grown on Al_2O_3 (a,d), MgO (b,e) and quartz (c,f) substrates. The inset shows corresponding cross-section SEM images. The circles in red color indicate the hexagonal grains of the nanostructures.	120
5.5	UV-Visible spectra of ZnO nanostructures deposited on (a) quartz and (b) sapphire substrates. The inset shows a linear fit of the graph $(\alpha hv)^2$ versus (hv) for the optical band gap (Eg) calculation.	121
5.6	(a) Photoluminescence spectra of ZnO nanostructures deposited on different substrates. (b) De-convoluted PL spectra of ZnO nanostructures grown on MgO substrate	122
5.7	Schematic representation of the various emission lines from the different energy levels of ZnO.	123
5.8	I-V characteristics of ZnO nanostructures deposited on (a) sapphire and MgO, (b) quartz substrate.	125
5.9	Transient photoresponse characteristic curves of ZnO nanostructures grown on different substrates. The solid line represents the fitting of the curves using eq. 3.2.	126
5.10	Transient photoresponse characteristic curves of the sample ZnO/MgO under the illumination of different lights	129

LIST OF TABLES

Table No.	Table caption	Page No.
3.1	Derived parameters from the transient photoresponse characteristic curves of ZnO nanostructures.	66
3.2	Obtained values for porosity, dark current and a photo-to-dark current ratio of ZnO nanostructures.	81
4.1	Derived parameters from the transient photoresponse characteristic curves of undoped ZnO and Ga-doped ZnO nanostructures.	101
4.2	Comparison of the reported performance of various UV photodetectors based on different ZnO nanostructures	103
5.1	Derived parameters from the transient photoresponse characteristic curves of ZnO nanostructures grown on different substrates.	127
5.2	Comparison of the reported performance of various UV photodetectors based on different ZnO samples	128

ACRONYMS

Zinc Oxide	ZnO
Pulsed Laser Deposition	PLD
Glancing Angle Deposition	GLAD
X-ray Diffraction	XRD
Scanning Electron Microscopy	SEM
Atomic Force Microscopy	AFM
Photoluminescence	PL
Ultraviolet	UV
Ultraviolet-Visible	UV-Vis
Near Band Edge	NBE
Deep Level Emission	DLE
Full Width at Half Maximum	FWHM
Current-Voltage	I-V

Chapter 1

Introduction

This chapter presents a brief review of the nanostructures and their remarkable features. The material of interest, *i.e.* Zinc Oxide (ZnO), has been explored in detail with its properties and applications. A brief discussion of the synthesis technique used in the present thesis is also highlighted. The general background and theory of glancing angle deposition technique along with its unique features have also been summarized.

1.1 Nanostructures: A brief overview

In 1959, a famous physicist Richard Feynman (Noble prize winner of Physics in 1965) while referring to the physics of materials coined a sentence "there is plenty of room at the bottom" during his talk in a conference at the American Physical Society. This encouraged the scientists, and since then the research on nanomaterials boosted up. The term 'Nano' generally refers to the structure of a material having at least one dimension between 1 and 100 nm. The study and technology which encompasses such dimensions of structures are known as 'Nanoscience' and 'Nanotechnology', respectively. From the past few years, the field of nanotechnology has spread its feathers into the various areas of science and engineering including, bio, civil, military, astronomy *etc*.

The technology enables to produce the nanostructures not only with unique designs but with fascinating functional properties of materials. Therefore, depending on the properties of nanostructures, the technology can be categorized into nanoelectronics and nanophotonics *etc*. With the advancement of this technology, various applications of nanostructures have been realized and implemented too. Till now, the nanostructures of different materials, including oxides and nitrides, have been prepared using various synthesis techniques, and a variety of morphologies have been obtained (Fig. 1.1). The functional nanostructures of semiconductor materials play a vital role in device-based technology. In recent years, the growth of low dimensional semiconductor nanostructures and their integration into working devices have revolutionized the semiconductor technology. Therefore, the low dimensions (*e.g.* 1D) of nanostructures such as wires, tubes, rods and belts have significantly stimulated the basic research in the scientific as well as industrial communities.



Figure 1.1: Assembly of nanostructures showing different types of morphology [1].

1.1.1 Features of Nanostructures

The nanostructure materials have interesting and applicable properties which make them distinct from the bulk and thin film structures. Few of the key properties of nanostructures are listed as below:

- Low dimension (size effects): In bulk materials, the electronic energy levels have a continuum, whereas, for nanostructured materials, the case is different owing to the quantum size effect [2]. When the size of any material is reduced to the de-Broglie wavelength, the discrete electronic energy levels are realized due to the spatial confinement of electrons and holes. The reduced size may occupy any shape, *e.g.* nanowire, nanorod, nanotube, nanosheet *etc*. A blue-shift in the band gap of semiconductor materials is one of the examples of size-effects [3].
- Large surface-to-volume ratio: The reduction in the size of material has a direct relation with the surface-to-volume ratio. As

the size reduces, the ratio increases due to the increase in surface area per unit volume. Consequently, the increased surface area induces porosity in the material. This porosity is essential for the ultraviolet photo-detection and gas sensing applications [4,5].

• **Boundary effects:** Grain boundaries play a crucial role in the properties of material because a significant portion of atoms resides in the grain boundaries. Therefore, with the reduction in grain size, the interfacial region must be considered for the nano grain size of materials. For example, the reduction in grain size increases the surface activity of adsorption and desorption [6].

1.2 Material

The choice of material and understanding its properties are the important aspects for an efficient device application. In other words, the applicability of any device is fully dependent on the properties and characteristics of the selected materials. Therefore, the materials must be chosen so wisely that they fulfill the criteria and live up to the expectations. For example, designing of ultraviolet (UV) photodetector require a wide band gap material having defect-free and highly crystalline nature with strong absorption of UV light. Hence, zinc oxide (ZnO) at a certain extent proves its applicability in UV photodetectors with significant absorption of UV light due to its wide band gap nature [7].

1.2.1 Zinc Oxide (ZnO): The material of choice

Zinc Oxide (Chemical formula: ZnO) is a semiconductor material and has been studied for decades. The research on ZnO was initiated in the early 1900s, and it came up with the first electronic application in radio sets during the 1920s [8]. The number of relevant publications on ZnO is the evidence of its competency and applications in various fields [9,10]. Therefore, among the existing semiconductor materials, ZnO is still being researched by many scientists and engineers due to its attractive properties. The advancement in technology with various new synthesis techniques made possible the growth of ZnO nanostructures with high-quality and crystallinity. However, ZnO finds its application in both forms, *i.e.* bulk as well as nanostructures. One-dimensional (1D) ZnO nanostructures such as nanowires and nanorods have attracted considerable research interest due to their efficient charge carrier transport properties [11,12]. Moreover, many nanostructures of ZnO have needle-like tips or nanocone shapes, which enhances the electron field emission due to local field enhancement on their tips [13]. Therefore, by using the properties of such 1D-nanostructures, various semiconductor devices based on ZnO can be fabricated, for example, solar cells, light-emitting diodes, photodetectors, gas/chemical sensors *etc.* [14].

In general, ZnO is an *n*-type semiconductor material with band gap falls in the UV region. Along with UV emission, it also shows emissions in the visible region of the electromagnetic spectrum. The intrinsic defects of ZnO are mainly responsible for this visible emission [15]. The researchers have made full efforts leaving no stone unturned for obtaining *p*-type ZnO [16,17]. However, the self-compensation of charge carriers in ZnO made this not possible to some extent. Many impurity elements of group-I and group-V have also been doped in ZnO to obtain *p*-type nature [18], but the low reproducibility and poor stability of *p*-type conductivity is still a milestone in this field. The intrinsic conductivity combined with optical characteristics led to the new applications of ZnO. This conductive and optically transparent nature of ZnO reserved its place amongst the various transparent conductive oxide (TCO) materials. The applications of TCO include flat panel display, smart windows, transparent electrodes, window defrosters, light-emitting diodes *etc.* [19,20].

All such aforesaid applications of ZnO have been perceived due to its enthralling fundamental properties as listed in the discussion below.

1.3 Overview of the Properties of ZnO

1.3.1 Crystal Structure

ZnO belongs to the category of II-VI group of binary compounds. It crystallizes in three different structures, *i.e.* wurtzite, zinc blende, and rocksalt structures, as shown in Fig. 1.2 [9]. At ambient conditions, the most stable and most commonly observed phase is the wurtzite with hexagonal structure. The latter two structures form cubic structure and can be realized at relatively different thermodynamic conditions.



Figure 1.2: Different crystal structures of ZnO: (a) cubic-rocksalt, (b) cubic zinc blende, and (c) hexagonal wurtzite [9], (d) representing lattice parameters 'a (=b)' and 'c' of hexagonal wurtzite.

The wurtzite structure of ZnO consists of a hexagonal unit cell having two lattice parameters, '*a*' and '*c*' (Fig. 1.2d), typically with a ratio

of c/a=1.63. However, the lattice constants of an ideal wurtzite ZnO depend on the various parameters, *i.e.* temperature, impurity, *etc.* The value of lattice constants for an ideal and ordered ZnO are a=3.25 Å and c=5.21 Å with c/a ratio of nearly 1.6 at the temperature of 297 K [21]. The wurtzite structure of ZnO comprises of two interpenetrating hexagonal-closed-pack (hcp) sublattices of Zn²⁺ and O²⁻ ions arranged such that each Zn ion is surrounded by a tetrahedron of oxygen ions and vice versa. In this structure, the directions parallel to the *c*-axis are denoted by [000*l*]. The *ab-initio* calculations for ZnO showed that it has a natural tendency to grow in the [000*l*] directions due to the highest surface energy compared to all lowindex planes of the wurtzite structure [22]. This surface energy plays a vital role in the nucleation and growth process of ZnO nanostructures. It should be noted here that all the ZnO nanostructures studied for this thesis are crystallized in the wurtzite structure and have crystal orientation along the *c*-axis with prominent (002) plane.

1.3.2 Vibrational Properties

A phonon refers to the elementary excitation of the lattice vibration, and the lattice dynamics of any structure are mainly associated with the Ramanactive phonon modes. In the hexagonal wurtzite structure of ZnO, the arrangement of Zn²⁺ and O²⁻ ions produces a polar symmetry along the hexagonal vertical axis (*i.e. c*-axis). The structure has four atoms (*i.e.* 2 pairs of Zn-O) in the hexagonal unit cell leading to the twelve phonon branches, out of which nine are the optical and three are the acoustic [23]. The symmetry representation of the fundamental optical phonon modes of ZnO is given by $\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1$. The A₁ and E₁ modes are both Raman and IR active, whereas E₂ modes are Raman active only, and the B₁ branches are inactive (also known as silent modes). The polar A₁ and E₁ modes further split into LO (longitudinal optical) and TO (transverse optical) modes with different frequencies due to the long-range electrostatic forces [24]. Hence, the eight sets of characteristic optical phonon modes are $A_1(TO)$, $A_1(LO)$, $E_1(TO)$, $E_1(LO)$, $E_2(high)$, $E_2(low)$, $B_1(high)$ and $B_1(low)$. Importantly, the first six modes are also known as first-order Raman active vibrational modes. All the modes correlate with a band of wavenumbers (in the unit of cm⁻¹) with varying intensities in the Raman spectrum. Fig. 1.3 schematically depicts the characteristic Raman vibrational modes of wurtzite ZnO.



Figure 1.3: Optical phonon modes of wurtzite ZnO. Green and red spheres represent the oxygen and zinc atoms, respectively. Blue arrows represent the dominating displacement vectors. The vibrations of A_1 and B_1 modes are directed towards the *c*-axis whereas, the E_1 and E_2 modes have vibrations perpendicular to the *c*-axis.

Generally, in Raman spectrum of ZnO, the E_2 modes are very intense which particularly represents the chemical composition of Zinc (*i.e.* $E_2(low)$ mode) and Oxygen (*i.e.* $E_2(high)$ mode) in the wurtzite crystal structure. These E_2 modes are also defined as non-polar modes due to the mutual compensation of the displacement vectors within each sub-lattice (Fig. 1.3) and therefore have no net induced polarization. Similarly, the silent B_1 modes are also non-polar; however, for these modes, one sublattice is essentially at rest while the other neighboring ions move opposite
to each other (Fig. 1.3). For the $B_1(low)$ and $B_1(high)$ phonon modes the displacements are caused by the heavier sub-lattice (*i.e.* Zn) and lighter sub-lattice (*i.e.* O), respectively. On the other hand, the A₁ and E₁ phonon modes arise due to oscillations of rigid sub-lattices and are mainly dominated by the oxygen ions. These modes are polar in nature, where the Zn and O ions both move parallel and perpendicular to the *c*-axis for the A₁ and E₁ phonon vibrations, respectively.

Practically, the Raman shift for all these modes (*i.e.* the vibrational properties) of ZnO is strongly affected by the doping or by the microscopic nature (*i.e.* nanostructure form) also [25,26].

1.3.3 Optical Properties

1.3.3.1 Band Structure

ZnO is known to be a wide band gap semiconductor material and have its place in the family of II-VI compounds. It has a direct band gap (E_g) of 3.4 eV at room temperature [16]. This band gap corresponds to the UV light of wavelength 365 nm and is transparent throughout the visible spectrum of light. The term 'wide band gap' referred to those semiconductors having a band gap about twice or three times the band gap of conventional semiconductor Si, the most commonly and widely used semiconductor having band gap of ~1.12 eV [27]. The other examples of wide band gap semiconductors are GaN (E_g =3.39 eV) and SiC (E_g =2.9 eV) widely studied among the family of indirect band gap semiconductors [28].

The direct and indirect band gaps are defined depending on the position of extrema and minima of valence band and conduction band. Fig. 1.4 shows a schematic representation for the direct and indirect band gap of semiconductors. The photon emission in the indirect band gap semiconductors is accompanied by the phonon emission, as shown in Fig. 1.4(b).



Figure 1.4: Schematic representation for the (a) direct and (b) indirect band gap of semiconductors.

1.3.3.2 Photoluminescence

The emission spectrum of ZnO is characterized by near-band emission (NBE) and deep-level emission (DLE). The NBE consists of an intense emission peak in the UV wavelength range and arises due to the band-to-band transition or excitons emission [29]. The various intrinsic and/or extrinsic defect states located at the deep levels causes a broad emission in the visible region of the electromagnetic spectrum. Fig. 1.5 shows the typical photoluminescence (PL) spectra of ZnO at room temperature. For more understanding of defect-assisted emissions along with UV emission, a schematic has been presented in Fig. 1.6 showing the various energy levels of ZnO. For a perfect crystalline ZnO, the emission from DLE can be highly suppressed. Therefore, the high intense UV emission with suppressed visible emission can be considered as an indication for the crystallinity of ZnO.



Figure 1.5: Typical photoluminescence spectra of bulk ZnO.



Figure 1.6: Schematic representation for various energy levels of ZnO.

The elementary deep level defects of ZnO include zinc vacancies (V_{Zn}) , interstitial zinc (Zn_i) , oxygen vacancies (V_o) and interstitial oxygen (O_i) [30,31] These defects can affect the position of band edge emission as well as the shape/width of luminescence spectra. Therefore, the point defects play a crucial role in determining the optical properties of ZnO and

strongly depend on the growth conditions and synthesis methods [32]. All the ZnO nanostructures presented in this thesis show intense UV emission with suppressed visible emission, indicating the crystallinity and quality of prepared nanostructures. This feature is attributed to the pulsed laser deposition technique, as discussed in the chapters.

1.3.4 Other Properties

Besides the above-mentioned properties of ZnO, it has many other important and applicable properties too, as listed below.

- *Large exciton binding energy* (60 meV) which is much suitable for efficient excitonic emission at room temperature.
- *High radiation hardness*, making it more appropriate for use in space applications.
- *Piezoelectricity* makes it applicable for sensors and actuators.
- *High thermal conductivity* ensures the high efficiency for heat removal during the device operation.
- *Highly sensitive* for adsorbed gas species and has utility in sensing of various gases such as CH₄, CO, NO₂ *etc*. [33]
- *Bio safe and biocompatible* for biomedical applications. For example, biomedical imaging and drug delivery [10].

1.4 Doping in ZnO

In this section, a brief review on the doping in ZnO is given, also providing a visual background for an understanding of chapter-4. Implementing the impurities by doping is one of the most efficient ways to modify and tune the optical and electrical properties of ZnO. Since it is a wide band gap material and doping can efficiently tune such band gap by modifying the defect states. Moreover, with appropriate doping of selective elements, the electrical properties of ZnO can be precisely tailored with keeping its optical properties unaffected.

Usually, the resistivity (ρ) for any material having electrons as the majority of charge carriers, is given by $\rho = (1/ne\mu)$, where *n* is the carrier concentration, e is the elementary charge and μ is the mobility. It is clear that with an increase of carrier concentration and/or mobility, the resistivity can be reduced. For ZnO, it should be noted that, even without any doping, it shows *n*-type conductivity with typical resistivity of the order of 10^{-2} Ω .cm. However, the intrinsic conductivity can be increased by suitable doping of group-III elements (B, Al, Ga and In) acting as electron donors [34]. Such dopants can occupy the Zn sites due to similarity in ionic radii of respective elements. The dopant also donates one of its electrons to the conduction band, thereby increasing the carrier concentration and hence the conductivity. Similarly, doping of group-IV elements (Si, Ge, Sn) in ZnO has also been reported [35]. Moreover, the doping of group-I (Li, Na, K, Cu, Ag) and group-V elements (N, P, As and Sb) with the efforts to fabricate *p*-type ZnO have also been well documented [17,36]. To study the magnetic properties of doped ZnO, transition metal elements have also been used as a dopant [37].

The influence of doping in ZnO is not limited. The doping may modify the carrier concentrations, electronic structure, luminescence properties and structural parameters (*i.e.* lattice constants). The modified properties have their own feasibility and applicability. For example, the increased conductivity along with inadequacy and low-cost of doped-ZnO has replaced the devices based on indium tin oxide (ITO) materials.

1.5 Synthesis Mechanism and Techniques

A wide variety of synthesis techniques with unique growth mechanism have been developed and used for the growth of ZnO nanostructures. In general, the methods for the fabrication of nanostructures are categorized by the two approaches, namely, 'top-down' and 'bottom-up'. In top-down synthesis method, the nanostructures are fabricated by etching out the crystal planes which are already present on the substrate. This patterning can be done using optical or electron beam lithography techniques which however are very costly and have long processing time. The main drawbacks of the topdown approach are imperfections of crystals, impurities and contamination caused during the interaction processes. The bottom-up approach includes the synthesis of nanostructures on the substrates by precisely stacking the atoms onto each other. This approach produces the defect-free, homogeneous and long-range ordered nanostructures.

The synthesis techniques depending on its growth mechanism may involve some type of catalyst for the growth of nanostructures. Furthermore, based on the phase of catalyst (*i.e.* liquid or solid), there can be two types of mechanisms, namely, vapor-liquid-solid (VLS) and vapor-solid-solid (VSS). The nanostructure growth in such type of catalyst-assisted growth mechanisms can be controlled by controlling the properties of the catalyst material. However, the presence of catalyst particles in the nanostructures may result in impurity and hinders the device performance. Therefore, to avoid such issues, modern research efforts have been heading for the catalyst-free or self-catalyzed nanostructure growths. In this process, the semiconductor material or its element itself is used as a promoter instead of external catalyst elements, ensuring both controlled and impurity-free growth.

Depending on the processing methods of nanostructures, the synthesis techniques can be classified as shown in the chart (Fig. 1.7). Each of the method presented in the chart has different growth process and different requirements for the synthesis. The chemical methods use a chemical form (either liquid or vapor) of the starting material, whereas the

other methods use solid target materials. Explaining each of these methods is beyond of this thesis.



Figure 1.7: Various synthesis techniques of nanostructures.

It must be added here that other than the techniques reported above, the nanostructures can be prepared by the combination of different methods too. For example, ZnO nanorods have been fabricated by mixing laser ablation and chemical synthesis techniques [38]. Similar other variants of PLD such as RF plasma-assisted PLD, bias voltage-assisted PLD, *etc.* have also been reported to grow ZnO [39–41].

In the work of the present thesis, the glancing angle deposition (GLAD) technique [42] has been adopted by utilizing the conventional pulsed laser deposition (PLD) setup. PLD is known to produce highly crystalline samples [43]. On the other hand, GLAD assists in the formation of pores during the deposition. Thus the crystallinity, as well as porosity in

the grown nanostructures, can be realized by the combinatorial effect of GLAD and PLD. The details of PLD with its schematic and real experimental setup have been presented in chapter-2 of the thesis. The basic theory and principle of growth by GLAD technique has been described in the following subsection.

1.5.1 Theory of Glancing Angle Deposition (GLAD)

The GLAD technique was first developed by M. J. Brett's group around the 1990s by using the sputtering setup [44,45], and since then it has been extensively used in combination with various PVD systems including thermal evaporation, PLD, *etc.* [46–49].



Figure 1.8: Schematic of a basic GLAD apparatus, where ' α ' defines the angle between the axis of vapor flux and substrate' normal.

Usually, in the GLAD technique, the vapor-flux arrives at the surface of the substrate at a glancing angle as schematically shown in Fig. 1.8. The substrate, however, may be stationary or may have rotations during the deposition [50]. The GLAD technique is a promising way of obtaining

a variety of nanostructures for different materials with controlled synthesis. This technique also enables to tune the surface anisotropy by varying the surface morphologies [51].



Figure 1.9: Schematic view of GLAD growth: (a) vapor flux arrives at an angle ' α ' and produces a random distribution of nuclei on the substrate' surface, (b) nuclei grow and evolve shadows, (c) columnar growth with partial suppression of neighboring, (d) inclined columnar structures and growth restrictions for smaller columns [42].

The growth of columnar structures by GLAD takes places due to a combination of the ballistic shadowing effect and the limited surface diffusion. Fig. 1.9 represents a schematic view of growth by GLAD technique. The vapor-flux is incident at an angle (α) and forms nuclei on the substrate surface through a random process (Fig. 1.9a). These nuclei grow into small columns and develop shadows with size distribution (Fig. 1.9b). Consequently, the growth of smaller columns is suppressed and restricted by the screening of neighboring nuclei from the incoming vapor-flux (Fig. 1.9c). At some instant, the smaller nuclei and columns become totally shadowed and stop growing (Fig. 1.9d). With continuing the process and at sufficient deposition, a self-reinforcement causes the development of

isolated columnar structures. Moreover, with the extreme of the shadow, porous nanostructures of isolated columns inclined towards the vapor-flux can be obtained [45,52]. The induced porosity and column spacing depends on the incident flux angle, with a decrease of the incidence angle the nanostructures may lose porosity and become dense [44,53]. Therefore, the morphology and density of GLAD produced nanostructures are unlike the normally deposited films.

The thickness of nanostructures produced by GLAD technique is associated with the two competing factors. The first factor is porosity produced by the shadowing effect at higher incidence angles, and the second is a geometrical factor (*i.e.* incidence angle) which causes the thickness to decrease with increasing the incidence angle. The reduction in thickness can be attributed to the low flux capture at higher incidence angles, as shown in Fig. 1.10.



Figure 1.10: Schematic representation for the lower flux capture to tilted substrates compared to the normally oriented substrates [50].

1.5.1.1 Advanced GLAD Processes

Nowadays, the advanced GLAD processes have been spaciously used with the aim to improve the quality of nanostructures [42]. The advanced approach includes the processing of nanostructures before, during or after the GLAD process. Few of the advanced processes are listed below:

- Pre-deposition treatment (substrate seeding): In this process, seeds of the desired materials are first deposited on the substrates, and then nanostructures are produced on these seeded substrates using GLAD. The seeds act as forced nucleation sites for the growth of nanostructures. Moreover, with proper designing of seeds, the shape and size of nanostructures can be precisely controlled. There are numerous methods by which seeds can be prepared [42]. However, in the present work, a PLD has been used to deposited the seeds onto the substrate by keeping the substrate parallel to the target' surface. More details with experimental parameters have been presented in chapter-2 of the thesis.
- Controlling substrate motion and temperature.
- External shadowing.
- GLAD co-deposition, *i.e.* deposition of single/two materials from similar/different directions.
- Post-deposition treatments such as annealing, etching, oxidation and GLAD templating.
- Sequential GLAD *i.e.* deposition of different materials sequentially.

Due to the flexibility of GLAD technique the fabricated nanostructures show *improved quality*, *crystallinity* and *high surface-to-volume ratio* (*i.e. porosity*). Such properties are very essential for the electrical and optical applications, for example, electrical/optical sensors, solar cells *etc*.

1.6 Utility of ZnO

Based on the intriguing properties, as discussed in section 1.3, ZnO proves to be a good contender of next-generation optoelectronic devices. However,

the utility of ZnO is not limited to a specific field. It has applications in various sectors including engineering, medicinal, bioscience, food industry, cosmetics, electronics, optics and many more [54]. There are various devices based on ZnO have been fabricated, such as solar cells, lasers, field emission devices and UV photodetectors [55–57]. Here, we constrained ourselves to discuss on the UV photodetectors. The following sections describe the basics of UV photodetectors and their functioning.

1.6.1 Ultraviolet Photodetectors

Strictly speaking, a photodetector is a kind of device which converts the optical signal into an electrical signal either in the form of a current or a voltage. The ultraviolet (UV) photodetectors are meant to measure the UV light. The electromagnetic spectrum of UV light lies in the wavelengths ranging from 100-400 nm. A wavelength range from 400-700 nm is identified as the visible region; therefore, the photodetectors having a response only for UV photons are known as visible-blind detectors. This character of visible-blindness for UV detection is very useful and applicable in various fields in order to avoid an expensive process of filtering. The UV range can be further divided into three subcategories depending on their energy and wavelengths. For example, UV-A is assigned for the wavelength range of 400-315 nm, similarly for UV-B (315-280 nm) and UV-C (280-100 nm). UV-C is also called a deep UV. In the present work of thesis, specifically, we have used two different wavelengths of UV light, *i.e.* UV-A (365 nm) and UV-C (254 nm) for the sensing measurements.

ZnO is a widely studied material for the fabrication of UV photodetectors, and numerous efforts have been put in the direction to improve the performance of ZnO based UV photodetectors. For example, a low dark current is one of the key factors to improve the sensitivity of such photodetectors. The earlier reports suggested that the surface electrons of ZnO have a tendency of depletion by the adsorbed oxygen on the surface states [57–60]. Therefore, the UV photodetectors which have been fabricated using low-dimensional nanostructures of ZnO such as nanowires and nanotubes show high performance than the conventional bulk structures [61,62]. The increased performance of photodetectors based on such nanostructures is attributed to the large surface-to-volume ratio, which contains a high concentration of surface states and is therefore propitious to the depletion of electrons under dark conditions. However, the performance can be further improved by precise tuning of preparation conditions and doping of selective elements.

1.6.1.1 Mechanism and Working Principle of UV Photodetection

The photoresponse in ZnO has been identified due to the two mechanisms, namely *i*) a rapid band-to-band recombination with very short time constants, and *ii*) photo-desorption of oxygen molecules from the surface. In the first mechanism, when a photon of incident energy (E_{Ph}) greater than the band gap energy (E_g) of the material, falls on the surface of a semiconductor material it gets absorbed and generates an electron-hole pair, *i.e.* the excitation of an electron from the valence band to the conduction band, leaving a hole in the valence band. These charge carriers (*i.e.* electrons and holes) then drift towards the respective electrodes under the applied electric field and generate a signal in the form of a photocurrent in the circuit.

The second mechanism is considered to be dominant in the ZnO nanostructures as schematically shown in Fig. 1.11. In this mechanism, the adsorption and desorption of oxygen molecules play a major role in the photoresponse process. ZnO has free electrons, and in the surroundings, there are plenty of oxygen molecules available (Fig. 1.11a). At ambient conditions, the oxygen molecules get attached to the surface of nanostructures as negatively charged ions by the *adsorption* process. The

adsorption takes place due to the presence of trap levels and oxygen vacancy states near the surface, resulting in the trapping of free electrons and thereby creating a depletion layer on the surface of nanostructures as schematically represented in Fig. 1.11b. This process can be written as,

$$O_2(gas) + e^- \to O_2^-(ads)$$
 1.1

The depletion layer causes a reduction in the conductivity of a material. Moreover, the oxygen adsorption also results in the band bending due to the formation of a potential barrier near the surface of nanostructures [57].

Now, when the UV light with energy equal to or greater than the band gap of material is illuminated on the samples, numerous electron-hole pairs are generated by the absorption of photons.

$$h\nu \rightarrow e^- + h^+$$
 1.2

The generated electrons and holes take part in the photo-desorption process and increase the current. Therefore, the increase in photocurrent upon UV illumination is attributed to the supply of necessary photon energy and thereby, the *desorption* of oxygen molecules from the surface of nanostructures. The holes further oxidize the ionized adsorbed-oxygen, known as the photo-desorption process, shown in Fig. 1.11c.

$$h^+ + O_2^-(ads.) \to O_2(gas)$$
 1.3

In this way, the depletion region is eliminated, and the photo-generated electrons remain, which actually contribute to the increase in photocurrent. On the contrary, when the supply of photons is stopped, the re-adsorption of oxygen molecules takes place, resulting in a decrease of photocurrent.



Figure 1.11: Schematic representation for photo-generation mechanism in ZnO nanostructures: (a) in the dark condition, (b) oxygen adsorption and formation of the depletion layer, and (c) during UV illumination process.

1.7 Motivation and Objectives

ZnO nanostructures perform the most exclusive role in the advancement of semiconductor nanotechnology. Therefore, considering ZnO as an important wide band gap semiconductor material for various optoelectronic applications, we have selected this material for our present investigations. To date, the nanostructures of ZnO have been grown using various synthesis techniques including chemical and physical deposition techniques, and a variety of morphologies such as nanorods, nanotubes, nanowires, nanowalls *etc.* have been obtained [63–65]. Notably, the controlled synthesis of these nanostructures is still a foremost challenge to the researchers.

Most of the synthesis method includes some sort of catalyst to initiate the growth process, which may degrade the crystallinity and add impurities in the samples. Consequently, the poor crystalline nature and availability of defects hinder the performance of the ZnO based devices. The pulsed laser deposition (PLD) method can overcome such issues, as the PLD grown nanostructures prove high-crystallinity and quality due to the defect-free nature, which especially suits for UV photo-detection. Furthermore, the high surface-area-to-volume ratio is encouraged for ZnO nanostructures in the photo- and gas-sensing applications. The glancing angle deposition (GLAD) technique in combination with PLD can help produce the highly porous as well as crystallographically oriented nanostructures. Further, this technique also provides flexibility on the shape and size of nanostructures by tuning the various deposition parameters. In the present work, synthesis of self-seeded, highly porous and crystallographically oriented ZnO nanostructures have been performed, without the aid of any catalyst, using the GLAD-assisted PLD technique. Further, the UV photo-detection on fabricated photodetectors has been performed, and the influence of various atmospheric conditions on the UV performance has also been investigated.

Objectives

The adopted technique is aimed towards fabricating the crystallographically oriented, defect-free and visible-blind ZnO nanostructures and providing the direct implementation of the fabricated nanostructures for multifunctional applications. The precise objectives of this work are as follows:

I. To produce porous and yet crystallographically oriented visibleblind ZnO nanostructures by GLAD-assisted PLD by varying several deposition parameters and study the influence of deposition parameters such as oxygen partial pressure and deposition-angle on the growth and optical properties.

- II. To study the crystalline growth, porosity and UV photosensitivity of ZnO nanostructures on different substrates.
- III. To study the role of Ga doping in ZnO nanostructures and further to investigate the influence of different gas atmospheres and temperature on UV photo-sensing properties of these nanostructures.

1.8 Organization of the Thesis

The above objectives of the work have been presented in the form of six chapters, including the introduction and conclusion. The brief on chapter contents are given below:

Chapter 1 entitled 'Introduction' presents a brief review of the nanostructures and their remarkable features. The material of interest, *i.e.* ZnO, has been explored in detail with its fundamental properties and applications. The general background and theory of glancing angle deposition (GLAD) technique, along with its unique features, have also been summarized.

Chapter 2 entitled 'Experimental and Characterization Techniques' consists of a detail description of the experimental setup and method used to synthesize the ZnO nanostructures. It also provides a brief detail of various analytical tools such as X-ray diffraction (XRD), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), UV-Visible (UV-Vis) and Photoluminescence (PL) Spectroscopy, and the time-dependent photo-sensing measurements used to characterize the fabricated samples.

Chapter 3 describes the study on the role of deposition parameters such as oxygen partial pressure and seeding-angle on the growth and optical

properties of ZnO nanostructures.

Chapter 4 contains the study of undoped ZnO and Ga-doped ZnO nanostructures. It describes the influence of Ga doping on the growth and photoresponse properties of nanostructures. It also shows the comparative study on the UV performance under various environmental conditions such as in vacuum, air, oxygen and nitrogen. Further, the study of photoresponse properties at low temperature (*i.e.* 10K) has also been presented.

Chapter 5 describes the study on the growth of ZnO nanostructures deposited on various substrates, *i.e.* quartz, sapphire and MgO. The photoresponse study for the nanostructures grown on these substrates has also been discussed.

Chapter 6 entitled 'Conclusions and Future Prospects' summarize the concluding remarks of the thesis and highlight the possible future directions of the present study.

Chapter 2

Experimental and Characterization Techniques

This chapter delivers a brief insight into the experimental techniques to synthesize and characterize the ZnO nanostructures used for the present research work. The substrate preparation procedure and synthesis methods have been described in detail. The synthesis methods include preparation of bulk pellets of target materials and fabrication of nanostructures. In characterization techniques, X-ray diffraction (XRD) and Raman spectroscopy for structural analysis, scanning electron microscopy (SEM) and atomic force microscopy (AFM) for surface analysis, UV-Visible (UV-Vis) and Photoluminescence (PL) spectroscopy for optical analysis, transient photocurrent studies with ultraviolet (UV) and visible light exposure have been discussed. A brief introduction with the principle of operation and the experimental setups used for the various characterization techniques has also been described.

2.1 Substrate Preparation

The selection of a substrate is a primary requirement for the growth of nanostructures and device applications. There is a variety of substrates available, including amorphous and crystalline substrates to synthesize the nanostructures. In the present work of thesis, different substrates have been used such as quartz (HHV, India), sapphire (Al₂O₃) (MTI Corp. Germany) and MgO (MTI Corp. Germany). These substrates were cut into the desired size using a low-speed diamond wheel saw (SYJ-150). Usually, the size of the substrate is chosen depending on the requirement for characterization. For example, for optical measurements, the size of substrates was kept as $10 \times 10 \times 0.5$ mm, and for SEM it was kept smaller as $2.0 \times 5.0 \times 0.5$ mm. A glass desiccator filled with silica gel was used to store the substrates and samples. One substrate of each batch is kept for reference or background. After cutting the substrates, they were chemically cleaned in an ultrasonic bath (TELSONIC Ultrasonics), sequentially with acetone and propanol in each for 10 minutes at 30 °C. These substrates were then used for the growth of nanostructures, as discussed in the subsequent sections.

2.2 Synthesis Methods

The synthesis methods have been divided into two parts: i) synthesis of bulk target materials by solid-state reaction method and ii) synthesis of nanostructures by pulsed laser deposition (PLD) at a glancing angle, known as glancing angle deposition (GLAD) technique. Brief detail on both methods has been described as follows.

2.2.1 Synthesis of Bulk Targets

The bulk targets (*i.e.* pellets) of materials have been prepared by using a solid-state reaction route. For the present study, the powder of ZnO (99.999%, Aldrich) and Ga_2O_3 (99.999%, Aldrich) have been used to make

the target pellets. Firstly, the powders of chosen materials were taken in an appropriate ratio and weighed in analytical balances (AXIS, LCGC). For doped target materials, the powders were mixed and ground using a mortar and pestle to make the mixture homogeneous. The well-grinded powders were then poured into a cleaned die-set (Kimaya, India) to make the target pellets with dimensions of 3 mm in thickness and 20 mm in diameter. The hydraulic press (PCI Analytics, India) with an applied pressure of 5 tons was used to press the powder and make into the target pellets. These pellets were then sintered at 1000 °C for 12h in a box furnace (Nabertherm, Germany) with a controlled rate of heating and cooling program.

The bulk pellets of target materials used in the present study of the thesis are ZnO and 2% Ga-doped ZnO. These targets have been used in the second step for the synthesis of nanostructures in a pulsed laser deposition system.

2.2.2 Synthesis of Nanostructures

The synthesis of nanostructures has been performed by Glancing Angle Deposition (GLAD) technique in a Pulsed Laser Deposition (PLD) setup. The principle mechanism of the GLAD technique is already explained in chapter-1 of the thesis. In the present work, the PLD setup is utilized to synthesize the nanostructures at glancing angle geometry. However, PLD is generally known for fabrication of the thin films. Therefore, it is important to discuss first the underlying mechanism and experimental design of the PLD system before going into the details of nanostructure synthesis.

2.2.2.1 Experimental Setup of Pulsed Laser Deposition (PLD)

In 1965, Smith and Turner initiated the fabrication of thin films by utilizing the ruby laser. After that, PLD has been used to deposit many materials, including high-temperature superconductor materials and nitrides [43,66]. PLD provides a great range for the tunability of parameters which significantly affects the properties of deposited thin films. Fig. 2.1 and Fig. 2.2, respectively, show a schematic design and the real experimental setup of the PLD system used for the present work. The standard PLD setup consists of the following components:

- An ablation laser (*e.g.* KrF or ArF excimer lasers, Nd:YAG lasers, femtosecond lasers)
- A lens for focusing of a laser beam onto the target
- A vacuum chamber made of stainless steel
- Processing gas inlets
- A rotating target holder assembly
- A substrate holder connected through a programmed heater

For the present research work, a pulsed excimer laser (Compex Pro 102 F, Coherent, Germany) of wavelength λ =248 nm, pulse width=20 ns, has been used as an ablation source. A vacuum chamber (Excel Instruments, India) has been used as a deposition chamber. The vacuum chamber contains target holder, substrate holder, heating element, gate valves and the provisions for gas admission. A high vacuum of the order of $\sim 10^{-4}$ Pa is achieved using the efficient rotary and the turbomolecular pumps (Pfeiffer Vacuum GmbH). The laser beam is focused onto the target pellet using a focusing lens (focal length, f=30 cm). The beam impinges on the upper layers of target materials and generates a plasma plume through ablation of material. Fig. 2.3 shows a photograph of generated plasma plume from the ZnO target material. The generated plume has a nearly elliptical shape, and it contains the ejected species from the target materials. These species approaches towards the substrate which is kept at a particular temperature on a heating stage. During the deposition process, the target is continuously rotated in a raster as well as on-axis motion so as to ensure the uniform surface-ablation of material. The target material and substrate are kept at a fixed distance; however, this distance can be varied depending upon the

requirements of a deposition. The substrate is attached to the heating stage of a substrate holder, and the temperature is maintained through a controlled program.



Figure 2.1: Schematic representation of the experimental setup of a pulsed laser deposition system.

Generally, all the depositions are performed in the presence of a background gas. The metal-oxide materials are deposited with supplying an oxygen gas into the deposition chamber, and the gas pressure is maintained throughout the deposition process. Interestingly, the shape and focus of generated plasma plume can be modified by adjusting the partial pressure of background gas. Moreover, the color of this plasma plume may vary depending upon the target materials used for the deposition. For example, a violet-blue color of the plume can be seen for ZnO material (Fig. 2.3). The interaction of the laser light with the target material is quite complex. There are numerous models explaining the growth of thin films such as the Volmer-Weber growth model, Frenk-van der Merve growth model and Stranski-Krastanov growth model [67].



Figure 2.2: Experimental setup of pulsed laser deposition system at a thin film laboratory, IIT Indore.



Figure 2.3: Photograph of the plasma plume generated from a ZnO target.

The synthesis of nanostructures is completely different than the thin films when the GLAD technique is employed in a PLD setup. Fig. 2.4 shows the schematic presentation for the fabrication of nanostructures using the GLAD technique.



Figure 2.4: Schematic diagram of the experimental arrangement for the synthesis of nanostructures by GLAD-assisted PLD method.

The synthesis process has been divided into two stages, described as follows:

2.2.2.2: Pre-deposition Treatment (Stage-I: Substrate Seeding)

The process responsible for producing the GLAD nanostructures begins with the initial nucleation of the deposited material. In this stage, seeds of the target material grow at the surface of the substrate. Therefore, in order to produce highly ordered nanostructures, the seeds have been prepared by keeping the substrate parallel to the target's surface, as shown in Fig. 2.4 (stage-I). This stage can be considered as a normal PLD geometry with 0° (zero) deposition-angle. The deposition-angle ' α ' can be defined as the angle subtended between the substrate normal and the incident plume. These deposited seeds serve as nucleation sites and support the growth of nanostructures in the next stage. The quality of the seed layer is considered the dominating factor that influences the final growth of nanostructures [68]. The effect of a seed layer on the growth of nanorods has extensively investigated by Brett et al. [69], it has been shown that the individual nanocolumns are more uniform in the seeded substrates due to the reduction of competitive growth. Moreover, the seed layer provides smooth electrical conduction of electrons without the use of any conducting substrate. The seed layer can be deposited by any material or catalyst. However, in the present work, the target material is itself used as seeding material. Such type of self-seeding eliminates the possibility of any impurity in the samples and produces high-quality nanostructures without disorders.

2.2.2.3 Glancing Angle Deposition (Stage-II: Nanostructures Growth)

The ultimate growth of nanostructures depends on the formation of seeds during the first-stage. In stage-II, for the growth of nanostructures, the seeded substrate is kept at an angle of 85° with respect to the incident plume. Fig. 2.4 (stage-II) shows the schematic for the basic structure of GLAD. The mechanistic factor in this stage which controls the nanostructure growth is a 'shadowing effect', preventing the deposition of particles in the regions situated behind initially formed nuclei (*i.e.* shadowed regions) [42]. The ballistic deposition during this process gives rise to the tilted columnar and highly porous nanostructures of the target material. The underlying mechanism and the principle of GLAD have been discussed with detail in chapter-1 of the thesis. An important feature of this technique is that it does not require any catalyst to initiate growth. The self-seeded substrate itself works as nucleation sites for the growth of nanostructures. Till now, many

materials, including organic and inorganic, have been successfully deposited using the GLAD technique [42].

Based on the growth and quality of the synthesized nanostructures, this technique has some advantages and disadvantages discussed as follows:

Advantages:

- The growth of nanostructures is simple, and it gives flexibility in the deposition parameters such as laser energy density, pulse repetition rate, substrate temperature, background gas pressure *etc*.
- It is a clean process and no catalyst required to initiate the growth process.
- Stoichiometric transfer with exact chemical proportion.
- Production of highly crystalline and phase-pure nanostructures.
- Assists in the formation of porosity with high surface-to-volume ratio.
- High-quality and defect-free nature of nanostructures.
- Confer the shape and size control of nanostructures by tuning the various parameters.
- Multiple depositions can be performed using a single target material, *i.e.* no need to prepare the target pellet of the same material for every deposition process.

Disadvantages:

• The cross-section of the projected plume is generally small; therefore, it is difficult to grow the nanostructures on large area substrates.

2.3 Characterization Techniques

The synthesized nanostructures have been studied by a variety of characterization techniques. The phase purity or crystalline nature has been determined by the XRD measurements. The vibrational modes have been studied by Raman spectroscopy. The surface topography and growth has been determined by SEM and AFM. Optical properties such as band gap and defect analysis have been carried out by UV-Visible and PL spectroscopy. The ultraviolet photo-detection has been confirmed by performing transient ultraviolet photoresponse studies by illuminating the samples with UV (365/254 nm) lights. The visible-blindness of the detectors has been tested by exposing visible light of different colors (*i.e.* red, blue and green). The concise details of these techniques have been described in the following sub-sections.

2.3.1 Structural Characterization

2.3.1.1 X-ray Diffraction

The X-rays are scattered by successive atoms in the crystals which can interfere and give rise to the diffraction effects. This process is known as Xray diffraction (XRD). The underlying basic mechanism of XRD can be explained as follows; when the X-rays enter into a crystal, each atom behaves as a diffraction point, and the whole crystal behaves like a threedimensional diffraction grating. The obtained diffraction pattern provides information about the internal arrangement of atoms in the crystals, which helps to determine the crystal structure.

Bragg condition:

In 1912, W. L. Bragg predicted the relationship among various factors and proposed a diffraction law, known as Bragg's law [70]. According to this law, when a monochromatic X-ray of wavelength λ falls on a material, it

gets diffracted by the different set of atomic planes present in the crystal structure. Constructive interference occurs between the diffracted waves if the following Bragg relation is satisfied,

$$2dsin\theta = n\lambda$$
 2.1

where *d* is the inter-planer distance, θ is the incident angle (as shown in Fig. 2.5), *n* is a positive integer and λ is the X-ray wavelength. When the above criterion is fulfilled, a peak in the diffraction pattern appears at a particular angle. It is noteworthy that the XRD pattern of each material is different and unique, which validate the purity of the structural phase of that material. In addition to the phase purity, it also helps to confirm the chemical stoichiometry of particular material. The obtained diffraction pattern comprises of almost complete information about the crystal structure, for example, lattice parameter, bond angles, grain size, strain *etc*. The samples to be measured by XRD can be powders, pellets or thin films.



Figure 2.5: Schematic diagram of the experimental setup for XRD measurement for the θ -2 θ scan.

Fig. 2.5 shows the schematic diagram of a typical experimental setup for XRD measurement. In the diagram, θ is the angle between the

incident X-ray beam and sample's surface, ϕ is the angle of rotation about a plane perpendicular to the surface, ψ is the angle about a line parallel to the surface, and 2θ is the angle between the incident beam and diffracted beam. In θ - 2θ scan, the obtained intense peak corresponding to an angular position is the signature from the atomic crystal planes. These planes are generally denoted as (*hkl*) in the form of the numerical values.

In the present thesis, the structural phase purity and crystalline nature of prepared nanostructures have been examined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation (λ =1.54 Å) using a Rigaku SmartLab X-ray diffractometer.

2.3.1.2 Raman Spectroscopy

The Raman effect was detected in 1928 by the Indian physicist Sir Chandrasekhara Venkata Raman. In this technique, the sample is irradiated by a laser beam and the scattered light is observed. Due to the nature of the interaction of incident light with the sample, the scattered light can have identical, higher or lower frequency than the incident light frequency. The observed frequency shift provides the information on the vibrational, rotational and other low-frequency excitations of the sample. The conventional Raman spectroscopy measures intensity versus frequency or wavenumber.

Fig. 2.6 illustrates the different Raman scattering processes involved. The basics of Raman scattering can be explained as follows. When an electromagnetic wave of electrical vector **E** interacts with a molecule, an electric dipole moment $\mathbf{P}(=\alpha \mathbf{E})$ is induced, where α is a proportionality constant called 'polarizability' [71]. The deformations of the lattice due to phonons modulates this polarizability at the phonon characteristic frequency, v_m . Raman scattering is an inelastic scattering of photons. According to the classical theory of Raman scattering, a molecule with a dipole oscillating with three frequency components, known as (*i*) Rayleigh scattering (the scattered photon has same the frequency as the original incident photon), (*ii*) anti-Stokes Raman scattering with frequency, $v_0 + v_m$, (*i.e.* the frequency of the scattered photon is increased), and (*iii*) Stokes Raman scattering with frequency, $v_0 - v_m$ (*i.e.* the frequency of the scattered photon is decreased). Thus the Stokes and anti-Stokes scatterings are respectively referred as to whether the light-matter interaction and the transfer of energy and momentum involve the creation or annihilation of elementary photons.



Figure 2.6: Schematic representation of elastic and inelastic Raman scattering processes.

Raman Instrumentation

Depending on the type of investigation, different types of Raman setups can be used. For example, macro Raman setups are used to study the large crystalline samples and liquids. While micro Raman setups are generally used to probe the smaller samples. Fig. 2.7 shows the schematic diagram of a usual Raman spectrometer. A Raman spectroscopy setup typically consists of a He-Ne laser source (λ ~633 nm), spatial filters, microscope, sample stage, monochromator and charge-coupled device (CCD) detector. In the present thesis, a commercially available JOBIN-YVON HORIBA LabRAM HR Evolution micro Raman spectrometer has been used to study the Raman modes. An appropriate microscope objective, which mostly operates in the backscattering geometry, is used to focus the incident laser beam. In this thesis, the phonon excitations of ZnO nanostructures have been examined which are indicative of a particular structure.



Figure 2.7: Schematic diagram of a micro Raman spectroscopy setup.

2.3.2 Surface Morphology and Porosity Analysis

In the present thesis, the surface morphology of synthesized nanostructures has been characterized by scanning electron microscopy (SEM). However, the surface topography for a few of the samples has also been analyzed by atomic force microscopy (AFM). The SEM images have been further utilized for the porosity analysis by the help of ImageJ software. The brief detail on the above techniques is described as follows.

2.3.2.1 Atomic Force Microscopy

AFM is an experimental technique which characterizes the surface of a material down to nanometer scale and creates a 3D profile. It also provides the roughness and surface quality of the samples. Fig. 2.8(a) shows the schematic representation of an AFM setup. It uses a sharp cantilever tip to image the surface. This tip scans the surface very gently and measures the forces between the tip and the surface. The amount of force depends on the spring constant of the cantilever and the distance between the tip and surface. This result in the bending of a cantilever which is monitored by a laser beam reflected towards the position-sensitive detector, as shown in Fig. 2.8(a). Thus by measuring the cantilever deflections, the surface topography can be mapped out. An important feature of AFM is that it can image the electrically non-conductive materials too and does not require any sample preparations. AFM can be operated in different modes, as shown in Fig. 2.8(b). The brief detail on the operating modes is given below.

Operating modes of AFM

1. Contact mode: This is the simplest operating mode of AFM and also known as a static mode or repulsive mode. In this mode, a cantilever tip is scanned by making soft physical contact with the sample. This mode can work in two ways: *i*) *constant height* and *ii*) *constant force*. In constant height mode, the deflection of cantilever maps the topography of the surface. While in constant force mode, a feedback loop is provided to maintain a constant cantilever deflection so that the force between the probe and the sample remains constant. The contact mode provides fast scanning and is good for rough samples. However, the dragging of the probe can deform or damage the soft samples and can contaminate the surface. To overcome such issues, tapping or non-contact mode is generally preferred.



Figure 2.8: Schematic representation of (a) atomic force microscope and (b) contact and non-contact modes of AFM.

2. Tapping mode: Tapping mode or intermittent contact AFM is the most preferred mode of operation for the high-resolution images. In this mode, the cantilever tip oscillates up and down near its resonance frequency and intermittently contacts the sample. The image is obtained by variation in the amplitude of oscillations when the cantilever tip taps the sample surface during scanning.

In the present thesis, tapping mode has been used for imaging the nanostructures.

3. Non-contact mode: The non-contact mode is operated if the separation between tip and sample is increased. In this mode, the oscillation of cantilever is larger than its resonance frequency with small amplitudes.

2.3.2.2 Scanning Electron Microscopy

Imaging the microstructures require electron microscopes which have much higher resolving power than optical microscopes. The scanning electron microscope is one of the most important instruments used for the examination of micro/nano-structure morphology and analysis of their chemical compositions. In the SEM imaging method, a high energy electron beam hits the sample and either interacts with the whole volume of the sample or passes the sample unaffected. Fig. 2.9 schematically shows the possible interaction of the electron beam with an atom.



Figure 2.9: Schematic diagram showing the interaction of electrons with an atom.

The energy exchange between the primary electron beam and the sample results in the emission of secondary electrons by inelastic scattering processes. These secondary electrons can be detected by specialized detectors. Fig. 2.10 shows the schematic diagram of a scanning electron microscope. An electron gun of tungsten filament cathode emits the electron beam by thermionic emission. This electron beam which typically has an energy ranging from 0.2 keV to 40 keV, is focused by condenser lenses. The beam then passes through a pair of scanning coils which deflects the beam in x and y directions so that it scans in a raster motion over the sample surface area. The generated secondary electrons are mainly used as a signal to create the topography of the sample. These secondary electrons are collected by a collector grid which is kept at higher voltages to attract the low energy electrons. A scintillator is used to convert the electrons into photons. These photons are guided by the photomultiplier tube, where the photons are again converted to electrons and amplified to generate an

electrical current. The signal is translated into a grey value and displayed as variations in brightness on a screen of the computer.



Figure 2.10: Schematic representation of a scanning electron microscope.

In the present research work, Supra T M 55; Carl Ziess FESEM has been used to record the images of samples.

2.3.2.3 Porosity Analysis by ImageJ

The obtained SEM images have been further analyzed by using ImageJ software (IJ 1.46r) to determine the porosity of grown nanostructures. The software comes with different tools for analyzing the various properties of images. The brief detail on obtaining the porosity value by this software is given as follows.

Firstly, the desired SEM image for which porosity measurement is to be performed is opened. We then select the image type and use the rectangular selection tool to select the largest rectangular section of the image. After that, a threshold tool is selected to choose the area of porosity.
The grey/white values in the SEM image shows the grown structures while the dark area represents the void space in the structures. Initially, both the slider bars on the threshold menu are set to zero. Then the value on the lower slider is slowly increased. With this process, the darkest regions of the image become red. The value is continuously increased until all of the dark porosity spots become fully red. Fig. 2.11 gives a view of an original and ImageJ processed-SEM images. With this process, the area fraction value is observed and noted. This value shows the percentage (%) of porosity.



Figure 2.11: Evaluating the porosity value by processing the SEM image using ImageJ.

By repeating the above analysis at least three times, the average porosity of the sample can be determined. For the present work, the obtained values by this analysis show the average top to bottom porosity (%) for the vertically oriented nanostructures of low thickness.

2.3.3 Optical Characterization

2.3.3.1 Ultraviolet-Visible Spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy refers to the absorption/reflectance spectroscopy technique. As the name suggests, this spectroscopy utilizes the ultraviolet and visible electromagnetic spectral

regions for the measurements. It is a non-contact characterization technique to determine the optical band gap of semiconducting materials. In this technique, optical absorption spectra are recorded, which give an insight into the intrinsic properties of semiconducting samples. The obtained absorption spectra may be divided into three regions; *(i)* the main intense absorption indicates the optical band gap of the material, *(ii)* near absorption edge or Urbach tail represents the disorder in the material, and *(iii)* the lower absorption spectra with low intensities show the presence of defect states. The optical absorption spectra of any material depend on the internal and external parameters such as doping, thickness, structural transitions and temperature. Fig. 2.12 shows a schematic diagram of the typical UV-Vis spectroscopy setup with the key components. It consists of a light source, monochromator to disperse the incident light, sample holder, detector, and data display unit.

When a monochromatic light of intensity $I_0(\lambda)$ is incident on the sample, absorption takes place as per the Beer-Lambert law [72]. The absorbance (A) is defined via the incident intensity $I_0(\lambda)$ and the transmitted intensity $I(\lambda)$ by the following relation,



$$A = \log_{10}\left(\frac{I_0}{I}\right) \tag{2.2}$$

Figure 2.12: Schematic diagram of UV-Visible spectroscopy setup.

In work presented in this thesis, UV-Vis spectroscopy has been used to determine the optical band gap of grown ZnO nanostructures. The measurements were performed on Carry 60 (Agilent) UV-Vis spectrometer. Before placing the sample, a reference beam is used to set a baseline correction for the removal of absorption from the transparent substrate.

2.3.3.2 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a contactless, non-destructive and high-sensitive technique used for the characterization of electronic structure and optical properties of semiconductor materials. The luminescence from semiconductor materials is obtained by the photo-excitation process. When a semiconductor material absorbs an electromagnetic light with energy equal or greater than the band gap of the semiconductor, an electron is excited to the conduction band leaving a hole in the valence band. The material can dissipate this energy through radiative/non-radiative transition of electrons either to defect states or valence band. In radiative decay a light of particular wavelength is emitted while in a non-radiative decay phonons are emitted instead of photons. Fig. 2.13 schematically represents the basic principle of PL spectroscopy.



Figure 2.13: Principle of photoluminescence spectroscopy.

A schematic diagram of the typical PL setup is shown in Fig. 2.14. For the present work, PL spectroscopy has been used to ensure the intense UV emission from the grown ZnO nanostructures. The intense UV emission validates the quality of samples. The PL measurements were performed using DongWoo Optron DM 500i PL spectrometer with (He-Cd) laser (λ =325 nm).



Figure 2.14: Schematic diagram of photoluminescence spectroscopy setup.

A typical PL setup consists of two main components: Excitation source and Detection system.

Excitation source

In a PL spectrometer, Helium-Cadmium (He-Cd) laser is used as a source of ultraviolet light (λ =325 nm). He-Cd lasers with UVA wavelength have an excellent beam quality and have been extensively used for many applications such as holography, spectroscopy, non-destructive testing, diffraction grating fabrication, microlithography *etc*. The 'Cd' atoms play the role of the lasing element and are heated to convert into the gas phase to start the lasing action. The laser tube contains a reservoir for Cd metal and a heater for vaporization. The 'He' atoms are excited by collisions with the accelerated electrons generated through gas discharge. These He atoms then pass their energies to Cd atoms by collisions. The emission takes place in the ultraviolet region.

Detection system

The luminescence collection system consists of a pair of lenses, mirrors, filters, monochromators, a photomultiplier tube (PMT), and a computer. The excited and emitted wavelengths are separated by using the filters. A collimating mirror is used to collimate the light to a parallel beam. This collimated beam falls on a monochromator with a diffraction grating. The desired emission wavelength is selected by the monochromator. Photomultiplier tubes are used as the detectors. The output from the detector is amplified and displayed on a digital display.

2.3.4 Transient Ultraviolet Photo-detection Studies

ZnO is a wide band gap semiconductor material and quite suitable for detecting the ultraviolet (UV) light. The photocurrent mechanism in ZnO nanostructures includes the photo-generation of free charge carriers and it is governed by the *adsorption* and *desorption* processes, as described schematically in chapter-1 of the thesis.

The time-dependent photocurrent characteristic curves help in determining the various parameters for a specific UV photodetector, for example, dark/photo-current, photosensitivity, switching time (*i.e.* rise and decay-time) *etc*. The parameters of the fabricated photodetector and sensing experimental setup with its working principle have been described in the following subsections.

2.3.4.1 Photodetector Fabrication

In order to study the UV light-sensing, the UV photodetectors have been fabricated using the grown nanostructures. The gold (Au) electrodes with

50 μ m spacing were deposited on the samples using a physical vapour deposition (PVD) sputtering system. The channel width for all the detectors was 2 mm, and the total active area of the device was 0.001 sq. cm. The step-III of Fig. 2.15(a) shows a schematic diagram of the fabricated photodetector.

2.3.4.2 Photo-sensing Setup and Working Method

Fig. 2.15(b) schematically represents the home-made sensing experimental setup where the fabricated photodetectors have been tested. The detectors were placed in a measurement chamber and connected through a Keithley meter (4612A). The meter is connected through a computer having KickStart software where the data is stored and displayed on the monitor. The Keithley meter is also used to record the current-voltage (I-V) characteristics of detectors. The sensing measurements have been performed in darkness and under the exposure of different lights. The UV photo-detectors were tested for deep-UV sensing using 254 nm UV light. The visible lights, *i.e.*, red, blue and green LEDs (light-emitting diodes) were used to test the visible-blindness of detectors.

The experimental setup has a provision for gas admittance into the measurement chamber. It also has a facility of connecting a vacuum pump to perform the measurement under vacuum. With the use of the above facilities, few of the photodetectors were tested under different atmospheres such as in vacuum, air, nitrogen and oxygen gas. The detectors have also been tested at low-temperature (10K) to ensure the reproducibility and sustainability of the photocurrent. For the low-temperature measurements, a closed-cycle cryostat system (JANIS) was used. Importantly, the measurement chamber consists of a platform where a maximum of two samples can be connected and measured at a time. This simultaneous measurement helps for a comparative study of results and also ensures the

identical conditions for the detectors. The chamber was also covered with a black rectangular wooden-box to avoid the obstruction of light from outside.



Figure 2.15: Schematic diagram of (a) fabricated photodetector and (b) photo-sensing experimental setup.

Working Method:

The following steps were followed while performing the measurements:

• Initially, under the dark condition (*i.e.* when the light source is switch-off) with a suitable bias voltage, the current is stabilized for

a few minutes and then recorded. The obtained current is known as the dark current.

- A UV light is then switched on, this changes the dynamic response of the material, and the photocurrent is recorded in the meter.
- After saturation under UV exposure, the light is again switched off. This brings down the current at its lower or initial level. In this way, the first cycle is completed.
- The above procedures are again followed, and at least two or three photocurrent switching cycles are obtained to ensure the repeatability of photocurrent and switching.
- The same setup has also been used to study the current-voltage (I-V) characteristics.

Chapter 3

Influence of Deposition Parameters on the Growth and Properties of ZnO Nanostructures

In the present chapter, the role of deposition parameters, *i*) oxygen partial pressure and *ii*) deposition-angle (seeding-angle) have been investigated. The effects of these deposition parameters in controlling the growth, porosity, crystallinity and optical properties of ZnO nanostructures have been studied systematically. The nanostructures have been synthesized on quartz substrates by using the GLAD technique with PLD setup. The influence of the above deposition parameters on the growth has been studied by field emission scanning electron microscope (FESEM). The crystallinity has been verified by X-ray diffraction (XRD) studies. Study of vibrational modes has been performed by Raman spectroscopy. Further, the optical properties have been studied by UV-Visible and photoluminescence (PL) spectroscopy.

It has been demonstrated here that both the deposition parameters strongly influence the morphology and hence the ultraviolet photo-detection properties of ZnO nanostructures. The results presented in this chapter are published in peer-reviewed journals^{* \$}.

^{*} Soni et al., Scripta Materialia, **162** (2019) 24-27.

^{\$} Soni et al., Materialia, **6** (2019) 100326.

3.1 Introduction

The nanostructure forms of ZnO semiconductor play a significant role in the development of device-based technology. The high surface-area-tovolume ratio can be utilized for many optoelectronic and gas sensing applications [33,73–76]. Therefore, controlling the porosity becomes important in nanostructured ZnO materials. Till now, many nanostructures of ZnO with different surface morphologies including nanorods, nanowires, nanowalls, nanosheets and many more have been fabricated and studied [63,77-81]. These nanostructures have been prepared by variety of synthesis techniques such as hydrothermal method [63,75], chemical deposition method [77,82], sputtering [64,83], electrospinning method [84,85], and pulsed laser deposition (PLD) method [49,62,65,78,79,86,87]. Each synthesis methods have different growth mechanism which results in different morphology of resultant nanostructures. However, the physical properties of these nanostructures can be controlled by the various synthesis parameters. For example, tapered tips and flat tips of ZnO nanorods have been observed, respectively, under Ar and N₂ ambient during the growth by PLD [88].

Crystallinity is one of the important properties of ZnO nanostructures which determine their applicability for visible-blind ultraviolet photodetectors. Large attention has been paid by the scientific and industrial community for the improvement of optoelectronic devices based on the various ZnO nanostructures. One reason for the low performance of the devices can be identified as poor crystalline nature and lower surface area of the grown nanostructures [89,90]. The samples grown by PLD method are highly crystalline in nature. PLD offers a variety of tunable parameters such as laser energy, background gas pressure, substrate temperature, deposition time *etc*. These parameters can be controlled, and thereby the growth and the properties of the resultant nanostructure samples can also be controlled. For example, the effects of substrate temperature on

the growth-morphology and properties have been reported by many researchers [91–94]. Besides, the doping can also influence the structure and properties of nanostructures. For example, Gondoni *et al.*, in their study, reported the structure-property relation of crystalline and oriented nanostructured Al-doped ZnO thin films for the applications in photovoltaic devices [95,96].

Another advantage of the PLD method is that it does not require any catalyst to initiate the growth process, while the other methods use some chemicals for the growth of nanostructures. Therefore, PLD helps self-seeding; this is a key parameter for the catalyst-free growth of nanostructures. In the present work of the thesis, the target material itself is used as a seed material. The seeding usually provides nucleation sites which help for the *directionality* to the nanostructures and also supports the growth. Moreover, connected seeding also helps in the smooth electrical conduction without the need of any conducting substrate. Such type of catalyst-free growth not only eliminates the possibility of unexpected doping but also provides pure nanostructures.

Here, we have used glancing angle geometry in a PLD setup for the growth of porous and *c*-axis oriented ZnO nanostructures. This technique is generally known as glancing angle deposition (GLAD) [42]. The details with geometrical representation and the working principle of this technique have already been described in chapter-2 of the thesis. As discussed above, the PLD method offers control by tuning a variety of deposition parameters which directly affects the properties of the grown samples. The processing parameters also play an important role during the deposition process in texturing the ZnO. Therefore, the deposition conditions must be chosen in such a way that the desired properties can be obtained. In the present study, the oxygen partial pressure and the deposition-angle (seeding-angle) have been varied to study the growth and the optical properties of ZnO

nanostructures. The influence of each of these two parameters has been discussed in detail as below:

PART-A

3.2 Influence of Oxygen Partial Pressure

The oxygen partial pressure is considered to be the most crucial parameter of PLD growth process. It can affect the oxygen stoichiometry, crystal structure and can also tune the defects. In this section, for investigating the influence of oxygen partial pressure on the ZnO nanostructures, only the oxygen partial pressure was varied, and the other parameters were kept constant. For the part-A, the detail information on the experimental parameters and results have been described as follows.

3.2.1 Experimental

A disc-shaped bulk pellet of ZnO was synthesized by pressing the ZnO powder and sintered at 1000 °C for 10 hours. Using this pellet, ZnO nanostructures were grown on quartz substrates by the GLAD-assisted PLD method. The schematic representation for this combination is given in Fig. 2.4 of chapter-2. The quartz substrates were sequentially cleaned with acetone and propanol for 10 minutes in an ultrasonic bath to remove dirt and impurities. The base pressure of the vacuum chamber was achieved at 10^{-4} Pa. The pulsed KrF excimer laser ($\lambda = 248$ nm) was used to ablate the ZnO target material. A focused laser beam hits the rotating target at an angle of 45° with respect to the target normal. Before starting the deposition, the target pellet was ablated by a few laser shots to clean the surface. The ZnO nanostructures were grown in two stages as described in chapter-2. For stage-I, all the substrates were seeded by ZnO by exposing the target with a laser at a repetition rate of 8 Hz for 5 min. In the same condition, the ZnO stage-II), and the ZnO starget to glancing angle (stage-II), and the ZnO

nanostructures were grown on ZnO seeded substrate with a laser repetition rate of 10 Hz for 30 min. The substrate temperature and target to substrate distance were kept at 650 °C and 4 cm, respectively. During the growth of nanostructures (*i.e.* stage-II), the oxygen partial pressure (P_{O2}) in the growth chamber was varied to study the effects on ZnO nanostructures. For a comparative study, the nanostructures were grown at three different oxygen partial pressures, *i.e.* 7.5 Pa, 10.0 Pa and 15.0 Pa, and the samples were denoted as ZnO-7.5, ZnO-10 and ZnO-15, respectively.

The crystallographic structure of samples was characterized by Xray diffraction (XRD) using a Rigaku SmartLab X-ray diffractometer. The surface morphology was investigated by a Field Emission Scanning Electron Microscope (FESEM, Supra 55 Ziess). Optical properties were UV-Vis spectrometer 60. studied by (Carry Agilent) and Photoluminescence (PL) spectrometer (DongWoo Optron DM 500i). Photocurrent measurements were performed using Keithley meter in the dark and under UV illumination (365 nm, < 4 mW) at ambient atmosphere and temperature. A detail description of the above experimental techniques is described in chapter-2.

3.2.2 Results and Discussion

In this section, the structural, morphological and optical properties are discussed for the nanostructures grown on quartz substrates with different oxygen partial pressure.

3.2.2.1 Structural Analysis

X-ray Diffraction

Fig. 3.1 shows the X-ray diffraction (XRD) patterns of ZnO nanostructures grown by varying the oxygen partial pressure. The XRD peaks at $2\theta \approx 31.09^{\circ}$ and 34.5° represents (100) and (002) peaks, respectively for ZnO crystal

planes. The absence of a substrate's peak in the spectra is due to the amorphous nature of quartz substrates.



Figure 3.1: XRD patterns of ZnO nanostructures grown at different oxygen partial pressure.

The present XRD results are clear evidence for the crystallinity of grown nanostructures. The intense (002) peak shows that the ZnO nanostructures are predominantly oriented along the *c*-axis and demonstrate the wurtzite structure of ZnO. Moreover, the narrow full width at half maximum (FWHM) of (002) peaks clearly represent the quality and crystalline nature of present ZnO nanostructures. The XRD results also reveal that the nanostructures are free of any impurity. Such type of impurity-free and crystalline nature of ZnO nanostructures are highly commendable for the UV photo-sensing applications. From XRD results, it is also observed that the lattice parameters have no significant variations in spite of the different oxygen partial pressure. It has already been reported that an increase of oxygen partial pressure (Po₂) beyond a certain limit reduces the kinetic energy of the ablated species to occupy the lowest energy sites which may result into the degradation of crystallinity at higher Po₂ [79].

3.2.2.2 Morphological Analysis

Scanning Electron Microscopy

In order to understand the influence of oxygen partial pressure (P_{O2}) on the growth and surface morphology, the samples were characterized by scanning electron microscope (SEM). Fig. 3.2 shows the SEM images of grown ZnO nanostructures with varying P_{O2} .



Figure 3.2: Scanning electron micrographs with surface morphology (left panel) and cross-sectional view (right panel) of ZnO nanostructures grown at 7.5 Pa (a,b), 10.0 Pa (c,d), and 15.0 Pa (e,f).

The micrographs confirm the growth of ZnO nanostructures like nanowalls which are porous in nature. The average height of these nanowalls as measured from the cross-section images were found in the range 0.6-1.0 μ m. It is evident from the SEM images that the samples form stacked structures with porosity and connectivity throughout the sample. Importantly, the porosity exists for all the samples without losing crystallinity. The porosity enhances the surface area, and the connectedness of walls helps in the smooth electrical conduction. The value of porosity was determined by using ImageJ software as discussed in chapter-2. The obtained porosity (%) values were 41.2, 34.5, and 23.8 for ZnO-7.5, ZnO-10 and ZnO-15, respectively. This induced porosity is attributed to the GLAD technique.

In the present case, both the porosity and the growth were observed to be different for the different P_{02} . Initially, at low P_{02} the nanostructures are aligned, creating the caves like structures and for the sample grown at elevated P_{02} show some vertically open structural growth. The sample ZnO-10 shows the mixed type of morphologies, which can be seen in the other two samples. Such trend shows that the increase in P_{02} transfers the one type of morphology into another type. It is evident from the cross-sectional SEM images that the low P_{02} favors porous and rough structures. Theoretically, it has also been reported that the diffusion coefficients of Zn or O atom decrease with decreasing partial pressure of oxygen [97]. Thus the growth of ZnO under oxygen-poor condition is more likely results into the rougher surface. It has also been suggested that the growth and morphology of nanostructures greatly depend on the type and pressure of gas employed during the fabrication process [98–101].

The variation in surface morphology and growth can be understood as follows. The oxygen pressure greatly influences the kinetic energy of ejected species. Moreover, the mean free path of ejected species depends upon the processing gas pressure and increases with decreasing the pressure [102]. When the nanostructures are processed under high Po₂, the ejected species undergo a large number of collisions with the background gas molecules. The particles after collisions reach to the surface of the substrate and promote the growth. The nucleation of these particles is either controlled by the seed layer or by the processing conditions. Depending on the kinetic energy of ablated species, interesting nanostructures can be realized with different surface morphology and porosity. The effect of processing gas pressure can also be visualized on the size of ablated plume. The size of plume decreases with an increase in gas pressure. For the present case, the surface morphology is different due to the growth kinetics involved in the process as discussed above.

3.2.2.3 Optical Analysis

UV-Visible Spectroscopy

To determine the optical band gap, room-temperature UV-Visible (UV-Vis) spectroscopic study is carried out on the grown ZnO nanostructures. The details of UV-Vis spectroscopy are described in chapter-2. Fig. 3.3 shows the absorbance spectra of samples ZnO-7.5 and ZnO-15. Clearly, a sharp absorption edge appears at about 378 nm, which is attributed to the band gap of ZnO.

In order to determine the optical band gap (E_g) of grown ZnO nanostructures, a Tauc plot has been made using the following equation [103,104]:

$$(\alpha h \upsilon) = A (h \upsilon - E_a)^n \tag{3.1}$$

where E_g is an optical band gap for the particular transition, A is the proportionality constant, v is the transition frequency, h is the Planck's constant and n determines the nature or type of transition-band. For example, if n=1/2 and 3/2, the transitions are direct allowed and direct

forbidden, respectively, while for n=2 and 3 the transitions are indirect allowed and indirect forbidden respectively. The optical band gap E_g can be calculated by plotting $(\alpha h \upsilon)^2$ on y-axis and photon energy $(h \upsilon)$ on xaxis [103]. The intercept of the linear region of this graph gives the value of optical band gap, as shown in the inset of Fig. 3.3. The calculated optical band gap is 3.19 and 3.17 eV for the samples ZnO-7.5 and ZnO-15, respectively. The obtained values of the band gap lie in the UV region and agree well with the reported values of ZnO [105,106]. The strong absorption in the UV range and visible-blind character makes these samples more suitable for UV light-sensing applications.



Figure 3.3: UV-Visible spectra of ZnO nanostructures grown at different oxygen partial pressure. The inset shows a linear fit of the graph $(\alpha h \upsilon)^2$ versus $(h\upsilon)$ for the optical band gap (E_g) calculation.

Photoluminescence Spectroscopy

The information regarding the defects involved in ZnO nanostructures such as oxygen vacancy and other defects can be determined from the photoluminescence (PL) measurements. The PL spectroscopy enables to study the various emission processes involved in the system. The details of PL spectroscopy have been described in chapter-2. Fig. 3.4 represents the room-temperature PL spectra of the samples ZnO-7.5 and ZnO-15 excited at 325 nm using He-Cd laser.



Figure 3.4: Photoluminescence spectra of ZnO nanostructures grown at different oxygen partial pressure.

It can be seen from the PL graph that the spectrum consists of two emission peaks. Notably, an intense emission peak in the UV region, centered at about 382.5 nm, was observed for both the samples. This intense ultraviolet peak is attributed to the recombination of free excitons through exciton-exciton collision process [29] due to the 3.26 eV wide direct band gap transition of ZnO. This high intense UV peak also indicates the crystallinity and quality of grown ZnO nanostructures. It is evident from the PL graph that the excitonic emission is predominant from the high intensity of UV emission and is much higher than the visible luminescence. A weak and broad peak in the green-red range is also observed from the PL spectra which are referred as the deep-level emission (DLE), as it involves electron transition from the various defects of ZnO. The DLE is generally created by impurities and defects such as zinc interstitials and mainly from oxygen vacancies [30,107]. It is clear from the spectra that the emission in the visible region is comparatively negligible, which authenticates that the samples have negligible defects. In the present case, the visible emission is highly suppressed for all the samples. This type of features generally is never reported for the nanostructures grown by other methods [31]. Thus, these PLD grown nanostructures are completely visible-blind and quite suitable for the application of visible-blind UV light detection.

3.2.2.4 Transient Ultraviolet Photo-detection Studies

In order to study the photoresponse properties, the transient photocurrent was measured for the fabricated photodetectors. The measurement was performed in darkness and under the exposure of UV light (365 nm). Fig. 3.5 shows the transient photocurrent characteristic curves taken at 5 V of applied bias voltage. It was noticed that the current after switching on UV light was greater than the observed dark current. The light was kept on for nearly two hours to achieve a saturation condition, and then the photocurrent cycles were taken to assure the repeatability and reproducibility of the photocurrent. In Fig. 3.5, three cycles of photocurrent switching clearly demonstrate the reproducibility of UV photoresponse for all the samples.

The adsorption and desorption dynamics are considered to be responsible for the rise and decay of photocurrent. For example, the increase in current upon the illumination of UV light is attributed to the desorption of oxygen molecules from the surface that governs the generation of free charge carriers for ZnO. In ambient conditions, the oxygen molecules are adsorbed onto the surface of nanostructures and capture the free electrons creating a depletion layer on the surface with low conductivity. This mechanism has already been explained in detail in chapter-1 of the thesis. However, the adsorption and desorption of oxygen molecules are well established and reported very long back [108].



Figure 3.5: Transient photoresponse characteristic curves of ZnO nanostructures grown at different oxygen partial pressure.

The bi-exponential function [109], given by the following equation, has been used to determine the rise time constants for the present photodetectors.

$$I = I_0 + A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2)$$
 3.2

where I_0 is the steady-state photocurrent, t is the time, A_1 and A_2 are the constants, τ_1 and τ_2 are the relaxation time constants. The average-weighted rise time (τ_r) has been evaluated by using the following expression [62]:

$$\tau_r = \frac{A_1 t_1 + A_2 t_2}{A_1 + A_2} \tag{3.3}$$

For the present study, the saturation takes place in seconds of rise time (τ_r), which is comparable to that of single nanowire [82]. Thus, in spite of the thickness of the present samples is nearly 1 µm, τ_r is comparable to the single nanowire' response, due to the high crystallinity of these nanostructures. Table 3.1 shows the various parameters calculated from the photocurrent curves. It is clear from the table that the sample grown at low P₀₂ (7.5 Pa) exhibits a higher photo-to-dark current ratio (I_p/I_d), however the rise time is sacrificed for this sample due to lower electrical conductivity. This lower conductivity is attributed to poor connectivity amongst the nanostructures. Thus, a lower P_{O2} brings more porosity to the nanostructures and enhances the UV photoresponse. In the present case, these parameters tune very systematically with P_{O2} .

Table 3.1: Derived parameters from the transient photoresponse characteristic curves of ZnO nanostructures.

Sample	Dark current	Rise time	Photo-to-dark current ratio
	I_d (μ A)	$\tau_r(sec)$	I_p/I_d
ZnO-7.5	0.14	36	94.38
ZnO-10	0.48	20	47.50
ZnO-15	0.77	18	25.37

3.2.3 Summary

Highly *c*-axis oriented ZnO nanostructures were successfully grown using the GLAD technique with varying P_{02} . Different oxygen partial pressure results in a variation in surface morphology and porosity. The crosssectional SEM images confirm the interconnected nano-walls of grown ZnO nanostructures. The transient photocurrent study revealed that the fabricated photodetectors have appreciable UV response due to the defectfree and crystalline nature. The nanostructures, grown at low P_{02} show the highest photoresponse due to increased porosity. The UV-Visible spectra confirmed the optical band gap in the UV range with no significant variations. Photoluminescence spectra show that the samples are highly sensitive for the UV light and thus can be used in the application of visibleblind ultraviolet light-detection. This study opens an avenue for studies on PLD-grown oxide nanostructures with desired control on crystalline growth and porosity.

PART-B

3.3 Influence of Deposition-angle (Seeding-angle)

Deposition-angle or seeding-angle is one of the most important parameters of GLAD technique which must be chosen very carefully. The seedingangle determines the shape, size and the growth of nanostructures. In the present section of the thesis, the seeding-angle has been varied from 0°-75° during the first stage of a deposition only. The GLAD technique has been utilized in stage-II (85°) for the growth of nanostructures. The details of synthesis and obtained results of Part-B have been discussed in the following subsections.

3.3.1 Experimental

The same prefabricated ZnO pellet was used here to synthesize the ZnO nanostructures. All the nanostructures were grown on the quartz substrates. The growth of ZnO nanostructures for the present study was performed by following the two stages, as described below:

Stage-1: This includes the same seeding process of ZnO, as discussed earlier. However, in the present case, the seeding has been performed at different deposition-angles, *i.e.* during the process of seeding the substrate were kept at fixed angles of 0° (ZnO-0), 30° (ZnO-30), 45° (ZnO-45), 60° (ZnO-60) and 75° (ZnO-75). The pictorial representation for the different seeding conditions has been schematized in Fig. 3.6. For seeding, the nucleation seeds of ZnO were deposited at a repetition rate of 8 Hz, and oxygen partial pressure of 5 Pa. The target was ablated for 5 min during the seed layer formation for all the samples.

Stage-2: In this stage, the ZnO-seeded quartz substrates, as obtained from stage-I, were used for the growth of ZnO nanostructures using a GLAD geometry (*i.e.* 85°). The repetition rate and deposition time for this stage

were kept at 10 Hz and 10 min, respectively. During the growth of nanostructures, the oxygen partial pressure in the growth chamber was fixed at 15 Pa for all the samples. Based on our earlier study, optimized deposition time and oxygen partial pressure have been used to obtain porous as well as conductive nanostructures. In the present case, the growth of seeds is different due to different back-scattering of molecules/particles and a lower flux captured for tilted substrates compared to the normally oriented substrates. Thus the growth of crystalline-seeds (*i.e.* size, shape, porosity and distribution) is different at different deposition angles which eventually influence the further growth of material at a glancing angle in the second stage. These nucleated seeds support the growth of nanostructures.



Figure 3.6: Schematic representation of the seeding-angles for the first-stage of deposition.

The rest of the deposition parameters and characterization techniques are the same as discussed in section 3.2.1. However, in this study, the samples have also been characterized by Raman spectroscopy using LabRam HR Evolution spectrometer (HORIBA Scientific) with an excitation wavelength of 633 nm.

3.3.2 Results and Discussion

In this section, the structural properties using XRD and Raman spectroscopy, morphological analysis by SEM, and optical properties using UV-Vis, PL and ultraviolet photo-detection have been discussed for the samples grown at different seeding-angles.

3.3.2.1 Structural Analysis

X-ray Diffraction

Fig. 3.7 shows the XRD patterns of ZnO nanostructures grown by varying the seeding-angle. An intense (002) peak shows the ZnO nanostructures are preferentially oriented along the c-axis; although a structural alignment along (100) direction is also visible.



Figure 3.7: XRD patterns of ZnO nanostructures grown at different seeding-angles.

The narrow full width at half maximum (FWHM) and intense peaks in XRD patterns demonstrate the good crystallinity of present nanostructures. The obtained crystallinity of these nanostructures is better than that of many reported ZnO nanostructures [110–113]. That is because of seeding and two-stage deposition in the present work. However, in any condition, the (002) peak remains predominant, this is due to the highest surface energy of {0001} basal planes of ZnO as compared to the all lowindex planes of the wurtzite ZnO crystal [22]. In addition, the seed-layer also helps the *c*-axis growth of nanostructures due to the highly oriented grains of ZnO seed-layer along the (002) direction [115].

The abstracted information form the XRD patterns are presented in Fig. 3.8 which shows the variation in the crystallite-size, FWHM and the intensity ratio of (002) and (100) peaks at different seeding-angles. Comparatively narrow FWHM and large crystallites were obtained for the sample grown at the condition of 0° seeding-angle. Interestingly, the ratio of intensity for (002) and (100) peak is found to decrease in a strikingly systematic manner with increasing the seeding-angle. Moreover, it clearly shows that the sample grown at higher seeding-angle exhibits only one crystallographic orientation. These XRD patterns suggest that the crystallographic orientation is controlled by the seeding-angle during the first-stage of deposition.

The crystallite size of the samples has been calculated using the Scherrer equation [116] as given below,

$$D = \frac{\kappa\lambda}{\beta \cos\theta}$$
 3.4

where *D* is the mean size of the crystalline domains, *K* is a dimensionless shape factor with a value close to unity, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity and θ is the Bragg angle. The lattice parameter '*c*' was calculated using 2θ values of intense (002) peak and found nearly constant for all the samples. This insignificant change in the lattice parameter shows that the ZnO lattice is free from strain. This feature signifies that the obtained nanostructures are highly crystalline and pure.



Figure 3.8: Variation in crystallite size, FWHM of (002) peak, and intensity ratio of (002) and (100) peaks with changing seeding-angle.

Raman Spectroscopy

In order to understand the vibrational modes and related structure of grown nanostructures, the samples were characterized by Raman spectroscopy technique. The technical details of Raman spectroscopy measurements have been described in chapter-2 of the thesis. Fig. 3.9 shows the room-temperature micro-Raman spectra of ZnO nanostructures grown by varying the seeding-angle.

At ambient conditions, ZnO crystallizes in the wurtzite structure. It has a hexagonal lattice which is characterized by the two interpenetrating sub-lattices of Zn^{2+} and O^{2-} ions. Each Zn ion is surrounded by a tetrahedron of oxygen ions and vice versa, generating the polar symmetry along the hexagonal vertical *c*-axis. According to the group theory, for the wurtzite symmetry of ZnO, the optical modes (Γ_{opt}) can be represented by the following equation [23]:

$$\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1 \tag{3.5}$$

where A_1 and E_1 are polar modes and are both infrared and Raman active, while E_2 modes are non-polar and Raman active only. The B_1 modes are called silent modes and are both Raman and infrared inactive. The non-polar E_2 mode split into two branches and show two wavenumbers, namely E_2 (high) and E_2 (low). The A_1 and E_1 modes are translated into longitudinal optical (LO) and transverse optical (TO) due to long-range electrostatic field. A detailed study on Raman modes has been reported by Russo *et al.*, [25] where the modes are excited by varying different wavelengths too.



Figure 3.9: Room-temperature Raman spectra of ZnO nanostructures grown at different seeding-angles. A Raman spectrum of the quartz substrate is also plotted for the comparison.

In Fig. 3.9, the intense and prominent peaks of ZnO are observed at 98 cm⁻¹ and 436 cm⁻¹. These characteristic Raman frequencies have been denoted as $E_2(low)$ and $E_2(high)$ modes respectively, which are attributed to the non-polar E_2 vibrational modes of the wurtzite ZnO. The $E_2(low)$ mode is related to the vibration of heavy Zn sub-lattices, and E₂(high) mode is associated with the motion of oxygen atoms [25,81]. However, the E_2 (high) Raman peak was found to slightly shift for the sample ZnO-45; this could be due to the variation in morphology (Fig. 3.10) and presence of defects, as confirmed by PL studies, discussed in later sections. Moreover, a very less intense peak near about 330-340 cm⁻¹ was also observed in all the samples, which is assigned as $E_2(high)-E_2(low)$ mode due to the secondorder Raman processes [117]. The intense peak of quartz substrate was observed at 489 cm⁻¹ due to the Si-Si stretching vibrations of the quartz substrate [118]. These results show that all the nanostructures are highly crystalline as indicated by the sharp E₂ phonon peaks, which are the significant feature for the wurtzite lattice structure of hexagonal ZnO. This Raman results also agree with the XRD results.

3.3.2.2 Morphological Analysis

Scanning Electron Microscopy

Fig. 3.10 shows the SEM images of ZnO nanostructures grown on the quartz substrate with a variation of the seeding-angle from 0° to 75° . The micrographs confirm the growth of ZnO nano-network. It is also apparent that the growth is gradually varied for the different seeding-angles. At 0° seeding-angle, hollow structures with nanowall-network are clearly visible in top-view SEM image. At 30° seeding-angle, the surface morphology of nanostructures seems like the series of peaks and valleys with decreased porosity; and at higher seeding-angles, the surface morphology is entirely different albeit with a connecting network of nanowalls and porosity. The variation in surface morphology upon changing the seeding-angle is

attributed to the growth of seeds at different angles, influencing the growth of nanostructures at stage-II. The cross-sectional view of SEM images (Fig. 3.10) explicitly shows the growth of nanostructures is perpendicular to the substrates' surface.



Figure 3.10: Surface morphology (left panel) and cross-sectional view (right panel) of ZnO nanostructures grown at 0° (a,b), 30° (c,d), 45° (e,f), 60° (g,h), and 75° (i,j) seeding-angle.

The porous areas of obtained SEM images were analyzed using ImageJ software, and it was found that the porosity decreases with the increase in seeding-angle. The induced porosity increases the surface-tovolume ratio and thus, the photocurrent. Table 3.2 shows the variation in porosity (% area) with changing the seeding-angle. Since all the deposition parameters were kept constant in both the stages, no significant variation in the thickness was observed. The measured thickness of all the samples was found to be in the range of 400-420 nm by cross-section SEM. For the present samples, the thickness is much smaller; therefore, the variation in the surface porosity of these thin structures can be considered to reflect the variation in the volume porosity. The variation in porosity entirely depends on the experimental conditions used during the growth of nanostructures [49]. In the present case, the porosity is maximum for the samples grown at lower seeding-angles. It is also confirmed from the SEM images that the samples show the distinguishing interconnection of morphology over the entire sample surface area. The cross-sectional view shows the density and well-connectedness of grown nano-network. Such type of variations in the physical parameters can be utilized to design efficient optoelectronic devices.

3.3.2.3 Optical Analysis

UV-Visible Spectroscopy

In order to obtain the optical quality and band-gap of these samples, UV-Visible spectroscopic measurements were performed. Fig. 3.11(a-e) shows the UV-Vis spectra of ZnO nanostructures grown at different seedingangles. An intense UV absorption has been observed for all the samples, which is attributed to the band-edge absorption of ZnO. The variation in band-tails suggests defects such as oxygen vacancies, interstitial *Zn*, and impurity-induced disorder in ZnO [119]. At lower seeding-angles, *i.e.* ZnO- 0 and ZnO-30 samples show very feeble absorption in the visible region as compared to the other samples deposited at higher seeding-angle.



Figure 3.11: (a-e) UV-Visible spectra of ZnO nanostructures grown at different seeding-angles. The inset shows a linear fit of the graph $(\alpha h \upsilon)^2$ versus $(h\upsilon)$ for the optical band gap (E_g) calculation. (f) Absorbance ratio in UV and visible wavelengths.

This clearly indicates the presence of defects in the samples at higher seeding-angles. Also, as mentioned earlier, the surface morphology of ZnO-

0 and ZnO-30 is different from that of the rest of the samples. Hence, in the present case, the surface morphology becomes an indirect indication for the level of defects. In order to evaluate the visible-blindness of these samples, we have also calculated the absorbance ratio in UV (A_{UV}) and visible (A_{Vis}) wavelength region and plotted as in Fig. 3.11(f). The value of this ratio was found to decrease with increase in seeding-angle and decreasing porosity. This change in ratio clearly indicated the nature of visible-blindness of the PLD-grown nanostructures.

The optical band gap (E_g) was calculated using the eq. 3.1 and with Tauc plots, as shown in the inset of Fig. 3.11. The variation in E_g with respect to seeding-angle was found in the range of 3.16 to 3.26 eV. It is observed that as the seeding-angle increases, the band gap variation goes through the highest value at 30° and then it decreases systematically. This variation is although small, but noticeable, and it can be attributed to the potential fluctuations in the electronic band structure of ZnO nanostructures [120]. Except for the as-grown ZnO-0, the obtained band gaps were in accordance with the crystallite size variation estimated from the XRD patterns. Such size-dependent variations in the band gap are earlier observed for semiconducting nanostructures [110,121,122]. It is also clear from the band gap calculations that all the samples have strong absorption for UV wavelength and thus are very appropriate for optoelectronic applications in the UV range.

Photoluminescence Spectroscopy

Fig. 3.12(a) shows the room-temperature photoluminescence (PL) spectra of ZnO nanostructures grown at different seeding-angles. Each spectrum consists of two different emission peaks. A strong emission peak centered around 382.5 nm is attributed to the recombination of free excitons through exciton-exciton collision process due to the wide direct band-gap transition of ZnO [29]. The broad peak appearing in the visible range of wavelength

indicates the presence of defects. It is also observed from the PL graphs that the excitonic emission is leading with the high intensity of UV emission and is much higher than the luminescence in the visible range for ZnO-0, ZnO30 and ZnO-75 samples.



Figure 3.12: (a) Photoluminescence spectra of ZnO nanostructures grown at different seeding-angles. (b) The ratios of intensities for near-band emission to deep-level emission. (c) Normalized PL plot.

The high intense UV emission of these samples is in good agreement with the reported ZnO nanorod arrays [65]. Additionally, these three samples also show a feeble and broad peak in the wavelength of the visible region. Sun and Tsui have also reported similar kind of weak visible emission for porous nanostructured ZnO thin films grown by pulsed laser deposition [49]. Thus the PLD-grown samples have a very low level of defects. On the other hand, samples ZnO-45 and ZnO-60 show an intense peak in the green-red wavelength range (Fig. 3.12c) which is referred to as deep-level emission (DLE), as it involves electron transition from the defects in the grown nanostructures. The DLE is generally created by various kinds of defects such as impurities, zinc interstitials and mainly from oxygen vacancies. This is a useful finding where the level of defects can be controlled by tuning the seeding-angle during PLD process. Here, the near band emission (NBE) is predominant for the samples grown at lower seeding-angles (*i.e.* 0° and 30°).

The intensity of the visible emission is desired to be low for many applications. Therefore the intensity ratio of UV emission to the visible emission is usually considered as an important criterion to indirectly assess the quality and crystallinity of ZnO [123]. The intensity ratio of NBE to DLE (I_{NBE}/I_{DLE}) is calculated and presented in Fig. 3.12(b) which clearly indicates high crystallinity and quality of present ZnO nanostructures grown by GLAD technique. The above studies show that the selective samples show the character of visible-blindness due to which they do not need any kind of filtering of visible light.

3.3.2.4 Transient Ultraviolet Photo-detection Studies

To study the photosensitivity of these nano-networks, photocurrent measurements were performed by illuminating the samples with UV light of 365 nm wavelength. Fig. 3.13 represents the photocurrent cycles taken under the bias voltage of 1.5 V at ambient temperature and atmosphere.

The current was found to increase as the UV light was switched on. The light was kept on nearly for 2 h to check the saturation, and then the photocurrent cycles were taken to ensure the repeatability and reproducibility of the curves (Fig. 3.13). The increase or decrease in current is attributed to desorption or adsorption of oxygen molecules from the surface. The phenomenon is explained in detail in chapter-2 of the thesis. Table 3.2 shows the obtained parameters from the photocurrent switching curves.



Figure 3.13: Transient photoresponse characteristic curves of ZnO nanostructures grown at different seeding-angles.

It was found that the photosensitivity is higher for the sample grown at lower seeding-angle, and then it decreases systematically with the increase in seeding-angle. The increase in photosensitivity is attributed to the increase in surface porosity of the nano-networks. The increased surface-area helps adsorption and desorption of oxygen more promptly on the surface and pores, and thus increases the response [124]. The slow decay of photocurrent could be due to the delayed re-adsorption process. This
measurement clearly shows that the grown samples have a strong influence of UV light and quite suitable for UV light-detection due to the visibleblindness character.

Table 3.2: Obtained values for porosity, dark current and a photo-to-dark current ratio of ZnO nanostructures.

Sample	Porosity	Dark current	Photo-to-dark current ratio
	(%)	I_d (µA)	(I_p/I_d)
ZnO-0	31.42	0.071	57.67
ZnO-30	30.28	0.072	31.42
ZnO-45	20.32	75.32	4.72
ZnO-60	10.31	58.23	1.53
ZnO-75	9.81	53.65	1.16

3.3.3 Summary

The catalyst-free crystalline and porous ZnO nanostructures were successfully grown by a two-stage PLD. In the first stage, the depositionangle was varied during self-seeding, and in the second stage, the nanostructures were prepared by glancing angle PLD. The cross-sectional SEM confirms the growth of the wall/stack-like nanostructure network. The top view of the surface shows a porous network of these nanostructures, and the porosity exists without losing crystallinity and without any impurity in these samples. The growth and optical properties highly depend on this seeding-angle (first-stage). Thus, by varying the seeding-angle during PLD, the gradual and systematic variations were observed for the crystallographic orientation, porosity, defect-level and visible-blindness. The UV photocurrent studies show that seeding at an angle facing the plume provides a defect-free crystalline growth of ZnO nanostructures with maximum porosity and maximum photosensitivity for the application in visible-blind UV photo-detection, whereas a high defect-level and luminescence can be attained for visible-light at higher seeding-angle. Thus, this geometrical variation during PLD has proved to be highly effective in tuning almost all the functional properties of ZnO nanostructures.

Chapter 4

UV Photo-detection by ZnO and Ga-doped ZnO Nanostructures: A Comparative Study under Different Gas Atmospheres and Temperatures

In this chapter, the effects of Ga doping in ZnO and various properties of prepared nanostructures have been discussed. These nanostructures have been grown on the quartz substrates by the GLAD-assisted PLD method. The fabricated photodetectors have been tested for deep-UV photo-sensing. In the previous chapter, a discussion on the photo-detection performed at ambient temperature and atmosphere (*i.e.* in the air) have been discussed. While the present study manifests the performance of photodetectors under different gas atmospheres such as in vacuum, air, nitrogen and oxygen. The UV photo-detection has also been tested at low temperature (10 K) to validate their applicability for space applications and atmospheric study. To prove the visible-blindness of present photodetectors, the photo-detection measurements have been performed under the exposure of visible lights such as blue, red and green light-emitting diodes (LEDs). More importantly, these detectors need a very low operational voltage and do not need any filtering to low energy photons.

Hence, the present study significantly contributes to the synthesis and designing of an efficient deep-UV photodetector which can sustain at diverse environmental conditions without letting down its performance. The results presented in this chapter are published in peer-reviewed journal^{#.}

[#] Soni et al., J. Mater. Chem. C, 2020, 8, 7837.

4.1 Introduction

Usually, the UV light-sensing is performed by using silicon-based photodetectors. It has a low sensitivity for UV lights due to its small band gap (1.1 eV). Moreover, the drawback of such photodetectors is their sensitivity towards visible and infrared regions too. Therefore, ZnO with a wide band gap of 3.37 eV is a good substitute for such photodetectors. ZnO is a binary semiconductor material having hexagonal wurtzite crystal structure [16]. The pure and defect-free ZnO nanostructures are highly transparent for the visible spectrum of light. Such crystalline ZnO nanostructures with high surface-to-volume ratio find broad applications in visible-blind UV photodetectors and various gas/chemical sensors [33]. As discussed in chapter-3, the different morphologies and properties of ZnO nanostructures can be obtained by tuning the various deposition parameters. Therefore, based on the different shapes and size of nanostructures, an efficient device can be designed for optoelectronic applications. For example, 1D ZnO nanostructures are very useful for field emission device applications due to their sharp tips [125].

The enhancement in the performance of photodetectors can also be obtained by impurity doping, coating, annealing *etc.* [126–128] Also, the incorporation of selective elements has become one of the crucial parameters to improve and control the optoelectronic properties of ZnO. Doping has shown tremendous influence on the photo-detection and other optical properties of ZnO. For example, many elements such as Ni, Cu, V *etc.* have been used as a dopant for ZnO to fabricate efficient UV photodetectors and various gas sensors also [129–131]. Till now, different studies have been carried out with doping in ZnO such as the study of luminescence and light guiding properties based on Er and Li codoped ZnO nanostructures [132].

The type and amount of doping have a rigorous impact on the overall properties of ZnO, including, structural, optical and electrical properties. Therefore, the choice of suitable dopants with desired properties is very essential for any applications. Among the elements of group III, Al tends to form its own oxides, and In^{3+} has a large size (0.8Å), which causes more lattice distortion. Ga is comparatively suitable dopant since the ionic radius of Ga^{3+} (0.62 Å) is comparable to Zn^{2+} (0.74 Å), and therefore it is easy to dope Ga impurity in ZnO lattice without much lattice distortion. Besides, this does not lose its attractive optical and electrical properties after a fractional Ga doping. It is an effective *n*-type dopant in ZnO, which helps to increase the electrical conductivity by increasing the carrier density [133]. The earlier reports suggested that Ga doping in ZnO significantly enhanced the field emission (FE) properties, and it is found the best suitable for the UV photo-detection and FE-based device applications [134–137]. Thus an understanding of the impression of dopants on the optical properties of ZnO nanostructures can help to materialise and fabricate new devices for optoelectronic applications. Recently, remarkable efforts have been made to improve the performance of ultraviolet photodetectors. Therefore, with the continuing research into this field and the development of various synthesis methods have led to an increased interest in using the various ZnO nanostructures for UV sensing and other applications. For example; Chiu et al. reported the improved performance of Ga-doped ZnO nanopagodas by enhanced O₂ and H₂O chemisorption reactivity of different crystal planes [138].

UV photodetectors find their applicability in various fields including biomedical instrumentation, missile launching and testing, space communications *etc.* [139]. Therefore, with a motivation to compare the properties, the undoped ZnO and 2% Ga-doped ZnO nanostructures have been synthesized and studied for the deep-UV photoresponse properties under different environmental conditions, including various gas atmospheres and at low-temperature.

4.2 Experimental

4.2.1 Bulk $Zn_{1-x}Ga_xO(x=0.00, 0.02)$

The bulk target pellets of $Zn_{1-x}Ga_xO$ (x= 0.00, 0.02) were prepared using solid-state reaction method. The powders of ZnO and Ga₂O₃ were mixed in appropriate molar ratios and then ground for 4-5 hours to make a homogeneous mixture. This mixture was pressed into pellet form with 5 tons of pressure using a hydraulic press and kept in a box furnace at the temperature of 1000 °C for 10 hours for the densification of pellets. These pellets were then used as a target material for the synthesis of nanostructures.

4.2.2 Nanostructure Synthesis

The synthesis of undoped ZnO and 2% Ga-doped ZnO nanostructures were carried out using the GLAD-assisted PLD method. The quartz substrates were sequentially sonicated in acetone and propanol for 10 min, before loading into the deposition chamber. The base pressure of the deposition chamber was attained at the order of 10⁻⁴ Pa. The laser ablation was performed using a pulsed KrF excimer laser (λ = 248 nm) at an energy fluence of $\sim 3 \text{ J/cm}^2$. For the present study, two samples were prepared, namely, ZnO and Ga:ZnO for undoped ZnO and Ga-doped ZnO, respectively. The nanostructural growth takes place in the two stages as described in detail with schematically in chapter-2 of the thesis. Firstly, the nucleation seeds of target material were deposited on the substrate at a repetition rate of 8 Hz with 5 Pa partial oxygen pressure. The target was ablated for 5 min for the formation of crystalline seeds. The nanostructures were then grown on the seeded substrates with a GLAD geometry. The laser repetition rate and deposition time for this stage were kept at 10 Hz and 10 min, respectively. During the growth of nanostructures, the oxygen partial pressure in the growth chamber was maintained at 15 Pa for both the

samples. The photodetectors were fabricated based on ZnO and Ga-doped ZnO nanostructures using Au electrodes for the photo-detection studies. The schematic representation of fabricated detectors has been depicted in chapter-2 of the thesis.

The as-prepared samples were investigated systematically using XRD, Raman spectroscopy, SEM, UV-Visible and PL spectroscopy. The current-voltage (I-V) characteristics were recorded using Keithley meter by sweeping the voltage from -2 to 2 mV. The visible-blindness of detectors was confirmed by performing the measurements with LEDs of three different visible lights (*i.e.* red, green and blue). The deep-UV sensing was tested by the exposure of UV light (254 nm, 5 mW cm⁻²) under diverse atmospheric conditions such as in a vacuum, air, nitrogen and oxygen. The photodetectors were also tested at low-temperature (10K) using a closed-cycle cryostat system. The schematic for sensing experimental setup has been shown in chapter-2 of the thesis. Notably, the photocurrent measurements were performed simultaneously, keeping both undoped and doped samples in a single chamber. This simultaneous measurement ensures the identical conditions for both the detectors.

4.3 Results and Discussion

In this section, the various experimental results have been discussed and analyzed in detail. The structural, morphological and optical properties along with the peculiarity of visible-blindness and deep-UV photo-sensing for undoped ZnO and Ga-doped ZnO nanostructures have been described in the following subsections.

4.3.1 Structural Analysis

X-ray Diffraction

Fig. 4.1 shows the X-ray diffraction (XRD) patterns of ZnO and Ga:ZnO nanostructures grown on quartz substrates. The samples show (002) and (004) peaks which correspond to the hexagonal wurtzite crystal structure. In addition to these peaks, another peak at (101) with lower intensity is observed for Ga:ZnO. The absence of impurity peaks in the XRD patterns clearly demonstrates the purity of the nanostructures and decisively suggests the applicability of present nanostructures to fabricate visible-blind UV photodetectors. The present glancing angle deposited nanostructures have a lot better crystallinity as compared to the other ZnO based nanostructures grown by using various synthesis techniques [140,141].



Figure 4.1: XRD patterns of undoped and Ga-doped ZnO nanostructures.

From XRD figure, it is also evident that the preferential orientation of the crystallites is along the *c*-axis, representing the (002) plane of wurtzite ZnO. The FWHM (full width at half maximum) of (002) peak was calculated from the Gaussian fit of the curve and found ~0.17° and 0.23° for ZnO and Ga:ZnO, respectively. However, the intensity of this peak slightly decreased with Ga doping. The crystallite size as calculated from the Scherrer's formula (eq. 3.4) was ~50.83 and 38.16 nm for ZnO and Ga:ZnO, respectively. This variation in crystallite size is corroborated to the difference in ionic radii of Zn and Ga.

Raman Spectroscopy

To study the vibrational modes, Raman spectroscopy of undoped and Gadoped ZnO nanostructures were performed. Fig. 4.2 shows the roomtemperature micro Raman spectra of the two samples along with a quartz substrate. For a perfect ZnO crystal with wurtzite symmetry, a total of six Raman active modes are present, given as. $A_1(TO)+A_1(LO)+E_1(TO)+E_1(LO)+2E_2$ [23]. The origin and significance of each of these modes have been discussed in chapter-1 of the thesis. The present Raman spectra consist of the peaks at different wavenumbers emanated from the samples and quartz substrate. The obtained peaks are represented by the dashed lines in Fig. 4.2, where the letter 'S' represents the contribution of the quartz substrate. The two most prominent peaks are observed for undoped ZnO at about 97 cm⁻¹ and 436 cm⁻¹ which are assigned as $E_2(low)$ and $E_2(high)$ modes, respectively. The $E_2(low)$ mode involves the vibrations of Zn sub-lattice, while E₂(high) mode arises due to the motion of oxygen atoms [25]. It is seen that the frequency of $E_2(low)$ mode shifted at 99 cm⁻¹ upon Ga doping. As the $E_2(low)$ mode is associated with the vibration of Zn atoms, therefore substitutional doping of the Zn atoms changes the vibrational frequencies of the Ga-doped sample. Such a significant shift clearly indicates that Ga dopant atom has been successfully substituted at Zn atom sites. On the other hand, the frequency of $E_2(high)$ mode (436 cm⁻¹) remains unaltered with Ga doping. As the E_2 (high) mode is dominantly related to the vibration of oxygen atoms, the presence of Ga atom does not change the frequency of this mode. However, the $E_2(high)$ mode becomes less intense and broader, which indicates a slight decline in the crystallinity of Ga:ZnO. An analogous feature also observed earlier by Horzum *et al.* with Ga doping in ZnO thin films [142].

For the highly oriented ZnO nanostructures, when the incident light is normal to the surface, only E_2 and $A_1(LO)$ modes can be monitored, and other modes are forbidden due to the Raman selection rules. Thus the absence of $A_1(TO)$ mode in the present spectra suggests the vertical growth of nanostructures along the *c*-axis. The peak located at 573 cm⁻¹ observed for the undoped ZnO is assigned as $A_1(LO)$ mode, which arises due to the intrinsic defects of oxygen vacancies and zinc interstitials. The disappearance of LO mode for Ga:ZnO indicates the variation in inherent lattice defects related to the oxygen vacancies and interstitial zinc due to the screening of internal electric fields by the free charge carriers. Hence, these Raman results explicitly show the presence of Ga into ZnO and also confirm the wurtzite structure of grown nanostructures, supporting the XRD findings.



Figure 4.2: Room-temperature Raman spectra of undoped and Ga-doped ZnO nanostructures. A Raman spectrum of the quartz substrate is also plotted for the comparison.

4.3.2 Morphological Analysis

Scanning Electron Microscopy

Fig. 4.3 illustrates the surface morphologies and cross-sectional view of undoped ZnO and Ga-doped ZnO nanostructures by scanning electron microscope. The top view of undoped ZnO nanostructures (Fig. 4.3a) explicitly shows hexagonal facets indicating the wurtzite structure. A distinct change in the surface morphology was observed by the incorporation of Ga into ZnO, as seen in SEM of Ga:ZnO (Fig. 4.3c), and a wedge-shaped morphology originated due to the mixed orientations and doping. The obvious change in morphology upon Ga doping has also been reported earlier for ZnO nanostructures grown by the hydrothermal method [143]. The cross-sectional view (Fig. 4.3(b, d)) confirms the perpendicular growth of nanostructures on the quartz substrate. The total thickness of samples as measured from the cross-sectional SEM lies in the range of 400-500 nm. It is also evident from the SEM images that, the grown nanostructures exhibit a porous structure with void spaces. The porosity analysis was performed by using ImageJ software and found to be ~6.20% and 20.88% for ZnO and Ga:ZnO, respectively. The details for analysis of porosity by ImageJ is presented in chapter-2 of the thesis.

In the present case, the induced porosity is attributed to the change in morphology of nanostructures upon Ga doping. A similar result has also been observed earlier for Al-doped ZnO [144], where doping significantly affected the surface morphology and porosity. It should be noted here that, the growth of these nanostructures is uniform throughout the thickness; hence, the porosity analysis applies the volume of the 400-500 nm thin structures above the seeding layer. Fig. 4.3(e) shows the energy-dispersive X-ray spectroscopy (EDX) results for Ga:ZnO sample. The spectra confirm the presence of Ga in ZnO nanostructures with a required amount as presented in the inset table.



Figure 4.3: (a-d) Surface morphologies and the cross-sectional view of undoped ZnO and Ga-doped ZnO nanostructures. (e) EDX spectra image of Ga-doped ZnO nanostructures grown on a quartz substrate.

4.3.3 Optical Analysis

UV-Visible Spectroscopy

The optical quality and band gap of grown nanostructures have been determined by UV-Visible (UV-Vis) spectroscopy technique. Fig. 4.4 shows the absorbance spectra in the wavelength range of 300-800 nm. The sharp absorption-edge in the UV region confirms the high-quality and crystallinity of both the samples. Such intense UV absorption and crystalline nature make the present nanostructures more suitable for UV light-sensing applications. The optical band gap (E_g) was calculated from the Tauc relation (eq. 3.1). The inset of Fig. 4.4 represents the Tauc plots

which determine the value of optical band gap (E_g) . The value of E_g was found to be nearly 3.24 eV for both the samples, representing the wide band gap of the nanostructures. Also, these values of optical band gap are close to the band gap of intrinsic ZnO and are in good agreement with the reported works of literature [105,106].



Figure 4.4: UV-Visible spectra of undoped ZnO (left) and Ga-doped ZnO (right) nanostructures. The inset shows a linear fit of the graph $(\alpha h \upsilon)^2$ versus $(h\upsilon)$ for the optical band gap (E_g) calculation.

Photoluminescence Spectroscopy

Fig. 4.5 shows the representative photoluminescence (PL) spectra of undoped ZnO and Ga-doped ZnO nanostructures. Generally, the room temperature PL of ZnO exhibits two emission peaks. The first peak in the UV range called near-band emission (NBE) due to the recombination of free excitons. Another emission in the visible range of spectrum called deeplevel emission (DLE) due to defect-assisted broad emission [145]. In the present case, both the samples show an intense and prominent UV emission peak at about 380 nm, suggestive of the movement of electrons from the conduction band to the valence band. However, the intensity of NBE increases for Ga:ZnO sample. The increase in intensity and broadening of UV emission upon Ga doping has also been reported earlier by EscobedoMorales *et al.* [143]. The Ga atoms occupied at Zn vacancies defect position and increased the donor-related defects (such as shallow donor and zinc interstitials) in ZnO nanostructures which lead to an intense UV emission in the PL spectra. The high-intense UV signal as compared to the visible emission is an indication for the quality of grown nanostructures. It is clear from the PL graph that both the samples show negligible defect-assisted emission. Therefore, it can be deduced that the nanostructures by the GLAD technique are visible-blind and highly crystalline. Such merits make these nanostructures more suitable for highly sensitive UV photo-detection applications.



Figure 4.5: Photoluminescence spectra of undoped ZnO and Ga-doped ZnO nanostructures.

4.3.4 Electrical and Photo-detection Studies

In this section, a comparative study of various measurements performed on the fabricated photodetectors has been discussed. Firstly, the currentvoltage (I-V) characteristics of the detectors have been analyzed. Secondly, the visible-blindness character of the detectors has been determined by exposing under different visible lights (*i.e.* blue, red and green LEDs). At last, the deep-UV (254 nm) photo-sensing has been performed under various atmospheric conditions such as in air, oxygen, nitrogen and vacuum. The photodetectors have also been tested at low-temperature (10K) to confirm their suitability for low-temperature applications. The physical significance of all the obtained results has also been explained in detail.

For every measurement, initially, a dark current has been stabilized and observed for 10 minutes, and then lights were switched on. More importantly, these photo-detection studies have been performed with a minimal applied bias of 2 mV. Generally, a high bias voltage of several volts is applied to detect the signal, whereas here only a few millivolt of operating voltage for the detection is required. The bias voltage usually creates an electric field near the surface. The larger voltage creates a large electric field, and the high field may result to damage the device. The high bias voltage also results in self-heating of the device, which eventually hinders the photocurrent switching cycle too [146]. Therefore, to keep the device at safe, a low or zero bias voltage is preferred for highly sensitive photodetectors.

4.3.4.1 I-V Characteristics

Fig. 4.6 shows the current-voltage (I-V) characteristics of detectors taken in the air under darkness. The linearity of the I-V graph clearly suggests the ohmic nature of contacts. A manifold decrease in the dark current (I_d) was clearly observed upon Ga doping. Generally, the low dark current is considered very helpful to enhance the detector's signal-to-noise ratio. In the present case, the reduction in dark current for Ga-doped ZnO nanostructures is ascribed to the increased amount of porosity and large grain boundaries which scatters the charge carriers and reduces the conductivity. Further, the large surface area helps in the diffusion of oxygen gas promptly into the grain boundaries, which expands the amount of adsorbed oxygen at the grain boundaries, resulting in the increase of depletion width and hence favouring the low dark current [147–149].



Figure 4.6: I-V characteristics of undoped ZnO and Ga-doped ZnO nanostructures.

4.3.4.2 Study of Visible-blindness

In order to confirm the visible-blindness of present photodetectors, the timedependent photo-detection has been performed in the air under three different lights, *i.e.* red, green and blue LEDs. Fig. 4.7 shows the performance of both photodetectors under different visible lights. It is clear that both the detectors show absolutely no response for red and green lights. However, under blue exposure, the signal response is extremely low, and notably, the generated photocurrents are comparable to the dark currents itself. The minor response can be due to the wide band gap nature of ZnO material (3.24 eV for the present case). More importantly, this response is negligible as compared to the deep-UV photoresponse.

As clear from Fig. 4.8 (a, b), the photoresponse under blue light is insignificant compared to the UV photoresponse, and this is true for both the detectors. For example, the UV response for Ga:ZnO is nearly 3 times compared to the blue light (Fig. 4.8b). Likewise, when comparing only the UV performance of both the detectors, it is observed that Ga:ZnO have a maximum photo-to-dark current ratio (I_p/I_d) under UV light illumination (Fig. 4.8(a,b)).



Figure 4.7: Transient photoresponse characteristic curves of (a) undoped ZnO and (b) Ga-doped ZnO nanostructures under red, green and blue lights.



Figure 4.8: Comparison of photoresponse under blue and UV light for (a) undoped ZnO and (b) Ga-doped ZnO nanostructures.

Thus, a much larger response to UV light ensures the applicability of these detectors for visible-blind UV photo-detection applications. A detailed mechanism of photoresponse, including in air, is explained in the next sections.



4.3.4.3 Photo-detection under Various Atmospheres

Figure 4.9: Room-temperature transient photoresponse characteristic curves of undoped ZnO and Ga-doped ZnO nanostructures under different atmospheric conditions. The gases are at ambient conditions. The increase in response upon Ga doping is denoted by a vertical arrow in the figure.

In order to test the performance versatility of these visible-blind photodetectors, a comparative study on the photo-detection under diverse atmospheric conditions such as in air, oxygen, nitrogen, and vacuum has been performed. All these measurements have been performed at room-temperature under the illumination of deep-UV (254 nm) light. The obtained results are shown in Fig. 4.9.

The adsorption process under different medium is schematized in Fig. 4.10. The values of I_p/I_d derived from the adsorption and desorption dynamics of the characteristic curves under the different conditions are reported in Table 4.1. The influence on the performance of photodetectors under different atmospheric conditions, and the mechanism is explained as follows:



Figure 4.10: Schematic representation of the adsorption process under different medium. The red color spheres represent adsorbates, bottom layer (green color) represents the quartz substrate, and the thick top layer (yellow color) represents the depletion width.

Sample		I_p/I_d at roo	I_p/I_d at 10K		
	air	vacuum	nitrogen	oxygen	vacuum
ZnO	1.59	2.22	1.75	1.22	1.6
Ga:ZnO	3.10	12.42	3.30	2.58	10.5

Table 4.1: Derived parameters from the transient photoresponse characteristic curves of undoped ZnO and Ga-doped ZnO nanostructures.

Photoresponse in Air:

Fig. 4.9(a) shows the photoresponse behavior of both detectors in the air as the surrounding medium. A weak current is detected in the absence of UV light, while upon UV illumination, the current suddenly increased and saturated at a certain level. Noticeably, for an individual detector, compared to the dark current, the photocurrent increased enormously upon UV light exposure. This clearly demonstrates that the samples have an appreciable deep UV photo-detection under an open environment. Moreover, the multiple illumination cycles exhibit nearly identical photocurrent switching, as shown in Fig. 4.11, which certifies the repeatability and reproducibility of the rise in photocurrent.

The mechanism responsible for the rise and decay of photocurrent is attributed to the desorption and adsorption processes of the constituent adsorbates of the medium. For the present case of air, at normal conditions, the volume contains the essential adsorbates, mostly nitrogen (~78%) and oxygen (~22%). However, the adsorption/desorption is mainly dominated by oxygen adsorbates.



Figure 4.11: Transient photoresponse characteristic curves in the air at room temperature for undoped ZnO and Ga-doped ZnO nanostructures.

The observed steady-state dark current is nearly 26.3 and 1.3 μ A for ZnO and Ga:ZnO, respectively. Thus, the photo-generated current of the device can be calculated as

$$\Delta I = (I_{UV} - I_{dark}) \tag{4.1}$$

where I_{UV} is the current under UV light and I_{dark} is the dark current. Then the sensitivity (*S*) of the detectors can be defined as [150]

$$S(\%) = \left(\frac{\Delta I}{I_{dark}}\right) \times 100$$
 4.2

The calculated percentage sensitivity of the detectors is approximately 59 and 210 for ZnO and Ga:ZnO, respectively. Table 4.2 summarizes the UV response performance of present and different UV photodetectors based on various ZnO nanostructures. It is seen that Ga doping has significantly improved the sensitivity of a detector. The obtained values of sensitivity for the present detectors are pretty higher than the reported values of the detectors based on Ga-doped ZnO films [152]. Moreover, the dark current and photo-to-dark current ratio for the present detectors are far better than the reported Mg-doped ZnO thin films [153]. The present results are also comparable to the single nanowires and other nanostructures [159,160]. Notably, the fabrication of single nanowires and making electrodes on them is itself a problematic and tedious task along with a challenge to upkeep the device. However, the similar results are obtained here with the nanostructures of high porosity and crystallinity acquired by the GLAD technique.

Photodetector sample	Fabrication method	Photo- to-dark current ratio (l_p/l_d)	Bias voltage	Wavelength	Sensitivity (%)	Ref.
ZnO:AuNPs	Sputtering	1.46	-	254 nm	46	[151]
GZO nanopagodas	MOCVD	1.26	1 V	254 nm	26.82	[138]
GZO/ZnO heterojunction	PLD	-	-	UVA	29.10	[152]
MgZnO/ZnO thin film	Spin coating	1.23	4 V	365 nm	23	[153]
Al/ZnO nanorods/Pt	Hydrothermal	1.3	2 V	365 nm	34.1	[154]
ZnO nanowire	Hydrothermal	1.4	-3 V	254 nm	40	[155]
Ag/ZnO/Ag	Thermal evaporation	-	0-30 V	365 nm	0	[156]
Ga-doped ZnO films	MBE	1.06	20 V	374 nm	6.03	[157]
Au/GaZnO NRs/Au	Hydrothermal	1.18	3 V	200-400 nm	18.1	[158]
ZnO	GLAD-	1.59	2 mV	254 nm	59 (210)	This
(Ga:ZnO) nanostructures	assisted PLD	(3.10)				work

Table 4.2: Comparison of the reported performance of various UV photodetectors based on different ZnO nanostructures.

Photoresponse in Oxygen:

Fig. 4.9(b) shows the photo-detection performance of both detectors under an oxygen atmosphere. Under this circumstance, the surface of nanostructures has abundant oxygen, creating a thick depletion layer with an increased potential barrier (Fig. 4.10). With UV light exposure, these oxygen molecules get desorb and initiate the photocurrent. The calculated sensitivity (%) (by eq. 4.2) under this medium is 22 and 158 for ZnO and Ga:ZnO photodetectors, respectively. It is clear that the photo-to-dark current ratio (Table 4.2) and sensitivity are reduced as compared to the air medium. This reduction is originated due to the sufficient and continuous re-adsorption of oxygen molecules during the UV illumination.

Photoresponse in Nitrogen:

Fig. 4.9(c) shows the photo-detection measurements performed in nitrogen gas-ambient. It is observed that the photoresponse in nitrogen is comparable to the response in air and much higher to the oxygen atmosphere (Table 4.1). From the studies of density functional theory by Breedon *et al.*, it has been deduced that the binding energy of stable nitrogen is -1.42 eV and for oxygen is -2.47 eV [161]. This shows that the adsorption rate and interaction of nitrogen on the surface is very weak as compared to the oxygen molecules. Moreover, the adsorption of nitrogen adsorbates is directed by the physisorption process while for oxygen adsorbates it is due to the chemisorption process. Therefore, due to the weak bonding of nitrogen adsorbates, a thinning in the depletion width can be observed (Fig. 4.10). This is the reason that ZnO based photodetectors possess better photoconductivity in a nitrogen atmosphere as compared to the oxygen/air media. The calculated sensitivity (%) under this medium is 75 and 230 for ZnO and Ga:ZnO photodetectors, respectively.

Photoresponse in Vacuum:

Fig. 4.9(d) demonstrates the performance of photodetectors when tested in a vacuum. The detectors are found to be highly sensitive under vacuum with sensitivity (%) values of 122 and 1142 for ZnO and Ga: ZnO, respectively. It is noteworthy that among all the mediums, the maximum photo-detection is observed in a vacuum condition. This increase in response is attributed to the vacuum-assisted easy desorption of oxygen molecules from the surface. Additionally, by the release of trapped electrons, more carriers are generated through the photo-generation process, which increases the photocurrent and hence the photosensitivity. It has been suggested that UV exposure removes the loosely bound oxygen from the surface and in vacuum further removes the lattice oxygen via surface hydrocarbons [162].

In the present case, the photoresponse for Ga:ZnO was found to be roughly 4 times more to that in air. Whereas, compared to the undoped ZnO, this response increased by roughly 6 times (Table 4.1). The slow or nonsaturation behavior of the photoresponse in a vacuum is representing the non-equilibrium between desorption of oxygen molecules and photogenerated electron-hole pairs. Moreover, the photocurrent decays very slowly when the UV light was turned off. It should be noted here that this decay was considerably slower as compared to the decay in other mediums. This slow decay of photocurrent may reflect the residual oxygen in the vacuum chamber. However, the current comes to its initial value after a very long time due to the slow re-adsorption process, indicating the persistent photoconductivity to some extent in the samples.

4.3.4.4. Photo-detection at Low-temperature

In order to test the suitability of present photodetectors for space applications, the photo-detection is performed at the lower temperature (10K). A closed-cycle cryostat has been used here to perform the lowtemperature measurements. The samples were kept on a stage which was connected through a temperature controller. The measurement was performed in a vacuum chamber, and a high vacuum of the order of 10^{-7} mbar was attained before starting the sensing measurements. Fig. 4.12 shows the measured transient photoresponse at 10K, along with the results obtained at 300K for a comparison. It is observed that both the detectors show significant response even at the low-temperature. However, the response at 10K is slightly reduced compared to the response at room temperature. ZnO and Ga-doped ZnO are both semiconducting materials; hence, this reduction in response is corroborated to the increased resistance at low temperatures [163]. The typical semiconducting nature of ZnO material is shown in the resistivity (ρ) versus temperature (T) curve (inset of Fig. 4.12). It is further clear from Table 4.1 that a remarkable photo-to-dark current ratio is obtained without a major change even at 10K. Hence, this measurement clearly demonstrated the applicability of present photodetectors even at low-temperatures.



Figure 4.12: Temperature-dependent transient photoresponse characteristic curves of undoped ZnO and Ga-doped ZnO nanostructures. The inset shows a typical semiconducting behavior of ZnO in resistivity (ρ) versus temperature (T) curve.

4.3.4.5 Role of Ga Doping in Improving the UV Photoresponse

It is clear from the above photo-detection studies that Ga doping significantly improved the photoresponse of ZnO. It was also noticed that the detector Ga:ZnO attains a maximum photo-detection in all the atmospheric conditions. The advantage of Ga doping in ZnO can be understood by the following arguments.

Primarily, the Ga³⁺ ions at Zn²⁺ site in ZnO account for the increase in this photoresponse. These ions act as the cationic dopants in the ZnO lattice, permitting the electrons to transport easily to the conduction band [164]. Therefore, this leaves the more electrons of the pair in the conduction band. The photo-carrier generation increases the conductivity of Ga:ZnO nanostructures under UV illumination by increasing the carrier number and simultaneously reducing the depletion width or barrier height under different atmospheres.

It should also be noted here that, in addition to the surrounding gases, the depletion width is also affected by the surface morphology, grain size and surface-to-volume ratio (*i.e.* porosity) of nanostructures [165,166]. In the present case, Ga doping significantly changes these parameters as discussed in the above studies. Fig. 4.13 shows the basic mechanism for the improvement of photoresponse upon Ga doping under air. When the nanostructures are exposed with an open environment, the adsorption by oxygen molecules forms a potential barrier with band-bending across the grain boundaries. For smaller grain size, higher will be the adsorption rate due to the improved density of adsorption sites per unit area of the surface. Thus the higher adsorption rate causes a higher rate of desorption upon UV exposure which releases more number of electrons contributing the photoresponse.



Figure 4.13: Schematic representation for the principal mechanism of photoresponse for different grain size of nanostructures.

4.4 Summary

In summary, undoped and Ga-doped crystalline ZnO nanostructures were successfully grown by the GLAD-assisted PLD method. The fabricated photodetectors were visible-blind and demonstrated substantial photocurrent generation under UV illumination in diverse atmospheric conditions. This kind of visible-blind UV photo-detection may less expensive as compared to the Si-based technology where filtering is required.

The Ga doping significantly influenced the porosity and photoresponse of ZnO nanostructures. Both the detectors were tested simultaneously under identical conditions for a comparative study on the performance. There is a manifold enhancement in the current gain and sensitivity by only fractional Ga doping in ZnO. Moreover, both the photodetectors possess reversible switching characteristics with UV on/off. The thermal stability shows the applicability of photodetectors in the application area, where the temperature is sufficiently low. Our results suggest a high possibility of using these UV active visible-blind photodetectors to perform specific functions in optoelectronic applications. These results also suggest the potentiality of harnessing the GLAD technique in combination with PLD for an efficient UV photodetector. The study can be extended to encompass the growth of other types of materials and to further investigate the ability of nanostructures to sense other gases.

Chapter 5

Fabrication of Ultraviolet Photodetectors of ZnO Nanostructures on Different Substrates

In this chapter, a comparative study on the growth and photo-sensing properties of ZnO nanostructures fabricated on different types of substrates has been presented. The GLAD-assisted PLD method has been used to synthesize these nanostructures on the various substrates such as quartz, sapphire (Al₂O₃) and MgO. The quartz substrate has an amorphous nature, while the latter two substrates have crystalline nature with (001) and (100) crystal orientation for sapphire and MgO, respectively. Using the grown nanostructures on different substrates, three photodetectors have been fabricated and studied for deep-UV photo-detection. This study provides an idea on the selection of substrates for the crystalline growth of nanostructures and their UV performance comparison. The results presented in this chapter are published in peer-reviewed journal^{Ψ}.

^Ψ Soni et al., Sensors and Actuators A: Physical 313 (2020) 112140, (doi.org/10.1016/j.sna.2020.112140).

5.1 Introduction

Highly oriented, aligned and ordered ZnO nanostructures attracted huge attention of the scientific community due to their fundamental properties and potential device applications which shows incredible performance. Apart from the piezoelectric nature and biomedical applications, the ZnO has gas sensing and light-sensing applications too [167]. Owing to its wide band gap (~3.37 eV) nature, it is used for ultraviolet (UV) photo-detection that covers diverse fields of application regions including environmental monitoring, solar astronomy, missile warning system and air quality monitoring [74,168]. For any of the applications, the morphology of ZnO is a crucial parameter in determining the physical and optoelectronic properties. Furthermore, this can be grown in various nanoforms, and their properties can also be tuned by tuning the synthesis conditions [110,169–171].

The shape and morphology of ZnO nanostructures are much dependent on the quality and the type of substrate used. Till date, in the device perspective, different kinds of substrates, including solid and flexible substrates, have been used to grow the ZnO nanostructures. These nanostructures have been grown using different methods, and various morphologies have been obtained [172,173]. The solid substrates can be of amorphous or crystalline nature. Moreover, it may have conductive or nonconductive nature depending on the applications. For example, Cu and n/ptype Si substrates have been used to grow ZnO nanorods by hydrothermal and PLD method [65,113,172,174]. Amorphous quartz and glass substrates have been used for the growth of different ZnO nanostructures [94,174,175]. On the other hand, in spite of large lattice mismatch, the ZnO nanostructures have also been grown on single crystals including sapphire [64], MgO [176] and perovskite crystal SrTiO₃ [177]. Yang et al. reported the oriented growth of ZnO nanostructures on different substrates via hydrothermal method [172]. More recently, Cossuet et al. studied the

growth and nucleation of ZnO nanowires on the poorly and highly textured polycrystalline ZnO seed layer and showed that the vertical directional growth dominates on the highly textured ZnO seed layer [178].

For an effective growth of ZnO nanostructures on various substrates, coating of a seed layer has become the modern approach. The seed layer can be formed by using any catalyst, but this may cause unintentional doping and impurity in the resultant nanostructures. Therefore, the catalyst-free growth can be realized by self-seeding of the target material. The seed layer also assists in the smooth electrical conduction along with supporting the growth of nanostructures. Therefore, the directional growth of high-quality nanostructures with excellent electrical conduction on self-seeded solid substrates has become an essential and promising way. However, there are still many factors, including deposition methods and processing environment which directly or indirectly affect the properties of ZnO nanostructures.

For the present investigation, we purposely chose two kinds of substrates (*i.e.* amorphous and crystalline). Therefore, total three different substrates, *i.e.* quartz, sapphire (hexagonal) and MgO (cubic) have been used for a comparative study on the growth and UV performance of ZnO nanostructures fabricated by the GLAD-assisted PLD method. The quartz substrate is amorphous and from our earlier studies (as discussed in chapter 3 and 4) it is apparent that the GLAD-assisted PLD helps the highly-oriented growth on ZnO even on the quartz [170,171,179]. On the other hand, sapphire and MgO substrates are single crystals with different crystal structures, *i.e.* hexagonal for sapphire and cubic for MgO; hence that can affect the crystalline growth of ZnO. A pre-treatment of substrate, *i.e.* formation of ZnO seeds ensures the directionality and electrical conduction. This crystalline ZnO-seeding further makes sure the crystallinity of nanostructures. The morphological and structural properties are characterized and discussed in detail. The electronic properties of

synthesized nanostructures are probed by the optical band gap and luminescence studies. Finally, the deep-UV photo-sensing properties with the sensing mechanism have been discussed, and the results are analyzed.

5.2 Experimental

A disc-shaped bulk pellet of ZnO was synthesized by pressing the ZnO powder and sintered at 1000 °C for 10 hours. The prepared ZnO bulk pellet was then used as a target material for the synthesis of nanostructures. The nanostructures were deposited on the quartz, sapphire (Al₂O₃) (001) and MgO (100) substrates under identical growth conditions by the GLADassisted PLD method. All the substrates were sequentially sonicated in acetone and propanol for 10 min, before loading into the deposition chamber. The base pressure of the vacuum chamber was attained at the order of 10⁻⁴ Pa. The laser ablation was performed using a pulsed KrF excimer laser source of 248 nm wavelength and energy fluence of $\sim 3 \text{ J/cm}^2$. The nanostructural growth takes place in the two stages as described in chapter-2 of the thesis. Firstly, all the three substrates were loaded into the PLD chamber, and the self-seeding of ZnO target material was performed at a repetition rate of 8 Hz with 5 Pa oxygen partial pressure. The target was ablated for 5 min for the formation of crystalline seeds. The geometry was then changed to glancing angle and nanostructures were grown on ZnO seeded substrates. The repetition rate and deposition time for this stage were kept at 10 Hz and 10 min, respectively. The background oxygen partial pressure was maintained at 15 Pa during the growth process. The prepared nanostructures on quartz, Al_2O_3 and MgO substrates were named as ZnO/Q, ZnO/ALO and ZnO/MgO, respectively. To study the ultraviolet (UV) photo-sensing properties of these nanostructures, photodetectors were fabricated as discussed in chapter-2.

The deposited nanostructures were then systematically investigated by the various experimental techniques such as XRD, Raman spectroscopy, SEM, AFM, UV-Visible and PL spectroscopy. The photo-detection measurements of the fabricated detectors were performed under deep-UV (254 nm) and visible light exposure. All the measurements were performed in air at room temperature.

5.3 Results and Discussion

In this section, the results of various experiments and characterizations performed on ZnO nanostructures have been discussed. The structural, morphological and optical properties have been explained in detail one by one in the following subsections.

5.3.1 Structural Analysis

X-ray Diffraction

Fig. 5.1 shows the XRD patterns of ZnO nanostructures synthesized on the different substrates. The absence of any impurity peaks in the diffraction pattern confirms the formation of pure ZnO nanostructures. In addition to the substrate' peaks, the nanostructures show intense peaks corresponding to ZnO (002) and (004) planes. The produced ZnO nanostructures are crystallographically oriented, and the grain-growth direction is vertical in the same direction making columnar structures. This shows that the grown nanostructures are preferentially oriented along the *c*-axis and indicating the hexagonal wurtzite structure of ZnO.

A strong relationship with (00*l*) orientations is the key evidence for the vertical growth rate of ZnO [68]. Notably, all three samples are crystallographically oriented towards (002) plane in spite of different types of substrates. Nistor *et al.* reported the formation of (002) plane of ZnO on MgO (100) substrate, attributing the high flux of incident species and therefore favouring the (002) ZnO growth rate [176]. It is important to note here that, the ZnO nanostructures on quartz substrate also show crystallinity regardless of the amorphous nature of the substrate. This interesting feature is attributed to the growth of nanostructures using the GLAD-assisted PLD method and self-seeding of the highly crystalline thin seed layer. The crystallinity of present nanostructures on the amorphous quartz/glass substrate is far better than the crystallinity of reported ZnO nanostructures synthesized by different methods [110–112,156]. For example, the ZnO nanostructures grown by a hydrothermal method generally show several diffraction peaks [180,181], clearly indicating that the orientation of nanostructures is deviating from the substrate' normal. In the present case, the underlying ZnO seed layer helps to improve the crystallinity, which can be identified as the controlling parameter for the crystal quality too [182].



Figure 5.1: XRD patterns of ZnO nanostructures grown on the quartz, MgO and Al₂O₃ substrates.

Fig. 5.2(a) shows the magnified part of XRD patterns around (002) Bragg peak. The 2 θ position of (002) peak slightly differs for different samples. The broadening in this peak is an indication of crystallite size distribution towards smaller size, causing the higher density of nanostructures as also seen in the scanning micrographs discussed latter. The average value of crystallite size is calculated from the Scherrer formula (eq. 3.4) and shown in Fig. 5.2(b). The comparatively smaller full width at half maximum (FWHM) indicates that the crystalline substrates have significantly affected the growth and hence the nanostructures on quartz show wider FWHM. The lattice constants were estimated as a~0.32 nm and c~0.52 nm with minimal variation in these three samples. These values are in good agreement with the values reported in the literature [21].



Figure 5.2: (a) Enlarged view of ZnO (002) XRD peak, (b) Crystallite size and FWHM of (002) peak of ZnO nanostructures grown on different substrates.

Raman Spectroscopy

Fig. 5.3 shows the Raman spectra of ZnO nanostructures grown on different substrates. The spectra consist of the peaks at different wavenumbers represented by the black dashed lines. It is observed that all three samples show typical peaks associated with the wurtzite ZnO. The physical significance of Raman modes of ZnO has been given in chapter-1 of the thesis. In Fig. 5.3, the two most prominent peaks are associated with E_2 phonon modes, namely, $E_2(low)$ and $E_2(high)$ located at wavenumbers ~98 cm⁻¹ and ~437 cm⁻¹, respectively. There is no significant variation observed in the position of E_2 modes for these three different samples. A very less intense peak near about 330-340 cm⁻¹, though absent in ZnO/Q, is assigned
as $E_2(high)-E_2(low)$ mode due to the second-order Raman processes [117]. The $E_2(low)$ and $E_2(high)$ modes are basically related to the vibrations of the heavy Zn sub-lattice and the oxygen atoms, respectively. These modes are also known as non-polar modes due to the opposite motion of neighbouring ions of each sub-lattice, resulting in finally a net-zero polarization. It is observed that the intensity of the $E_2(low)$ mode is stronger than the intensity of $E_2(high)$ mode, and this is a typical case of non-resonant Raman scattering [183]. The high intense $E_2(low)$ mode represents a high degree of local order in the Zn sub-lattice.



Figure 5.3: Room-temperature Raman spectra of ZnO nanostructures deposited on different substrates. The letter 'S' represents the contribution from individual substrates.

On the contrary to E_2 modes, the A_1 and E_1 are the polar modes commonly assigned to the defect complexes containing oxygen vacancy and zinc interstitials in ZnO [184]. This modes further split into TO (transverse optical) and LO (longitudinal optical) components. As the measurements are performed in backscattering geometry, the absence of TO modes in the present Raman spectra further confirms the highly *c*-axis orientation of grown ZnO nanostructures corroborating the XRD results. In Fig. 5.3, a broad signal also appears in between 500 cm⁻¹ and 600 cm⁻¹ with center frequency at about 575 cm⁻¹. Specifically, the LO phonon modes are located in this region with high phonon density of states. This band is attributed to the disorder-induced Raman scattering [185]. The mode at frequency 575 cm⁻¹ is assigned as A₁(LO) phonon mode and is observed for all the three samples. However, the intensity of this mode is very low for the samples ZnO/Q and ZnO/ALO, while it is broadened and red-shifted for the sample ZnO/MgO. Such a shift and broadening in the A₁(LO) branch outside the Brillouin zone center [185] which represents the extent of intrinsic defects or disorder in ZnO/MgO sample.

5.3.2 Morphological Analysis (by SEM and AFM)

Fig. 5.4 shows the surface morphologies obtained by SEM and AFM techniques for the ZnO nanostructures grown on different substrates. The SEM images (a-c) reveal the formation of ZnO nanostructures, which accords with the AFM results (d-f). These micrographs also indicate the facile growth of ZnO nanostructures on the entire substrate with perpendicular direction, *i.e.* oriented along the *c*-axis, which is also confirmed from the XRD analysis. The top view of different SEM images shows the grains are hexagonal on the top and have columnar like shape perpendicular to the substrate as seen in the cross-sectional SEM images The root mean square (rms) surface roughness as determined by AFM is 38.2, 35.4 and 16.8 nm for ZnO/ALO, ZnO/MgO and ZnO/Q, respectively. Maximum surface roughness provides a more effective surface area and thus improves UV photoresponse. It is observed that the grown nanostructures are porous, unlike any solid film; however, the porosity

values are different for the different samples. The estimated values for porosity are 26.32%, 15.72% and 6.20% for ZnO/ALO, ZnO/MgO and ZnO/Q, respectively. The porosity analysis was performed on SEM micrographs by using ImageJ software as discussed in chapter-2 of the thesis. The pores occupy volume within vertically grown crystalline grains of ZnO. For the present thin vertical nanostructures, the pores are also vertical. Hence the present porosity analysis shows the average top to bottom porosity (%) for the vertically oriented nanostructures. The thickness is determined using cross-sectional SEM images with an average value of 350 nm for all the samples (inset Fig. 5.4). The formation of such porous yet crystalline nanostructures with large surface area is encouraging for UV photo-detection applications.

From the SEM images, some intermittent particles with hexagonal shape typical for crystalline ZnO are evident. For ZnO/ALO, some of these hexagonal particles have sharp edges (Fig. 5.4a), and it is little distorted for the other two samples and therefore exhibit a different surface morphology. The present results show that the size and number of particles are strongly influenced by the substrate and the ZnO seeding-template. The variation in morphology is ascribed to the difference in lattice mismatch between the substrate and the seed layer [56,186]. Well-separated nanostructures are produced due to a large lattice mismatch for sapphire, while comparatively less lattice mismatch for MgO substrate resulted in the less separation of nanostructures. On the other hand, ZnO/Q shows the coalescence of nanostructures with few existing pores. It should be noted here that all vertically standing nanostructures are connected through the seed layer, which helps in the electrical conduction of electrons. The above study showed that growth and morphologies are significantly influenced by the type of substrate and nevertheless providing the highly directional growth with crystallinity and porosity.



Figure 5.4: SEM (top) and AFM (bottom) images of ZnO nanostructures grown on Al_2O_3 (a,d), MgO (b,e) and quartz (c,f) substrates. The inset shows corresponding cross-section SEM images. The circles in red color indicate the hexagonal grains of the nanostructures.

5.3.3 Optical Analysis

UV-Visible Spectroscopy

Fig. 5.5 shows the UV-Vis spectra of ZnO nanostructures grown on quartz and sapphire substrates. The substrate MgO was not polished on both the sides and hence UV-Vis spectroscopic measurements were not possible for ZnO/MgO sample. It is observed that the absorption edge for both the samples lies in the UV range, representing the visible-blind, defect-free and wide band gap of present nanostructures. Moreover, the UV absorption intensity of sample ZnO/ALO is much stronger than the sample ZnO/Q, indicating the synthesized nanostructures on a sapphire substrate have comparatively good optical properties. The band gap of grown ZnO nanostructures is calculated using the Tauc plot by eq. 3.1 and shown in the inset figures. A vertical straight portion in higher energy region confirms the direct allowed transition in ZnO nanostructures. The obtained value of band gap is 3.24 and 3.25 eV for ZnO/Q and ZnO/ALO samples, respectively. The present values of the optical band gap agree well with the reported band gap of ZnO [105].



Figure 5.5: UV-Visible spectra of ZnO nanostructures deposited on (a) quartz and (b) sapphire substrates. The inset shows a linear fit of the graph $(\alpha h \upsilon)^2$ versus $(h \upsilon)$ for the optical band gap (E_g) calculation.

Photoluminescence Spectroscopy

get more insight into the optical characteristics, In order to photoluminescence (PL) spectroscopy of grown ZnO nanostructures was performed, as shown in Fig. 5.6(a). Generally, the room-temperature PL of ZnO exhibits two emission peaks. The first peak in the UV range is called near-band emission due to the recombination of free excitons and another emission in the visible range is called deep-level emission due to the presence of defects [31]. In the present case, a sharp and intense peak centered at ~380 nm related to the UV emission is observed for all the three samples. This intense UV emission is ascribed to the dominant recombination of free excitons through exciton-exciton collision process [29]. This indicates the wide direct band gap transition of ZnO and represents the high crystallinity of present nanostructures. Moreover, the absence or suppression of visible emission in the samples ZnO/ALO and ZnO/Q reveals that the concentration of defects is negligible here, representing the visible-blindness of nanostructures.



Figure 5.6: (a) Photoluminescence spectra of ZnO nanostructures deposited on different substrates, (b) De-convoluted PL spectra of ZnO nanostructures grown on MgO substrate.

ZnO/MgO show a highly asymmetric PL feature along with few emissions in the visible region. To study this, the PL curve has been deconvoluted into several distinct individual peaks by Gaussian fit. Fig. 5.6(b) highlights the possible de-convoluted components of the PL curve, indicated by the peak numbers as P₁, P₂ and P₃. The peaks P₁ and P₂ are very close to each other and located at ~380 and 392 nm respectively, representing the UV/UV-violet emission attributed to the band-edge and near band emission. The peak P₃ of low intensity spanning from 300-650 nm is ascribed to the point defects related to the Zn interstitials or oxygen vacancies [187]. The broad spectrum of P₃ assisted in the emissions related to the green-yellow and orange-red levels. The earlier studies on ZnO reported the green emission possibly due to the substrate surface effect [188,189]. However, in the present case, the intensity of the latter two emissions can be considered very feeble as compared to the band-edge emissions.



Figure 5.7: Schematic representation of the various emission lines from the different energy levels of ZnO.

Hence, the high intensity in the UV region implied the optical quality and crystallinity of the present nanostructures. The different PL

features for these three nanostructures are attributed to the difference in morphology and defect-level. The possible emissions from different energy levels of ZnO have been schematized in Fig. 5.7. The contribution of UV and visible lights has been further determined by the time-dependent photodetection on these nanostructures, as explained in the next section.

5.3.4 Electrical and Photo-detection Studies

Three different photodetectors have been fabricated (the fabrication method has been described in chapter-2) to study their electrical and photo-sensing properties. The following subsections represent a comparative study of various measurements performed on the fabricated photodetectors.

5.3.4.1 I-V Characteristics

To investigate the electrical properties of these photodetectors, the I-V characteristics are measured in the dark from -0.1 to 0.1 V, as shown in Fig. 5.8. The linearity of the I-V curve demonstrated the ohmic nature of contacts. The different values of dark current (I_d) are observed for these nanostructures, as reported in Table 5.1. The smaller dark current helps in the reduction of noise and therefore enhances the signal-to-noise ratio and performance of the device. It is noticed that the dark current is quite low for ZnO/ALO, which is due to the lower connectivity of grains and higher porosity as compared to the other two samples. The lower connectivity is originated due to the large lattice mismatch, which resulted in the separated nanostructures as revealed by SEM also. Moreover, the large surface-areato-volume ratio helps in the diffusion of oxygen gas promptly into the grain boundaries, which expands the amount of adsorbed oxygen at the grain boundaries, resulting in the increase of depletion width and hence favouring the low dark current [147–149]. On contrast, ZnO/Q shows a higher dark current, which is attributed to the higher density of nanostructures without many pores.



Figure 5.8: I-V characteristics of ZnO nanostructures deposited on (a) sapphire and MgO, (b) quartz substrates.

5.3.4.2 Photo-detection Studies under Ultraviolet and Visible Lights

From the above optical studies, it has been clear that the detectors are highly responsive for UV light. Therefore, based on their properties, all three detectors have been tested for deep-UV sensing. However, the detector ZnO/MgO has also been tested underexposure of visible light due to its photoluminescence behavior in the visible region of the electromagnetic spectrum (as seen in Fig. 5.6b).

Photo-detection in UV Light:

The transient photoresponse under deep-UV (254 nm) of the three detectors is measured in air at room temperature, as shown in Fig. 5.9. The measurement is performed with only 0.1 V applied bias voltage. The dark current is stabilized with a duration of 5 minutes by retaining the detectors in dark condition. The UV light is switched on and off for every 10 minutes so as to saturate the current to its maximum/minimum value. It is clear from Fig. 5.9 that the detectors have appreciable photocurrent response. Also, the photoinduced switching is very quick (Table 5.1). The repetitive photocurrent switching cycles ensure the stability of photocurrent with UV on/off. The adsorption and desorption of oxygen molecules are accountable for the rise and decay of photocurrent with UV on/off.



Figure 5.9: Transient photoresponse characteristic curves of ZnO nanostructures grown on different substrates. The solid line represents the fitting of the curves using eq. 3.2.

The generation and decay of photocurrent are accompanied by desorption and adsorption process of oxygen molecules through the surface. At ambient condition, the free electrons are seized by the oxygen molecules through adsorption, finally creating a depletion region on the surface, which affects the current. Upon UV light exposure, numerous electron-hole pairs are generated, and the oxygen gets desorbed from the surface, which decreases the width of the depletion region and hence promotes the photocurrent. The above process has been described schematically in chapter-2 of the thesis.

Sample	Porosity	Dark	Photo-to-dark	Sensitivity
	(%)	current	current ratio	(<i>S</i>) (%)
		(I_d)	(I_p/I_d)	
ZnO/ALO	26.32	0.14 nA	2.82	182
ZnO/MgO	15.72	45.2 μΑ	1.53	53
ZnO/Q	6.20	1.57 mA	1.32	32

Table 5.1: Derived parameters from the transient photoresponse characteristic curves of ZnO nanostructures grown on different substrates.

Table 5.1 shows the extracted parameters from the photocurrent switching curves of Fig. 5.9. The rise and decay-time constants are determined by fitting the curves using a bi-exponential function (eq. 3.2) [109]. The photoresponse processes are well fitted with the equation, as shown by the solid lines in the first cycle of Fig. 5.9. The rise and decay of photocurrent consist of two components, *i.e.* the fast and slow-response components, respectively denoted as τ_{r1} and τ_{r2} for the rise, and τ_{d1} and τ_{d2} for the decay of photocurrent. Clearly, the sample having high porosity shows the fast rise and decay-time as compared to the other samples. Moreover, the high photo-to-dark current ratio (I_p/I_d) and the highest photosensitivity is evidence of the highly porous and crystalline nanostructures. The sensitivity (*S*) of the detectors is determined by using eq. 4.2.

Table 5.2 shows a comparative performance with different parameters of present and similar ZnO-based UV photodetectors fabricated by different methods. It is apparent that the present nanostructures show improved performance in terms of photo-to-dark current ratio, sensitivity and response times as compared to the ZnO based samples grown by other synthesis routes. In Fig. 5.9, it is also noticed that the response slightly increases after each cycle which could be due to the non-equilibrium between adsorption and desorption. The transient photoresponse characteristics for ZnO/Q show a slow saturation as compared to the other two samples, representing a slow transfer of charge carriers between the

conduction band and the valence band. The slow decay of photocurrent on switching off the UV light is also an indication of a slow re-adsorption process.

Table 5.2: Comparison of the reported performance of various UV photodetectors based on different ZnO samples.

Photodetector samples	Fabrication method	Rise time constants	Decay time constants	Ref.
U-ZnO NWs (ZnO NWs)	Electrodeposition and atomic layer deposition	28.49 s (83.33 s)	$\tau_{d1} = 60.29 \text{ s},$ $\tau_{d2} = 700.47 \text{ s}$ $(\tau_{d1} = 120.05 \text{ s}, \tau_{d2} = 1372 \text{ s})$	[190]
ZnO nanowires Ga- incorporated ZnO nanowires	Vapor transport method	$\tau_{r1} = 52 \text{ s},$ $\tau_{r2} = 121 \text{ s}$ $\tau_{r1} = 164 \text{ s},$ $\tau_{r2} = 250 \text{ s}$	$\tau_{d1} = 59 \text{ s},$ $\tau_{d2} = 347 \text{ s}$ $\tau_{d1} = 124 \text{ s},$ $\tau_{d2} = 243 \text{ s}$	[191]
N:ZnO thin film	Radio Frequency (RF) Sputtering	$ au_{r1} = 18 \text{ s}, \ au_{r2} = 285 \text{ s}$	$ au_{d1} = 67 \text{ s}, \ au_{d2} = 680 \text{ s}$	[192]
ZnO Nws	Vapor Liquid Solid (VLS) method	$\tau_{r1} = 24.7 \text{ s},$ $\tau_{r2} = 295 \text{ s}$	$ au_{d1} = 25.7 \text{ s}, \ au_{d2} = 347.9 \text{ s}$	[57]
ZnO/Q ZnO/MgO	GLAD-assisted PLD	$\tau_{r1} = 42 \text{ s},$ $\tau_{r2} = 251 \text{ s}$ $\tau_{r1} = 12 \text{ s},$ $\tau_{r2} = 59 \text{ s}$	$\tau_{d1} = 27 \text{ s},$ $\tau_{d2} = 243 \text{ s}$ $\tau_{d1} = 12 \text{ s},$ $\tau_{d2} = 158 \text{ s}$	This work
ZnO/ALO		$ au_{r1} = 9 \text{ s}, \ au_{r2} = 48 \text{ s}$	$ au_{d1} = 7 ext{ s}, au_{d2} = 130 ext{ s}$	

Photo-detection of ZnO/MgO under Visible Lights

From the optical properties, as discussed in PL spectroscopy of section 5.3.3, it was observed that the sample ZnO/MgO show defect-assisted lowintense emissions. Therefore, a transient photocurrent is measured under the illumination of visible lights of different LEDs (*i.e.* red, green and blue), and the obtained results are compared with the UV measurements to see whether such sample can be useful for UV light-detection. It is found that this photodetector shows a huge response to UV light as compared to any visible light, as shown in Fig. 5.10.



Figure 5.10: Transient photoresponse characteristic curves of the sample ZnO/MgO under the illumination of different lights.

It is also evident that both the rise and decay of photocurrent in the case of visible light is much slower as compared to the UV light response. The response in the visible light has been attributed to the emission from the existing different illumination centres in the sample. This result also agrees with the PL spectra. This finding implies that all three nanostructures grown by the GLAD-assisted PLD method have reasonable UV photodetection performance for an application.

5.4 Summary

In summary, porous ZnO nanostructures have been successfully grown on three different substrates by the GLAD-assisted PLD method. Due to this combination of GLAD and PLD, the nanostructures grew vertical with highly crystalline and yet porous morphology even for the amorphous nature of the quartz substrate. The absence of TO modes and high intense fundamental E_2 modes in the Raman spectra confirmed the *c*-axis growth and the wurtzite structure of grown nanostructures, which also corroborate well with the XRD results. However, due to different substrates, the morphology and porosity were different for the nanostructures. These nanostructures were used to fabricate UV photodetectors. Although the same techniques were employed in preparing these photodetectors, the photodetector with sapphire substrate exhibited extremely low dark current with high UV photosensitivity as compared to the other two samples. Mainly, the growth on sapphire is much porous and defects-free, causing a high surface-to-volume ratio for effective UV photo-detection. This study highlighted the importance of the GLAD-assisted PLD method for maintaining the quality with the porosity in the nanostructures grown on any type of substrates.

130

Chapter 6

Conclusions and Future Prospects

This chapter concludes the present work with highlights. It also provides an outlook for future prospects that can be carried out in this area. The key objectives of this thesis were to produce highly porous and yet crystallographically oriented ZnO nanostructures using the GLAD-assisted PLD method. Further, to explore the structural, morphological, optical and photo-sensing properties of fabricated nanostructures to make them applicable for various optoelectronic applications even at diverse environmental conditions.

6.1 Conclusions

The present study significantly contributed to the study and development of visible-blind ultraviolet photo-detection of glancing angle deposited ZnO nanostructures. The study also accomplishes the prime objectives and validates the title of the dissertation. These objectives were chosen in the form of different studies to investigate the ZnO nanostructures and their properties. The main highlights of the work presented in the thesis are listed as follows:

- The produced ZnO nanostructures by the GLAD-assisted PLD method are crystallographically oriented and show crystallinity. A pre-deposition treatment (*i.e.* substrate seeding) with usual PLD geometry significantly help in the formation of crystalline seeds and directionality to the nanostructures. Moreover, the prodigious ability of PLD to produce impurity-free samples made the present nanostructures highly pure and defect-free.
- Specifically, the GLAD technique is a kind of constructive inclusion to the PLD. This technique assisted in the formation of pores during the deposition and also produced the nanostructures with isolated columnar structures. Importantly, the porosity exists without losing the crystallinity. The induced porosity and high surface-to-volume ratio make the samples fairly suitable for photo-sensing applications.
- In chapter 3, the effects of deposition parameters such as oxygen partial pressure and seeding-angle are discussed. The variation in growth and properties of ZnO nanostructures is clear evidence of the effects of these deposition parameters. The difference in growth process resulted in the difference in morphology and properties. The obtained nanostructures are vertical, crystallographically oriented

and show the preferential orientation of the wurtzite ZnO. The increase in porosity helps the adsorption of oxygen molecules and increases the photosensitivity upon photo-desorption.

- In chapter 4, the effects of Ga doping in ZnO and their properties are discussed. In particular, the results obtained in chapter 3 encouraged us to study the effects of doping on the morphological and UV photo-sensing properties. In the study, a multifold enhancement of UV photosensitivity and a substantial reduction in dark current by Ga substitution is observed. Moreover, the Ga doping significantly changed the surface morphology and grain size, which resulted in the increased adsorption and photo-desorption activity. For Ga-doped ZnO nanostructures, the photoresponse in a vacuum is increased roughly by 4 times as compared to the air medium. Also, the UV photo-detection study under different atmospheric conditions (such as in vacuum, air, nitrogen and oxygen) and temperature variation revealed the applicability of the photodetectors for a diverse environment.
- Lastly, in chapter 5, a comparative study on the growth and UV photosensitivity of ZnO nanostructures grown on various substrates is presented and discussed. These nanostructures are deposited on amorphous (quartz) and crystalline (Al₂O₃ and MgO) (of different crystal structures) substrates. All the deposited nanostructures are porous and crystallographically oriented. This study suggested that the crystalline substrates, especially Al_2O_3 (in the present study), is the most suitable option for the growth of highly crystalline, defectfree and porous ZnO nanostructures, also exhibit high UV photosensitivity. Moreover, despite the amorphous nature of quartz substrates. the grown nanostructures on quartz are crystallographically oriented, suits for commercialization or

industrial applications. These results represented the ability and efficiency of the GLAD-assisted PLD method.

6.2 Future Prospects

The present work of the thesis opens an avenue for the studies on PLDgrown various oxide nanostructures with desired control on the crystalline growth and porosity. Assimilating the benefits from various aspects of this study, there is still room to further direct the work in future. Some possible studies can be as follows:

- As discussed in the dissertation, PLD offers a variety of tunable deposition parameters, including GLAD; therefore, it is possible to further tune the various properties of fabricated nanostructures by tuning the other deposition parameters.
- The fabricated nanostructures can be further explored for the application of gas-sensing, including harmful gases.
- It would be of great interest to fabricate heterostructures or p-n junction by a suitable combination of different materials.
- In addition, these nanostructures can be grown on soft substrates to study their applications in flexible electronics.
- Following a similar approach, the other oxide materials can also be fabricated with unique morphologies and properties.

REFERENCES

- Z.L. Wang, Nanostructures of zinc oxide, Materials Today. 7 (2004)
 26–33. https://doi.org/10.1016/S1369-7021(04)00286-X.
- [2] Kumar M. (2016) Metal Oxide Nanostructures: Growth and Applications. In: Husain M., Khan Z. (eds) Advances in Nanomaterials. Advanced Structured Materials, vol 79. Springer (ISBN: 978-81-322-2668-0).
- [3] M. Li, J.C. Li, Size effects on the band-gap of semiconductor compounds, Materials Letters. 60 (2006) 2526–2529. https://doi.org/10.1016/j.matlet.2006.01.032.
- [4] N. Nasiri, R. Bo, F. Wang, L. Fu, A. Tricoli, Ultraporous Electron-Depleted ZnO Nanoparticle Networks for Highly Sensitive Portable Visible-Blind UV Photodetectors, Advanced Materials. 27 (2015) 4336–4343. https://doi.org/10.1002/adma.201501517.
- [5] M. Tiemann, Porous Metal Oxides as Gas Sensors, Chemistry A European Journal. 13 (2007) 8376–8388. https://doi.org/10.1002/chem.200700927.
- [6] J. Xu, Q. Pan, Ya Shun, Z. Tian, Grain size control and gas sensing properties of ZnO gas sensor. Sens. Actuators B: Chem. 66 (2000) 277– 279. https://doi.org/10.1016/S0925-4005(00)00381-6.
- [7] B.D. Boruah, Zinc oxide ultraviolet photodetectors: rapid progress from conventional to self-powered photodetectors, Nanoscale Advances. 1 (2019) 2059–2085. https://doi.org/10.1039/C9NA00130A.
- [8] C. Jagadish, S. Pearton, (2006) Zinc Oxide Bulk, Thin Films and Nanostructures, first ed, Elsevier Science, pp. 600 (ISBN 9780080464039).
- [9] Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, H. Morkoç, A comprehensive review of ZnO materials and devices, Journal of Applied Physics. 98 (2005) 041301. https://doi.org/10.1063/1.1992666.

- [10] D.M. Cruz, E. Mostafavi, A. Vernet-Crua, H. Barabadi, V. Shah, J.L. Cholula-Díaz, G. Guisbiers, T.J. Webster, Green nanotechnology-based zinc oxide (ZnO) nanomaterials for biomedical applications: a review, J. Phys. Mater. 3 (2020) 034005. https://doi.org/10.1088/2515-7639/ab8186.
- [11] P.-C. Chang, Z. Fan, C.-J. Chien, D. Stichtenoth, C. Ronning, J.G. Lu, High-performance ZnO nanowire field effect transistors, Appl. Phys. Lett. 89 (2006) 133113. https://doi.org/10.1063/1.2357013.
- [12] W.I. Park, J.S. Kim, G.-C. Yi, M.H. Bae, H.-J. Lee, Fabrication and electrical characteristics of high-performance ZnO nanorod field-effect transistors, Appl. Phys. Lett. 85 (2004) 5052–5054. https://doi.org/10.1063/1.1821648.
- [13] N. Pan, H. Xue, M. Yu, X. Cui, X. Wang, J.G. Hou, J. Huang, S.Z. Deng, Tip-morphology-dependent field emission from ZnO nanorod arrays, Nanotechnology. 21 (2010) 225707. https://doi.org/10.1088/0957-4484/21/22/225707.
- [14] Ü. Özgür, D. Hofstetter, H. Morkoç, ZnO Devices and Applications: A Review of Current Status and Future Prospects, Proceedings of the IEEE. 98 (2010) 1255–1268. https://doi.org/10.1109/JPROC.2010.2044550.
- [15] F.A. Selim, M.H. Weber, D. Solodovnikov, K.G. Lynn, Nature of Native Defects in ZnO, Phys. Rev. Lett. 99 (2007) 085502. https://doi.org/10.1103/PhysRevLett.99.085502.
- [16] A. Janotti, C.G.V. de Walle, Fundamentals of zinc oxide as a semiconductor, Rep. Prog. Phys. 72 (2009) 126501.
 https://doi.org/10.1088/0034-4885/72/12/126501.
- [17] J.C. Fan, K.M. Sreekanth, Z. Xie, S.L. Chang, K.V. Rao, p-Type ZnO materials: Theory, growth, properties and devices, Progress in Materials Science. 58 (2013) 874–985. https://doi.org/10.1016/j.pmatsci.2013.03.002.

- [18] C.H. Park, S.B. Zhang, S.-H. Wei, Origin of p-type doping difficulty in ZnO: The impurity perspective, Phys. Rev. B. 66 (2002) 073202. https://doi.org/10.1103/PhysRevB.66.073202.
- [19] T. Minami, Transparent conducting oxide semiconductors for transparent electrodes, Semicond. Sci. Technol. 20 (2005) S35–S44. https://doi.org/10.1088/0268-1242/20/4/004.
- [20] M.K. Roul, B. Obasogie, G. Kogo, J.R. Skuza, R.M. Mundle, A.K. Pradhan, Transparent and flexible heaters based on Al:ZnO degenerate semiconductor, Journal of Applied Physics. 122 (2017) 135110. https://doi.org/10.1063/1.4992007.
- [21] R.R. Reeber, Lattice parameters of ZnO from 4.2° to 296°K, Journal of Applied Physics. 41 (1970) 5063–5066. https://doi.org/10.1063/1.1658600.
- [22] B. Meyer, D. Marx, Density-functional study of the structure and stability of ZnO surfaces, Phys. Rev. B. 67 (2003) 035403. https://doi.org/10.1103/PhysRevB.67.035403.
- [23] T.C. Damen, S.P.S. Porto, B. Tell, Raman Effect in Zinc Oxide, Phys.
 Rev. 142 (1966) 570–574. https://doi.org/10.1103/PhysRev.142.570.
- [24] M. Šćepanović, M. Grujić-Brojčin, K. Vojisavljević, S. Bernik, T. Srećković, Raman study of structural disorder in ZnO nanopowders, Journal of Raman Spectroscopy. 41 (2010) 914–921. https://doi.org/10.1002/jrs.2546.
- [25] V. Russo, M. Ghidelli, P. Gondoni, C.S. Casari, A. Li Bassi, Multiwavelength Raman scattering of nanostructured Al-doped zinc oxide, Journal of Applied Physics. 115 (2014) 073508. https://doi.org/10.1063/1.4866322.
- [26] H.-Y. Shin, E.-L. Shim, Y.-J. Choi, J.-H. Park, S. Yoon, Giant enhancement of the Raman response due to one-dimensional ZnO nanostructures, Nanoscale. 6 (2014) 14622–14626. https://doi.org/10.1039/C4NR04527K.

- [27] W. Bludau, A. Onton, W. Heinke, Temperature dependence of the band gap of silicon, Journal of Applied Physics. 45 (1974) 1846–1848. https://doi.org/10.1063/1.1663501.
- [28] F. Roccaforte, P. Fiorenza, G. Greco, R. Lo Nigro, F. Giannazzo, F. Iucolano, M. Saggio, Emerging trends in wide band gap semiconductors (SiC and GaN) technology for power devices, Microelectronic Engineering. 187–188 (2018) 66–77. https://doi.org/10.1016/j.mee.2017.11.021.
- [29] W. Shan, W. Walukiewicz, J.W. Ager, K.M. Yu, H.B. Yuan, H.P. Xin, G. Cantwell, J.J. Song, Nature of room-temperature photoluminescence in ZnO, Appl. Phys. Lett. 86 (2005) 191911. https://doi.org/10.1063/1.1923757.
- [30] F. Oba, M. Choi, A. Togo, I. Tanaka, Point defects in ZnO: an approach from first principles, Sci. Technol. Adv. Mater. 12 (2011) 034302. https://doi.org/10.1088/1468-6996/12/3/034302.
- [31] A.B. Djurišić, Y.H. Leung, K.H. Tam, Y.F. Hsu, L. Ding, W.K. Ge, Y.C. Zhong, K.S. Wong, W.K. Chan, H.L. Tam, K.W. Cheah, W.M. Kwok, D.L. Phillips, Defect emissions in ZnO nanostructures, Nanotechnology. 18 (2007) 095702. https://doi.org/10.1088/0957-4484/18/9/095702.
- [32] C.H. Ahn, Y.Y. Kim, D.C. Kim, S.K. Mohanta, H.K. Cho, A comparative analysis of deep level emission in ZnO layers deposited by various methods, Journal of Applied Physics. 105 (2009) 013502. https://doi.org/10.1063/1.3054175.
- [33] L. Zhu, W. Zeng, Room-temperature gas sensing of ZnO-based gas sensor: A review, Sensors and Actuators A: Physical. 267 (2017) 242– 261. https://doi.org/10.1016/j.sna.2017.10.021.
- [34] P. Nunes, E. Fortunato, P. Tonello, F. Braz Fernandes, P. Vilarinho, R. Martins, Effect of different dopant elements on the properties of ZnO thin films, Vacuum. 64 (2002) 281–285. https://doi.org/10.1016/S0042-207X(01)00322-0.

- [35] H. Sato, T. Minami, S. Takata, Highly transparent and conductive group IV impurity-doped ZnO thin films prepared by radio frequency magnetron sputtering, Journal of Vacuum Science & Technology A. 11 (1993) 2975–2979. https://doi.org/10.1116/1.578678.
- [36] B.K. Meyer, J. Stehr, A. Hofstaetter, N. Volbers, A. Zeuner, J. Sann, On the role of group I elements in ZnO, Appl. Phys. A. 88 (2007) 119– 123. https://doi.org/10.1007/s00339-007-3962-4.
- [37] C.G. Jin, Y.Gao, X.M. Wu, M.L. Cui, L.J. Zhuge, Z.C. Chen, B. Hong, Structural and magnetic properties of transition metal doped ZnO films, Thin Solid Films. 518 (2010) 2152–2156. https://doi.org/10.1016/j.tsf.2009.09.047.
- [38] T. Hirate, T. Kimpara, S. Nakamura, T. Satoh, Control of diameter of ZnO nanorods grown by chemical vapor deposition with laser ablation of ZnO, Superlattices and Microstructures. 42 (2007) 409–414. https://doi.org/10.1016/j.spmi.2007.04.011.
- [39] G. Epurescu, G. Dinescu, A. Moldovan, R. Birjega, F. Dipietrantonio,
 E. Verona, P. Verardi, L.C. Nistor, C. Ghica, G. Van Tendeloo, M. Dinescu, p-type ZnO thin films grown by RF plasma beam assisted
 Pulsed Laser Deposition, Superlattices and Microstructures. 42 (2007) 79–84. https://doi.org/10.1016/j.spmi.2007.04.072.
- [40] H. Yamaguchi, T. Komiyama, M. Yamada, K. Sato, T. Aoyama, Fabrication of ZnO films by PLD method with bias voltage, Physica B: Condensed Matter. 401–402 (2007) 391–394. https://doi.org/10.1016/j.physb.2007.08.195.
- [41] K. Suzuki, M. Inoguchi, K. Kageyama, H. Takagi, Y. Sakabe, Wellcrystallized zinc oxide quantum dots with narrow size distribution, J Nanopart Res. 11 (2009) 1349–1360. https://doi.org/10.1007/s11051-008-9521-x.
- [42] M.T. Taschuk, M.M. Hawkeye, M.J. Brett (2010) Glancing Angle Deposition. In: P.M. Martin (ed.), Handbook of Deposition Technologies for Films and Coatings, 3rd edn. William Andrew

Publishing, Boston, pp. 621–678. https://doi.org/10.1016/B978-0-8155-2031-3.00013-2.

- [43] R. Eason, Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials, John Wiley & Sons, 2007.
- [44] K. Robbie, M.J. Brett, Sculptured thin films and glancing angle deposition: Growth mechanics and applications, Journal of Vacuum Science & Technology A. 15 (1997) 1460–1465. https://doi.org/10.1116/1.580562.
- [45] K. Robbie, J.C. Sit, M.J. Brett, Advanced techniques for glancing angle deposition, Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena. 16 (1998) 1115–1122. https://doi.org/10.1116/1.590019.
- [46] P.C.P. Hrudey, K.L. Westra, M.J. Brett, Highly Ordered Organic Alq3 Chiral Luminescent Thin Films Fabricated by Glancing-Angle Deposition, Advanced Materials. 18 (2006) 224–228. https://doi.org/10.1002/adma.200501714.
- [47] D. Vick, Y.Y. Tsui, M.J. Brett, R. Fedosejevs, Production of porous carbon thin films by pulsed laser deposition, Thin Solid Films. 350 (1999) 49–52. https://doi.org/10.1016/S0040-6090(99)00274-6.
- [48] M. Tyagi, M. Tomar, V. Gupta, Fabrication of an efficient GLADassisted p-NiO nanorod/n-ZnO thin film heterojunction UV photodiode, J. Mater. Chem. C. 2 (2014) 2387–2393. https://doi.org/10.1039/C3TC32030H.
- [49] Y.W. Sun, Y.Y. Tsui, Production of porous nanostructured zinc oxide thin films by pulsed laser deposition, Optical Materials. 29 (2007) 1111–1114. https://doi.org/10.1016/j.optmat.2006.05.011.
- [50] C. Buzea, K. Kaminska, G. Beydaghyan, T. Brown, C. Elliott, C. Dean, K. Robbie, Thickness and density evaluation for nanostructured thin films by glancing angle deposition, Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing,

Measurement, and Phenomena. 23 (2005) 2545–2552. https://doi.org/10.1116/1.2131079.

- [51] R. El Beainou, A. Chargui, P. Pedrosa, A. Mosset, S. Euphrasie, P. Vairac, N. Martin, Electrical resistivity and elastic wave propagation anisotropy in glancing angle deposited tungsten and gold thin films, Applied Surface Science. 475 (2019) 606–614. https://doi.org/10.1016/j.apsusc.2019.01.041.
- [52] K. Robbie, L.J. Friedrich, S.K. Dew, T. Smy, M.J. Brett, Fabrication of thin films with highly porous microstructures, Journal of Vacuum Science & Technology A. 13 (1995) 1032–1035. https://doi.org/10.1116/1.579579.
- [53] D.J. Poxson, F.W. Mont, M.F. Schubert, J.K. Kim, E.F. Schubert, Quantification of porosity and deposition rate of nanoporous films grown by oblique-angle deposition, Appl. Phys. Lett. 93 (2008) 101914. https://doi.org/10.1063/1.2981690.
- [54] A. Kołodziejczak-Radzimska, T. Jesionowski, Zinc Oxide—From Synthesis to Application: A Review, Materials. 7 (2014) 2833–2881. https://doi.org/10.3390/ma7042833.
- [55] K. Matsubara, P. Fons, K. Iwata, A. Yamada, K. Sakurai, H. Tampo, S. Niki, ZnO transparent conducting films deposited by pulsed laser deposition for solar cell applications, Thin Solid Films. 431–432 (2003) 369–372. https://doi.org/10.1016/S0040-6090(03)00243-8.
- [56] T. Premkumar, Y.S. Zhou, Y.F. Lu, K. Baskar, Optical and Field-Emission Properties of ZnO Nanostructures Deposited Using High-Pressure Pulsed Laser Deposition, ACS Appl. Mater. Interfaces. 2 (2010) 2863–2869. https://doi.org/10.1021/am100539q.
- [57] S. Dhara, P. Giri, Enhanced UV photosensitivity from rapid thermal annealed vertically aligned ZnO nanowires, Nanoscale Research Letters. 6 (2011) 504. https://doi.org/10.1186/1556-276X-6-504.

- [58] S. Chaudhary, A. Umar, K.K. Bhasin, S. Baskoutas, Chemical Sensing Applications of ZnO Nanomaterials, Materials (Basel). 11 (2018). https://doi.org/10.3390/ma11020287.
- [59] D.H. Zhang, Adsorption and photodesorption of oxygen on the surface and crystallite interfaces of sputtered ZnO films, Materials Chemistry and Physics. 45 (1996) 248–252. https://doi.org/10.1016/0254-0584(96)80115-5.
- [60] X.G. Zheng, Q.Sh. Li, J.P. Zhao, D. Chen, B. Zhao, Y.J. Yang, L.Ch. Zhang, Photoconductive ultraviolet detectors based on ZnO films, Applied Surface Science. 253 (2006) 2264–2267. https://doi.org/10.1016/j.apsusc.2006.04.031.
- [61] Z. Bai, X. Chen, X. Yan, X. Zheng, Z. Kang, Y. Zhang, Self-powered ultraviolet photodetectors based on selectively grown ZnO nanowire arrays with thermal tuning performance, Physical Chemistry Chemical Physics. 16 (2014) 9525–9529. https://doi.org/10.1039/C4CP00892H.
- [62] T.H. Flemban, M.A. Haque, I. Ajia, N. Alwadai, S. Mitra, T. Wu, I.S. Roqan, A Photodetector Based on p-Si/n-ZnO Nanotube Heterojunctions with High Ultraviolet Responsivity, ACS Appl. Mater. Interfaces. 9 (2017) 37120–37127. https://doi.org/10.1021/acsami.7b09645.
- [63] L. Zhu, Y. Li, W. Zeng, Hydrothermal synthesis of hierarchical flowerlike ZnO nanostructure and its enhanced ethanol gas-sensing properties, Applied Surface Science. 427 (2018) 281–287. https://doi.org/10.1016/j.apsusc.2017.08.229.
- [64] R. Nandi, S.K. Appani, S.S. Major, High resolution X-ray diffraction studies of epitaxial ZnO nanorods grown by reactive sputtering, Journal of Applied Physics. 121 (2017) 215306. https://doi.org/10.1063/1.4984935.
- [65] Q. Li, K. Gao, Z. Hu, W. Yu, N. Xu, J. Sun, J. Wu, Photoluminescence and Lasing Properties of Catalyst-Free ZnO Nanorod Arrays Fabricated

by Pulsed Laser Deposition, J. Phys. Chem. C. 116 (2012) 2330–2335. https://doi.org/10.1021/jp210377s.

- [66] T. Venkatesan, Pulsed laser deposition—invention or discovery?, J.
 Phys. D: Appl. Phys. 47 (2013) 034001. https://doi.org/10.1088/0022-3727/47/3/034001.
- [67] A.C. Levi, M. Kotrla, Theory and simulation of crystal growth, J.
 Phys.: Condens. Matter. 9 (1997) 299–344. https://doi.org/10.1088/0953-8984/9/2/001.
- [68] J. Song, S. Lim, Effect of Seed Layer on the Growth of ZnO Nanorods,
 J. Phys. Chem. C. 111 (2007) 596–600. https://doi.org/10.1021/jp0655017.
- [69] M.O. Jensen, M.J. Brett, Periodically structured glancing angle deposition thin films, IEEE Transactions on Nanotechnology. 4 (2005) 269–277. https://doi.org/10.1109/TNANO.2004.842061.
- [70] C. Kittel, (2004) Introduction to Solid State Physics, 8th ed. Wiley (ISBN: 978-0-471-41526-8).
- [71] W.M. Saslow, (2002) Electricity, Magnetism, and Light, 1st ed. Elsevier, pp. 800 (ISBN: 9780080505213).
- [72] D.F. Swinehart, The Beer-Lambert Law, J. Chem. Educ. 39 (1962) 333. https://doi.org/10.1021/ed039p333.
- [73] Y.H. Ko, G. Nagaraju, J.S. Yu, Fabrication and Optimization of Vertically Aligned ZnO Nanorod Array-Based UV Photodetectors via Selective Hydrothermal Synthesis, Nanoscale Research Letters. 10 (2015) 323. https://doi.org/10.1186/s11671-015-1032-y.
- [74] Y. Ning, Z. Zhang, F. Teng, X. Fang, Novel Transparent and Self-Powered UV Photodetector Based on Crossed ZnO Nanofiber Array Homojunction, Small. 14 (2018). https://doi.org/10.1002/smll.201703754.
- [75] S.H. Ko, D. Lee, H.W. Kang, K.H. Nam, J.Y. Yeo, S.J. Hong, C.P. Grigoropoulos, H.J. Sung, Nanoforest of Hydrothermally Grown Hierarchical ZnO Nanowires for a High Efficiency Dye-Sensitized

Solar Cell, Nano Lett. 11 (2011) 666–671. https://doi.org/10.1021/nl1037962.

- [76] X.-Y. Liu, C.-X. Shan, S.-P. Wang, H.-F. Zhao, D.-Z. Shen, Intense emission from ZnO nanocolumn Schottky diodes, Nanoscale. 5 (2013) 7746–7749. https://doi.org/10.1039/C3NR02263C.
- [77] B. Liu, C. Feng, X. Zhang, L. Zhu, X. Wang, G. Zhang, D. Xu, Seedless growth of ZnO nanorods on TiO 2 fibers by chemical bath deposition, CrystEngComm. 18 (2016) 1215–1222. https://doi.org/10.1039/C5CE01866H.
- [78] C.C. Weigand, M.R. Bergren, C. Ladam, J. Tveit, R. Holmestad, P.E. Vullum, J.C. Walmsley, Ø. Dahl, T.E. Furtak, R.T. Collins, J. Grepstad, H. Weman, Formation of ZnO Nanosheets Grown by Catalyst-Assisted Pulsed Laser Deposition, Crystal Growth & Design. 11 (2011) 5298–5304. https://doi.org/10.1021/cg2013073.
- [79] B. El Zein, S. Boulfrad, G.E. Jabbour, E. Dogheche, Parametric study of self-forming ZnO Nanowall network with honeycomb structure by Pulsed Laser Deposition, Applied Surface Science. 292 (2014) 598– 607. https://doi.org/10.1016/j.apsusc.2013.12.014.
- [80] A. Shkurmanov, C. Sturm, H. Franke, J. Lenzner, M. Grundmann, Low-Temperature PLD-Growth of Ultrathin ZnO Nanowires by Using ZnxAl1-xO and ZnxGa1-xO Seed Layers, Nanoscale Res Lett. 12 (2017). https://doi.org/10.1186/s11671-017-1906-2.
- [81] Y. Peng, G. Wang, C. Yuan, J. He, S. Ye, X. Luo, Influences of oxygen vacancies on the enhanced nonlinear optical properties of confined ZnO quantum dots, Journal of Alloys and Compounds. 739 (2018) 345–352. https://doi.org/10.1016/j.jallcom.2017.12.250.
- [82] S.N. Das, K.-J. Moon, J.P. Kar, J.-H. Choi, J. Xiong, T.I. Lee, J.-M. Myoung, ZnO single nanowire-based UV detectors, Appl. Phys. Lett. 97 (2010) 022103. https://doi.org/10.1063/1.3464287.
- [83] M. Masłyk, M.A. Borysiewicz, M. Wzorek, T. Wojciechowski, M. Kwoka, E. Kamińska, Influence of absolute argon and oxygen flow

values at a constant ratio on the growth of Zn/ZnO nanostructures obtained by DC reactive magnetron sputtering, Applied Surface Science. 389 (2016) 287–293. https://doi.org/10.1016/j.apsusc.2016.07.098.

- [84] P. Shankar, J.B. Balaguru Rayappan, Electrospun tailored ZnO nanostructures – role of chloride ions, RSC Advances. 5 (2015) 85363– 85372. https://doi.org/10.1039/C5RA15697A.
- [85] Y.-J. Liu, H.-D. Zhang, J. Zhang, S. Li, J.-C. Zhang, J.-W. Zhu, M.-G. Gong, X.-X. Wang, Y.-Z. Long, Effects of Ce doping and humidity on UV sensing properties of electrospun ZnO nanofibers, Journal of Applied Physics. 122 (2017) 105102. https://doi.org/10.1063/1.5000443.
- [86] J.H. Noh, J.H. Park, H.S. Han, D.H. Kim, B.S. Han, S. Lee, J.Y. Kim, H.S. Jung, K.S. Hong, Aligned Photoelectrodes with Large Surface Area Prepared by Pulsed Laser Deposition, J. Phys. Chem. C. 116 (2012) 8102–8110. https://doi.org/10.1021/jp211233s.
- [87] S. Inguva, S.K. Marka, R.K. Vijayaraghavan, E. McGlynn, V.V.S.S. Srikanth, J.-P. Mosnier, Crystalline ZnO/Amorphous ZnO Core/Shell Nanorods: Self-Organized Growth, Structure, and Novel Luminescence, J. Phys. Chem. C. 119 (2015) 4848–4855. https://doi.org/10.1021/jp511783c.
- [88] R. Mannam, E.S. Kumar, D.M. Priyadarshini, F. Bellarmine, N. DasGupta, M.S. Ramachandra Rao, Enhanced photoluminescence and heterojunction characteristics of pulsed laser deposited ZnO nanostructures, Applied Surface Science. 418 (2017) 335–339. https://doi.org/10.1016/j.apsusc.2017.01.029.
- [89] M. Ladanov, M.K. Ram, G. Matthews, A. Kumar, Structure and Optoelectrochemical Properties of ZnO Nanowires Grown on n-Si Substrate, Langmuir. 27 (2011) 9012–9017. https://doi.org/10.1021/la200584j.
- [90] Y. Zhang, M.K. Ram, E.K. Stefanakos, D.Y. Goswami, Synthesis, Characterization, and Applications of ZnO Nanowires, Journal of

 Nanomaterials.
 2012
 (2012)
 e624520.

 https://doi.org/10.1155/2012/624520.

- [91] C. Li, G. Fang, Q. Fu, F. Su, G. Li, X. Wu, X. Zhao, Effect of substrate temperature on the growth and photoluminescence properties of vertically aligned ZnO nanostructures, Journal of Crystal Growth. 292 (2006) 19–25. https://doi.org/10.1016/j.jcrysgro.2006.03.061.
- [92] A. Mortezaali, R. Moradi, The correlation between the substrate temperature and morphological ZnO nanostructures for H2S gas sensors, Sensors and Actuators A: Physical. 206 (2014) 30–34. https://doi.org/10.1016/j.sna.2013.11.027.
- [93] P. Ghosh, A.K. Sharma, Effect of substrate temperature on the growth of pulsed-laser deposited ZnO nanostructures, Appl. Phys. A. 116 (2014) 1877–1884. https://doi.org/10.1007/s00339-014-8347-x.
- [94] R. Sivakumar, T. Tsunoda, Y. Kuroki, T. Okamoto, M. Takata, ZnO nanowire growth by electric current heating method: A study on the effect of substrate temperature, Materials Chemistry and Physics. 134 (2012) 345–349. https://doi.org/10.1016/j.matchemphys.2012.02.075.
- [95] P. Gondoni, M. Ghidelli, F.D. Fonzo, M. Carminati, V. Russo, A.L. Bassi, C.S. Casari, Structure-dependent optical and electrical transport properties of nanostructured Al-doped ZnO, Nanotechnology. 23 (2012) 365706. https://doi.org/10.1088/0957-4484/23/36/365706.
- [96] P. Gondoni, M. Ghidelli, F. Di Fonzo, V. Russo, P. Bruno, J. Martí-Rujas, C.E. Bottani, A. Li Bassi, C.S. Casari, Structural and functional properties of Al:ZnO thin films grown by Pulsed Laser Deposition at room temperature, Thin Solid Films. 520 (2012) 4707–4711. https://doi.org/10.1016/j.tsf.2011.10.072.
- [97] Q. Ruan, J. Ye, D.-J. Shu, M. Wang, Influence of oxygen partial pressure on the adsorption and diffusion during oxide growth: ZnO(0001) surface, Phys. Rev. B. 96 (2017) 115412. https://doi.org/10.1103/PhysRevB.96.115412.

- [98] S. Choopun, H. Tabata, T. Kawai, Self-assembly ZnO nanorods by pulsed laser deposition under argon atmosphere, Journal of Crystal Growth. 274 (2005) 167–172. https://doi.org/10.1016/j.jcrysgro.2004.10.017.
- [99] X. Peng, B. Yang, J. Chu, P. Feng, Effects of nitrogen pressure during pulsed laser deposition on morphology and optical properties of Ndoped ZnO nanostructures, Surface Science. 609 (2013) 48–52. https://doi.org/10.1016/j.susc.2012.11.002.
- [100] R. O'Haire, E. McGlynn, M.O. Henry, J.-P. Mosnier, ZnO nanostructured thin films grown by pulsed laser deposition in mixed O2 / Ar background gas, Superlattices and Microstructures. 42 (2007) 468– 472. https://doi.org/10.1016/j.spmi.2007.04.020.
- [101] A. Klamchuen, T. Yanagida, M. Kanai, K. Nagashima, K. Oka, T. Kawai, M. Suzuki, Y. Hidaka, S. Kai, Role of surrounding oxygen on oxide nanowire growth, Appl. Phys. Lett. 97 (2010) 073114. https://doi.org/10.1063/1.3474605.
- [102] V. Gupta, K. Sreenivas (2006) Pulsed Laser Deposition of Zinc Oxide (ZnO). In: C. Jagadish, S. Pearton (Eds.), Zinc Oxide Bulk, Thin Films and Nanostructures, Elsevier Science Ltd, Oxford, pp. 85–174. https://doi.org/10.1016/B978-008044722-3/50004-X.
- [103] J. Tauc, R. Grigorovici, A. Vancu, Optical Properties and Electronic Structure of Amorphous Germanium, Physica Status Solidi (b). 15
 (1966) 627–637. https://doi.org/10.1002/pssb.19660150224.
- [104] B.D. Viezbicke, S. Patel, B.E. Davis, D.P. Birnie, Evaluation of the Tauc method for optical absorption edge determination: ZnO thin films as a model system, Physica Status Solidi (b). 252 (2015) 1700–1710. https://doi.org/10.1002/pssb.201552007.
- [105] K. Davis, R. Yarbrough, M. Froeschle, J. White, H. Rathnayake, Band gap engineered zinc oxide nanostructures via a sol–gel synthesis of solvent driven shape-controlled crystal growth, RSC Adv. 9 (2019) 14638–14648. https://doi.org/10.1039/C9RA02091H.

- [106] M.K. Kavitha, P. Gopinath, H. John, Reduced graphene oxide–ZnO self-assembled films: tailoring the visible light photoconductivity by the intrinsic defect states in ZnO, Phys. Chem. Chem. Phys. 17 (2015) 14647–14655. https://doi.org/10.1039/C5CP01318F.
- [107] M.D. McCluskey, S.J. Jokela, Defects in ZnO, Journal of Applied Physics. 106 (2009) 071101. https://doi.org/10.1063/1.3216464.
- [108] D.A. Melnick, Zinc Oxide Photoconduction, an Oxygen Adsorption Process, J. Chem. Phys. 26 (1957) 1136–1146. https://doi.org/10.1063/1.1743483.
- [109] D. Guo, Z. Wu, P. Li, Y. An, H. Liu, X. Guo, H. Yan, G. Wang, C. Sun, L. Li, W. Tang, Fabrication of β-Ga₂O₃ thin films and solar-blind photodetectors by laser MBE technology, Opt. Mater. Express, OME. 4 (2014) 1067–1076. https://doi.org/10.1364/OME.4.001067.
- [110] M.A. Desai, S.D. Sartale, Facile Soft Solution Route To Engineer Hierarchical Morphologies of ZnO Nanostructures, Crystal Growth & Design. 15 (2015) 4813–4820. https://doi.org/10.1021/acs.cgd.5b00561.
- [111] Z. Yi, J. Luo, X. Ye, Y. Yi, J. Huang, Y. Yi, T. Duan, W. Zhang, Y. Tang, Effect of synthesis conditions on the growth of various ZnO nanostructures and corresponding morphology-dependent photocatalytic activities, Superlattices and Microstructures. 100 (2016) 907–917. https://doi.org/10.1016/j.spmi.2016.10.049.
- [112] F.N. Jiménez-García, C.L. Londoño-Calderón, D.G. Espinosa-Arbeláez, A. Del Real, M.E. Rodríguez-García, Influence of substrate on structural, morphological and optical properties of ZnO films grown by SILAR method, Bull Mater Sci. 37 (2014) 1283–1291. https://doi.org/10.1007/s12034-014-0073-7.
- [113] A. Echresh, M. Zargar Shoushtari, M. Farbod, Effect of growth angle and post-growth annealing on the structural and optical properties of ZnO nanorods grown hydrothermally on p-Si substrate, Materials

Letters. 110 (2013) 164–167. https://doi.org/10.1016/j.matlet.2013.08.020.

- [114] S. Bang, S. Lee, Y. Ko, J. Park, S. Shin, H. Seo, H. Jeon, Photocurrent detection of chemically tuned hierarchical ZnO nanostructures grown on seed layers formed by atomic layer deposition, Nanoscale Res Lett. 7 (2012) 290. https://doi.org/10.1186/1556-276X-7-290.
- [115] A. Mohanta, R.K. Thareja, Photoluminescence study of ZnO nanowires grown by thermal evaporation on pulsed laser deposited ZnO buffer layer, Journal of Applied Physics. 104 (2008) 044906. https://doi.org/10.1063/1.2969908.
- [116] R. Jenkins, R. L. Snyder, (1996) Introduction to X-Ray Powder Diffractometry, 1st ed. Wiley, (ISBN: 0471513393).
- [117] R. Cuscó, E. Alarcón-Lladó, J. Ibáñez, L. Artús, J. Jiménez, B. Wang, M.J. Callahan, Temperature dependence of Raman scattering in ZnO, Phys. Rev. B. 75 (2007) 165202.
 https://doi.org/10.1103/PhysRevB.75.165202.
- [118] D. Hardcastle, I.E. Wachs, Raman spectroscopy of chromium oxide supported on Al2O3, TiO2 and SiO2: A comparative study, Journal of Molecular Catalysis. 46 (1988) 173-186.
- [119] S. Benramache, A. Rahal, B. Benhaoua, The effects of solvent nature on spray-deposited ZnO thin film prepared from Zn (CH3COO)2, 2H2O, Optik. 125 (2014) 663–666. https://doi.org/10.1016/j.ijleo.2013.07.085.
- [120] J. Duraimurugan, G.S. Kumar, M. Venkatesh, P. Maadeswaran, E.K. Girija, Morphology and size controlled synthesis of zinc oxide nanostructures and their optical properties, J Mater Sci: Mater Electron. 29 (2018) 9339–9346. https://doi.org/10.1007/s10854-018-8964-9.
- [121] B.S. Mwankemwa, S. Akinkuade, K. Maabong, J.M. Nel, M. Diale, Effects of surface morphology on the optical and electrical properties of Schottky diodes of CBD deposited ZnO nanostructures, Physica B:

Condensed Matter. 535 (2018) 175–180. https://doi.org/10.1016/j.physb.2017.07.030.

- [122] R. Vinodkumar, I. Navas, K. Porsezian, V. Ganesan, N.V. Unnikrishnan, V.P. Mahadevan Pillai, Structural, spectroscopic and electrical studies of nanostructured porous ZnO thin films prepared by pulsed laser deposition, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 118 (2014) 724–732. https://doi.org/10.1016/j.saa.2013.08.090.
- [123] W.S. Shi, B. Cheng, L. Zhang, E.T. Samulski, Influence of excitation density on photoluminescence of zinc oxide with different morphologies and dimensions, Journal of Applied Physics. 98 (2005) 083502. https://doi.org/10.1063/1.2089160.
- [124] A. Wei, L. Pan, W. Huang, Recent progress in the ZnO nanostructurebased sensors, Materials Science and Engineering: B. 176 (2011) 1409– 1421. https://doi.org/10.1016/j.mseb.2011.09.005.
- [125] H. Jin, Y. Li, J. Li, C. Gu, Field emission from ZnO nanostructures with different morphologies, Microelectronic Engineering. 86 (2009) 1159–1161. https://doi.org/10.1016/j.mee.2009.02.005.
- [126] C.-L. Hsu, S.-J. Chang, Doped ZnO 1D Nanostructures: Synthesis, Properties, and Photodetector Application, Small. 10 (2014) 4562– 4585. https://doi.org/10.1002/smll.201401580.
- [127] A. Bera, D. Basak, Photoluminescence and Photoconductivity of ZnS-Coated ZnO Nanowires, ACS Appl. Mater. Interfaces. 2 (2010) 408–412. https://doi.org/10.1021/am900686c.
- [128] S.-H. Tsai, S. Basu, C.-Y. Huang, L.-C. Hsu, Y.-G. Lin, R.-H. Horng, Deep-Ultraviolet Photodetectors Based on Epitaxial ZnGa2O4 Thin Films, Sci Rep. 8 (2018) 14056. https://doi.org/10.1038/s41598-018-32412-3.
- [129] R.S. Ganesh, E. Durgadevi, M. Navaneethan, V.L. Patil, S. Ponnusamy, C. Muthamizhchelvan, S. Kawasaki, P.S. Patil, Y. Hayakawa, Controlled synthesis of Ni-doped ZnO hexagonal

microdiscs and their gas sensing properties at low temperature, Chemical Physics Letters. 689 (2017) 92–99. https://doi.org/10.1016/j.cplett.2017.09.057.

- [130] R.S. Ganesh, E. Durgadevi, M. Navaneethan, V.L. Patil, S. Ponnusamy, C. Muthamizhchelvan, S. Kawasaki, P.S. Patil, Y. Hayakawa, Tuning the selectivity of NH3 gas sensing response using Cu-doped ZnO nanostructures, Sensors and Actuators A: Physical. 269 (2018) 331–341. https://doi.org/10.1016/j.sna.2017.11.042.
- [131] Z. El khalidi, E. Comini, B. Hartiti, A. Moumen, H.M.M. Munasinghe Arachchige, S. Fadili, P. Thevenin, A. Kamal, Effect of vanadium doping on ZnO sensing properties synthesized by spray pyrolysis, Materials & Design. 139 (2018) 56–64. https://doi.org/10.1016/j.matdes.2017.10.074.
- [132] F. Pavón, A. Urbieta, P. Fernández, Luminescence and light guiding properties of Er and Li codoped ZnO nanostructures, Journal of Luminescence. 195 (2018) 396–401. https://doi.org/10.1016/j.jlumin.2017.11.059.
- [133] M. Gabás, P. Díaz-Carrasco, F. Agulló-Rueda, P. Herrero, A.R. Landa-Cánovas, J.R. Ramos-Barrado, High quality ZnO and Ga:ZnO thin films grown onto crystalline Si (100) by RF magnetron sputtering, Solar Energy Materials and Solar Cells. 95 (2011) 2327–2334. https://doi.org/10.1016/j.solmat.2011.04.001.
- [134] Y.-H. Liu, S.-J. Young, L.-W. Ji, S.-J. Chang, Enhanced Field Emission Properties of Ga-Doped ZnO Nanosheets by using an Aqueous Solution at Room Temperature, IEEE Transactions on Electron Devices. 61 (2014) 4192–4196. https://doi.org/10.1109/TED.2014.2362134.
- [135] S.-J. Young, C.-L. Chiou, Synthesis and optoelectronic properties of Ga-doped ZnO nanorods by hydrothermal method, Microsyst Technol. 24 (2018) 103–107. https://doi.org/10.1007/s00542-016-3183-x.

- [136] Y.-H. Liu, S.-J. Young, L.-W. Ji, S.-J. Chang, Ga-Doped ZnO Nanosheet Structure-Based Ultraviolet Photodetector by Low-Temperature Aqueous Solution Method, IEEE Transactions on Electron Devices. 62 (2015) 2924–2927. https://doi.org/10.1109/TED.2015.2457441.
- [137] S.-J. Young, Y.-H. Liu, Ultraviolet photodetectors with Ga-doped ZnO nanosheets structure, Microelectronic Engineering. 148 (2015) 14–16. https://doi.org/10.1016/j.mee.2015.07.009.
- [138] H.-M. Chiu, J.-M. Wu, Opto-electrical properties and chemisorption reactivity of Ga-doped ZnO nanopagodas, J. Mater. Chem. A. 1 (2013) 5524–5534. https://doi.org/10.1039/C3TA01209C.
- [139] M. Razeghi, Short-wavelength solar-blind detectors-status, prospects, and markets, Proceedings of the IEEE. 90 (2002) 1006–1014. https://doi.org/10.1109/JPROC.2002.1021565.
- [140] R. Khokhra, B. Bharti, H.-N. Lee, R. Kumar, Visible and UV photodetection in ZnO nanostructured thin films via simple tuning of solution method, Scientific Reports. 7 (2017) 15032. https://doi.org/10.1038/s41598-017-15125-x.
- [141] Y.-J. Liu, H.-D. Zhang, X. Yan, A.-J. Zhao, Z.-G. Zhang, W.-Y. Si, M.-G. Gong, J.-C. Zhang, Y.-Z. Long, Effect of Ce doping on the optoelectronic and sensing properties of electrospun ZnO nanofibers, RSC Adv. 6 (2016) 85727–85734. https://doi.org/10.1039/C6RA16491A.
- [142] S. Horzum, F. Iyikanat, R.T. Senger, C. Çelebi, M. Sbeta, A. Yildiz, T. Serin, Monitoring the characteristic properties of Ga-doped ZnO by Raman spectroscopy and atomic scale calculations, Journal of Molecular Structure. 1180 (2019) 505–511. https://doi.org/10.1016/j.molstruc.2018.11.064.
- [143] A. Escobedo-Morales, U. Pal, Defect annihilation and morphological improvement of hydrothermally grown ZnO nanorods by Ga doping, Appl. Phys. Lett. 93 (2008) 193120. https://doi.org/10.1063/1.3026746.
- [144] B. Chouchene, T.B. Chaabane, K. Mozet, E. Girot, S. Corbel, L. Balan, G. Medjahdi, R. Schneider, Porous Al-doped ZnO rods with selective adsorption properties, Applied Surface Science. 409 (2017) 102–110. https://doi.org/10.1016/j.apsusc.2017.03.018.
- [145] H. Usui, Y. Shimizu, T. Sasaki, N. Koshizaki, Photoluminescence of ZnO Nanoparticles Prepared by Laser Ablation in Different Surfactant Solutions, J. Phys. Chem. B. 109 (2005) 120–124. https://doi.org/10.1021/jp046747j.
- [146] A.M. Bazargan, F. Sharif, S. Mazinani, N. Naderi, High-performance transparent ultraviolet photodetector based on thermally reduced graphene oxide and ZnO thin films, J Mater Sci: Mater Electron. 28 (2017) 11108–11113. https://doi.org/10.1007/s10854-017-6896-4.
- [147] F. Zahedi, R.S. Dariani, S.M. Rozati, Structural, Optical and Electrical Properties of ZnO Thin Films Prepared by Spray Pyrolysis: Effect of Precursor Concentration, Bull Mater Sci. 37 (2014) 433–439. https://doi.org/10.1007/s12034-014-0696-8.
- [148] S. Mridha, D. Basak, Thickness dependent photoconducting properties of ZnO films, Chemical Physics Letters. 427 (2006) 62–66. https://doi.org/10.1016/j.cplett.2006.06.022.
- [149] S. Mridha, D. Basak, Effect of thickness on the structural, electrical and optical properties of ZnO films, Materials Research Bulletin. 42 (2007) 875–882. https://doi.org/10.1016/j.materresbull.2006.08.019.
- [150] K. L, A. M v, P.K. Basu, Microwave assisted synthesis of ZnO and Pd-ZnO nanospheres for UV photodetector, Sensors and Actuators A: Physical. 264 (2017) 90–95. https://doi.org/10.1016/j.sna.2017.06.013.
- [151] E. Wongrat, N. Chanlek, C. Chueaiarrom, B. Samransuksamer, N. Hongsith, S. Choopun, Low temperature ethanol response enhancement of ZnO nanostructures sensor decorated with gold nanoparticles exposed to UV illumination, Sensors and Actuators A: Physical. 251 (2016) 188–197. https://doi.org/10.1016/j.sna.2016.10.022.

- [152] K. Singh, I. Rawal, R. Punia, R. Dhar, X-ray photoelectron spectroscopy investigations of band offsets in Ga 0.02 Zn 0.98 O/ZnO heterojunction for UV photodetectors, Journal of Applied Physics. 122 (2017) 155301. https://doi.org/10.1063/1.4990757.
- [153] V.S. Rana, J.K. Rajput, T.K. Pathak, L.P. Purohit, Multilayer MgZnO/ZnO thin films for UV photodetectors, Journal of Alloys and Compounds. 764 (2018) 724–729. https://doi.org/10.1016/j.jallcom.2018.06.139.
- [154] H. Zhou, G.-J. Fang, N. Liu, X.-Z. Zhao, Effects of thermal annealing on the performance of Al/ZnO nanorods/Pt structure ultraviolet photodetector, Materials Science and Engineering: B. 176 (2011) 740– 744. https://doi.org/10.1016/j.mseb.2011.03.003.
- [155] W. Lin, X. Yan, X. Zhang, Z. Qin, Z. Zhang, Z. Bai, Y. Lei, Y. Zhang, The comparison of ZnO nanowire detectors working under two wavelengths of ultraviolet, Solid State Communications. 151 (2011) 1860–1863. https://doi.org/10.1016/j.ssc.2011.10.010.
- [156] S.K. Panda, C. Jacob, Preparation of transparent ZnO thin films and their application in UV sensor devices, Solid-State Electronics. 73 (2012) 44–50. https://doi.org/10.1016/j.sse.2012.03.004.
- [157] L.J. Mandalapu, F.X. Xiu, Z. Yang, J.L. Liu, Ultraviolet photoconductive detectors based on Ga-doped ZnO films grown by molecular-beam epitaxy, Solid-State Electronics. 51 (2007) 1014– 1017. https://doi.org/10.1016/j.sse.2007.05.009.
- [158] Z. Song, H. Zhou, C. Ye, L. Yang, M. Xue, J. Mei, H. Wang, Surface treatment for Schottky barrier photodetector based on Au/GaZnO nanorods/Au structure, Materials Science in Semiconductor Processing. 64 (2017) 101–108. https://doi.org/10.1016/j.mssp.2017.03.023.
- [159] G.Y. Chai, L. Chow, O. Lupan, E. Rusu, G.I. Stratan, H. Heinrich, V.V. Ursaki, I.M. Tiginyanu, Fabrication and characterization of an individual ZnO microwire-based UV photodetector, Solid State

 Sciences.
 13
 (2011)
 1205–1210.

 https://doi.org/10.1016/j.solidstatesciences.2011.01.010.

- [160] S. Singh, Y. Kumar, H. Kumar, S. Vyas, C. Periasamy, P. Chakrabarti, S. Jit, S.-H. Park, A study of hydrothermally grown ZnO nanorod-based metal-semiconductor-metal UV detectors on glass substrates, Nanomaterials and Nanotechnology. 7 (2017) 1847980417702144. https://doi.org/10.1177/1847980417702144.
- [161] M. Breedon, M.J.S. Spencer, I. Yarovsky, Adsorption of atomic nitrogen and oxygen on ZnO (2110) surface: a density functional theory study, J. Phys.: Condens. Matter. 21 (2009) 144208. https://doi.org/10.1088/0953-8984/21/14/144208.
- [162] J. Bao, I. Shalish, Z. Su, R. Gurwitz, F. Capasso, X. Wang, Z. Ren, Photoinduced oxygen release and persistent photoconductivity in ZnO nanowires, Nanoscale Res Lett. 6 (2011) 404. https://doi.org/10.1186/1556-276X-6-404.
- [163] H. Gupta, J. Singh, R. N. Dutt, S. Ojha, S. Kar, R. Kumar, V. R. Reddy, F. Singh, Defect-induced photoluminescence from galliumdoped zinc oxide thin films: influence of doping and energetic ion irradiation, Physical Chemistry Chemical Physics. 21 (2019) 15019– 15029. https://doi.org/10.1039/C9CP02148E.
- [164] S.-J. Young, C.-C. Yang, L.-T. Lai, Review—Growth of Al-, Ga-, and In-Doped ZnO Nanostructures via a Low-Temperature Process and Their Application to Field Emission Devices and Ultraviolet Photosensors, J. Electrochem. Soc. 164 (2017) B3013–B3028. https://doi.org/10.1149/2.0051705jes.
- [165] A. Katoch, J.-H. Kim, Y.J. Kwon, H.W. Kim, S.S. Kim, Bifunctional Sensing Mechanism of SnO2–ZnO Composite Nanofibers for Drastically Enhancing the Sensing Behavior in H2 Gas, ACS Appl. Mater. Interfaces. 7 (2015) 11351–11358. https://doi.org/10.1021/acsami.5b01817.

- [166] C.T. Quy, N.X. Thai, N.D. Hoa, D.T.T. Le, C.M. Hung, N.V. Duy, N.V. Hieu, C2H5OH and NO2 sensing properties of ZnO nanostructures: correlation between crystal size, defect level and sensing performance, RSC Adv. 8 (2018) 5629–5639. https://doi.org/10.1039/C7RA13702H.
- [167] R.T. Candidato, J.P. Ontolan, P. Carpio, L. Pawłowski, R.M. Vequizo, Effects of precursor composition used in solution precursor plasma spray on the properties of ZnO coatings for CO2 and UV light sensing, Surface and Coatings Technology. 371 (2019) 395–400. https://doi.org/10.1016/j.surfcoat.2018.10.009.
- [168] P.-N. Ni, C.-X. Shan, S.-P. Wang, B.-H. Li, Z.-Z. Zhang, D.-X. Zhao, L. Liu, D.-Z. Shen, Enhanced Responsivity of Highly Spectrum-Selective Ultraviolet Photodetectors, J. Phys. Chem. C. 116 (2012) 1350–1353. https://doi.org/10.1021/jp210994t.
- [169] M. Guo, P. Diao, S. Cai, Hydrothermal growth of well-aligned ZnO nanorod arrays: Dependence of morphology and alignment ordering upon preparing conditions, Journal of Solid State Chemistry. 178 (2005) 1864–1873. https://doi.org/10.1016/j.jssc.2005.03.031.
- [170] A. Soni, K.R. Mavani, Controlling porosity and ultraviolet photoresponse of crystallographically oriented ZnO nanostructures grown by pulsed laser deposition, Scripta Materialia. 162 (2019) 24– 27. https://doi.org/10.1016/j.scriptamat.2018.10.026.
- [171] A. Soni, K. Mulchandani, K.R. Mavani, Crystallographically oriented porous ZnO nanostructures with visible-blind photoresponse: Controlling the growth and optical properties, Materialia. 6 (2019) 100326. https://doi.org/10.1016/j.mtla.2019.100326.
- [172] J. Yang, J. Zheng, H. Zhai, X. Yang, L. Yang, Y. Liu, J. Lang, M. Gao, Oriented growth of ZnO nanostructures on different substrates via a hydrothermal method, Journal of Alloys and Compounds. 489 (2010) 51–55. https://doi.org/10.1016/j.jallcom.2009.08.159.

- [173] G. Fiaschi, S. Mirabella, G. Franzò, L. Maiolo, A. Chitu, Y. Komem,
 Y. Shacham-Diamand, Effect of laser annealing on ZnO nanorods grown by chemical bath deposition on flexible substrate, Applied Surface Science. 458 (2018) 800–804. https://doi.org/10.1016/j.apsusc.2018.07.092.
- [174] A. Soni, K. Mulchandani, K.R. Mavani, Ultraviolet photo response of crystallographically oriented nanostructured thin films of ZnO grown by pulsed laser deposition, AIP Conference Proceedings. 2100 (2019) 020077. https://doi.org/10.1063/1.5098631.
- [175] S. Baruah, J. Dutta, Hydrothermal growth of ZnO nanostructures, Science and Technology of Advanced Materials. 10 (2009) 013001. https://doi.org/10.1088/1468-6996/10/1/013001.
- [176] M. Nistor, N.B. Mandache, J. Perrière, C. Hebert, F. Gherendi, W. Seiler, Growth, structural and electrical properties of polar ZnO thin films on MgO (100) substrates, Thin Solid Films. 519 (2011) 3959–3964. https://doi.org/10.1016/j.tsf.2011.01.266.
- [177] Y.-C. Liang, C.-Y. Hu, H. Zhong, Effects of ultrathin layers on the growth of vertically aligned wurtzite ZnO nanostructures on perovskite single-crystal substrates, Applied Surface Science. 261 (2012) 633– 639. https://doi.org/10.1016/j.apsusc.2012.08.072.
- [178] T. Cossuet, H. Roussel, J.-M. Chauveau, O. Chaix-Pluchery, J.-L. Thomassin, E. Appert, V. Consonni, Well-ordered ZnO nanowires with controllable inclination on semipolar ZnO surfaces by chemical bath deposition, Nanotechnology. 29 (2018) 475601. https://doi.org/10.1088/1361-6528/aadf62.
- [179] A. Soni, K. Mulchandani, K.R. Mavani, UV activated visible-blind Ga:ZnO photodetectors using the GLAD technique: a comparative study in different gas atmospheres and temperatures, J. Mater. Chem. C. 8 (2020) 7837–7846. https://doi.org/10.1039/D0TC00990C.
- [180] Z. Cao, Y. Wang, Z. Li, N. Yu, Hydrothermal Synthesis of ZnO Structures Formed by High-Aspect-Ratio Nanowires for Acetone

Detection, Nanoscale Research Letters. 11 (2016) 347. https://doi.org/10.1186/s11671-016-1563-x.

- [181] W. Li, Y. Sun, J. Xu, Controllable Hydrothermal Synthesis and Properties of ZnO Hierarchical Micro/Nanostructures, Nano-Micro Lett. 4 (2012) 98–102. https://doi.org/10.1007/BF03353699.
- [182] Z. Yu, H. Li, Y. Qiu, X. Yang, W. Zhang, N. Xu, J. Sun, J. Wu, Size-controllable growth of ZnO nanorods on Si substrate, Superlattices and Microstructures. 101 (2017) 469–479. https://doi.org/10.1016/j.spmi.2016.12.005.
- [183] A. Peleš, V.P. Pavlović, S. Filipović, N. Obradović, L. Mančić, J. Krstić, M. Mitrić, B. Vlahović, G. Rašić, D. Kosanović, V.B. Pavlović, Structural investigation of mechanically activated ZnO powder, Journal of Alloys and Compounds. 648 (2015) 971–979. https://doi.org/10.1016/j.jallcom.2015.06.247.
- [184] S.U. Awan, S.K. Hasanain, M.S. Awan, S.A. Shah, Raman scattering and interstitial Li defects induced polarization in co-doped multiferroic Zn0.96-yCo0.04LiyO (0.00 ≤ y ≤ 0.10) nanoparticles, RSC Adv. 5 (2015) 39828–39839. https://doi.org/10.1039/C5RA03691G.
- [185] Schumm M. (2008) ZnO-based semiconductors studied by Raman spectroscopy: semimagnetic alloying, doping and nanostructures, PhD Dissertation, JuliusMaximilians-Universität Würzburg.
- [186] O.F. Farhat, M.M. Halim, M.J. Abdullah, M.K.M. Ali, N.K. Allam, Morphological and structural characterization of single-crystal ZnO nanorod arrays on flexible and non-flexible substrates, Beilstein J Nanotechnol. 6 (2015) 720–725. https://doi.org/10.3762/bjnano.6.73.
- [187] S. Vempati, A. Celebioglu, T. Uyar, Defect related emission versus intersystem crossing: blue emitting ZnO/graphene oxide quantum dots, Nanoscale.
 7 (2015) 16110–16118. https://doi.org/10.1039/C5NR04461H.
- [188] H. Zhou, H.-Q. Wang, L. Wu, L. Zhang, K. Kisslinger, Y. Zhu, X. Chen, H. Zhan, J. Kang, Wurtzite ZnO (001) films grown on cubic MgO

(001) with bulk-like opto-electronic properties, Appl. Phys. Lett. 99(2011) 141917. https://doi.org/10.1063/1.3647846.

- [189] J.-H. Shen, S.-W. Yeh, H.-L. Huang, D. Gan, Structure, interface, and luminescence of (0111) ZnO nanofilms, Thin Solid Films. 519 (2010) 549–555. https://doi.org/10.1016/j.tsf.2010.08.098.
- [190] H. Makhlouf, C. Karam, A. Lamouchi, S. Tingry, P. Miele, R. Habchi, R. Chtourou, M. Bechelany, Analysis of ultraviolet photo-response of ZnO nanostructures prepared by electrodeposition and atomic layer deposition, Applied Surface Science. 444 (2018) 253–259. https://doi.org/10.1016/j.apsusc.2018.02.289.
- [191] J.B. Park, Y.T. Chun, Y.B. Lee, J.I. Sohn, W.-K. Hong, Defectmediated modulation of optical properties in vertically aligned ZnO nanowires via substrate-assisted Ga incorporation, Nanotechnology. 26 (2015) 145202. https://doi.org/10.1088/0957-4484/26/14/145202.
- [192] S. Dhara, P.K. Giri, Stable p-type conductivity and enhanced photoconductivity from nitrogen-doped annealed ZnO thin film, Thin Solid Films. 520 (2012) 5000–5006. https://doi.org/10.1016/j.tsf.2012.02.081.
