# INVESTIGATIONS ON HYDROTHERMALLY GROWN ZnO NANOSTRUCTURES TOWARDS DEVELOPMENT OF UV/BROADBAND PHOTODETECTORS

Ph.D. Thesis

By JITESH AGRAWAL



## DISCIPLINE OF ELECTRICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE JANUARY, 2020

# INVESTIGATIONS ON HYDROTHERMALLY GROWN ZnO NANOSTRUCTURES TOWARDS DEVELOPMENT OF UV/BROADBAND PHOTODETECTORS

A THESIS

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

> *by* JITESH AGRAWAL



## DISCIPLINE OF ELECTRICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE JANUARY, 2020



## INDIAN INSTITUTE OF TECHNOLOGY INDORE

## **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled INVESTIGATIONS ON HYDROTHERMALLY GROWN ZnO NANOSTRUCTURES TOWARDS DEVELOPMENT OF UV/BROADBAND PHOTODETECTORS in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF ELECTRICAL ENGINEERING, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July, 2015 to January, 2020 under the supervision of Dr. Vipul Singh, Associate Professor, IIT Indore and Dr. I. A. Palani, Associate Professor, IIT Indore.

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.

DAgrawal 31-01-2020

signature of the student with date (JITESH AGRAWAL)

This is to certify that the above statement made by the candidate is correct to the best of my/our

knowledge.

31/01/2020

Signature of Thesis Supervisor #1 with date

(Dr. VIPUL SINGH)

Signature of Thesis Supervisor #2

(Dr. I. A. PALANI)

JITESH AGRAWAL has successfully given his/her Ph.D. Oral Examination held on 28/05/2020.

Signature of Chairperson (OEB) Date: 29.05, XIZO

of PSPC Member #1 28/5/ Date:

Signature of Head of Discipline Date:

Signature of PSPC Member #2

Date: 28 05 2020

Signature of External Examiner 05 2020 Date:

Signature(s) of Thesis Supervisor(s)

Date:

Signature of Convener, DPGC Date: 28 5 19870

## ACKNOWLEDGMENTS

I owe it all to the almighty for blessing me with this opportunity to pursue Ph.D. in a prestigious institute IIT Indore.

I would like to express my sincere gratitude to my supervisors **Dr. Vipul Singh** and **Dr. I. A. Palani** whose invigorating motivation and valuable ideas kept me on track during this journey. Dr. Vipul Singh has been a tremendous mentor for me. His constant support, valuable advices, constructive criticism and extensive discussion helped me in accomplishing my PhD. Moreover, his principles, noble thoughts, politeness and simplicity always influenced me and will always help me in becoming a good person. The joy and enthusiasm he has for his research was contagious and motivational for me. I sincerely thank Dr. I.A. Palani for sharing his deep knowledge. His keen interest in research and deep understanding of the subject always encouraged me to become a good research scientist.

I would like to express my gratitude to **Director**, **IIT Indore** who has been highly encouraging during the entire course of my doctoral work.

I express my deepest gratitude to my parents **Shri Hari Shankar Agrawal** and **Smt. Manju Agrawal** and my little sister **Ms. Surbhi Agrawal** for all the sacrifices they made on my behalf and making me what I am today. They are a source of encouragement and inspiration to me throughout my life. This thesis was not possible without their support and help.

Writing PhD thesis without the help of colleagues is not possible. I am thankful to my colleagues from the **Molecular and Nanoelectronics Research Group (MNRG)**, Dr. Kshitij Bhargava, Dr. Anubha Bilgaiyan, Dr. Tejendra Dixit, Dr. Ashish Kumar, Dr. Mayoorika Shukla Bharadwaj, Dr. Pramila, Dr. Shalu Chaudhary, Mr. Akash Tripathi, Ms. Nidhi Yadav, Ms. Tejswini K. Lahane and Mr. Anil Yadav for their company and being supportive all the time. I would like to specially thank **Dr**. **Tejendra Dixit** for his incouragement, ideas and mentorship, **Dr**. **Ashish Kumar** for his support in the initial days of Ph.D. and **Mr**. **Akash Tripathi** for his company and intellectual discussions.

I would further like to thank my friends **Mr. Adarsh Nigam and Mr. Harsh Mathur** for always being enthusiast and encouraging.

My sincere thanks and appreciation to the PSPC (Ph.D. Student Progress Committee) members, **Dr. Srivathsan Vasudevan** and **Dr. Rajesh Kumar** for their precise observations and valuable suggestions to improve the quality of my doctoral work.

I extend my gratitude to **Prof. M. S. R. Rao** (IIT Madras) for allowing me to acess the research facilities in his well equipped laboratory.

I thank SIC IIT Indore, most specifically **Mr. Kinny Pandey**, **Mr. Nitin Upadhyay**, **Mr. Ravindra**, **Sarita Batra mam and Mr. Ghanshyam** for their support.

I want to express my gratitude towards **Dr. Shilpa, Dr. P. Matkar** and other staff members of Health Center ,IIT Indore, who kept me physically fit.

I want to thank all staff member of IIT Indore for providing all comfort and convenience. Beside this, several people have knowingly and unknowingly helped me in successful completion of my thesis.

I would like to express my gratitude towards **Mr. Prit Jain** for his mentorship during my M.E. (2011-2013) which sowed seeds of research and encouraged me to pursue Ph.D.

I also acknowledge **University Grants Commission (UGC)**, **New Delhi**, for providing me financial assistance.

Dated:

(Jitesh Agrawal)

## Dedicated

to my family

## ABSTRACT

The photodetectors are one of the key components in modern technologies and are widely used in military and civil fields such as optical imaging, fire detection, optical communication, missile guidance and positioning system etc. Currently, Si-based photodetectors and photomultipliers are dominant in the market due to their extremely mature processing techniques and low cost. However, due to the lower bandgap of 1.1 eV to 1.3 eV, Si can only be used for detection in visible and near-infrared (NIR) spectral range. Additionally, with the continuous evolution of the technology, the demand for high performing UV and broadband photodetectors have been increasing in the diverse applications. Therefore, wideband metal oxide semiconductors like  $WO_3$ ,  $SnO_2$ , NiO, ZnO, Nb<sub>2</sub>O<sub>5</sub> Ga<sub>2</sub>O<sub>3</sub> etc. have been explored. Due to simple and low-cost fabrication processes, biocompatibility and enriched physical, optical, electrical and chemical properties, ZnO has emerged as a promising material for sensors. It has a wide and direct bandgap of 3.37 eV at room temperature, which makes it suitable for various optoelectronic applications especially in UV region, including UV photodetectors.

One dimensional (1D) and two dimensional (2D) nanostructured materials have gained a lot of interest in the past several decades due to better physical, chemical and electrical properties. Generally, the surface of a material is more sensitive to the external changes, therefore larger surface area of the nanostructures has made them more sensitive to these changes. This work is mainly focused on the development of high responsivity UV and broadband photodetectors over flexible and rigid substrates, using varieties of ZnO nanostructures obtained by simple and low-cost hydrothermal process. In the first part of work, the ZnO nanostructures growth process has been optimized towards synthesis of complex nanostructures with higher surface area, to control the intrinsic defect density and to improve the adhesivity of nanostructures with the substrate. The obtained nanostructures have demostrated significantly high UV and broadband photoresponse, which was found to be comparable to commercially available photodetectors. In next part, the impact of high energy UV radiation over the device performance has been investigated and a suitable solution to overcome this issue has been proposed. Moreover, considering the increasing demand of flexible photodetectors for various wearable applications, highly sensitive and ultra low power, flexible UV photodetector have been synthesised. The device exhibited remarkably high photo-sensitivity of 348 and photo-responsivity 265 mA/W at just 0.1V applied bias.

## LIST OF PUBLICATIONS

#### Peer-reviewed Journals: From Thesis Work

- Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Development of reliable and high responsivity ZnO based UV-C photodetector", IEEE J. Quantum Electron, 56 (1), 2019, 4000105.
- Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Electron depleted ZnO nanowalls-based broadband photodetector", IEEE Photon. Technol. Lett., 31 (20), 2019, 1639-1642.
- Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Development of Al doped ZnO nanowalls based flexible, ultralow voltage UV photodetector", IEEE Sens. Lett., 3 (9), 2019, 3501504.
- 4. Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Systematic investigations on the effect of prolong UV illumination on optoelectronic properties of ZnO honeycomb nanostructures", Scr. Mater., 163, 2019, 1-4.
- 5. Jitesh Agrawal, Tejendra Dixit, Anand Iyamperumal Palani, Mamidanna Sri Ramachandra Rao and Vipul Singh, "Zinc interstitial rich ZnO honeycomb nanostructures for deep UV photodetection", Phys. Status Solidi RRL, 12 (10), 2018, 1800241.
- Jitesh Agrawal, Tejendra Dixit, I. A. Palani, M S Ramachandra Rao, and Vipul Singh, "Fabrication of high responsivity deep UV photo-detector based on Na doped ZnO nanocolumns", Phys. D: Appl. Phys. 51 (18), 2018, 185106.

#### Peer-reviewed Journals: Outside of Thesis Work

 C Shalu, Mayoorika Shukla, Ananya Tiwari, Jitesh Agrawal, Anubha Bilgaiyan and Vipul Singh, "Role of solvent used to cast P3HT thin films on the performance of ZnO/P3HT hybrid photo detector", Physica E low Dimens. Syst. Nanostruct., 115, 2020, 113694.

- 2. Akash Tripathi, **Jitesh Agrawal**, Tejendra Dixit and Vipul Singh, "Trap assisted persistent photo-conductivity in solution-processed CuO thin film", IEEE J. Quantum Electron, 56 (1), 2019, 7000105.
- Tejendra Dixit, Jitesh Agrawal, Miryala Muralidhar, Masato Murakami, Kolla Lakshmi Ganapathi, Vipul Singh and MS Ramachandra Rao, "Exciton lasing in ZnO-ZnCr<sub>2</sub>O<sub>4</sub> nanowalls", IEEE Photon. J., 11 (6), 2019, 4501307.
- Tejendra Dixit, Jitesh Agrawal, Swanand V Solanke, K Lakshmi Ganapathi, M. S. Ramachandra Rao and Vipul Singh, "ZnO/Au/ZnO configuration for high performance multiband UV photodetection", IEEE Sens. Lett., 3 (9), 2019, 3501604.
- Ashish Kumar, Jitesh Agrawal, Ashok Kumar Sharma, Vipul Singh and Ajay Agarwal, "A cost-effective and facile approach for realization of black silicon nanostructures on flexible substrate", J. Mater. Sci.: Mater. Electron, 30 (17), 2019, 16554–16561.
- Tejendra Dixit<sup>\*</sup>, Jitesh Agrawal<sup>\*</sup>, Vipul Singh and M S Ramachandra Rao, "High-performance broadband photodetection in solution processed ZnO-ZnCr<sub>2</sub>O<sub>4</sub> nanowalls", IEEE Electronic Device Lett., 40 (7), 2019, 1143-1146. (\*, equal contribution)
- Mayoorika Shukla, Pramila, Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Facile hydrothermal synthesis of Mn doped ZnO nanopencils for development of amperometric glucose biosensors", Mater. Res. Express, 5, 2018, 055031.

### **Conference proceedings: From Thesis Work**

 Jitesh Agrawal, I. A. Palani and Vipul Singh, "Growth of ZnO nanowalls over rigid and flexible substrate for high responsivity photodetectors", 6<sup>th</sup> International Conference on Advanced Nanomaterials and Nanotechnology (ICANN), 18-21 Dec. 2019, Indian Institute of Technology Guwahati.

- Jitesh Agrawal, I. A. Palani and Vipul Singh, "Hydrothermal growth of ZnO nanostructures over the Al foil for the development of flexible UV photodetectors", International Conference on Precision, Meso, Micro & Nano Engineering (COPEN), 12-14 Dec. 2019, Indian Institute of Technology Indore.
- Jitesh Agrawal, I. A. Palani and Vipul Singh, "UV treatment of ZnO nanostructure surface towards enhancing UV photodetectors responsivity", 10<sup>th</sup> International Conference on Materials for Advanced Technologies (ICMAT), 23-28 Jun. 2019, Marina Bay Sands, Singapore.
- Jitesh Agrawal, I. A. Palani and Vipul Singh, "Fabrication of ZnO nanocolumns for high sensitivity deep UV photodetectors", 27<sup>th</sup> DAE-BRNS National Laser Symposium (NLS-27), 3-6 Dec. 2018, RRCAT, Indore.
- 5. Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Optical and structural analysis of surfactant assisted hydrothermal growth ZnO nanostructures", 19<sup>th</sup> International Workshop on the Physics of Semiconductor Devices (IW-PSD), 11-15 Dec. 2017, Indian Institute of Technology Delhi, New Delhi.
- Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Hydrothermal growth of complex ZnO nanostructures for the optoelectronic and sensing applications", International Conference On LASER Deposition (ICOLD), 20-22 Nov. 2017, Indian Institute of Technology Madras, Chennai.
- Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Investigation on the effect of thermal annealing and metal coating on the optoelectronic properties of ZnO nanostructures", 4<sup>th</sup> International Conference on Nanoscience and Nanotechnology (ICONN), 9-11 Aug. 2017, SRM University, Chennai.
- Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Cu or Au: A systematic comparison on various aspects of optoelectronic properties of metal coated ZnO nanocolumns", 9<sup>th</sup> International Conference on Materials for Ad-

vanced Technologies (ICMAT), 18-23 Jun. 2017, Suntec Singapore.

9. Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Citrate assisted hydrothermal growth of ZnO nanostructures for optical gas sensing", International Conference on Emerging Trends in Materials and Manufacturing Engineering (IMME), 10-12 Mar. 2017, National Institute of Technology Trichi, Tiruchirappalli, India. (Won first prize in poster presentation)

### **Conference proceedings: Outside of Thesis Work**

- Akash Tripathi, Jitesh Agrawal, Tejendra Dixit, I. A. Palani and Vipul Singh, "Evidence of large and persistent photoconductivity in CuO thin films", 10<sup>th</sup> International Conference on Materials for Advanced Technologies (ICMAT), 18-23 Jun. 2019, Marina Bay Sands, Singapore.
- Tejendra Dixit, Jitesh Agrawal, I. A. Palani and Vipul Singh, "Insight on the plasmon-exciton coupling of nonnoble metal coated ZnO nanorods for optoelectronic application", National Conference on Materials for Sustainable Development & New Technology (MSDNT-2017), 28-29 Apr. 2017, Jammu University, Jammu.

### **Book Chapter**

1. **Jitesh Agrawal**, Tejendra Dixit, I. A. Palani and Vipul Singh, Optical and structural analysis of surfactant assisted hydrothermal growth ZnO nanostructures, Springer Nature Switzerland AG, The Physics of Semiconductor Devices.

## TABLE OF CONTENTS

LIST OF FIGURES xv			
LIST OF TABLES xix			
LI	ST O	OF NOMENCLATURE & ACRONYMS	xx
1	Intr	roduction	1
	1.1	Photodetectors	1
		1.1.1 Classification of photodetectors	1
	1.2	Zinc oxide	3
		1.2.1 Lattice structures of ZnO	4
		1.2.2 Band structure and optoelectronic proper-	
		ties of $ZnO$	5
		1.2.3 ZnO nanostructures	6
		1.2.4 Working principle of ZnO based UV pho-	
		todetectors	8
		1.2.5 ZnO nanostructure synthesis techniques	10
		1.2.6 Hydrothermal synthesis of ZnO nanostruc-	
		tures	11
	1.3	Review of past work	15
	1.4	Challenges	17
	1.5	Objectives of this work	18
	1.6	Organization of the thesis	19
2	Exp	perimental methods and characterizations techniques	21
	2.1	Introduction	21
	2.2	Materials used for device fabrication	21
		2.2.1 ZnO	22
		2.2.2 Silver (Ag)	22
	2.3	Substrate preparation	22
		2.3.1 Cleaning of glass substrate	22
		2.3.2 Hydrothermal deposition of ZnO nanorods . 2	23
		2.3.3 Deposition of electrodes / Physical vapour	
		deposition	25
		2.3.4 DC sputtering	26
	2.4	Thin film and device characterization techniques 2	27

		2.4.1	UV-Vis absorption spectroscopy and diffuse	
			reflectance spectroscopy	27
		2.4.2	Fourier transform infrared spectroscopy	30
		2.4.3	Photoluminescence (PL) spectroscopy	31
		2.4.4	Field emission scanning electron microscopy	33
		2.4.5	XRD measurements	34
		2.4.6	Raman spectroscopy	36
		2.4.7	Confocal microscopy	37
		2.4.8	Electron paramagnetic resonance (EPR)	38
		2.4.9	Current-Voltage (I-V) characterization	40
3	Gro	wth of	f ZnO nanostructures and their structural	
	and	optica	l characterization	45
	3.1	Introc	luction	46
	3.2	Exper	imental details	49
	3.3	Resul	ts and discussion	50
		3.3.1	Growth of honeycomb structures	50
		3.3.2	Growth of nanocolumns	57
		3.3.3	I-V characterization of pristine ZnO	
			nanocolumns	74
	3.4	Concl	usions	76
4	Dev	velopm	ent of zinc oxide based broadband photode-	
	tect	ors		77
	4.1	Introc	luction	77
	4.2	Exper	imental details	79
	4.3	Resul	ts and discussion	80
		4.3.1	I-V response of the device	80
		4.3.2	Photosensing mechanism	82
		4.3.3	I-V response in deep UV-Visible-NIR region .	84
	4.4	Conci	llsions	88
5	Inv	estigati	on on the effect of prolong UV illumination	
	ove	r the pe	erformance of broadband photodetector	91
	5.1	Introc	luction	92
		5.1.1	Experimental details	93
	5.2	Resul	ts and discussion	94
		5.2.1	Optical characterization	94
		5.2.2	I-V characterization	100

		5.2.3 Pt/ZnO nanostructures for reliable device
		performance $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $102$
		5.2.4 Conclusions
6	Syn	hesis of Al-doped ZnO nanowalls for ultra-low
	pow	er, flexible UV photodetector 10
	6.1	Introduction
	6.2	Experimental details
	6.3	Results and discussion
		6.3.1 Structural analysis
		6.3.2 Growth mechanism
		6.3.3 Optical analysis
		6.3.4 I-V characterization $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 11^4$
	6.4	Conclusions
7	Con	clusions and future work 11
	7.1	Conclusions
	7.2	Future scope of the work

## LIST OF FIGURES

1.1	Commercially available photodetectors	4
1.2	The Wurtzite structure of ZnO	5
1.3	Various morphologies of ZnO nanostructures	7
1.4	(a) Schematic of a nanowire-based photoconductor.	
	(b, c) before and after UV illumination, respectively	9
1.5	Schematic of ZnO hydrothermal growth process	12
1.6	Schematic showing the role of hexamethylenete-	
	tramine as a capping agent	16
2.1	Schematic of ZnO hydrothermal growth process	24
2.2	Schematic of physical vapor deposition	26
2.3	Schematic of dc sputtering system	27
2.4	Instruments used for the fabrication of devices	27
2.5	Experimental set-up for UV-Vis absorption spec-	
	troscopy	28
2.6	Experimental set up for diffuse reflectance mea-	
	surement (a) Carry 60 UV-Vis spectrometer, (b) an	
	integrating sphere attachment to detect diffuse re-	
	flectance	30
2.7	Schematic of FTIR spectroscopy setup	31
2.8	Experimental set-up of PL measurement system	32
2.9	Schematic diagram of FESEM	34
2.10	Schematic of Bragg's law	35
2.11	Different kind of scattering phenomenon	36
2.12	Experimental set-up of Micro Raman spectroscopy .	37
2.13	Schematic diagram for a confocal microscope	38
2.14	Two energy level system in the varying magnetic	
	field	39
2.15	Photo current measurement setup	40
2.16	Instruments used for characterization of devices	41
3.1	Experimental procedure for the growth of ZnO	
	nanostructures	49

3.2	FESEM image of ZnO samples obtained using	
	0mM, 0.5 mM, 5mM and 10 mM concentration of	
	trisodium citrate in the precursor solution	51
3.3	Schematic representation of the growth of	
	nanorods and honeycomb nanostructures	51
3.4	XRD plot of the pristine ZnO nanorods, 0.5CA,	
	5CA and 10CA samples	52
3.5	Raman spectra of the pristine ZnO, 0.5CA, 5CA,	
	and 10CA samples	54
3.6	(a) Photoluminescence spectra and (b) normal-	
	ized photoluminescence spectra of pristine ZnO	
	nanorods, 0.5CA, 5CA and 10CA samples	55
3.7	Diffuse reflectance analysis of pristine ZnO	
	nanorods, 0.5CA, 5CA, and 10CA samples	56
3.8	FE-SEM images of the (a) 10ZC (b) 20ZC samples	57
3.9	Growth mechanism of ZnO nanocolumns $\ldots \ldots$	58
3.10	Scotch tape peel-off test of pristine ZnO, 10ZC and	
	20ZC samples	59
3.11	XRD plot of pristine ZnO, 10ZC, and 20ZC samples	60
3.12	XRD plot of the 10ZC sample grown for 3 hours	
	and 5 hours	62
3.13	XRD plot of the (a) 10ZC (before annealing), (b)	
	20ZC (before annealing), (c) 10ZC (after annealing)	
	and (d) 20ZC (after annealing)	63
3.14	FE-SEM images of the samples (a) 10ZC before an-	
	nealing, (b) annealed 10ZC, (c) 20ZC before anneal-	
	ing and (d) annealed 20ZC	65
3.15	TGA plot of pristine ZnO and 10ZC samples $\ldots$ .	66
3.16	FTIR spectra of pristine ZnO, 10ZC and 20ZC sam-	
	ples, (a) before annealing and (b) after annealing $\cdot$ .	67
3.17	Raman spectra of pristine ZnO, 10ZC and 20ZC	
	samples	68
3.18	Temperature-dependent Raman analysis of 10ZC	69
3.19	DRS spectra of (a) pristine ZnO, 10ZC and 20ZC	
	samples inset shows enlarged view of the visible	
	region and (b) 10ZC (before and after annealing),	
	Tauc plot of (c) pristine ZnO, 10ZC and 20ZC and	
	(d) 10ZC (before and after annealing)	71

3.20	ln ( $\alpha$ ) versus photon energy plot to calculate the	
	Urbach energy	72
3.21	(a) PL spectra of pristine ZnO, 10ZC and 20ZC sam-	
	ples. The inset shows the normalized PL plot of	
	pristine ZnO, 10ZC and 20ZC samples, (b) PL spec-	
	tra of annealed 10ZC and annealed 20ZC samples .	73
3.22	(a) Device schematic, (b) semilog I-V plot of pris-	
	tine ZnO nanorods and 10ZC sample	74
4.1	Device schematic	80
4.2	XRD plot of the Ag electrode coated 5CA sample	81
4.3	Semilog I-V plot of pristine ZnO and 5CA	81
4.4	Photosensing mechanism: (a) oxygen adsorption	
	and depletion region formation and (b) exciton	
	generation by UV illumination and oxygen desorp-	
	tion	82
4.5	(a) Charge carrier transportation in nanorods net-	
	work and (b) charge carrier transportation in HC	
	NSs	83
4.6	I-V response of the device in deep UV. Near UV.	
	Visible, NIR region	84
4.7	Specific detectivity plot at different wavelengths	85
4.8	Responsivity plot of at different wavelengths	86
49	Responsivity plot in deep IIV Near IIV Visible	00
1.7	NIR and IR region at different voltages	86
4 10	Switching response of the device	87
<i>1</i> .10	EQE plot of the device at a different wavelength	87
7.11	EQE plot of the device at a different wavelength	07
5.1	Photoluminescence spectra of the 5CA sample,	
	taken at a different time interval of UV illumination	94
5.2	Normalized photoluminescence spectra of the 5CA	
	sample, taken at the different time interval of UV il-	
	lumination, inset shows magnified view of the near	
	band emission peak	95
5.3	Near band emission intensity to deep level emis-	
	sion intensity ratio variation with time	96
5.4	Absorption spectra of the 5CA sample before and	
	after 30 minutes of UV illumination	97
5.5	Tauc plot of pristine and UV illuminated 5CA sample	98

5.6	Electron paramagnetic resonance of the 5CA sam-
	ple before and after UV illumination
5.7	Raman analysis of the 5CA sample before and after
	UV illumination
5.8	Confocal analysis of the 5CA sample before and af-
	ter UV illumination
5.9	two-photon analysis of the 5CA sample before and
	after UV illumination
5.10	(a) The device schematic and (b) photoresponse of
	pristine 5CA samples
5.11	Switching response of the 5CA sample 102
5.12	Change in photo current with respect to time 102
5.13	PL spectra of the Pt/5CA sample just after and after
	15 minutes of continuous UV illumination 103
5.14	I-V response of the Pt nanoparticles coated 5CA
	sample
5.15	Switching response of the Pt nanoparticles covered
	5CA device
6.1	FESEM image of the AZO sample 111
6.1 6.2	FESEM image of the AZO sample
6.1 6.2 6.3	FESEM image of the AZO sample
<ul><li>6.1</li><li>6.2</li><li>6.3</li><li>6.4</li></ul>	FESEM image of the AZO sample
<ul><li>6.1</li><li>6.2</li><li>6.3</li><li>6.4</li></ul>	FESEM image of the AZO sample       111         EDX spectra of the AZO sample       111         XRD plot of the AZO sample       111         Schematic of the growth of ZnO nanorods and       112         AZO nanowalls       112
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> </ul>	FESEM image of the AZO sample111EDX spectra of the AZO sample111XRD plot of the AZO sample111Schematic of the growth of ZnO nanorods and112AZO nanowalls112Raman plot of the AZO sample113
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> </ul>	FESEM image of the AZO sample111EDX spectra of the AZO sample111XRD plot of the AZO sample111Schematic of the growth of ZnO nanorods and112AZO nanowalls112Raman plot of the AZO sample113DRS of AZO nanowalls. Inset shows the Tauc plot
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> </ul>	FESEM image of the AZO sample
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> </ul>	FESEM image of the AZO sample
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> </ul>	FESEM image of the AZO sample
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> </ul>	FESEM image of the AZO sample
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> <li>6.8</li> </ul>	FESEM image of the AZO sample
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> <li>6.8</li> </ul>	FESEM image of the AZO sample111EDX spectra of the AZO sample111XRD plot of the AZO sample111XRD plot of the AZO sample111Schematic of the growth of ZnO nanorods and112Raman plot of the AZO sample113DRS of AZO nanowalls11set shows the Tauc plotof the sample114(a) Device schematic, (b) I-V response of the PD inthe dark and under 350 nm and 410 nm light illumination115Photoresponsivity plot of the sample for 200 nm to800 nm wavelength light illumination
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> <li>6.8</li> <li>6.9</li> </ul>	FESEM image of the AZO sample
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> <li>6.8</li> <li>6.9</li> </ul>	FESEM image of the AZO sample111EDX spectra of the AZO sample111XRD plot of the AZO sample111XRD plot of the AZO sample111Schematic of the growth of ZnO nanorods and112Raman plot of the AZO sample113DRS of AZO nanowalls113DRS of AZO nanowalls. Inset shows the Tauc plot114(a) Device schematic, (b) I-V response of the PD in114the dark and under 350 nm and 410 nm light illumination115Photoresponsivity plot of the sample for 200 nm to800 nm wavelength light illumination116Switching response of the AZO based UV photodetector117
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> <li>6.8</li> <li>6.9</li> <li>6.10</li> </ul>	FESEM image of the AZO sample111EDX spectra of the AZO sample111XRD plot of the AZO sample111XRD plot of the AZO sample111Schematic of the growth of ZnO nanorods and112Raman plot of the AZO sample112Raman plot of the AZO sample113DRS of AZO nanowalls. Inset shows the Tauc plot114(a) Device schematic, (b) I-V response of the PD in114(a) Device schematic, (b) I-V response of the PD in115Photoresponsivity plot of the sample for 200 nm to800 nm wavelength light illumination116Switching response of the AZO based UV photode-117(a) Image of the sample, (b) piezoresponse of AZO117
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> <li>6.8</li> <li>6.9</li> <li>6.10</li> </ul>	FESEM image of the AZO sample111EDX spectra of the AZO sample111XRD plot of the AZO sample111XRD plot of the AZO sample111Schematic of the growth of ZnO nanorods and112AZO nanowalls112Raman plot of the AZO sample113DRS of AZO nanowalls. Inset shows the Tauc plot114(a) Device schematic, (b) I-V response of the PD in114(a) Device schematic, (b) I-V response of the PD in115Photoresponsivity plot of the sample for 200 nm to800 nm wavelength light illumination116Switching response of the AZO based UV photode-117(a) Image of the sample, (b) piezoresponse of AZO117(a) Image of the sample, (b) piezoresponse of AZO117
<ul> <li>6.1</li> <li>6.2</li> <li>6.3</li> <li>6.4</li> <li>6.5</li> <li>6.6</li> <li>6.7</li> <li>6.8</li> <li>6.9</li> <li>6.10</li> </ul>	FESEM image of the AZO sample111EDX spectra of the AZO sample111XRD plot of the AZO sample111XRD plot of the AZO sample111Schematic of the growth of ZnO nanorods and112Raman plot of the AZO sample113DRS of AZO nanowalls1nset shows the Tauc plotof the sample114(a) Device schematic, (b) I-V response of the PD inthe dark and under 350 nm and 410 nm light illumination115Photoresponsivity plot of the sample for 200 nm to800 nm wavelength light illumination116Switching response of the AZO based UV photode-117(a) Image of the sample, (b) piezoresponse of AZO117(a) Image of the sample, (b) piezoresponse of AZO117

## LIST OF TABLES

2.1	LASER specifications	32
3.1	Lattice parameters of as-prepared samples	61
3.2	Lattice parameters of 10ZC samples, before and af-	
	ter annealing	64
4.1	Comparison with recently reported UV and broad-	
	band photodetectors	88
6.1	Comparison of recently reported UV photodetectors.	118

# LIST OF NOMENCLATURE & ACRONYMS

#### NOMENCLATURE

α	Absorption coefficient
λ	Wavelength [nm]
$\mu_B$	Bohr magneton
θ	Angle of incidence between the incident ray and scat- tering planes [degree/radian]
A	Absorbance
С	Speed of light in vacuum
D	Crystallite size
d	Lattice spacing
е	Electronic charge
$E_g$	Bandgap energy
$E_U$	Urbach energy
$E_{ph}$	Photon energy
F(R)	Kubelka–Munk function
<i>g</i> e	g-factors
h	Planck's constant
Ι	Incident light intensity
$I_d$	Dark current

$I_{ph}$	Photo current
т	Mass of electron
R	Reflectance
Т	Transmittance
$V_O$	Oxygen vacancy
$Zn_i$	Zinc interstitial

#### ACRONYMS

AZO	Aluminum doped zinc oxide
$D^*$	Specific detectivity
DC	Direct current
DI	De-ionised
DLE	Defect level emission
DRS	Diffused reflectance spectroscopy
EDX	Energy dispersive X-ray
EPR	Electron paramagnetic resonance
EQE	External quantum efficiency
FESEM	Field emisson scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
НС	Honeycomb nanostructure
HMTA	Hexamethylenetetramine
IPA	Iso-propyl alcohol
KMnO <sub>4</sub>	Potassium permanganate
LDR	Linear dynamic range
Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate

NBE	Near-band emisson
NIR	Near-infrared
NPs	Nanoparticles
NSs	Nanostructures
PD	Photodetector
PL	Photoluminescence
PVD	physical vapor deposition
R	Photoresponsivity
S	Photosensitivity
TGA	Thermogravimetric analysis
UV	Ultraviolet
Vis	Visible light
XRD	X-ray diffraction
$Zn(NO_3)_2$	Zinc nitrate
ZnO	Zinc oxide

## $Na_3C_6H_5O_7$ Trisodium citrate

## **Chapter 1**

## Introduction

### 1.1 Photodetectors

Photodetectors are the devices that convert the incident optical signals into another form of signals such as heat, electrical signals etc. The photodetectors are one of the critical components in modern technologies and are widely used in military and civil fields such as optical imaging, optical communication, missile guidance and positioning system, etc [1]. Basically, photodetectors operate on the principle of transfer of photon energy to the electrons in the lower energy state, to excite them to available higher energy states.

## 1.1.1 Classification of photodetectors

Based on the transition of electrons to higher energy levels, photodetectors can be classified into one of the following categories [4].

- 1. **Photoconductive or photovoltaic:** When the incident light energy is higher than the bandgap of material, electrons in the valence band are excited to the conduction band, which resulted in the generation of excitons. The photogenerated charge carriers reduce the overall resistance of the device.
- 2. Photoelectric (photoemissive): In the photoelectric effect,

when the energy of incident light is sufficiently high, the electrons in the conduction band are transferred to the vacuum level. The excess energy of the photon is transformed into the kinetic energy of the emitted photon.

- 3. **Polarization:** These photodetectors work on the principle of photorefractive effect, which describes the change in refractive index upon photoexcitation. These kinds of photodetectors are used to detect light of desired polarization.
- 4. Phonon generation: When the power of incident photon is less than the bandgap then, the electrons are excited to the midgap energy states and return to the initial energy level by releasing the energy in the form of heat.
- 5. **Other:** There could be several other possible forms of energy transitions such as the generation of excitons.

Furthermore, based on the device architectures, semiconductor-based photodetectors could be classified into the following three categories:

- 1. **Photoconductors:** The photoconductor configuration consists of two symmetrical ohmic contacts, deposited over the active layer of the device. An external bias voltage is applied to drift the photo-excited electrons and holes towards their respective electrodes, which leads to the flow of photo current. Usually, one type of photo-excited charge carriers are trapped by a variety of defects or trap states in the bandgap of the active layer, which significantly increase the lifetime of the charge carriers, facilitated the recirculation of other charge carriers in the external circuit, resulting in higher responsivity [5].
- 2. **Photodiodes:** The photodiode consists of a pn junction between a p-type and n-type semiconductor or a Schottky

junction between a semiconductor and metal. The built-in electric field at the interface drifts the photo-excited charge carriers in the opposite directions, towards their respective electrodes to generate photo current.

3. **Phototransistors:** Phototransistors are generally used as optoelectronic amplifier and switches in which the output signal can be amplified and modulated by incident light.

Currently, Si-based photodetectors and photomultipliers are generally used as commercial UV photodetectors due to their extremely mature processing techniques and low cost [6]. However, due to the smaller bandgap of 1.1 eV to 1.3 eV, Si can only be used for detection in visible and near-infrared (NIR) spectral range [7]. Silicon-based devices also have low intrinsic quantum efficiency and poor robustness [2]. Additionally, with the continuous evolution of the technology, the demand for high performing photodetectors have been increasing in the diverse application. Moreover, conventional Si-based photodetectors could not fulfill the requirement of emerging portable and wearable optoelectronic technologies such as low manufacturing cost, transparency and flexibility. Therefore, to satisfy the need for modern UV photodetectors, wideband metal oxide semiconductors like WO<sub>3</sub>, SnO<sub>2</sub>, NiO, ZnO, Nb<sub>2</sub>O<sub>5</sub> and Ga<sub>2</sub>O<sub>3</sub> etc. have been explored [8-19]. The wide bandgap semiconducting materials exhibit strong radiation hardness, high thermal and chemical stability, therefore can be used in a harsh environment. Additionally, ZnO is low cost and biocompatible material.

## 1.2 Zinc oxide

ZnO is a key technological material and has received widespread attention due to exceptional electrical, mechanical, and optical properties. Zinc oxide is a unique optoelectronic ma-



Fig. 1.1: Commercially available photodetectors

terial with varied applications such as light-emitting diodes, photodetectors, photodiodes, optical modulator waveguides, chemical and biosensors, gas sensors, energy harvesting devices including solar cells and nanogenerators, electromagnetic coupled sensors, actuators, and so on [20-27].

## 1.2.1 Lattice structures of ZnO

Zinc oxide crystallizes in the hexagonal  $C_{6v}^4$  or  $P6_3mc$  space group. It has wurtzite structure with lattice parameters a = 3.296 Å and c = 5.207 Å [28]. As shown in Fig. 1.2, one  $Zn^{2+}$  atom is tetrahedrally coordinated with four  $O^{2-}$  atoms. Such tetrahedral coordination leads to the noncentrosymmetric structure, which gives rise to the piezoelectric nature of ZnO [29, 30]. The ZnO lattice consists of alternating planes of zinc and oxygen atoms along the c-axis, which is the cause of polar nature of (0001) and (0001) faces. This polarity gives rise to normal dipole moment, polarization and piezoelectricity, and also an important factor in crystal growth, defect generation, plasticity, etching, etc. In addition to polar surfaces, it also has non-polar surfaces. The other facets such as  $(2\overline{1}\overline{1}0)$  (a-axis) and  $(01\overline{1}0)$  contain an equal number of Zn and O atoms, therefore these are nonpolar in nature. A significant variation in the growth rate of different planes has been observed. The growth along the polar facets is much faster comparing to the nonpolar factes.



Fig. 1.2: The Wurtzite structure of ZnO

# 1.2.2 Band structure and optoelectronic properties of ZnO

- Direct and wide-bandgap: ZnO has a wide bandgap of 3.37 eV at room temperatures. Such large and direct bandgap makes ZnO suitable for various optoelectronic applications, especially in the UV region, including UV photodetectors, solar cells, flame detectors, LEDs and laser diodes [31, 32].
- 2. High exciton binding energy: ZnO has a much higher free-

exciton binding energy of 60 meV then 25 meV in GaN. Such a large exciton binding energy signifies highly efficient excitonic recombination and emission, which can persist at room temperature and higher. The large exciton binding energy makes ZnO a promising material for optical devices that are based on excitonic effects [31].

- 3. Large piezoelectric constants: A small deformation in a piezoelectric crystal generates a potential difference in the material and vice versa. Owing to the noncentrosymmetricity in hexagonal Wurtzite structure, ZnO possesses large piezoelectric constant, which makes ZnO a potential material for nanogenerators, transducers, sensors and actuators [31].
- 4. **Strong luminescence:** Due to a direct and wide bandgap of 3.37 eV at room temperature, ZnO has a strong luminescence in the near UV region. The band-edge emission peak is centered at around 385 nm and a very broad peak in the visible area, which is due to the presence of various intrinsic defects [31, 33]. These defects lead the n-type conductivity in ZnO, which makes it suitable for applications in vacuum fluorescent displays and field emission displays.

### 1.2.3 ZnO nanostructures

One dimensional (1D) and two dimensional (2D) nanostructured materials have gained a lot of interest in the past several decades. Compare to thin films, the nanostructures possess better physical, chemical, and electrical properties due to larger surface area and quantum confinement effect [34]. Generally, the surface of a material is more sensitive to external changes. Therefore the larger surface area of the nanostructures has made them more susceptible to these changes. A lot of work has been done in the field of 1D nanostructure-based UV detectors. Researchers have generally used ZnO nanowires,  $Ga_2O_3$  nanowires and nanobelts or other metal-oxide nanostructures towards obtaining high sensitivity in the UV region [3, 35-38].



Fig. 1.3: Various morphologies of ZnO nanostructures <sup>1</sup>

Due to simple and low-cost fabrication process, and enriched physical, optical, electrical and chemical properties, ZnO has been emerged as a promising material for sensors applications with high performance and employed as the building unit in many electronic and optoelectronic devices, such as solar cells, photodetectors and field-effect transistors.

The research on nanostructured ZnO has been started with the growth of ZnO thin film in the 1960s. After that, over the last few decades, ZnO nanostructures have gained a lot of interest from the research community owing to their wide range of applications. Further, the physical and electrical properties of ZnO varies significantly with the morphology of nanostructures. Therefore, a variety of nanostructures morphologies like nano combs, nanorings, nano helixes/nano springs, nanobelts, nanowires, nanotubes, nanotips, nanoflow-

<sup>&</sup>lt;sup>1</sup>Reprinted from Materials Today, Volume 7, Issue 6, Zhong Lin Wang, Nanostructures of zinc oxide, 26-33, Copyright (2004), with permission from Elsevier.

ers, nanosheets, nanoporous, nanocages, etc., were obtained. Owing to attractive optoelectronic characteristics, 1D ZnO nanostructures were highly explored.

## 1.2.4 Working principle of ZnO based UV photodetectors

ZnO based1D and 2D nanostructures possess a high surface to volume ratio, which has made them more sensitives to the optical, physical and chemical changes in the vicinity. Therefore, ZnO has been widely used for the development of high sensitivity and responsivity nanometer-scale light sensors. The basic working principle of photodetection process is an internal photoelectric effect: when light falls on the surface of semiconductor material, and if the energy of the incident photons (i.e.,  $E_{ph} = hc\lambda$ ) exceeds the energy bandgap of the material (i.e., Eg), it gets absorbed. This absorption generates an electron-hole pair for each absorbed photon i.e. an electron is excited from the valance band to the conduction band and as a result, a hole is created in the valence band Fig. 1.4. These generated electron-hole pair separates and drifts to the respective electrodes under the intrinsic or externally-applied electric field. This carrier drift gives rise to the photo current in the external circuit. This photo current is directly proportional to the intensity of the incident light.

The photodetection mechanism in a nanorod is shown in Figure 1.4 [39]. In ZnO nanorods based photodetectors the adsorption and desorption of oxygen play a crucial role [40]. As the ZnO nanorods come in contact with air, the oxygen molecules get adsorbed over its surface while capturing free electrons from the nanorods. Therefore, the surface of the nanorods would get depleted of free electrons to form the depletion region over the surface, resulting in reduced conductivity of nanorods. This would result in a reduced dark current [36].



*Fig. 1.4:* (a) Schematic of a nanowire-based photoconductor. (b, c) before and after UV illumination, respectively <sup>2</sup>

$$O_2(g) + e^- \longrightarrow O_2^-(ad) \tag{1.1}$$

Now, as the samples were illuminated by photon energy higher than the bandgap (hv > Eg), the electron-hole pairs were generated. Under the inbuilt electric field, the holes were pushed towards the surface, where they migrated with the negatively charged adsorbed oxygen molecule. Consequently, the oxygen molecules were desorbed from the surface and electron concentration increases. This phenomenon would reduce the depletion width at the surface and increase the conductivity of the nanorods, which would significantly enhance the photo current [36, 41].

$$e^- + h^+ + O_2^-(ad) \longrightarrow O_2(g) + e^- \tag{1.2}$$

Further, under the externally applied bias, the photogenerated electron-hole pairs are separated and leading to photo current flow along the nanostructures. Moreover, there are numerous reports, indicating the role of ambient conditions. The photoresponse was observed to be slower in a vacuum and much quicker in the air, which again indicates the critical role of oxygen in the

<sup>&</sup>lt;sup>2</sup>Reprinted (adapted) with the permission from (Nano Letters, Volume 7, Issue 4, C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P. Aplin, J. Park, X.Y. Bao, Y.H. Lo, D. Wang, ZnO nanowire UV photodetectors with high internal gain, 1003-1009). Copyright (2007) American Chemical Society.

photosensing mechanism.

#### 1.2.5 ZnO nanostructure synthesis techniques

The morphologies, defect states, and crystallinity of the nanostructures significantly affect the optoelectronic and sensing properties of ZnO. Therefore, numerous efforts have been made towards obtaining a variety of highly crystalline ZnO nanostructures morphologies such as nanorods, nanoplates, nanowires, nanoflowers, tetrapods etc. The ZnO nanostructures synthesis techniques can be broadly classified in the two categories: gas-phase synthesis and liquid phase synthesis. The gas-phase synthesis techniques include chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD), physical vapor deposition (PVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), electron beam deposition and organometallic vapor epitaxy (OMPVE). [28, 42, 43].

The physical vapor deposition techniques like thermal evaporation have been used for the deposition of a variety of ZnO nanostructures. In such systems, the target materials are heated to their evaporation temperature that leads to the deposition of thin-film or nanostructures over the substrate. However, there is a high possibility of incorporation of catalyst and impurities in the ZnO lattice.

Another well-established technique for excellent crystallinity, uniformity and control over defect density is the chemical vapor deposition method. The simplest CVD system consists of a vacuum chamber, precursor gases and substrate heaters. The chemical reactions take place near or at the heated substrate (temperature ranging from 200 °C to 1600 °C), which resulted in the growth of uniform and high crystallinity thin film. The major advantage of the CVD process is that it provides excellent coverage. Therefore substrates with different features can be uni-
formly coated. Additionally, deposition takes place at lower vacuum pressure than required for PVD systems. Variety of ZnO nanostructures like nanorods, nanotips, nanowalls, nanonails, nanowires, nanoropes and nanolawns could be synthesized by using this system [44, 45]. However, the CVD suffers from low product yield and limited choice of substrate.

Although, the gas phase deposition techniques like CVD, thermal evaporation and MBE could produce highly crystalline thin films and variety of nanostructures, but the deposition takes place at high vacuum pressure of around  $10^{-6}$  mbar and at high temperature ranging from 200 °C to 1600 °C, which makes the system quite complicated, that leads to significant enhancement in the device fabrication cost. Additionally, most of the gas phase deposition techniques are not suitable for flexible organic substrates.

In contrast to the gas phase synthesis techniques, the liquid phase deposition techniques offer several advantages such as scalability, low production cost, low-temperature synthesis (< 200 °C). The liquid phase synthesis includes spray pyrolysis, sol-gel technique, hydrothermal growth, electrospinning, etc [46]. However, hydrothermal growth has gained more attention due to ease processing and verity of nanostructures which can be obtained by altering the growth parameters and precursor solution.

### 1.2.6 Hydrothermal synthesis of ZnO nanostructures

The wet chemical methods have received a lot of attention from the researchers due to several reasons: compatibility with flexible organic substrates; less hazardous; no need of a metal catalyst, which allows easy integration of obtained nanostructures with well-established silicon technology. These methods involve different chemical reactions in reversible equilibrium and are driven by the minimization of free energy for the entire growth environment. The hydrothermal technique is preferred over other deposition techniques because it can produce a large variety of nanostructures and provide excellent control over the points defects, which significantly affect the optoelectronic properties of ZnO [46, 47]. Due to the presence of these mid-gap defect states ZnO nanostructures are capable of using visible light for photocatalysis applications, even without doping with transition metals.



Fig. 1.5: Schematic of ZnO hydrothermal growth process

The hydrothermal process for the synthesis of ZnO nanostructures consist of the following steps:

- Deposition of a thin layer of ZnO nanoparticles over the substrate by sputtering, spin coating, or other thin film deposition techniques. The ZnO nanoparticles act as a seed for the nucleation of ZnO nanowires growth.
- Annealing of the seed layer at high temperature (180 °C 250 °C) for better crystallinity and orientation of the ZnO nanoparticles.
- 3. Aqueous precursor solution of the alkaline reagents (e.g., NaOH, KOH, hexamethylenetetramine, or HMTA  $((CH_2)_6N_4))$  and Zinc salts (e.g., ZnCl<sub>2</sub>, ZnSO<sub>4</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>) is prepared. The alkaline solution provides OH<sup>-</sup> ions

whereas Zn salts act as the source of  $Zn^{2+}$  ions for the growth of ZnO nanowires.

- The seed layer coated substrate is kept in the precursor solution at fixed temperature and pressure for a specified time duration.
- 5. After growth, the as-grown samples are rinsed with deionized water and dried in air.

The growth process of ZnO nanorods can be explained as follows: The  $\pm$ (0001) planes in the wurtzite structure of ZnO are the high energy polar surfaces, consisting either  $Zn^{2+}$  or  $OH^$ ions. As the ZnO nucleus is formed, OH<sup>-</sup> ions are preferentially adsorbed over the polar planes to minimize the surface energy. As a result, the polarity of the surface is inverted and OH<sup>-</sup> terminated plane becomes Zn<sup>2+</sup> terminated plane and vice versa. The process is repeated over the course of time, which resulted in the fast growth of ZnO along c-axis, exposing nonpolar facets (1100 and  $2\overline{1}\overline{1}0$  [48]. Therefore, the preferential growth in one direction resulted in the formation of ZnO nanorod like structures. However, the hydrothermal technique is a versatile technique which allows the usage of different surfactant to obtain different kinds of nanostructures. Further, the different salts can be added to the precursor solution to obtain doped ZnO nanostructures. During the hydrothermal growth, the following reactions take place in the precursor solution [46]:

$$Zn^{2+} + 2OH^{-} \longleftrightarrow Zn(OH)_2 \tag{1.3}$$

$$Zn(OH)_2 + 2OH^- \longleftrightarrow [Zn(OH)_4]^{2-}$$
 (1.4)

$$[Zn(OH)_4]^{2-} \longleftrightarrow ZnO_2^{2-} + 2H_2O \tag{1.5}$$

$$ZnO_2^{2-} + H_2O \longleftrightarrow ZnO + 2OH^-$$
(1.6)

$$ZnO + OH^- \longleftrightarrow ZnOOH^-$$
 (1.7)

In the eq. 1.3,  $OH^-$  ions come from alkali, not from the H<sub>2</sub>O. Therefore, other organic solvents like ethanol, butanol or other ionic liquids can be used in place of water in order to obtain different aspect ratios of ZnO nanowires. As the polar solvent has strong interaction with the polar surface, they absorbed over the polar surface to hinder the growth alone c-axis. This resulted in the lower aspect ratio of the nanorods [48]. In the eq. 1.4, different species of zinc hydroxides  $(Zn(OH)_2, Zn(OH)^+ \text{ and } [Zn(OH)_4]^{2-})$ could be formed, which depends on the pH of the precursor solution, that can be controlled by changing alkaline reagent concentration. The major challenge in hydrothermal growth is to control the growth rate and to avoid homogeneous nucleation, which is responsible for the precipitate formation and to encourage heterogeneous growth over the seed layer to obtain high aspect ratio nanorods. The alkali solutions such as KOH and NaOH get dissolve in water instantly and increase the pH of the solution, which leads to rapid precipitate formation. Therefore there is a need for different alkali reagents which can control the pH and therefore growth rate of ZnO. Interestingly, Liu et al., have reported that NH<sub>3</sub>.H<sub>2</sub>O could not only provide a basic environment for growth but also mediate heterogeneous nucleation [49]. The most commonly used reagents for hydrothermal growth are HMTA and zinc nitrate. During the ZnO nanostructure using HMTA as alkali reagent, the following reactions occur:

$$(CH_2)_6N_4 + 4H_2O \longleftrightarrow (CH_2)_6N_4 - 4H^+ + 4OH^-$$
(1.8)

$$(CH_2)_6N_4 + 6H_2O \longleftrightarrow 6HCHO + 4NH_3 \tag{1.9}$$

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$$
 (1.10)

$$Zn^{2+} + 4NH_3 \longleftrightarrow Zn[(NH_3)_4]^{2+}$$
(1.11)

$$Zn^{2+} + 2OH^{-} \longleftrightarrow Zn(OH)_{2} \tag{1.12}$$

$$Zn(OH)_2 \longleftrightarrow ZnO + H_2O$$
 (1.13)

Unlike, the growth in alkali solution, the OH<sup>-</sup> ions are provided by the H<sub>2</sub>O molecules in the solution. HMTA acts as a pH buffer and ensures the constant supply of OH<sup>-</sup> ions in the precursor solution (eq. 2.1). Further, the hydrolysis of HMTA produces ammonia and HCHO in the solution. The decomposition of HMTA is dependent on the pH and temperature of the solution. The ammonia plays two major roles: firstly, to maintain a constant supply of OH<sup>-</sup> ions and secondly to make a complex with  $Zn^{2+}$  ions, to ensure a timely and steady supply of  $Zn^{2+}$  ions. After that,  $Zn^{2+}$  ions react with  $OH^{-}$  ions, which resulted in the formation of  $Zn(OH)_2$ . However,  $Zn(OH)_2$  is thermodynamically unstable and transformed into ZnO [50]. As shown in Figure 1.6, The HMTA has not only to accelerate the growth alone c-axis but also adhere over nonpolar side facets to inhibit the growth in the lateral direction and allow access of ZnO molecules over (0001) place, which resulted in the growth of high aspect ratio nanorods [51, 52].

#### 1.3 Review of past work

The one dimensional ZnO nanostructures have gained a lot of attention from the research community owing to novel physical and chemical properties and higher sensing response comparing to ZnO thin films. Therefore, a significant amount of effort was made to obtain a variety of nanostructures. Due to the simple and low-cost synthesis process, the hydrothermal technique has become popular among the researchers. Further, by using different organic and inorganic additives in the precursor solution, a variety of ZnO nanostructures such as nanorods, nanotowers, nanovolcanoes, nanopipes, dumbbell-like, flower-like, disk-



*Fig. 1.6:* Schematic showing the role of hexamethylenetetramine as a capping agent

like, nanorings, nanobows, nanohelixes, nanosprings, nanocages, nanobelts have been synthesized using hydrothermal technique [53-60]. However, the major disadvantage with hydrothermal growth was that it is prone to the variety of intrinsic defects such as oxygen vacancies, zinc vacancies, oxygen interstitials, zinc interstitials, oxygen antisites and zinc antisites [61]. Therefore, several efforts were made to decrease the defect concentration and to improve the crystallinity of hydrothermally obtained ZnO nanostructures [62].

Broadband photodetectors are essential components of optoelectronic systems and find extensive applications in optical communication, environmental monitoring, image sensing, foldable displays, surveillance, remote sensing, ecological monitoring, astronomical detection, photometers, analytical applications, energy harvesting, biological research and chemical analysis [63-68]. A substantial amount of work has been done towards the synthesis of broadband photodetectors. ZnO is a wide bandgap material. Therefore, it is a potential material for broadband photodetection. Generally, pristine ZnO is sensitive to only near UV radiation. Therefore, in order to make ZnO responsive towards the visible and NIR region, ZnO has been used with several other materials such as graphene, perovskite, PbS quantum dots,  $Co_3O_4$ and so on [69-73]. However, there are quite a few studies on using pristine ZnO nanostructures as broadband photodetector [74].

### 1.4 Challenges

ZnO is a wide bandgap material, therefore it has become material of interest for near UV detection. However, pristine ZnO is not sensitive towards deep UV, visible and near IR region of the electromagnetic spectrum. Therefore, in order to develop a broadband photodetector, it has been doped or used with other visible and NIR sensitive materials. This process is quite complicated and increases the complexity and cost of device fabrication.

Usually, researchers have used basic 1D nanostructures such as nanorods, nanopillars, nanocolumns, nanotubes etc. for the development of photodetector, which eventually could not generate high sensing response due to their low charge transportation efficiency and several other factors. Therefore, it has become quite critical to synthesize more complex nanostructures that could provide a larger surface area and better charge transportation between the electrodes at lower fabrication costs. However, the development of such high responsivity and low-cost broadband photodetector is still a big challenge.

Further, the nanostructures obtained by hydrothermal growth are prone to low adhesivity with the substrate and variety of intrinsic defects which could significantly impact the device performance. Therefore, it is highly desirable to improve the thin film adhesion and reduce the inherent defect concentration in the hydrothermally grown ZnO nanostructures. Additionally, while developing UV photodetectors, device reliability is a major issue because the high energy UV radiation could be extremely harmful and could significantly hamper the device functioning. Therefore, it has become essential to investigate and minimize the effect of UV radiations over the device performance, towards the development of highly reliable UV sensor.

Moreover, considering the increasing application of batteryoperated flexible and wearable UV sensors such as wearable UV dosimeters, a variety of flexible substrates e.g., polyimide, cellulose paper, PET, plastic etc. have been reported. However, no significant growth has been achieved in this direction. Therefore, it is vital to synthesis ZnO nanostructures over a flexible substrate which could produce high UV sensing response and consume low electricity to reduce the power consumption, therefore lengthen the battery life of the device.

### 1.5 Objectives of this work

The main objective of this work is to develop ZnO based high responsivity and reliable broadband photodetector. The other goals of this work are as follows:

- To control the intrinsic defect density and to improve the adhesivity with the substrate of the hydrothermally grown ZnO nanostructures.
- 2. To synthesis complex ZnO nanostructures with larger surface area and high charge transport efficiency.
- To develop a high responsivity and low-cost broadband photodetector using complex ZnO nanostructures obtained by simple and economic hydrothermal process.
- 4. To investigate the effect of prolonging UV illumination over the ZnO nanostructures characteristics and the device re-

sponse. Additionally, to find a way to stop ZnO degradation due to UV exposure.

5. To develop highly sensitive UV photodetector for flexible and wearable electronics over a flexible substrate, which could operate at low power to lengthen the battery discharge time.

### **1.6** Organization of the thesis

- 1. **Chapter 1** includes the introduction to a different class and working principle of a photodetector. A detailed discussion about the material properties and different growth techniques, especially hydrothermal growth of ZnO nanostructures, has been done.
- 2. **Chapter 2** discussed the material and the deposition process used during this work. Further, the different structural and optical techniques used for device characterization have been briefly discussed.
- 3. **Chapter 3** discusses the hydrothermal growth to a variety of ZnO nanostructures by using additives in the precursor solution. The effect of additives over the structural and optical properties of ZnO nanostructures has also been discussed in detail.
- 4. **Chapter 4** has demonstrated ZnO honeycomb nanostructures for broadband photodetectors.
- 5. **Chapter 5** discussed the effect of high energy UV radiations over ZnO nanostructures characteristics and also about the prevention techniques.
- 6. **Chapter 6** demonstrate Al foil as a flexible substrate. The growth mechanism of the Al-doped nanoplate network has

been discussed. Further, a brief discussion about low power operation and piezoresponse has been added.

7. **Chapter 7** is the conclusion of the work that has been presented in the thesis and a small description of the future scope of this work.

### **Chapter 2**

## Experimental methods and characterizations techniques

### 2.1 Introduction

There are several key points which are needed to be considered for the development of a high-performance photodetector, like the selection of proper material, the material synthesis and deposition processes and the characterization techniques used to evaluate various device parameters. This chapter discussed a variety of materials employed in the presented research work. Further, it describes various material synthesis and nanostructures fabrication processes. After that, different characterization tools that have been used throughout the work are discussed in detail.

### 2.2 Materials used for device fabrication

The properties of material control the device physics; therefore, the selection of proper material is criteria for efficient device fabrication. Only those materials which satisfy the necessary condition of the energy bandgap, energy levels, and emission/absorption spectra peaks can be selected for an active layer of the device. The other properties like surface tension, solubility, melting point and evaporation, are essential when solutionprocessed device fabrication techniques are used. For the design of UV photodetector, it is crucial to select the material which is capable of the strong UV absorption and have low defect density [75]. All the materials are used as received without any further process or purification.

### 2.2.1 ZnO

ZnO is a metal oxide semiconducting material with unique optical and electrical properties. It can be grown in a variety of highly crystalline nanostructures. It is a wide bandgap semiconductor with a bandgap of 3.37 eV and therefore, its absorption and emission lie in the UV region which makes it a suitable material for UV emission and detection based applications [76]. It has a large exciton binding energy of 60 meV. Therefore, it is suitable for a variety of applications, which operate at room temperature. Further, it is a highly stable and biocompatible material.

### 2.2.2 Silver (Ag)

The noble metal Ag with a work function ranging from  $\sim$  4.20 eV to 4.78 eV, is used as an electrode for making Ohmic contacts with ZnO based devices, especially planar photodetectors and is deposited by physical vapor deposition technique (melting point: 962 °C).

### 2.3 Substrate preparation

### 2.3.1 Cleaning of glass substrate

Glass is the most commonly used substrate for device fabrication due to its smooth surface and is transparent to the spectral range of interest, i.e. ultraviolet A, visible and near-infrared. The glass pieces of 1.2 cm $\times$ 1.2 cm $\times$ 0.1 cm (L $\times$ W $\times$ H) were used as substrate. The cleaning of substrates is critical for the consistent growth of nanostructures and reliable device performance. Cleaning of the substrates was performed to remove inorganic and organic impurities clinging to their surface. The substrates were firstly cleaned in an ultrasonic bath of detergent in water, after that rinsed with deionized (DI) water. Afterward, the samples are sequentially ultrasonicated in DI water, acetone, and isopropanol (10 min each). The cleaned substrates were dried in nitrogen gas and placed in a desiccator.

### 2.3.2 Hydrothermal deposition of ZnO nanorods

The hydrothermal processing is a non-conventional, solution-based approach for the growth of nanostructures of inorganic materials under maintained temperature and pressure. The hydrothermal technique has become an essential tool for advanced materials processing, owing to its cost-effectiveness and low thermal budget processing of nanostructured materials for a wide variety of technological applications. Hydrothermal growth process consists of heterogeneous chemical reactions taking place in the presence of an aqueous solvent in a closed system above the room temperature and a pressure greater than 1 atm. In this work, the hydrothermal growth of a variety of ZnO nanostructures was accomplished in two major steps:

1. **Deposition of seed layer:** Initially for the growth of ZnO seed layer, 2 mM solution of zinc acetate [Zn(CH<sub>3</sub>COO)<sub>2</sub>, Sigma-Aldrich, 99 % purity] and equimolar ethanolamine was prepared in 2-methoxy ethanol. The solution was stirred using a magnetic stirrer at 700 rpm for 6 hours. After that, the solution was spin-coated on a clean glass substrate using a spin coater and further heated at 250 °C in an oven for 5 minutes to ensure the proper adhesion of the seed layer with the substrate [77].

2. Growth of ZnO nanostructures: For the growth of ZnO nanostructures, the precursor solution of 1 mM zinc nitrate hexahydrate [Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Sigma-Aldrich, 99% purity] and 1mM of hexamethylenetetramine (HMTA, Sigma-Aldrich, 99% purity) in 25 ml distilled water has been prepared. The Apex series balance (APX-60, Denver instrument) has been used for the measurement of all chemicals. The solution was mixed in the sealed glass beaker using a magnetic stirrer at room temperature for 15 minutes. As the growth solution is adequately mixed, the seed layer coated samples were immersed and placed upside down in the bottom of the beaker, sealed by plastic wrap to avoid evaporation of water during the hydrothermal process. After that, the glass beaker was kept in an oven at a temperature of 110 °C for 4 hours. Then, the samples were taken out from the glass beakers and rinsed in DI water for the removal of precipitates from the surface of samples. A schematic of the growth setup used in this thesis is shown in Figure 2.1.



Fig. 2.1: Schematic of ZnO hydrothermal growth process

## 2.3.3 Deposition of electrodes / Physical vapour deposition

Thermal evaporation is a conventional method for the deposition of metals, metal oxides and small organic molecules on the variety of rigid as well as flexible substrate. The deposition process involves two major steps: evaporation and condensation of the target material. In the first steps, the target material is kept in the boat made of high resistance materials like tungsten (W) and molybdenum (Mo). The boat is heated to the melting temperature of the target material for its evaporation (see Figure 2.4). The boat temperature is controlled by changing the input electrical power. The deposition process takes place in the ultra-high vacuum condition (usually  $10^{-6}$  mbar to  $10^{-7}$  mbar), to avoid interactions between the evaporated material and impurities present in the air. Further, the mean free path of the vapor under the high vacuum conditions is longer than the distance between boat and samples. Therefore, the vapor of the target material could travel without colliding with foreign species from the source to the substrate. In the second step of the deposition process, the material vapor condenses and deposited over the substrate surface. A crystal oscillator monitors the film thickness and deposition rate. One of the major advantages of PVD techniques is that the evaporated material has a gentle impact over the substrate surface, therefore it is more suitable for soft substrates materials. Two planner Ag electrodes of 50  $\mu$ m×2 mm×100 nm (channel length × width × thickness) for the development of planar photodetector was deposited using PVD system purchased from Hind High Vacuum Private Limited Company, India. The schematic of the thermal evaporation set-up is shown in Figure 2.2. The initial rate of Ag deposition was kept at 0.1 Å/s, which was increased up to 1 Å/s, as the thickness reaches 10 nm.



Fig. 2.2: Schematic of physical vapor deposition

### 2.3.4 DC sputtering

DC or direct current sputtering system is generally used for high crystallinity thin film deposition by the sputtering process. The sputtering system consists of a vacuum chamber, a pellet of target material, a sample holder attached to the cathode and anode electrodes. Initially, after loading the target pellet and the substrates, the chamber pressure is reduced to  $10^{-6}$  mbar. After that, Argon gas is purged in the chamber. Now, as a high DC bias is applied between the electrodes, the intrinsic electrons and the Argon molecules are accelerated and the interaction of Argon with electrons and other charged species ionized the Ar atoms to Ar<sup>+</sup> ions. The plasma of ionized Ar atoms (violet/blue) is visible from the optical window, provided in the vacuum chamber. Under the influence of high electric field between the electrodes, the Ar<sup>+</sup> ions bombarded over the target pallet which was connected to the cathode and ablates the target material, which in turn deposited over the substrate. As a result, a highly homogeneous and crystalline thin is obtained over the substrate. The schematic of the DC sputtering is shown in Figure 2.3. In this work, Pt nanolayer (non-continuous film) was deposited using the dc-sputtering technique.







Fig. 2.4: Instruments used for the fabrication of devices

## 2.4 Thin film and device characterization techniques

## 2.4.1 UV-Vis absorption spectroscopy and diffuse reflectance spectroscopy

When electromagnetic waves incident over a matter, a variety of phenomenon could take place like scattering, reflection, transmission, absorption and fluorescence/ phosphorescence. The incident wave would be absorbed by the matter when the energy of the wave is equal to or more than the bandgap of matter. The schematic of the operation of a typical UV-Vis spectrophotometer is shown in Figure 2.5. As the light is incident on the sample, it would transmit through the sample or adsorb by it. Therefore, the amount of light absorbed by the sample could be calculated as the difference between the incident light intensity ( $I_o$ ) and the transmitted light intensity (I). Quantitatively absorbance is described by the equation:

$$A = -\log(T) = -\log(I/I_o) \tag{2.1}$$



*Fig. 2.5:* Experimental set-up for UV-Vis absorption spectroscopy

In the above equation, A is absorbance, T is transmittance,  $I_o$  and I are the intensity of the incident light and the transmitted light, respectively, at a given wavelength. The absorbance A of material is a dimensionless quantity. In general, a UV-Vis spectrophotometer consists of a broadband light source such as a tungsten-halogen or deuterium lamp, a dispersion device for the separation of different wavelengths and a detector to convert visible light intensity into an electrical signal. Firstly, the absorption of the bare substrate has been taken as a baseline, which would be subtracted from the sample data to obtain the absorption data

of the sample only. The monochromatic light coming from the dispersion device is passed through a beam splitter, which would split the beam and now one beam fall on the sample and another one would fall on the reference cell. The light transmitted through the sample and reference cell is detected and recorded by the detectors. Absorption results of thin films are obtained by subtracting the reference spectra from the substrates. Absorption of the materials also depends on the sample thickness, which is given by the Beers-Lambert law:

$$I(\lambda) = I_o \times e^{-\alpha \lambda d} \tag{2.2}$$

Where  $I_o$  is the incident light intensity,  $\alpha$  is the absorption coefficient, and d is the thickness of the sample [78].

All absorption spectra included in this thesis were measured with a Varian Cary 300 UV-Vis spectrophotometer. Optical UV-Visible (UV-Vis) absorption measurements were taken within the wavelength range of 300-800 nm in normal incidence mode from ZnO honeycomb structures, nanorods, thin film and nanocolumns grown over glass substrates. Cleaned glass samples were used as a reference.

Low scattering of incident light by the solid thin film facilitates ease of the calculation of bandgap (Eg) for the absorption data. However, in the case of powder, nanostructures, or colloidal samples, where the scattering phenomenon is more dominant due to large surface area, the dispersed light also counted as absorbed light and is not distinguishable from each other. Therefore, to overcome these difficulties in the measurement of absorption spectra, diffuse reflectance spectroscopy (DRS) has been used, which is based on the theory proposed by Kubelka and Munk [79].

This theory uses the diffuse reflectance measurements to estimate the Eg values with good accuracy when the material scatters in a perfectly diffuse manner. The diffuse reflectance R is related to the Kubelka–Munk function F(R) by eq. (2.3):

$$F(R) = \frac{(1-R)^2}{2R}$$
(2.3)

Where R is the percentage reflectance from the sample [79, 80]. The graph of  $[F(R) \times E]^2$  versus energy E in electron-volt is used to measure the bandgap of the material. An attachment to a UV-Vis spectrometer has been used to measure the diffuse reflectance. Here an integrating sphere detector (Fig. 2.6(b)) is attached to Cary 60 (Agilent) UV-Vis instrument (Fig. 2.6(a))



*Fig. 2.6:* Experimental set up for diffuse reflectance measurement (a) Carry 60 UV-Vis spectrometer, (b) an integrating sphere attachment to detect diffuse reflectance

In Cary 60 white lamp source (xenon lamp) is used and the grating is used to select monochromatic wavelength. Here in this setup, the initial beam split into two parts, one is taken as a reference beam and the second goes on the sample. Finally, the output is compared to the reference beam and data has been collected. Since output photons come through scattering from the samples, so there is an integrating sphere detector.

### 2.4.2 Fourier transform infrared spectroscopy

The technique is used to obtain absorption or emission in the infrared region of the electromagnetic spectrum. In this technique, samples are shined by a light beam consisting of different wavelengths of light at once and the amount of light absorbed by the sample is measured with the help of a detector. The next beam contains a different combination of frequency, giving second data point and so on. To generate these beam patterns, a broadband light source such as tungsten or xenon lamp and a Michelson interferometer is used. The interferometer consists of a stable mirror, a movable mirror and a beam splitter. The output beam of the interferometer is passed through a sample and then to the detector. It requires Fourier transform to convert the raw data into the actual spectrum, therefore called Fourier transform infrared spectroscopy.



Fig. 2.7: Schematic of FTIR spectroscopy setup

### 2.4.3 Photoluminescence (PL) spectroscopy

Photoluminescence spectroscopy is a highly selective and extremely sensitive, non-destructive technique to investigate the presence of various midgap states, which requires minimal sample manipulation and environmental control. It can be used to probe surface and interface roughness, variety of impurities and doping levels in the direct bandgap materials. It works on the principle of spontaneous emission under optical excitation. When a laser light of photon energy higher than the bandgap of material, incident over the sample, electrons in the valence band are excited to the conduction band [81]. These excited electrons always seek to return the lowest available energy states. Therefore, in the case of direct bandgap material, electron recombines radiatively with the holes in the valence band. The energy of an emitted photon corresponds to the bandgap of the material. However, energy may also be lost through phonons (vibrations) in the lattice. Moreover, if the sample consist of impurities or defects than exciton recombination could also take place from the conduction band to midgap states or from midgap states to valence band, which resulted in low energy photon emission.

To investigate the emission characteristics, qualitative analysis of defects of ZnO nanocolumns, thin film, naorods and honeycomb structures, photoluminescence (PL) measurements were performed using a Dongwoo Optron PL system with an He-Cd laser (excitation wavelength of 325 nm). All measurements were taken at room temperature. The schematic of the PL measurement system is shown in Figure 2.8.

### Table 2.1: LASER specifications

Source	He-Cd LASER, CW
Power	20 mW
Wavelength	325 nm
Spot diameter	0.43 mm
Penetration depth	60 nm
1	



Fig. 2.8: Experimental set-up of PL measurement system

### 2.4.4 Field emission scanning electron microscopy

FE-SEM is a non-contact, non-destructive electron microscopy technique for obtaining the images of nanostructures surface. It consists of an electron gun that produces a focused beam of high energy electrons, which is directed and scanned over the surface of the nanostructures. The interaction between electron and surface atoms generates different signals, containing the topological and chemical composition of the material. These signals include (i) secondary electrons (SE) from which the images of nanostructures surface are obtained, (ii) backscattered electrons (BSE) which are used to determine crystal structures and orientation, (iii) photons i.e. the characteristic X-rays basically used for elemental analysis, (iv) visible light (cathodoluminescence (CL)), and (v) heat. In a typical FESEM system, an electron beam is thermionically emitted from an electron gun coupled with a tungsten filament cathode. Tungsten is normally used because it has the highest melting point and lowest vapor pressure of all metals, thereby making it suitable for electron emission. The schematic of the SEM is shown in Figure 2.9. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. The electron beam is passed through a multihole aperture, however standard aperture size is 30  $\mu$ m. Condense lens are used to control the demagnification. The electron beam of 1-20 KeV is focused in 1-10 nm diameter on the specimen with the help of an objective lens. The focused electron beam is scanned across the surface of the sample through the scan coil. The emitted electrons are collected by a detector and are converted to voltage. The SEM image is formed from a two-dimensional density distribution of detected electrons [82]. A variety of signals can be detected, including secondary electrons, backscattered electrons, x-rays, CL

and sample current. This technique is useful for producing relatively quick qualitative impressions of the surface.

The FESEM Supra55 Zeiss system has been used in the present study to investigate the morphology, lengths, size and orientation of the ZnO nanostructures. The FESEM characterization is performed at 5-10 kV acceleration voltage with a working distance of 1-10 mm. For cross-sectional SEM images, the samples are scratched at the backside with a diamond pen and then cracked. The samples for top views and cross-sectional views are stick onto an SEM stub with carbon tape and sputter with 2 nm Au films to reduce charging effects during the SEM measurements.



Fig. 2.9: Schematic diagram of FESEM

### 2.4.5 XRD measurements

X-ray diffraction (XRD) is a powerful, reliability, simplicity and non-destructive technique to determine the crystal structures, lattice constants, orientation of single crystals, defects, stresses and the chemical composition of the material. The wavelength of incident electromagnetic radiation onto the substrate is of only a few angstroms (ranging between 0.7-2 Å) i.e. the order of lattice spacing. In order to analyze a thin film or power sample, a monochromatic X-ray beam is directed at the sample and a detector is placed at the opposite angle of incidence. There are different metals like Cu, Co, Mo, Cr etc. which can be used as a cathode for X-ray generation. In our work, Cu has been used as an X-ray source, as its wavelength is near to the lattice parameters of ZnO, ease of cooling and availability of standard data. Generally, the X-ray incident angle ( $2\theta$ ) is varied from 10 to 90 degrees and the diffracted light intensity is measured from a detector to obtain a diffraction intensity plot with respect to different angles of incidence. Diffraction peaks occur only when constructive interference takes place between the reflected X-rays. The condition for constructive interference is given by Bragg's law, defined as:

$$n\lambda = 2d \times \sin(\theta) \tag{2.4}$$

where,

n = Order of refraction

- $\lambda$  = X-ray wavelength
- d = spacing between atomic planes
- $\theta$  = Angle between X-ray and scattering planes



Fig. 2.10: Schematic of Bragg's law

The relative intensity of diffraction peaks depends on the

type and arrangement of the atoms in the crystals [80]. The peak positions are compared with the standard JCPDS files of the material and based on the shift in peak position or broadening in the peak, useful information about the crystal lattice is obtained. In this work a Rigaku D/Max-2000 PC diffractometer was used, using CuK $\alpha$  radiation ( $\lambda$ = 1.54056 Å) at an X-Ray source operating voltage of 40 kV in the 2 $\theta$  range of 30°– 80°at a scanning rate of 2 °/min.

#### **Excited electronic states** Virtual electronic states **Excited phonon states** Phonon ground states Anti Resonant Stoke Rayleigh Stoke Stoke Raman Raman Raman Raman Shift Shift Shift Shift

### 2.4.6 Raman spectroscopy

Fig. 2.11: Different kind of scattering phenomenon

The Raman spectroscopy is used to analyze lattice dynamics, structural properties, chemical composition, orientation, or crystalline quality and electronic and magnetic properties of the system. Raman is the inelastic scattering of photons by phonons. As direct phonon- phonon coupling is weak for UV-Vis photons; their interaction takes place mainly with the mediation of electrons. As photons interact with the material, electron-hole pair created. The electron-hole pair is then scattered into another state by emitting or absorbing a phonon via electron-phonon interaction. Finally, it recombines radiatively, emitting the scatter phonon with lower or higher energy, while leaving the electronic states of the matter unchanged. If the scattered light is of lower frequency, then it is denoted as stoke Raman scattering and if scattered light exhibited higher frequency, then it is called anti-stoke Raman scattering.

The experimental set-up of Raman spectroscopy is shown in Fig. 2.12. In this work, the samples are shined by an intense 488 nm laser beam. The scattered light from the sample is collected with the help of lens. The major challenge here is to filter out the weak inelastic scattered light from intense Rayleigh scattered light. A notch or bandpass filter is used to filter the useful Raman scattered light and discard Rayleigh scattered light [83, 84]. In this work, Raman measurement was carried out on an RIR-M151 Research India micro-Raman system at room temperature, using a 532 nm line of diode laser as an excitation source with 75 mW power.



Fig. 2.12: Experimental set-up of Micro Raman spectroscopy

### 2.4.7 Confocal microscopy

It is an optical microscopy technique to obtain high resolution and contrast 3D images of the sample. In general, the resolution of optical microscopy is not excellent. Therefore, in order to improve the resolution, a pinhole is placed at the confocal plane of the lens, which eliminates the out of focus light and produces a very sharp and clear optical image of the sample. Further, it enables us to scan the sample at different heights to measure and plot the sample image at a different thickness. Also, the images can be combined to form a 3D image of the sample.

The primary issue with this technique is that due to the presence of pinhole, most of the sample emission is blocked and a minimal amount of emission reaches the detector. Therefore, to obtain a sufficient amount of radiation from the sample, long exposures are often required. Further, to sense such weak signals, highly sensitive detectors such as a photomultiplier tube (PMT) or avalanche photodiode are used, which convert the incident light signal into an electrical one. Confocal microscopy images were obtained by using a Leica TCS SP5 confocal microscope equipped with a PMT detector.



Fig. 2.13: Schematic diagram for a confocal microscope

### 2.4.8 Electron paramagnetic resonance (EPR)

Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy is a technique used to study paramagnetic centers on various oxides surfaces, which may include surface defects, metal ions and organic or inorganic radicals. Each paramagnetic center gives a specific EPR signature. Every electron has a magnetic moment and a spin quantum number S = 1/2, with the magnetic component  $m_s = 1/2$  and -1/2. In a stable molecule, where the atoms are bonded by paired electrons, no net electron spin is present. Henceforth, when the sample is placed under a high magnetic field, no magnetic moment could be observed. However, in the case of unpaired electrons, there exists a net electron magnetic moment. Therefore, as the sample is placed in the high magnetic field, the electron magnetic moment aligns itself either parallel ( $m_s = -1/2$ ) or antiparallel ( $m_s = 1/2$ ), to the field, each alignment has specific energy due to Zeeman effect. The Zeeman effect explains splitting a spectral line into several components in the presence of the static magnetic field. The separation between lower and upper energy states ( $\Delta E$ ) for an unpaired free electron is given by:

$$\Delta E = E_+ + E_- = g_e \mu_B B_o \tag{2.5}$$

 $g_e$  = dimensionless constant called electron g-factor. For freeelectron it is 2.0023

 $\mu_B$  = Bohr magneton =  $\frac{e\hbar}{2mc}$  = 0.92 × 10<sup>-23</sup> J.T<sup>-1</sup>



Fig. 2.14: Two energy level system in the varying magnetic field

The equation indicates that the separation between both en-

ergy states is proportional to the static magnetic field strength. Therefore, an unpaired electron can move between the two energy levels by either absorbing or emitting a photon of energy  $hv = \Delta E$ . The EPR spectra are measured by keeping incident photon frequency constant and varying the external magnetic field. Since there are typically more free electrons in the lower energy states, there is a net absorption of energy which is measured and plotted against the applied magnetic field.

### 2.4.9 Current-Voltage (I-V) characterization

I-V characterization is a widely used and essential method to measure various device parameters of a photodetector. The photo current measurement setup is shown in Figure 2.15. The electrical characteristics of the photodetectors are measured by a Keithley 2612B source meter unit. Current is measured under a swept voltage bias and constant bias voltage. All the devices are measured under dark first and then measured under the monochromatic light source. Systems used for characterization of semiconductor films and devices are shown in Figure 2.16.



Fig. 2.15: Photo current measurement setup

Further, in order to investigate the device photoresponse, I-V measurements have been taken, and various device parameters like sensitivity, responsivity, specific detectivity, external quantum efficiency (EQE) and linear dynamic range (LDR) were calculated which can be explained as follows:

 Dark Current (I<sub>d</sub>): The current present in the sample, when it is kept in dark conditions is known as dark current. The variety of defects causes the dark current in the samples and



Fig. 2.16: Instruments used for characterization of devices

when the operating temperature is more than absolute zero, which could produce a large number of charge carriers under dark conditions. It restricts the capability of the device to sense the low-intensity light and reduce the overall device performance.

- 2. Photo Current (I<sub>ph</sub>): As the samples are shined by the light of energy more than the bandgap of material, electron-hole pairs are generated. In the presence of external or built-in electric fields, the charge carriers are swept towards their respective electrodes, leading to large current flow, known as the photo current.
- 3. **Response Time:** A photodetector should be quick enough to respond to the input light signal. It is measured by sending light pulses to the photodetector, and measuring how fast the photodetector can respond to these signals. When the device is exposed to the light source, then the time taken by the detector to reach from 10% to 90% of maximum photo current is called rise time. As the light is switched off, photo current starts to decrease and the time required to reach from 90% to 10% of maximum photo current is called fall time.
- 4. Photosensitivity (S): It is defined as the ratio of the differ-

ence between photo current and dark current to the dark current.

Sensitivity = 
$$\frac{I_{ph} - I_d}{I_d}$$
 (2.6)

5. **Photoresponsivity (R):** It is given by the ratio of photo current to incident photon power (P<sub>o</sub>).

Responsivity = 
$$\frac{I_{ph}}{P_o} A.W^{-1}$$
 (2.7)

 Specific detectivity (D\*): It is another critical figure of merits for photodetectors. The device with larger specific detectivity can detect weak signals, which is comparable to the device noise [69, 85, 86].

$$D^* = R \sqrt{\frac{A}{2eI_d}} \ cm.Hz^{0.5}.W^{-1}$$
(2.8)

7. External quantum efficiency (EQE): It is defined as the ratio of photo generated charge carriers to the number of incident photons [87]. As all the photo generated electron-hole pairs do not contribute to photo current, some of them recombine in the traps. Hence the quantum efficiency is the probability of the generation of electron-hole pair on the incident of a single photon, which could produce current in the external circuit. It depends on the number of photons irradiated onto the semiconductor, the number of absorbed photons and converted to carriers and the number of carriers that reach the outer circuit before they recombine.

$$EQE = \frac{hcR}{e\lambda} \tag{2.9}$$

Where h, c, R, e and  $\lambda$  are plank's constant, velocity of light, photoresponsivity, a charge on the electron and wavelength of the incident light, respectively.

8. Linear dynamic range (LDR): It is defined as the range of device response where the photo current is linear to incident optical power [88, 89].

$$LDR = 20 \times \log\left(\frac{I_{ph}^*}{I_d}\right) dB$$
 (2.10)

Where  $I_{ph}^*$  is the photo current at an incident optical power of 1 mW/cm<sup>2</sup>.

\_

### **Chapter 3**

# Growth of ZnO nanostructures and their structural and optical characterization

In this chapter, we have discussed the growth process and optical characterization of complex zinc oxide nanostructures like ZnO nanorods, nanocolumns, and honeycomb structures. The nanostructures were synthesized using a hydrothermal growth technique. Detailed analysis of the effect of the inorganic (KMnO<sub>4</sub>) and organic (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) additives in the precursor solution has been performed. We have demonstrated that the nanostructures morphology and intrinsic defects in the crystal lattice which have a significant impact on the photoresponsivity, photoluminescence (PL) and adhesivity of the film on to the underlying substrate, can be expertly tuned by varying the concentration of additives in the precursor solution. Additionally, the effect of thermal annealing over the morphology, crystallinity and bandgap was also investigated. The structural analysis of the samples was performed using FESEM and XRD characterization and the optical characterization of the samples was performed using absorption spectroscopy, Raman spectroscopy and photoluminescence spectroscopy techniques. The work presented here has provided a subtle solution towards the rectification of various problems pertaining to hydrothermal processes like poor adhesivity, feeble UV emission and challenges in the precise tuning of the morphology along with the bandgap in one go.

### 3.1 Introduction

The morphologies of nanostructures have a significant impact on the optical and electrical properties of zinc oxide. Therefore, researchers have put a lot of effort into obtaining a variety of nanostructures like nanorods, nanopenciles, nanowires, nanoflowers, nanoplates etc. Several fabrication techniques have been successfully employed for the growth of such nanostructures, viz. pulse laser deposition (PLD) [90], RF-Magnetron sputtering [91], chemical vapor deposition (CVD) [92], thermal evaporation [93], hydrothermal technique [62] etc. However, conventional systems like PLD, CVD, and sputtering are much expensive and complicated due to their high material cost and the requirement of sophisticated systems to maintain highly critical growth conditions. Unfortunately, these processes were found to be restricted to the growth of basic nanostructures like nanorods, nanoneedles and nanowalls. In contrast to conventional methods, hydrothermal growth is a straightforward and inexpensive solution-based approach that requires lower temperature (70 - 150 °C) processing conditions to that of conventional methods which can profoundly surmount the total thermal budget incurred in such growth processes. Additionally, hydrothermal growth is suitable for the growth on the flexible substrate, large-area fabrication as well as for the synthesis of different kind of basic nanostructures (nanorods, nanoplates and nanoneedles) along with the growth of complex nanostructures (nanocombs and nanoflowers), just by varying the composition and concentration of additives and reagents in the precursor solution. Numerous attempts have been made towards the fabrication of the complex ZnO nanostructures by not only varying the concentration of  $Zn(NO_3)_2$  and HMTA in growth solution but also by using or-
ganic and inorganic additives i.e. morphology controlling agents like KMnO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>), TEA, DEA, CTAB and many more towards the improvement in the device performance [62, 94-97]. It is worthwhile to mention over here that most of the complex but efficient nanostructures were grown hierarchically using hydrothermal process. Therefore, it has become very crucial to develop a technique for the facile and discernible growth of complex nanostructures for efficient device fabrication.

Moreover, it was noticed that hydrothermally grown samples are prone to poor adhesion with the substrate, which is a critical and essential factor that has to be considered for reliable and optimum system performance. For this reason, several methodologies have been proposed towards the improvement of the adhesivity of nanostructures with the substrate like annealing of the seed layer at high temperature, increasing the pH value of precursor solution [98-100]. However, this critical issue has rarely been discussed and remains a challenging task for the researchers.

It was also observed that hydrothermally synthesized ZnO nanostructures were susceptible to various defect states, which are primarily responsible for the emission in the visible region with feeble UV emission [101]. In order to rectify the issues mentioned above, different post-growth treatments like dielectric coating, Ar and H<sub>2</sub> plasma treatment, and metal coating have been reported by various scientific groups [102-104].

Although numerous methods have been proposed to rectify the above-discussed problems about the hydrothermal process, the synchronous rectification of all issues, as mentioned earlier in a single take, was rarely reported. On that account, it has become essential to systematically develop a methodology for a singlestep growth of complex ZnO nanostructures aiming for all the critical issues viz. adhesivity, defect passivation along with variation in morphology towards the overall improvement in the device performance.

In this chapter, we have attempted to solve all the issues in one go by fabricating a variety of complex ZnO nanostructures comprising stacked nanoplates around the nanorods via the hydrothermal process with the incorporation of additives like trisodium citrate ( $Na_3C_6H_5O_7$ ) and potassium permanganate (KMnO<sub>4</sub>) in the precursor solution. The systematic analysis has been performed on the influence of the surfactant over the morphology and optical properties of nanostructures. Trisodium citrate has been chosen because it act as a chelating agent that can facilitate the growth of different kind of morphologies as well as profound improvement in the adhesion of thin-film with the substrate while on the other hand potassium permanganate can significantly suppress the defect states to upraise the NBE to DLE ratio along with the significant enhancement in the adhesivity of the thin film with the substrate. The technique as mentioned above, can provide a suitable solution for the one-step growth of ZnO nanocolumns. Further, the growth of ZnO nanocolumns was thoroughly investigated with the help of FESEM and XRD data of the samples and a plausible mechanism has been proposed. Scotch tape peel-off test results have shown the excellent adhesion of thin film with the substrate. PL spectra of the samples have shown remarkable suppression in the visible emission; however, annealing of the samples has resulted in significant blue emission. The as-prepared samples have demonstrated substantial improvement in the adhesivity, morphology and optoelectronic properties that have made them a potential candidate for optoelectronic device applications. This study has shed some light on the growth mechanism and other interesting issues like adhesion, defect assisted absorption and the optoelectronic properties of the as-grown and annealed samples.

# 3.2 Experimental details



*Fig. 3.1:* Experimental procedure for the growth of ZnO nanos-tructures

The sample preparation process involves three major steps: (1) Cleaning of the glass samples. (2) Deposition of the seed layer over the glass substrate. (3) Hydrothermal growth of ZnO nanostructures. The schematic representation of the hydrothermal growth process has been shown in Figure 3.1. Glass samples were properly cleaned via ultrasonication in acetone, isopropyl alcohol, and DI water for 10 min. each. The seed solution was prepared by mixing an equimolar solution of zinc acetate and ethanolamine in 2-methoxyethanol. After that, the seed layer was coated via spin coating the seed solution at 3000 rpm for 30 seconds. Afterward, spin-coated samples were annealed at 250 °C for better crystallinity and adhesivity of the seed layer over the substrate. The precursor solution for hydrothermal growth was prepared by mixing  $Zn(NO_3)_2.6H_2O(0.1M)$  and hexamethylenetetramine (HMTA)(0.1M) in DI water. Now, 0.1 mM, 1 mM, 5 mM and 10 mM concentrations of the Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> was added in the precursor solution and the samples were named as 0.1CA, 1CA, 5CA and 10CA, respectively. Further to investigate the effect of KMnO<sub>4</sub> over the growth process, 10 mM KMnO<sub>4</sub> along with 10 mM and 20 mM of  $Na_3C_6H_5O_7$ , was added to the solution. The samples were named as 10ZC and 20ZC, respectively. The solution was left on stirring for ten minutes. For hydrothermal growth, sealed glass beakers containing precursor solution and samples were kept in an over at 110 °C for five hours. Finally, after growth, samples were thoroughly washed using DI water and acetone, followed by drying at 110 °C.

Morphology and chemical composition of ZnO nanostructures were obtained using field emission scanning electron microscopy (FESEM), Zeiss Supra-55 equipped with energy dispersive X-ray (EDX). Crystallinity was analyzed using X-ray diffraction (XRD) having a Cu-K $\alpha$  source. Photoemission properties of the samples were measured using photoluminescence (PL) analyzer (Dongwoo Optron DM 500 i) equipped with a continuous wave He-Cd laser (excitation wavelength 325 nm) and a PMT detector. Raman analysis was performed by Horiba Jobin Yuon HR 800 UV Raman spectrometer. UV-Vis absorption spectra were obtained by (Cary 60 UV-Vis, Agilent Technologies) with a range of wavelengths from 200 nm to 800 nm. Fourier transform infrared spectroscopy was carried out using FT-IR, Tensor 27, BRUKER with the range of wave number from 400 – 4000 cm<sup>-1</sup>.

### 3.3 Results and discussion

### 3.3.1 Growth of honeycomb structures

Figure 3.2 shows the FESEM images of the ZnO samples. Randomly oriented ZnO nanorods (Figure 3.2(a)) with an average diameter of 50 nm were observed without any addition of the additives in the precursor solution, which is in good agreement with earlier reported work. As the small amount of trisodium citrate (0.5 mM) has been added in the precursor solution, the growth of nanoplates like structure was observed. On further increase in the concentration on trisodium citrate to 5 mM, nanoplates start to merge with nearby nanoplates, which resulted in the growth of honeycomb-like structures. On further increasing the concentration of trisodium citrate to 10 mM, precipitous growth was obChapter 3: Growth of ZnO nanostructures and their structural and optical characterization



*Fig. 3.2:* FESEM image of ZnO samples obtained using 0mM, 0.5 mM, 5mM and 10 mM concentration of trisodium citrate in the precursor solution

served. The average width of the nanoplates was found to be  $20\pm2$  nm.



*Fig. 3.3:* Schematic representation of the growth of nanorods and honeycomb nanostructures

A possible explanation of the growth of HC structures is as follows (Figure 3.3): citrate ions act as a chelating agent and therefore get preferentially adsorbed over the non-polar faces of ZnO nuclei and inhibits the growth along the preferential c-axis direction [105]. Now,  $ZnO_2^{2-}$  ions start to adsorbed over the non-polar face, thereby resulting in the growth of the nanoplates network. As the growth proceeds, the initially formed nanoplates merge at Chapter 3: Growth of ZnO nanostructures and their structural and optical characterization

the edges resulting in well-arranged honeycomb nanostructures, as shown in FESEM images.

XRD plots of the samples were presented in Figure 3.4. All XRD peaks can be assigned to the ZnO Wurtzite structure and were in good agreement with the JCPDS file of ZnO ((JCPDS 01-089-7102). The XRD plot of pristine ZnO nanorods has shown an intense peak at 34.38°, corresponds to (002) plane, which represents preferential growth along the c-axis. Interestingly, as the concentration of trisodium citrate has been increased, a significant suppression in (002) peak and enhancement in the (100) and (110) peak has been observed which also confirmed that the growth along polar c-axis has been suppressed and preferential growth along nonpolar a-plane. Moreover, on further increasing the concentration of trisodium citrate to 10 mM, all XRD peaks were heavily suppressed which shows that the crystallinity of the sample has been decreased.



*Fig. 3.4:* XRD plot of the pristine ZnO nanorods, 0.5CA, 5CA and 10CA samples

In order to confirm the presence of Zn interstitial in the samples and to analyze structural properties, chemical composition, and crystalline quality of the samples, Raman analysis was performed. Raman spectroscopy utilizes the inelastic scattering of photons, caused mainly by the electrons phonon interaction. ZnO has 12 phonon modes. At  $\Gamma$  point of Brillouin zone, phonon modes are represented as:

$$\Gamma_{out} = 2A_1 + 2B_1 + 2E_1 + 2E_2 \tag{3.1}$$

Where one  $A_1$  and one  $B_1$  mode are acoustic modes and the other 6 are optical modes. In  $E_1$  and  $E_2$  modes, phononic vibration takes place perpendicular to the c-axis. Both modes are doubly degenerated, as there are two-axis perpendicular to the c-axis which are energetically equivalent and linearly independent. Therefore vibration in the lattice can take place in both directions. In  $A_1$  and  $B_1$  modes, lattice vibrations are parallel to the c-axis and both are singly degenerated modes.  $A_1$  and  $E_1$  modes are polar modes, and both modes have longitudinal (LO) and transverse (TO) components [106].

The Raman spectra of pristine sample as presented in Figure 3.5 shows sharp peaks at 98.8 cm<sup>-1</sup>, 330 cm<sup>-1</sup>, 382 cm<sup>-1</sup> and 438.5 cm<sup>-1</sup> which correspond to E<sub>2</sub>(low), E<sub>2</sub>(high) - E<sub>2</sub>(low),  $A_1(TO)$  and  $E_2(high)$  modes of ZnO, respectively [107]. However, in Raman spectra of the 5CA and 10CA samples, some additional broad peaks around 160 cm<sup>-1</sup> and 270 cm<sup>-1</sup> were observed, which can be assigned to Zn interstitial defects [108]. Moreover, significant shift in 5CA and 10CA samples in E<sub>2</sub>(high) peak from  $438.5 \text{ cm}^{-1}$  to  $425.5 \text{ cm}^{-1}$  and  $E_2(\text{low})$  from  $98.8 \text{ cm}^{-1}$  to  $81.8 \text{ cm}^{-1}$ were observed which indicates the tensile stress in the sample due to the higher concentration of Zn interstitials in ZnO lattice and possibly because of the Na doping in the sample [109]. Furthermore, a distinguish peak at 583 cm<sup>-1</sup> corresponds to E<sub>1</sub>(LO) mode has been observed in the Raman plot of nanorods, which can be assigned to the significantly high concentration of oxygen vacancies in the sample. However,  $E_1(LO)$  mode peak was not observed in 5CA and 10CA samples, which was attributed to the absence or low concentration of oxygen vacancies.



*Fig. 3.5:* Raman spectra of the pristine ZnO, 0.5CA, 5CA, and 10CA samples

To examine the luminescence and defect states present in the samples, photoluminescence analysis of the samples was performed. The PL spectra of ZnO can be categorized into the following sections: near band emission (NBE) and deep level emission (DLE). NBE corresponds to the near band UV emission, which is the characteristic emission of ZnO, whereas the DLE is visible emission and can be assigned to the presence of various defect states viz.  $O_i$  (oxygen interstitial),  $V_O$  (oxygen vacancy),  $O_{Zn}$ (oxygen antisite),  $V_{Zn}$  (zinc vacancy),  $Zn_i$  (zinc interstitial) and  $Zn_{O}$  (zinc antisite) in ZnO lattice. The defect states form new recombination centers in the optical band gap which reduces the chances of direct recombination of excitons from the conduction band to the valence band, thereby leading to quenching of useful NBE emission. The PL spectra of the samples are shown in figure 3.6. The pristine ZnO has shown intense yellow emission, which can be ascribed to the higher concentration of oxygen vacancyrelated defects in the sample [110]. However, with the increasing concentration of trisodium citrate, the DLE peak intensity significantly reduced. In the PL spectra of 10CA, the DLE emission has been completely suppressed, which can be attributed to the elimination of the oxygen vacancies related defects in the samples.

Chapter 3: Growth of ZnO nanostructures and their structural and optical characterization



*Fig. 3.6:* (a) Photoluminescence spectra and (b) normalized photoluminescence spectra of pristine ZnO nanorods, 0.5CA, 5CA and 10CA samples

Furthermore, ZnO is a wide bandgap material and has a characteristic NBE peak in PL spectra around 385 nm. Therefore, any change in the NBE peak like the variation in the FWHM, peak intensity and peak shifting can provide critical information about the sample. In figure 3.6(b), normalized PL spectra of all the samples were shown. The pristine ZnO sample has shown a sharp NBE peak centered at 385 nm, which shows a high crystallinity of the sample. However, the NBE peak becomes broader with increasing trisodium citrate concentration which can be assigned to the high excitonic recombination and large crystal size distribu-

Chapter 3: Growth of ZnO nanostructures and their structural and optical characterization

tion [111, 112]. Moreover, the near band emission (NBE) region of 5CA and 10CA samples was observed to be extended in the visible region, which could be ascribed to the presence of Zn interstitial defect states in the samples [113]. The presence of a strong reducing agent i.e. tri-sodium citrate would lead to the reduction of Zn ions in the growth solution (equation 1), which in turn increases the density of neutral Zn atoms of growth solution. The high diffusivity of Zn atoms in the ZnO crystal lattice gives rise to Zn interstitial defect in the sample.

$$2Zn^{2+} + Na_3C_6H_5O_7 + 2H_2O \longrightarrow 2Zn + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2$$
(3.2)



*Fig. 3.7:* Diffuse reflectance analysis of pristine ZnO nanorods, 0.5CA, 5CA, and 10CA samples

Diffuse reflectance spectroscopy (DRS) analysis has been performed to investigate the absorption spectrum of the samples. As shown in Figure 3.7, the pristine ZnO sample has shown large near band UV absorption which is the band edge absorption of the ZnO. However, In contrast to pristine ZnO, the 5ZC sample showed remarkably high deep UV absorption along with near band UV absorption. Such high absorption at 260 nm can be ascribed to the higher concentration of Zn atoms in the sample [113]. Additionally, both samples have shown feeble absorption in the visible region.

### 3.3.2 Growth of nanocolumns



Fig. 3.8: FE-SEM images of the (a) 10ZC (b) 20ZC samples

FESEM images were taken in order to investigate the different morphology of the as-prepared samples. Interestingly, a complete transformation of the morphology of the nanostructures from nanorods to nanocolumns has been observed with the incorporation of additives (KMnO<sub>4</sub> and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) in the precursor solution. The FESEM images of the 10ZC sample have shown ZnO nanocolumns comprised of stacked nanoplates having the average base diameter of ~400 nm and the average length of ~2 µm, whereas the FESEM image of 20ZC has shown uniform and dense nanoplates.

The growth mechanism of nanocolumns with schematic diagram has been depicted in figure 3.9 and can be understood as follows: In the first step, KMnO<sub>4</sub> which is a strong oxidizing agent would notably increase the concentration of the OH<sup>-</sup> ions in the growth solution which in turn increases the rate of formation of Zn(OH)<sub>2</sub> thereby increasing forward reaction rate towards the rapid growth of ZnO nanorods [62]. Additionally, the oxygen-enriched environment produced by the decomposition of the KMnO<sub>4</sub> can certainly reduce various defect states in ZnO nanorods. The role of KMnO<sub>4</sub> in hydrothermal growth can be better understood by the following reactions [62]:

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$
(3.3)

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2 \tag{3.4}$$

Noteworthy, after initial rapid growth of nanorods, growth along the c-axis would be hindered very soon, as another additive i.e. trisodium citrate would produce citrate ions ( $C_6H_5O_7^{3-}$ ) which act as a chelating agent and further get adsorbed over the polar plane (0001) of nanorods (positively charged) and prevent the attack of  $ZnO_2^{2-}$  over the polar face of ZnO nanorods [114]. Now,  $ZnO_2^{2-}$  ions would be attracted to the side face of nanorods, which would result in a growth of ZnO nanoplates around nanorods to form nanocolumns (Figure 3.9) [115].



Fig. 3.9: Growth mechanism of ZnO nanocolumns

Adhesion of the ZnO film with the substrate is a critical issue for the fabrication of the devices. Here, the adhesivity of the ZnO nanostructures was probed via a scotch tape peel-off test that has revealed that the adhesion of the pristine ZnO sample was inferior over the glass substrate and almost completely peeled off from the substrate after the test. Sample 10ZC and 20ZC have shown excellent adhesion with the substrate, and a negligible amount of sample was peeled off from the substrate. Chapter 3: Growth of ZnO nanostructures and their structural and optical characterization



*Fig. 3.10:* Scotch tape peel-off test of pristine ZnO, 10ZC and 20ZC samples

The adhesion of the nanostructures over the substrate was accounted to be influenced by the pH value of the precursor solution [100]. It has been observed that the addition of KMnO<sub>4</sub> in precursor solution raise the pH of the solution. The pH of the solution was measured by pH meter and was found to be increased from 6.3 to 9.1 after the addition of KMnO<sub>4</sub>. Such noteworthy enhancement in the pH could be the plausible reason for better adhesion of the film with the substrate. Moreover, –COOH species in the precursor solution was also reported to improve the adhesion of the ZnO film [100]. Therefore, citrate ions with 3 -COOH groups would also facilitate significant improvement in the adhesion of the thin film with the substrate. Thus, the betterment in the adhesivity of nanostructures can be attributed to the combined effect of KMnO<sub>4</sub> and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>.

Figure 3.11 shows the XRD plots of pristine ZnO, 10ZC, and 20ZC samples. Intense ZnO diffraction peaks were observed at 31.72°, 34.38°, 36.20°, 47.45°, 56.52°, 62.74°, 67.88° and 68.97° that can be assigned to ZnO Wurtzite structure and were in good agreement with the JCPDS file of ZnO ((JCPDS 01-089-7102). No additional peak has been observed in the XRD plot of pristine ZnO sample which confirms the absence of any impurity in the pristine sample. In addition to this, diffraction peaks were found to be sharp and intense that can be attributed to the excellent crysChapter 3: Growth of ZnO nanostructures and their structural and optical characterization



Fig. 3.11: XRD plot of pristine ZnO, 10ZC, and 20ZC samples

tallinity of pristine ZnO samples. As mentioned in table 3.1, the peak intensity ratio of (002) peak to (100) peak of 10ZC has been significantly reduced as compared to that of the pristine ZnO sample. It shows that growth along the c-axis was heavily suppressed and growth along the a-axis was encouraged, which completely correlates with the proposed mechanism of ZnO growth along with the nonpolar faces of nanorods. However, the further increase in the concentration of trisodium citrate resulted in the formation of a poorly crystalline thin film. The reduced crystallinity can be ascribed to the incorporation of the impurities i.e. Na<sub>2</sub>CO<sub>3</sub> in the sample. A significant change observed in the FWHM value of the various diffraction peaks of 10ZC and 20ZC can be attributed to the difference in crystallite size and/or residual stress due to dislocations [116]. In order to verify the above statement, the average crystallite size of the nanostructures was calculated using Scherrer's equation [27]:

$$D = \frac{k \times \lambda}{\beta \times \cos\theta} \tag{3.5}$$

Where K is constant (0.90), λ is the wavelength of X-Ray (0.154 nm), β is the FWHM of the diffraction peak in radian and

 $\theta$  is the Bragg angle in degree. The calculated average crystallite size of the pristine ZnO sample (49.51 nm) was found to be much larger than that of 10ZC (26.52 nm). Therefore, the broadening of the diffraction peaks can be ascribed to the smaller crystallite size.

	Pristine ZnO	ZC10
a(Å)	3.2568	3.2715
c(Å)	5.2109	5.224
c/a	1.6	1.597
(100) peak position	31.71	31.61
FWHM of (100) Peak	0.18044	0.18768
(002) pek position	34.38	34.29
FWHM of (002) Peak	0.1747	0.30325
Relative peak intensity (002)/(100)	1.589	0.63
Crystallite size (n.m.)	49.51 26.52	

Table 3.1: Lattice parameters of as-prepared samples

In addition to this, a small peak shift towards the lower angle has been observed in the XRD plot of 10ZC. This peak shift can be attributed to the stress induced in the lattice. Therefore, for the systematic analysis of the peak broadening, lattice parameters have been calculated (Table 3.1). Lattice parameters are related to Miller indices and plane spacing by following equation [117]:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3} \left(\frac{h^2 + k^2 + hk}{a^2}\right) + \frac{l^2}{c^2}}}$$
(3.6)

Where d is plane spacing, h, k, and l are Miller indices and a, b and c are lattice constant. Bragg's law of diffraction was given by:

$$n\lambda = 2d \times \sin(\theta) \tag{3.7}$$

Where n is the order of diffraction (usually 1),  $\lambda$  is the X-Ray wavelength (.154 nm), d is lattice plane spacing, and  $\theta$  is the angle

of diffraction in degree. Lattice constant can be calculated using the following equations:

$$a = \frac{\lambda}{\sqrt{3}\sin\theta_{100}} \tag{3.8}$$

$$c = \frac{\lambda}{\sin \theta_{002}} \tag{3.9}$$

Interestingly, the diffraction peaks of the 10ZC sample were slightly shifted towards to smaller angle that was observed to result in an increment in lattice parameter a and c from 3.2568 Å to 3.2715 Å and from 5.2109 Å to 5.224 Å, respectively. Such a significant change in the lattice constant can be attributed to the strain induced in the ZnO lattice.



*Fig. 3.12:* XRD plot of the 10ZC sample grown for 3 hours and 5 hours

In order to further investigate the growth mechanism of the ZnO nanocolumns, a systematic analysis of the XRD plot of the samples grown for different time duration was performed. Figure 3.12 shows the comparison between the XRD analysis of the sample grown for 3 hours and 5 hours. XRD plot has shown no significant change in the (002) peak intensity, which indicates the formation of nanorods in the initial phase of the growth. Afterward, the growth along the c axis was heavily suppressed as the

negatively charged citrate ions tend to preferentially adsorb over the top surface of nanorods. A thorough investigation of XRD plot revealed that the intensity of (100) and (101) peaks of the sample grown for 5 hrs, were higher than that of the sample grown for 3 hrs while the intensity of (002) peak remains almost same. Therefore, it was concluded that in the second phase of the hydrothermal process, growth took place along the nonpolar side faces. The obtained results were completely correlated with the proposed growth mechanism.



*Fig. 3.13:* XRD plot of the (a) 10ZC (before annealing), (b) 20ZC (before annealing), (c) 10ZC (after annealing) and (d) 20ZC (after annealing)

Interestingly, in the XRD plot of 10ZC, a shoulder at  $33.16^{\circ}$  in the (002) XRD peak can be seen. Therefore, in order to get into more detail about it, XRD analysis of the 10ZC sample at relatively slower scan rate was performed. Figure 3.13 has shown the XRD plot of the 10ZC and 20ZC samples before and after annealing. A distinct peak at  $33.16^{\circ}$  corresponds to Na<sub>2</sub>CO<sub>3</sub> (JCPDS 01-086-0294) has been observed. The formation of Na<sub>2</sub>CO<sub>3</sub> can be understood as follows: As mentioned in Eq. (1.9) the hydrolysis of HMTA is producing HCHO, which in the presence of KMnO<sub>4</sub> (strong oxidizing agent) got oxidized into CO<sub>2</sub> [62]. Na<sup>+</sup> ions gen-

erated by the decomposition of trisodium citrate could react with  $CO_2$  molecules to form  $Na_2CO_3$ . Furthermore, in order to verify the presence of  $Na_2CO_3$ , XRD analysis of the samples heated at 450°C was performed. Had it been  $Na_2CO_3$ , it would have got decomposed into  $Na_2O$  and  $CO_2$  with the elimination of the corresponding peak due to thermal annealing. The decomposition of  $Na_2CO_3$  can be summarized as follows:

$$Na_2CO_3 \xrightarrow{\Delta} Na_2O + CO_2$$
 (3.10)

*Table 3.2:* Lattice parameters of 10ZC samples, before and after annealing

	ZC10	ZC10 Annealed
a(Å)	3.2715	3.263
c(Å)	5.224	5.2196
c/a	1.597	1.6
(100) peak position	31.61	31.62
FWHM of (100) Peak	0.18768	0.2859
(002) pek position	34.29	34.32
FWHM of (002) Peak	0.30325	0.35444
Relative peak intensity (002) / (100)	0.63	0.731
Crystallite size (n.m.)	26.52	30.66

Figure 3.13 shows the XRD plot of the annealed sample. As observed from the XRD plot, the diffraction peak corresponding to Na<sub>2</sub>CO<sub>3</sub> was eliminated, and not even a trace amount of Na<sub>2</sub>CO<sub>3</sub> was found. Henceforth, the presence of Na<sub>2</sub>CO<sub>3</sub> in the 10ZC was confirmed. Furthermore, significant enhancement in the average crystallite size of the samples after annealing at 450°C was observed. As shown in table 3.2, the calculated average crystallite size of the 10ZC sample was 26.52 nm, while after thermal annealing, the average crystallite size was found to increase to 30.66 nm. Additionally, a shift in the XRD peaks of the annealed sample towards the peak position of pristine ZnO showed that the stress present in the sample was reduced, which can be ascribed to the recrystallization of the sample [118]. XRD plot of

the annealed sample shows sharper diffraction peaks, which also signifies improved crystallinity of the sample.



*Fig. 3.14:* FE-SEM images of the samples (a) 10ZC before annealing, (b) annealed 10ZC, (c) 20ZC before annealing and (d) annealed 20ZC

In order to investigate the effect of annealing on the morphology of the ZnO nanostructures, FESEM analysis of the sample was performed. Substantial changes in the morphology of ZnO nanostructures were observed after annealing at 450 °C for 20 min. FESEM image of the 10ZC sample (figure 3.14 (a)) has shown nanocolumns comprising of stacked nanoplates. However, after annealing, the small grains appeared over the surface of nanocolumn (figure 3.14 (b)). Similarly, the FESEM image of the 20ZC sample (figure 3.14 (c)) showed dense and smoothsurfaced nanoplates that were transformed into granular surfaced nanoplates after thermal annealing (figure 3.14 (d)). The formation of grains over the surface can be explained by the coalescence and agglomeration of small size grain present over the surface of nanostructures to form larger grains [119, 120].

Hydrothermal growth is a solution-based approach that is prone to various impurities and defects due to the presence of  $OH^-$  ions,  $Zn(OH)_2$ ,  $H_2O$ , etc. in the precursor solution. Moreover, after annealing of the samples, significant changes were observed in the ZnO nanostructures morphology as seen from



Fig. 3.15: TGA plot of pristine ZnO and 10ZC samples

the FESEM images and XRD plots. Therefore, thermogravimetric analysis (TGA) was performed to investigate the chemical changes taking place on heating the samples. For the TGA analysis, samples were heated at the rate of 10 °C/min. in the temperature range from 40 – 600 °C. Figure 3.15 shows the TGA plot of the pristine ZnO and 10ZC samples. The loss of mass in both the samples in the temperature range of 30 °C < T < 110 °C was attributed to the evaporation of water content from the samples. Minimal change of mass at the temperature around 250 °C was observed, which could be due to the decomposition of the Zn(OH)<sub>2</sub> and the desorption of the CO<sub>2</sub> and O<sub>2</sub> gases from the sample [121].

Moreover, a significant change in mass percentage was detected in the temperature range from 250 °C - 350 °C that can be attributed to the presence of volatile organic compounds viz. citrate, carbonate and acetate ions in the samples which possibly decomposed at higher temperatures [122]. Weight loss around 400 °C can be referred to the decomposition of Na<sub>2</sub>CO<sub>3</sub> into CO<sub>2</sub> and Na<sub>2</sub>O, thereby verifying the results obtained in the XRD analysis. However, no separate XRD peak corresponds to Na<sub>2</sub>O was appeared in the XRD plot of the annealed sample, which can be referred to as the insignificant concentration of Na<sub>2</sub>O in the sample.

In the TGA analysis, remarkable changes in mass were observed after heating the sample at a higher temperature. Also, there were possibilities of diffusion of Na<sub>2</sub>O produced by the decomposition of Na<sub>2</sub>CO<sub>3</sub> in ZnO lattice. Therefore, FTIR analysis has been performed over two sets of samples, one was before annealing and the other one was after annealing at 450 °C. Figure 3.16(a) shows the FTIR spectra of the as-grown samples. The transmittance peak around 539 cm<sup>-1</sup> and 922 cm<sup>-1</sup> was related to the Zn–O bond [34]. Peak positioned at around 1600 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> can be assigned to the symmetric and asymmetric stretching modes of the carboxylate group of acetate and citrate bounded to the ZnO nanostructures [123]. FTIR spectra of the annealed samples were shown in figure 3.16(b). One additional transmittance peak was observed at 1541 cm<sup>-1</sup> in 10ZC and 20ZC samples, which can be referred to Na – O stretching, confirms the presence of Na<sup>+</sup> ions or Na<sub>2</sub>O in the samples [124]. Also, transmittance peaks of 10ZC were shifted from 528 cm<sup>-1</sup> to 560 cm<sup>-1</sup> also indicated the changes in the Zn-O bond stretching due to the incorporation of some foreign species, i.e. Na<sup>+</sup> ions or Na<sub>2</sub>O into the ZnO lattice.



*Fig. 3.16:* FTIR spectra of pristine ZnO, 10ZC and 20ZC samples, (a) before annealing and (b) after annealing

As shown in figure 3.17, the Raman spectra of ZnO consist of two dominant peaks, one at 98.80 cm<sup>-1</sup> (E<sub>2</sub>(low)), dominated by heavy Zn sublattice vibrations and another at

Chapter 3: Growth of ZnO nanostructures and their structural and optical characterization



*Fig. 3.17:* Raman spectra of pristine ZnO, 10ZC and 20ZC samples

438.52 cm<sup>-1</sup>(E<sub>2</sub>(high)), dominated by oxygen sublattice vibrations.  $E_2(low)$  and  $E_2(high)$  are the characteristic peaks of ZnO and indictate the crystallinity and defect states in the lattice structure. Intense and sharp peaks indicate the crystalline and defectfree growth of ZnO. The measured FWHM of the E<sub>2</sub>(low) and  $E_2$ (high) peaks of the pristine ZnO sample were observed to be 2.3  $\text{cm}^{-1}$  and 7.75  $\text{cm}^{-1}$ , respectively. However, in the case of ZC10, FWHM of E<sub>2</sub>(low) and E<sub>2</sub>(high) peaks increased to 17.54 cm<sup>-1</sup> and 13.32cm<sup>-1</sup>, respectively. Such significant enhancement in the FWHM of Raman peaks indicates reduced crystallinity and the presence of defects or impurities in the sample. Some smaller peaks were also observed at 201 cm $^{-1}$ , 338 cm $^{-1}$ , 380 cm $^{-1}$  and 410 cm<sup>-1</sup>, corresponds to the  $2^{nd}$  order of  $E_1(low)$  mode,  $E_2(high)$  $- E_2(low)$  mode,  $A_1(TO)$  mode and  $E_1(TO)$  mode, respectively. Another major peak observed at 581  $\text{cm}^{-1}$  can be ascribed to quasi LO mode as it appears in between  $A_1(LO)$  and  $E_1(LO)$  mode of ZnO.

Considering the annealing effect observed in previously discussed results, temperature-dependent Raman analysis of the samples was also performed to probe sodium doping in the



Fig. 3.18: Temperature-dependent Raman analysis of 10ZC

sample after annealing. In figure 3.18, it can be clearly observed that after annealing, Raman peaks became sharper and intensified that can be ascribed to the enhancement in the crystallinity and crystallite size of ZnO. Moreover, a remarkable shift in the  $E_2$ (high) peak from 441 cm<sup>-1</sup> to 431 cm<sup>-1</sup> was observed, signifying stress generated in the crystal lattice due to the incorporation of foreign species, i.e. Na<sub>2</sub>O or Na<sup>+</sup> ions [109]. Furthermore, one additional peak appeared around 569 cm<sup>-1</sup>, which points towards the presence of impurities in the sample. The intensity of the peak was observed to be increased with increasing annealing temperature, which can be ascribed to the incorporation of Na<sub>2</sub>O or Na<sup>+</sup> ions in ZnO lattice.

#### **Optical Analysis**

In order to systematically investigate the absorption characteristics and the bandgap of the samples, diffuse reflectance spectroscopic analysis was performed. Figure 3.19(a) shows the diffuse reflectance spectra of the samples. The spectra were plotted between F(R) and wavelength, where F(R) was known as Kubelka – Munk (KM) function, given by [125]:

$$F(R) = \frac{(1-R)^2}{2R}$$
(3.11)

Chapter 3: Growth of ZnO nanostructures and their structural and optical characterization

A thorough analysis of the absorption spectra of the pristine ZnO sample revealed a very sharp UV absorption peak centered at 358 nm wavelength. However, the absorption peak of the 10ZC and 20ZC samples were observed to get broader and blue-shifted from 358 nm to 310 nm, which can be attributed to the morphological changes and quantum confinement effect due to smaller crystallite size [126]. In addition to this, a significant difference in the slope of the UV absorption edge was observed. The absorption edge of the pristine ZnO sample was very steep. Notably, the slope of the absorption edge was found to get reduced with increasing concentration of trisodium citrate in growth solution which can be attributed to the reduced crystallinity of the sample [127]. The obtained results are in good correlation with the XRD data, stating that the crystallinity of the samples has been degraded after the addition of trisodium citrate in the precursor solution. The enlarged view of the absorption spectra of samples in the visible region is shown in the inset of figure 3.19(a). Two broad absorption peaks centered at 450 nm and 700 nm in ZnO spectra can be ascribed to the absorption due to the formation of zinc interstitial, oxygen vacancy i.e. neutral and doubly ionized oxygen vacancy and large dispersion of hybridized sporbital [128-131]. Furthermore, a considerable amount of absorption in the visible region at 570 nm was observed in both 10ZC and 20ZC samples (which was not present in pristine ZnO sample) that can be because of the presence of oxygen interstitial defect states. Moreover, incorporation of the sodium-related defect states can also be critical for absorption in the visible region.

The optical bandgap of the samples was calculated using the Tauc model [132] and Davis and Mott model [133]. Figure 3.19(c) shows a plot between  $[F(R) \times E]^2$  versus Energy in eV. The optical bandgap of the sample was obtained by extrapolation of the linear portion of the graph [134]. The estimated bandgap of all



*Fig. 3.19:* DRS spectra of (a) pristine ZnO, 10ZC and 20ZC samples inset shows enlarged view of the visible region and (b) 10ZC (before and after annealing), Tauc plot of (c) pristine ZnO, 10ZC and 20ZC and (d) 10ZC (before and after annealing)

the samples was found to be around 3.30 eV. However, annealing the samples resulted in a great impact on the bandgap of the samples. Figure 3.19(d) shows the Tauc plot of the as-grown and annealed 10ZC. The bandgap was observed to be narrow down to 3.1 eV after annealing, which can be attributed to the increased crystallite size of the nanostructures [111]. The results are in good agreement with the XRD data of annealed sample that has shown remarkable improvement in the crystallinity and increased crystallite size.

The absorption spectra of the 10ZC have shown an exponential curve at the end of band-edge absorption known as Urbach tail, which signifies either the formation of impurity bands or the crystal deformation and/or electron-phonon interactions [135, 136]. In order to develop a deeper understanding of the crystal deformation, Urbach energy of the samples have been calculated using Urbach empirical rule, given by,

$$\ln \alpha = \ln \alpha_o + \frac{hv}{E_U} \tag{3.12}$$

Chapter 3: Growth of ZnO nanostructures and their structural and optical characterization

Where  $\alpha$  is the absorption coefficient,  $\alpha_o$  is constant, hv is incident photon energy and  $E_U$  is the Urbach energy of localized states. The slope of the linear region, below fundamental absorption region is called Urbach slope, and reciprocal of the slope is called Urbach energy [137].



*Fig. 3.20:* In ( $\alpha$ ) versus photon energy plot to calculate the Urbach energy

Figure 3.20 shows  $\ln \alpha$  versus *hv* plot. The Urbach energy of pristine ZnO sample was calculated to be nearly 54 meV which was in good agreement with the previously published reports [138]. However, the calculated Urbach energy of the 10ZC and 20ZC samples was 114 meV and 120 meV, respectively, which is much larger than that of the pristine ZnO sample. Such noteworthy enhancement in the Urbach energy with the addition of the surfactant in the precursor solution can be ascribed to the defect states and/or crystal deformation. Additionally, the obtained Urbach energy of the annealed 10ZC was 135.53 meV, which was higher than that of the as-grown 10ZC sample. Such significant enhancement in the Urbach energy can be ascribed to the addition of Na<sup>+</sup> ions or Na<sub>2</sub>O in the ZnO lattice.

In order to analyze the optical properties and defects present in the samples, the photoluminescence (PL) analysis was per-



*Fig. 3.21:* (a) PL spectra of pristine ZnO, 10ZC and 20ZC samples. The inset shows the normalized PL plot of pristine ZnO, 10ZC and 20ZC samples, (b) PL spectra of annealed 10ZC and annealed 20ZC samples

formed. Figure 3.21 shows the PL spectra of various samples. PL spectra of the pristine ZnO sample have demonstrated broad and intense visible emission peak centered at 600 nm, corresponding to the doubly ionized oxygen vacancy [130]. However, mixing additives in the precursor solution has resulted in a significant blue shift in the DLE peak from 600 nm to 570 nm that can be assigned to reduced oxygen vacancy-related defect states [61]. As we have discussed previously, KMnO<sub>4</sub> is a potent oxidizing agent that tends to provide the oxygen-rich environment for hydrothermal growth, which resulted in significant suppression of oxygen vacancy-related defect states.

In order to analyze the defect density in the sample, NBE to DLE peak intensity ratio has been calculated. The ratio was observed to be very low (about 1.8) in pristine ZnO PL spectra, which indicated high defect density in the sample. However, 10ZC and 20ZC samples have shown remarkably high NBE/DLE ratio (11 and 9 respectively) which can be attributed to the oxidizing condition for hydrothermal growth caused by the presence of KMnO<sub>4</sub> in growth solution that has considerably reduced oxygen vacancy-related defect states [62, 139, 140]. Moreover, as discussed previously in DRS analysis, significant absorption in the visible region of 10ZC and 20ZC samples can also play a critical role in the suppression of the visible emission [141].

Pristine ZnO sample has shown a very sharp and intense NBE peak, which can be assigned to the high crystallinity of the sample. However, the NBE peak of 10ZC and 20ZC was observed to be wider compared to that of the pristine ZnO sample. Additionally, one shoulder appeared around 369 nm, which can be attributed to the excitonic recombination and the presence of different sizes of nanoparticles [111, 112].

Moreover, in order to examine the effect of the annealing over the luminescence properties of samples, PL analysis of the samples annealed at 450 °C was performed (Figure 3.21(b)). The spectra have shown intense blue emission that was not present in the as-grown sample. As we have discussed previously in the XRD, TGA and DRS analysis, Na<sub>2</sub>O produced by the decomposition of Na<sub>2</sub>CO<sub>3</sub> at high temperature, was possibly incorporated into the ZnO lattice. Henceforth, the defect-related blue emission peaks at 425 nm and 475 nm can be attributed to the Na<sub>2</sub>O defect states. This dramatic change in the PL spectra opens a new perspective on the optoelectronic properties and application based on the hydrothermal growth of ZnO nanostructures.

# 3.3.3 I-V characterization of pristine ZnO nanocolumns



*Fig. 3.22:* (a) Device schematic, (b) semilog I-V plot of pristine ZnO nanorods and 10ZC sample

Figure 3.22(a) has shown the device schematic of the pho-

todetector. We have deposited Ag electrode by thermal evaporation system. The channel length was kept at 50  $\mu$ m and channel width was around 2 mm. The total active area of the device was 0.001 cm<sup>2</sup>. The typical current-voltage (I-V) characteristic of ZnO photodetector measured under dark and deep UV light illumination (254 nm, 2.11 mW/cm<sup>2</sup>) conditions are shown in Fig.3.22(b). It is worthwhile to note that the dark current in pristine ZnO sample is around 0.19  $\mu$ A at 20V bias whereas photo current is measured 3.2  $\mu$ A, which is 16 times larger than dark current. Further, the dark current and photo current enhance exponentially with increasing applied bias. The measured photoresponsivity of ZnO nanorods is around 1.5 A/W. In contrast to pristine ZnO, dark current reduces by two orders of magnitude in 10ZC sample. Moreover, the photo current reaches to 1.02 mA after UV illumination. The photo current to dark current ratio increases to approx. 6 orders of magnitude. The calculated responsivity of 10ZC sample was observed to be as large as 507 A/W.

The charge trapping states over the surface are considered responsible for the observed variation in the photoconduction properties of ZnO nanostructures. In dark state, nanostructure surface gets oxidized by chemically adsorbing oxygen molecules over it which results in trapping of one electron which in turn reduces the conductivity of nanostructures. Further, after illumination with photon energy more than the band gap of ZnO, e-h pairs are generated and holes reach to the nanostructure surface to desorb the adsorbed oxygen and leave behind unpaired electrons. As a result, the conductance of the nanostructure gets enhanced. In case of 10ZC sample, the formation of nanoplates around the nanocolumns has significantly increased the surface area of the nanostructures which in turn improves the photoresponsivity of these devices.

# 3.4 Conclusions

We have successfully fabricated different ZnO nanostructures with different morphologies and improved optical and structural properties. The effect of the additives on the growth of ZnO nanostructures has been intensively analyzed and the plausible mechanism for the growth of nanocolumns has been proposed. It was found that the surfactant-assisted growth has induced some stress in the film, and further particle size of the nanostructures was observed to get reduced. In addition to oxidizing growth conditions, the presence of the citrate ions has ensured improved adhesion of the ZnO nanostructure film over the substrate. The post-growth annealing of the nanostructures has significantly modulated the morphology of nanostructures. The bandgap of the annealed 10ZC has been reduced from 3.3 eV to 3.1 eV. Urbach energy of the 10ZC sample was observed to be increased from 54 eV to 114 eV which indicates the addition of impurities in the sample. PL analysis of the samples has shown remarkable suppression in the related defect emission, which in turn improves the NBE to DLE ratio. Therefore, in addition to the fabrication of efficient photoconductors, we have successfully targeted the hydrothermal growth-related critical issues like poor adhesivity and low NBE to DLE ratio. The prepared nanostructures are potential candidates for other optoelectronic devices as well.

# **Chapter 4**

# Development of zinc oxide based broadband photodetectors

Photodetectors found applications in various medical, military, communication and environmental research fields. A variety of spectral range photodetector is required for different kinds of applications. Pristine ZnO has been extensively reported for high responsivity UV photodetectors based applications. However, in general, its photoresponse in deep UV, visible and NIR regions is inferior. Therefore, in this article, honeycomb nanostructure (5CA samples) have been demonstrated as high responsivity broadband (200 nm - 950 nm) photodetector. Further, the effect of morphology, doping and various defect states over the photosensing response has been discussed in detail. A significantly high photosensitivity in the deep UV to NIR region of the electromagnetic spectrum makes these devices a promising candidate for the development of broadband UV photodetectors for commercial applications.

### 4.1 Introduction

UV photodetectors find use in flame detection, missile launching systems, fire detection, spectroscopy, harmful UV radiation detection and many more [6, 65, 142, 143]. Researchers have extensively explored various binary wide-bandgap semiconductors like SnO<sub>2</sub>, GaN, ZnO and ZnS for UV sensing applications [144-147]. Owing to the wide bandgap of 3.37 eV, high exciton binding energy of 60 meV at room temperature, biocompatibility, low fabrication cost and variety of 1D and 2D nanostructures, ZnO emerges as one of the most promising candidates for near UV photodetection [31, 145, 148-151]. Further, several efforts have been made towards extending its applicability in deep UV region viz. doping of Cd, Mg, Be and Ge [146, 152-159]. However, in terms of photoresponsivity in the deep UV region, limited success has been achieved. The first and foremost possible solution for enhancing the photoresponsivity of the ZnO in the deep UV region is improving its absorption coefficient in the deep UV region. Secondly, increasing the surface to volume ratio of the NSs can be well utilized to improve its photosensitivity by significantly lowering the dark current. Recently, Zn/ZnO structures were reported by Zeng et al. to have an influence on the absorption coefficient of ZnO in the deep UV region.[11] Therefore, incorporation of the Zn atoms in ZnO NSs can provide a possible solution towards the enhancement of photoresponsivity in the deep UV region.

Additionally, pristine ZnO was rarely reported for visible and/or NIR sensing applications [74]. In order to extend its applicability in the visible and NIR region, a variety of ZnO based hybrid structures, heterostructures, and nanocomposites were reported [65, 143, 160-163, 72]. However, incorporating such configurations has significantly increased the complexity and the cost of device fabrication. Therefore, it is highly desirable to find a simple and economical, alternative approach to fabricate a device which is not only sensitive towards near UV region but also for deep UV, visible and NIR region. Though it remains a challenge for the research community. One possible solution could be the use of complex nanostructures e.g. nanosheets, nanoflowers, honeycomb etc. rather than conventional ZnO nanostructures viz. nanorods, nanowires, nanopillars etc. The larger surface area offered by these complex nanostructures could drastically improve the device performance.

Herein, we have extended the photodetection range of pristine ZnO from deep UV to NIR region, just by altering the morphology of the ZnO nanostructure. The honeycomb nanostructures provided high electron transportation efficiency resulting in large photoresponse. The proposed device architecture for broadband detection uses pristine ZnO nanostructure which eliminates the complexity and cost incurred in the development of the heterostructure, nanocomposites and hybrid structures. The device is a potential candidate for future optoelectronic applications, and also the performance is comparable to the existing commercial broadband photodetectors.

### 4.2 Experimental details

For the development of broadband photodetectors, honeycomb nanostructures, obtained by citrate assisted hydrothermal growth of ZnO, have been used. The detailed synthesis process of the nanostructures has been already discussed in chapter 3. For the I-V measurement, two silver electrodes of 50  $\mu$ m channel length and 2 mm width were deposited using shadow masks by physical vapor deposition (PVD) process.

Electrical characterization was performed in air at room temperature using a Keithley 2612A source meter. Incident light power was measured by TS2 LP 100, CNI laser, laser power meter. ISS P100 Xenon lamp power supply for the wavelength range from 200 to 950 nm was used to illuminate the samples.

# 4.3 Results and discussion

# 4.3.1 I-V response of the device



### Fig. 4.1: Device schematic

Figure 4.1 shows the schematic of the fabricated device. The calculated active area of the device was 0.001 cm<sup>2</sup>. The XRD plot shown in figure 4.2, has clearly indicated peak at 38.10°, which was assigned to the (111) orientation of the Ag electrodes whose work function is around 4.76 eV [44, 164], which is substantially larger than the electron affinity of ZnO (approx. 4.3 eV), i.e., sufficient for the formation of Schottky junction at the Ag/ZnO interface [165]. It is worthwhile to mention that the Schottky junction reportedly reduces the dark current, which significantly improves the device performance by providing a manifold increase in the photo current to dark current ratio [22].

In order to check the photoresponse of the samples, I-V measurements were performed in the dark as well as with deep UV ( $\lambda$  = 254 nm) illumination (Figure 4.3). Pristine ZnO has shown a dark current of approximately 0.19  $\mu$ A whereas the 5ZC sample has shown a significantly low dark current of around 5 nA. Such

Chapter 4: Development of zinc oxide based broadband photodetectors



Fig. 4.2: XRD plot of the Ag electrode coated 5CA sample



Fig. 4.3: Semilog I-V plot of pristine ZnO and 5CA

large difference in dark current was ascribed to the deceased barrier height of Schottky junction that can be explained as follows: The (0001) crystal orientation in ZnO nanorods consist of alternate layers of anions (Oxygen ions) and cations (Zn ions) that leads to the formation of dipoles. The net (nonzero) dipole moment makes polar surface unstable. Due to the highly unstable nature of the ZnO polar surface, Silver reacts strongly with the chalcogenides (Oxygen in ZnO) and thereby leaving behind dissociated Zn cations that typically result in lower barrier height in n-type ZnO, which in turn ceases the Schottky behavior and increases the dark current [166]. However, in the case of 5CA, crystal orientations are (100) and (110), which are nonpolar in nature due to the equal number of anion and cations. Therefore, no net dipole moment is present in these samples that make the nonpolar planes relatively more stable. Henceforth, Schottky barrier height remains the same that resulted in the lower dark current.



*Fig. 4.4:* Photosensing mechanism: (a) oxygen adsorption and depletion region formation and (b) exciton generation by UV illumination and oxygen desorption

Now, for the measurement of the photo current, samples were illuminated by 254 nm, 2.11 mW/cm<sup>2</sup> UV lamp. The photo current in pristine ZnO was approximately  $3.5 \,\mu$ A. Photo current to dark current ratio was ~ 18 and photoresponsivity was ~ 1.5 A/W. In comparison to the pristine ZnO, photo current in 5CA sample was enhanced to a value of 2.45 mA. The photo current to dark current ratio was  $4.9 \times 10^5$ , and photoresponsivity was 1.15  $\times 10^3$  A/W.

### 4.3.2 Photosensing mechanism

The remarkable enhancement in photoresponsivity can be explained as shown in Figure 4.4. Oxygen molecule in surrounding air gets chemically adsorbed over the ZnO NSs by trapping electrons from the ZnO surface that leads to the formation of de-
pletion region near the surface, which in turn significantly reduces the conductivity of the NSs. However, the small channel still existing in the center of nanorods facilitates the transport of charge carrier that leads to high dark current. However, in case of HC nanostrucutres, a fully depleted thinner nano-plates network restricts the flow of charge carriers. Additionally, Zn interstitials in ZnO act as a donor impurity, increasing the free electrons concentration at the surface that promotes the oxygen adsorption, results in a minimal dark current. Now, when the light source illuminates the samples, electron-hole pairs will generate. Due to the high electric field in the depletion region near the surface, holes move towards surface and electrons move towards the central part of the nanostructures that leads to the dissociation of the excitons [167]. The adsorbed oxygen molecules react with the existing holes and get desorbed, leaving behind unpaired electrons [149, 168]. As a consequence, channel width increases, and gets populated with unpaired electrons, increasing the conductivity of the NSs [169].



*Fig. 4.5:* (a) Charge carrier transportation in nanorods network and (b) charge carrier transportation in HC NSs

Further, as shown in Figure 4.5(a), in the nanorods network, electrons have to travel through a zig-zag path, which increases the distance to travel by an electron to reach the electrode. Additionally, in nanorods network, there exist interfaces between nanorods which offers high potential barrier in the path of electrons that hinder electrons transportation [170]. On the contrary, HC NSs consist of a well-connected nanoplates network which is free from such high potential barrier junction and provides a shorter and continuous conduction path for efficient carrier transportation, which in turn improves the photosensitivity of the device. Additionally, the sidewalls of the HC NSs act as low resistance conducting wire, which will also reduce the path resistance [171]. Henceforth, a substantial enhancement in the photo current to dark current ratio has been observed.



*Fig. 4.6:* I-V response of the device in deep UV, Near UV, Visible, NIR region

## 4.3.3 I-V response in deep UV-Visible-NIR region

Further, in order to investigate the device broadband photoresponse, the sample was illuminated with a wavelength ranging from 200 to 950 nm. The maximum photo current obtained at -10V bias in deep UV (at 250 nm) , near UV (at 350 nm), visible (at 550 nm), NIR (at 800 nm) and NIR (at 950 nm) region was  $6.8 \times 10^{-5}$  A,  $1.7 \times 10^{-4}$  A,  $4.9 \times 10^{-6}$  A,  $4 \times 10^{-7}$  A and  $5.3 \times 10^{-7}$  A, respectively. Accordingly, the photo current to dark current ratio was maximum ( $3.2 \times 10^7$ ) for near UV radiations, whereas for NIR regions, it was around  $9.5 \times 10^4$ , which was significantly higher than the previously published results [160, 172].

The device has shown significantly high specific detectivity, averaging around  $3 \times 10^{12} \text{ cm} \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$  in the near IR region.



Fig. 4.7: Specific detectivity plot at different wavelengths

However, the maximum D<sup>\*</sup> of  $2.07 \times 10^{15}$  cm·Hz<sup>1/2</sup>·W<sup>-1</sup> was observed at 300 nm, which was better than previously reported results [160, 172]. Further, the calculated average D<sup>\*</sup> in the visible region is  $7.7 \times 10^{13}$  cm·Hz<sup>1/2</sup>·W<sup>-1</sup>.

Figure 4.8 shows the responsivity (R) plot at different wavelengths. The device has shown a maximum responsivity of 115 A/W at 300 nm, which was superior to the other published reports [143]. The average responsivity in UV, visible and NIR regions was estimated to be 70 A/W, 4.3 A/W and 0.18 A/W, respectively. Moreover, the device performance was compared with the commercially available FDS010-Si photodiode (a product from Thorlabs), where we found our device performance superior in terms of dark current, responsivity, and detectivity.

Figure 4.9 shows the responsivity plot at different voltages for different wavelengths. The plot has shown exponential enhancement in the responsivity for 200 nm to 950 nm spectral range at 10 V applied bias. Additionally, the responsivity curve for different wavelengths was parallel to each other, which shows that the rate of change of responsivity with respect to the voltage was the same for the entire wavelength range.

Chapter 4: Development of zinc oxide based broadband photodetectors



Fig. 4.8: Responsivity plot of at different wavelengths



*Fig. 4.9:* Responsivity plot in deep UV, Near UV, Visible, NIR and IR region at different voltages

Figure 4.10 also shows the switching response of the device at 10 V bias for 350 nm wavelength. As the sample illuminated with a UV light source, current increases rapidly after that increase slowly with time. Similarly, slower fall time was observed, after the light source was turned off. This phenomenon can be attributed to the surface defect-related trapping centers, which retard the charge carrier collection speed upon UV illumination and the charge carrier recombination, as the light source was turned

Chapter 4: Development of zinc oxide based broadband photodetectors



Fig. 4.10: Switching response of the device

off [161, 173]. Additionally, after long UV illumination, a slight decrease in the photo current was observed. Also, the photo current in the next switching cycle was lower than the photo current in the first cycle. The observed phenomenon has been discussed in detail in the next chapter.



Fig. 4.11: EQE plot of the device at a different wavelength

Further, the linear dynamic range (LDR) or photosensitivity linearity of the device under the illumination of 350 nm was 128.9 dB, which was significantly higher than the previously published reports [86, 174]. The LDR of 128.9 dB is the record value for ZnO based detectors to the best of our knowledge. Moreover, higher photon-electron conversion rate is required for better sensing response which is determined by external quantum efficiency (EQE) [87, 175, 176]. The calculated EQE of the sample at 300 nm wavelength and 10 V applied bias was 47,583 %, which indicates higher photon-electron conversion efficiency, resulting in high device performance.

Materials	λ (nm)	S	R	D*	Ref.
Traterials	, intensity	U	I.	Ľ	11011
	$(mW/cm^2)$		$(\mathbf{A}.\mathbf{W}^{-1})$	$(cm.Hz^{0.5}.W^{-1})$	
Rhodamine	300-700,	$\sim 250$	5.5	$2.34 imes10^{11}$	[176]
<b>B</b> -sensitized	$\sim 2.4$				
ZnO					
Gd-ZnO/	250-1357,	$\sim 9$	28	$1.1 imes 10^{12}$	[177]
perovskite	$\sim 0.5$				
ZnO/PMMA	4000, 0.050	$\sim 1000$	8	-	[143]
/PbSe					
Inorganic	450, 16.42	$\sim 10000$	4.25	-	[178]
perovskite/ZnO					
n-3C-SiC/p-Si	375, 0.5	$\sim \! 500$	0.109	-	[179]
heterojunction					
n-ZnO NRs/	365, 0.0112	8000	0.32	$8 imes 10^{12}$	[180]
i- MgO/p-GaN					
ZnO/CsPbBr <sub>3</sub>	UV, 2	16527	231	$2.4 imes10^{13}$	[181]
n-Mn <sub>0.04</sub> Zn <sub>0.96</sub> O	365	46	0.8	$2.4 imes10^{12}$	[182]
/i-ZnGa <sub>2</sub> O <sub>4</sub> /n-GaN					
Pristine ZnO	250-950, 6	<b>3.2</b> ×10 <sup>7</sup>	115	$2.07  imes 10^{15}$	This
Nanowalls					Work

*Table 4.1:* Comparison with recently reported UV and broadband photodetectors

Table 4.1 shows a comparison of the device with some recently reported photodetectors based on photoresponsivity, sensitivity and detectivity. The comparative analysis has clearly revealed that our device performance is better than previously reported devices [143, 176-182].

## 4.4 Conculsions

In conclusion, we have successfully synthesized novel Zn rich ZnO HC NSs for high responsivity broadband photodetector applications. Background current has been significantly reduced that has been ascribed to the Ag/ZnO Schottky junction and high Zn concentration in ZnO. The as-fabricated device has shown significant improvement in the photo current to the dark current ratio from just 18 times in nano-rods to  $4.9 \times 10^5$  in HC NSs. The fabricated device has shown high photoresponsivity of  $1.15 \times 10^3$ A/W in the deep UV region of electromagnetic spectrum originating from the thinner nano-plate in HC NSs. The proposed device configuration has used pristine ZnO nanostructure which eliminates the complexities and the cost incurred in the development of complex heterostructure, nanocomposites, and hybrid structures. The device has demonstrated LDR of 128.9 dB and EQE of 47,583 %. The device performance was found to be comparable with the existing products and has tremendous potential to replace them with some modifications. \_

## **Chapter 5**

# Investigation on the effect of prolong UV illumination over the performance of broadband photodetector

Prolong UV irradiations could considerably modulate the optical and electrical properties of ZnO. Therefore, it was desirable to investigate the effect of prolonging UV exposer over ZnO characteristics towards the development of reliable ZnO based devices for various UV applications. This work is focused on the development of high-performance and dependable ZnO based deep UV (UV-C) photodetectors. Herein, hydrothermally synthesized ZnO honeycomb nanostructures were utilized to develop a high sensitivity UV-C photodetector. Photoluminescence studies of UV irradiated samples have suggested the formation of intrinsic defect states viz.  $V_O$  and  $Zn_i$  in ZnO, which were further confirmed by electron paramagnetic resonance, diffuse reflectance analysis, and photoresponse of the device. Further, we have demonstrated that the coating of Pt nanoparticles over ZnO nanostructures could significantly improve not only the device stability but also the response time and device endurance in deep UV radiations. The proposed device is a promising contender for future deep UV detector based optoelectronic products.

## 5.1 Introduction

ZnO is a low cost, biocompatible material with highly tunable structural and optical properties that have made the device suitable for an extensive range of applications. Especially in the UV region due to its wide bandgap and high exciton binding energy. However, the major issue with ZnO based deep UV sensors is their stability in deep UV radiations as when the devices are exposed to such high energy radiations, there are high chances of material to degrade. Therefore, before commercializing such devices, it is highly required to examine the device reliability and stability in such harsh environmental conditions. However, as per our knowledge, the issue has rarely been discussed. The metallic nanoparticles which are comprehensively explored in the last decade and have demonstrated significant improvement in UV emission and sensing response of ZnO, could pave the way to improve the device stability and reliability in deep UV radiations.

In the present work, we have used a simple and low-cost hydrothermal technique for the growth of ZnO honeycomb nanostructures by incorporating  $Na_3C_6H_5O_7$  i.e. trisodium citrate in the precursor solution. The obtained honeycomb nanostructures have provided not only a larger surface area but also facilitated efficient charge transportation between the electrodes, which was resulted in improved device performance. Moreover, to examine the device reliability in UV radiations, the samples were exposed to UV light for prolonging duration of time and were intensively characterized by PL and I-V characterization. Finally, we have demonstrated that the Pt NPs coating over ZnO nanostructures is an effective way to prevent material degradation and to improve the device performance and endurance in UV-C radiation.

## 5.1.1 Experimental details

The sample preparation process involves three major steps: (1) Cleaning of the glass samples. (2) Deposition of the seed layer over the glass substrate. (3) Hydrothermal growth of ZnO nanostructures. Glass samples were properly cleaned via ultrasonication in acetone, isopropyl alcohol and DI water for 10 min. The seed solution was prepared by mixing each. an equimolar solution of zinc acetate and ethanolamine in 2-Methoxyethanol. After that, the seed layer was coated via spin coating the seed solution at 3000 rpm for 30 seconds. Afterward, spin-coated samples were annealed at 250 °C for better crystallinity and adhesivity of the seed layer over the substrate. The precursor solution for hydrothermal growth was prepared by mixing  $Zn(NO_3)_2.6H_2O(0.1M)$ ,  $Na_3C_6H_5O_7$  (5 mM) and hexamethylenetetramine (HMTA) (0.1M) in DI water. The solution was left on stirring for ten mins. For hydrothermal growth, sealed glass beakers containing precursor solution and samples were kept in an over at 110 °C for three hours. Finally, after growth, samples were thoroughly washed using DI water and acetone, followed by drying at 110 °C. For the I-V measurement, two silver electrodes of 50  $\mu$ m channel length and 2 mm width were deposited using shadow masks by physical vapor deposition (PVD) process.

Photoemission properties of the samples were measured using photoluminescence (PL) analyzer (Dongwoo Optron DM 500 i) equipped with a continuous wave He-Cd laser (excitation wavelength 325 nm) and a PMT detector. Raman analysis was performed by Horiba Jobin Yuon HR 800 UV Raman spectrometer. UV-Vis absorption spectra were obtained by (Cary 60 UV-Vis, Agilent Technologies) with a range of wavelengths from 200 nm to 800 nm. EPR spectra were recorded on a JES FA200 computerChapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector

ized spectrometer at 9.3 GHz (X band). Electrical characterization was performed in air at room temperature using a Keithley 2612A source meter. Incident light power was measured by TS2 LP 100, CNI laser, laser power meter. ISS P100 Xenon lamp power supply for the wavelength range from 200 to 950 nm was used to illuminate the samples.

## 5.2 Results and discussion



## 5.2.1 Optical characterization

*Fig. 5.1:* Photoluminescence spectra of the 5CA sample, taken at a different time interval of UV illumination

In order to investigate the types of defects present in the sample, the PL analysis has been performed. The PL spectra in figure 5.1 show a sharp emission peak centered around 385 nm, which is the characteristic peak of ZnO. However, the Gaussian peak extended towards the higher wavelength region. The deconvolution of the peak has shown two separate peaks centered at 380 and 420 nm. The peak centered at 420 nm can be assigned to the Zn<sub>*i*</sub> defects present in the crystal lattice [44]. Further, a low-intensity deep-level emission (DLE) peak in the visible region has

been observed, which indicates the lower oxygen vacancy related defects concentration in the sample.

Further, towards analyzing the effect of UV illumination over the sample, PL characterization of the UV illuminated sample has been performed. Interestingly, in the inset of figure 5.2, a shoulder peak in the near band emission (NBE) region appears to be dominating as the UV illumination time has been increased. The shoulder peak corresponds to the increasing  $Zn_i$  defect states.



*Fig. 5.2:* Normalized photoluminescence spectra of the 5CA sample, taken at the different time interval of UV illumination, inset shows magnified view of the near band emission peak

Notably, significant enhancement in the DLE has been observed, which was attributed to the formation of new defect states in the sample. The DLE peak was centered nearly at 580 nm that has been assigned to the doubly ionized oxygen vacancies  $(V_O^{++})$ . Henceforth, increasing DLE peak intensity with UV illumination can be assigned to the formation of the doubly ionized oxygen vacancies [130, 183, 184]. Moreover, DLE was observed to increase for continuous illumination of the sample by 254 nm light for 1 hour. Therefore, it indicated that the intrinsic defects viz. Zn<sub>i</sub> and  $V_O$ , concentration can be efficiently tuned by controlling the UV illumination time. The formation of the doubly ionized oxygen vacancies on UV illumination can be explained via the following equations [185-187]:

$$hv \longrightarrow h^+ + e^-$$
 (Generation of excitons) (5.1)

$$O^{2-} + h^+ \longleftrightarrow O^- + h^+ \longleftrightarrow \frac{1}{2}O_2 + V_o \text{ (Formation of } V_O)$$
 (5.2)

$$V_O \longrightarrow V_O^{2+} + 2e^-$$
 (Photoexcitation of  $V_O$ ) (5.3)



*Fig. 5.3:* Near band emission intensity to deep level emission intensity ratio variation with time

As the ZnO sample surface comes in contact with atmospheric oxygen, the oxygen molecules get chemically adsorbed over the nanostructure surface and trap the free electron from the surface of ZnO, which leads to the formation of space charge region near the surface.[44] When the sample was exposed to UV light, excitons were generated over the surface (equation 5.1). The built-in electric field at the surface space charge region was high enough to surmount the coulombic attraction between the excitons, therefore increasing the dissociation rate to photo-excited charge carriers. Further, some of the holes reach lattice oxygen at the surface and release the lattice oxygen, which results in the formation of  $V_O$  (equation 5.2). Some of the  $V_O$  defect states were photo-excited to metastable defect states in the conduction band i.e.  $V_O^{2+}$  (equation 5.3), resulting in the enhanced DLE emission.[188]



*Fig. 5.4:* Absorption spectra of the 5CA sample before and after 30 minutes of UV illumination

In order to probe in more detail about the formation of defect states after UV illumination DRA analysis has also been performed. As shown in figure 5.4, UV illuminated samples showed a significant blue shift in the near UV absorption peak from 372 nm to 360 nm which was assigned to the high electron concentration in the conduction band that resulted in bandgap widening. Therefore, in order to estimate the variation in the bandgap, the Tauc plot technique has been used. Figure 5.5 has shown the Tauc plot of the samples before and after UV illumination. A significant enhancement in the bandgap from 3.21 to 3.32 eV has been observed which could be assigned to the Burstein-Moss effect.[189] Furthermore, UV illuminated samples have shown notable enhancement in the absorption in the visible region, indicating the formation of new defect states after UV exposure. The obtained results were utterly correlated with the PL analysis. Chapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector



Fig. 5.5: Tauc plot of pristine and UV illuminated 5CA sample

To further analyze the effect of UV illumination, EPR analysis has been performed (Figure 5.6). A sharp EPR peak at 1.96 g-factor has been observed. However, the origin of the peak is still unclear; several research groups have assigned this peak to the hole trapped at neutral  $V_O$  i.e.  $V_O^+$  [190-192]. The peak intensity of the pristine ZnO sample was quite low which has been significantly increased after 1 hour of UV illumination. Therefore, the EPR results show a correlation with the PL analysis and confirm the formation of oxygen vacancies after UV illumination. Furthermore, another peak close to the free-electron value (g  $\approx$ 2.005) has also been observed, which has been attributed to the electron trapped at oxygen vacancies [193-195]. A slight enhancement in the peak intensity has been attributed to the formation of oxygen vacancies.

Moreover, Raman spectroscopy is a powerful technique to probe surface defect states. Therefore, Raman analysis of the pristine and UV illuminated sample has been performed to confirm further the formation of the oxygen vacancies related to defect states over the surface. Figure 5.7 has shown the Raman plot of Chapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector



*Fig. 5.6:* Electron paramagnetic resonance of the 5CA sample before and after UV illumination



*Fig. 5.7:* Raman analysis of the 5CA sample before and after UV illumination

both the samples. Pristine sample Raman plot has shown a distinguished sharp peak at 438 nm which is corresponded to the  $E_2$ (high) phononic transition. The peak has been significantly suppressed after prolong UV illumination, which clearly shows that the surface of the ZnO has been degraded after extending UV illumination time.

Furthermore, confocal measurement of the samples by sub-

Chapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector



*Fig. 5.8:* Confocal analysis of the 5CA sample before and after UV illumination

bandgap excitation i.e. 559 nm and 635 nm, has been recorded and shown in figure 5.8. A significant enhancement in the luminescence of the photo-excited sample has been observed, which was assigned to the formation of  $V_O$  defects states in the bandgap. Moreover, 2-photon analysis has been performed for the confirmation of the formation of new energy states in the mid-bandgap due to the photo-induced  $V_O$  defects states. For the 2-photon analysis samples were photo-excited with different wavelengths ranging from 720 – 820 nm (figure 5.9). The pristine samples have shown feeble emission which clearly suggests the absence of defect states in 1.5 – 1.72 eV energy region above the valence band. However, the prolong UV irradiated sample showed significant enhancement in the luminescence intensity for the same excitation wavelength, which confirmed the incorporation of new defects i.e.,  $V_O$  in the samples.

## 5.2.2 I-V characterization

Figure 5.10(a) has shown the photodetector device schematic. The active device area was 2 mm  $\times$  50  $\mu$ m. As shown in figure 5.10(b), The dark current of the 5CA sample at 20 V applied bias was 5.17 nA. The Schottky junction at Ag/ZnO

Chapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector







*Fig. 5.10:* (a) The device schematic and (b) photoresponse of pristine 5CA samples

interface could be assigned to such low dark current. Further, as the device was shined by 254 nm, 2.11 mW/cm<sup>2</sup> light source, the photo current reaches to 2.45 mA. The photosensitivity of the device was  $4.9 \times 10^5$ . The responsivity and specific detectivity of the device were 1150 A/W and  $8.94 \times 10^{14}$  cm·Hz<sup>1/2</sup>·W<sup>-1</sup>, respectively. The significant improvement in the device performance can be assigned to larger surface area and high charge transport efficiency of the nanostructures [196].

Further, the switching response of the 5CA sample has been recorded to investigate the response time of the device (shown in Figure 5.11). The rise time and fall time of the device was 107 sec. and 160 sec., respectively. Notably, a significant decrease in photo current after each switching cycle has been observed. Moreover, as shown in figure 5.12, when the sample was continuously illu-

Chapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector



Fig. 5.11: Switching response of the 5CA sample



Fig. 5.12: Change in photo current with respect to time

minated for ten minutes, the photo current substantially increases with time till three minutes and thirty seconds, after that current suddenly starts to decrease with an increase in time and after 10 minutes the photo current value reaches to its initial value.

## 5.2.3 Pt/ZnO nanostructures for reliable device performance

In order to eliminate the effect of UV exposure and to stabilize the device performance, Pt was sputtered over the samples

Chapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector



*Fig. 5.13:* PL spectra of the Pt/5CA sample just after and after 15 minutes of continuous UV illumination

to obtain uniform deposition of Pt nanoparticles over ZnO nanostructures. As shown in figure 5.13, Pt coated 5CA (Pt/5CA) sample has shown no significant change in the emission spectra even after 15 min. of continuous exposure to UV radiations, which indicates that Pt nanoparticles have restricted the formation of oxygen vacancies, making the device stable in UV radiations.

After confirming the stability by PL analysis in the UV radiations, I-V response of the device at 254 nm wavelength, 2.11 mW/cm<sup>2</sup> power light source has been taken. The device dark current and photo current, at 20 V applied bias was 5.3 nA and  $3.13 \times 10^{-4}$  A, respectively. The calculated device photosensitivity and photoresponsivity were  $5.9 \times 10^4$  and 148 A/W, respectively. Moreover, the switching response under 254 nm light was recorded for several switching cycles. The plot has not shown any significant variation in the peak photo current even after several switching cycles, which has also confirmed the device stability in UV radiations. Further, a slight improvement in the device response speed has been observed. Comparing to bare 5CA samples, Pt NPs coated samples have shown a decrease in rise time from 107 sec. to 90 sec., whereas the fall time remains 160 sec. Chapter 5: Investigation on the effect of prolong UV illumination over the performance of broadband photodetector



*Fig. 5.14:* I-V response of the Pt nanoparticles coated 5CA sample



*Fig. 5.15:* Switching response of the Pt nanoparticles covered 5CA device

#### 5.2.4 Conclusions

In summary, the impact of UV radiations over device performance has been investigated using photoluminescence, diffuse reflectance and electron paramagnetic resonance characterization techniques. The formation of oxygen vacancies over the ZnO nanostructures surfaces due to prolong UV illumination was found responsible for a significant decrease in device performance. Therefore, in order to rectify this stability issue, the samples were coated with Pt NPs, which resulted in improved device stability. Additionally, the Pt NPs coating has significantly improved the device response speed. The as-prepared deep UV photodetector could be a promising contender for next-generation optoelectronic devices. \_

## Chapter 6

## Synthesis of Al-doped ZnO nanowalls for ultra-low power, flexible UV photodetector

The work is about the Al-doped ZnO nanowalls networkbased ultralow voltage, flexible UV photodetector. The photodetector is synthesized over Al foil by using a simple and lowcost hydrothermal process. The device has shown photo current to the dark-current ratio of 349, high responsivity (265 mA/W at just 0.1 V applied bias) and specific detectivity of  $4.5 \times 10^{10}$ cm·Hz<sup>1/2</sup>·W<sup>-1</sup> at 350 nm. The incident light power has been kept as low as 396  $\mu$ W·cm<sup>-2</sup> throughout the measurements. The external quantum efficiency (EQE) was 1827.8 % at 5V applied bias. The proposed ultralow voltage UV photodetector demands very low power and therefore could potentially lengthen the battery discharge time. Additionally, a prominent UV sensitive piezoelectric response, having dark voltage to photo voltage ratio of 24.5, has been demonstrated that has made the device a potential candidate for fast response time, self-powered photodetector.

#### 6.1 Introduction

The UV photodetectors (PD) find applications in flame detection, missile launching systems, space communication, harmful UV radiation detection, UV dosimeter, and many more civil and military applications [173, 196-199]. Further, UV radiation has a profound impact on the survival and development of humankind. For example, moderate skin exposure to natural or artificial UV light is advantageous for health. For instance, facilitating the synthesis of vitamin D, killing germs, treating or preventing rickets etc. By contrast, excessive UV radiation can cause various diseases, such as cataracts and skin cancer, and even accelerate the aging process. Therefore, for battery-powered PDs applications like wearable UV dosimeter, low powered flexible UV PDs are highly desirable to increase the battery discharge time. A wide bandgap of 3.37 eV and high exciton binding energy of 60 meV have made ZnO a suitable material for UV detection [148-150]. Therefore, various efforts have been made for improving its photosensitivity, photoresponsivity and response time. One of the easiest ways to improve ZnO based PDs performance is to increase the surface to volume ratio by developing complex nanostructures like nanocolumns, nanopenciles, nanoflowers, honeycomb structure etc., which could significantly enhance active device area [44, 105 200]. Interestingly, Wang et al., have reported that polar planes of ZnO lattice act as conducting wires and provide efficient charge transportation path [171]. Notably, in the case of nanowalls, the conduction path consists of a larger polar surface area; therefore, charge transportation efficiency of nanowalls is far better than other nanostructures. Thus, the ZnO nanowalls network could be a promising candidate for photosensing applications. Another possible way to improve the device characteristics is to dope ZnO with dopants e.g. Al, Ga, In, Sb etc. [150, 201, 202]. Among these materials, due to its feasibility and low fabrication cost, Al-doped ZnO (AZO) has emerged as a potential candidate and has shown significant improvement in the optical and electrical properties over the pristine counterparts [148].

Moreover, considering the increasing application of flexi-

ble devices in flexible screens, touch user interface, self-folding robotics, and various wearable devices, variety of flexible substrate e.g. polyimide, cellulose paper, PET, plastic etc. have been reported [203-206]. Herein, we have used Al foil as a substrate that has not only to provide flexibility to the ZnO film but also act as a source of Al ions during hydrothermal growth. Additionally, the Al substrate can also help to support the growth of nanowalls rather than the growth of the typical nanorods [207]. Choosing Al foil as a substrate has reduced the complexity and cut down the cost of device fabrication and has provided three-fold advantages viz. doping, nanowalls growth, and flexibility. Despite the enormous possibilities, Al foil as a flexible substrate for optoelectronic applications has not been given enough attention. The obtained device has shown good sensitivity even for low light intensity at very low applied bias. Moreover, the device exhibited a significantly high piezoelectric response that can be further utilized to make multifunctional devices that can function as self-powered UV photodetector and/or nano-generators.

## 6.2 Experimental details

The hydrothermal growth of ZnO nanowalls consists of 2 major steps. In the first step, Al foils of 1 cm × 1 cm × 18  $\mu$ m size, were spin-coated with seed solution prepared by mixing the equimolar concentration of zinc acetate, ethanolamine in 2-methoxy ethanol at 3000 rpm for 30 sec. and annealed at 240 °C. Afterward, the equimolar precursor solution of zinc nitrate and HMTA has been prepared and spin-coated samples were kept in the solution at 110 °C for 4 hrs. Then the samples were rinsed with DI water and dried in air. After that, the shadow mask of 50  $\mu$ m channel length and 2 mm width were employed to deposit Silver electrodes via a PVD system. In order to check the reproducibility of the samples, three different samples have been

prepared and characterized.

Morphology and chemical composition of ZnO nanostructures (NSs) were obtained using field emission scanning electron microscopy (FESEM), Zeiss Supra-55 equipped with energy dispersive X-ray (EDX). Crystallinity was analyzed using Rigaku Smartlab, an Automated multipurpose X-ray diffractometer (XRD) equipped with Cu-K $\alpha$  source. Raman analysis was performed by Horiba Jobin Yuon HR 800 UV Raman spectrometer at 488 nm wavelength. Photoemission properties of the samples were measured using the photoluminescence (PL) analyzer (Dongwoo Optron DM 500 i) equipped with a continuous wave He-Cd laser (excitation wavelength 325 nm) and a PMT detector. UV-Vis absorption spectra were obtained by (Cary 60 UV-Vis, Agilent Technologies) with a range of wavelengths from 200 nm to 800 nm. Electrical characterization was performed in air at room temperature using a Keithley 2612A source meter. Incident light power was measured by TS2 LP 100, CNI laser, laser power meter.

## 6.3 Results and discussion

## 6.3.1 Structural analysis

Figure 6.1 shows the FESEM image of the AZO nanowalls obtained by hydrothermal growth over the Al foil substrate. The nanowalls are uniformly distributed over the substrate and well-connected to each other. The average thickness of nanowalls was  $15 \pm 2$  nm. Figure 6.2 shows EDX spectra of the sample, which clearly indicates a peak corresponding to Al ions and atomic percentage of which was 3.92 in the sample.

XRD plot in figure 6.3 has shown diffraction peak at  $2\theta$  = 60.12° corresponds to the formation of aluminum oxide thin film



*Fig. 6.1:* FESEM image of the AZO sample



Fig. 6.2: EDX spectra of the AZO sample



Fig. 6.3: XRD plot of the AZO sample

over the Al foil. Notably, for optimum device performance, the current must pass through the active region (ZnO nanowalls) of the device and not from the Al foil. Therefore, a thin insulating layer of aluminum oxide at the Al/ZnO interface will cut off the pathway through Al foil, resulting in improved device performance.

### 6.3.2 Growth mechanism



*Fig. 6.4:* Schematic of the growth of ZnO nanorods and AZO nanowalls

The growth mechanism of the nanostructures is illustrated in Figure 6.4. As the top surface of ZnO nuclei is positively charged, the negatively charged  $ZnO_2^-$  ions would get coulombically attracted towards the top plane which results in the growth along c-axis [105]. Whereas, when Al foil is used as a substrate, in the initial phase of growth, Al<sup>3+</sup> ions form AlO<sub>2</sub><sup>-</sup> ions, which were adsorbed over the polar plane of ZnO nuclei and inhibited the growth along the c-axis. As a consequence, growth dominantly starts taking place over nonpolar (110) planes, resulting in the formation of nanowalls.

$$Al(s) + 3H_2O(l) \longrightarrow Al(OH)_3(aq) + 1.5H_2(g)$$
(6.1)

Chapter 6: Synthesis of Al-doped ZnO nanowalls for ultra-low power, flexible UV photodetector

$$Al(OH)_{3}(aq) \longrightarrow Al^{3+}(aq) + 3OH^{-}(aq)$$
(6.2)

$$Al^{3+}(aq) + OH^{-}(aq) \longrightarrow Al_2O_3 + H_2O \longrightarrow AlO_2^{-}$$
 (6.3)

Furthermore, the ionic radii of the Al ions (0.054 nm) are much smaller than that of Zn ions (0.074 nm) [208]. Therefore, there is a high probability of Zn ions substitution by small size Al ions that has leads to the doping of Al ions in ZnO lattice.

### 6.3.3 Optical analysis



Fig. 6.5: Raman plot of the AZO sample

In order to confirm the doping of Al in the samples, Raman analysis has been performed (shown in Figure 6.5). The Raman plot has shown intense  $E_2(low)$  and  $E_2(high)$  peaks at 100.95 cm<sup>-1</sup> and 442.26 cm<sup>-1</sup>. It is, in fact, noteworthy that these peaks were found to be shifted from their usual positions at 98 cm<sup>-1</sup> and 438 cm<sup>-1</sup> in pristine ZnO. The shift in peak positions has clearly indicated the compressive stress present in the sample due to the substitution of some Zn ions by Al ions in the lattice. The sample has also shown a peak at 525 cm<sup>-1</sup> that has been assigned to the Al incorporation in the ZnO lattice, which again confirms the presence of Al ions in the ZnO lattice. Chapter 6: Synthesis of Al-doped ZnO nanowalls for ultra-low power, flexible UV photodetector



*Fig. 6.6:* DRS of AZO nanowalls. Inset shows the Tauc plot of the sample

The absorption spectra are shown in figure 6.6, which clearly indicated the visible blind feature of the sample as no absorption has been observed in the visible region. Further, the sample has shown significantly high absorption in the UV region. Moreover, the bandgap of the sample has been estimated by the Tauc plot method and was estimated to be 3.15 eV. In Comparison to bulk ZnO bandgap of 3.37 eV, a significant decrease in the bandgap has been observed. As the samples were prepared by a hydrothermal process that is prone to crystal defects, the reduction in the bandgap can be assigned to the crystal defects e.g. oxygen vacancies [209, 210].

#### 6.3.4 I-V characterization

Figure 6.7(a) shows the device schematic. Figure 6.7(b) shows the I-V response of the AZO nanowalls sample. A low dark current of around 0.29 nA at an applied bias of 0.1 V has been observed. Non-polar planes of ZnO form Schottky contact with Silver electrodes, which could be the possible reason for such noteworthy small dark current. As the sample was il-

luminated with 350 nm UV light of 0.396 mW·cm<sup>-2</sup> power, the device has shown substantial enhancement in the photo current from 0.29 nA to 101.3 nA. The measured photosensitivity, specific detectivity and responsivity of the device were 348.3,  $4.5 \times 10^{10}$  cm·Hz<sup>1/2</sup>·W<sup>-1</sup> and 265 mA·W<sup>-1</sup>. The calculated external quantum efficiency at 0.1V bias was 92 %, which was exponentially increased to 1227.8 % at 5V applied bias.



*Fig. 6.7:* (a) Device schematic, (b) I-V response of the PD in the dark and under 350 nm and 410 nm light illumination

Further, as the sample was illuminated with 410 nm wavelength and a sharp decrease in the photo current to 5.57 nm has been observed. As shown in Figure 6.8, the device has not shown any noteworthy response throughout the visible and NIR region. UV to Visible rejection ratio of the device was 18.36. The device has demonstrated selective spectral response with an FWHM of 77 nm (296 nm-373 nm) [211]. Such substantial enhancement in the device performance can be explained as follows: the nanowalls network has provided a large surface area for the enhanced photon absorption which has resulted in high charge carrier concentration. Further, the well-connected network of the nanowalls would provide the continuous barrier-free path for the charge carrier transportation. Additionally, the (001) planes of the nanowalls will act as conducting wires, which would be resulting in a high photo current.

Another possible reason could be the doping of Al ions would increase the n-type character of the samples which would

Chapter 6: Synthesis of Al-doped ZnO nanowalls for ultra-low power, flexible UV photodetector



*Fig. 6.8:* Photoresponsivity plot of the sample for 200 nm to 800 nm wavelength light illumination

significantly increase the photo current. Moreover, as can be seen in the absorption spectra, the device has shown no absorption in the visible region, which could be the possible reason for low photoresponsivity in the visible region. Inset in Figure 6.8 has shown the device photoresponsivity at different applied biases. An exponential enhancement in the responsivity was observed with increasing the applied bias. Figure 6.9 has shown the switching response of the device. The rise time of the device was around 2 minutes 17 seconds, whereas the fall time of the device was 3 minutes 16 seconds. The slow response speed of the device could be attributed to the presence of various intrinsic defect states in the samples.

Further, for measuring the piezo-response, the device was pasted over 100  $\mu$ m thick OHP sheet for adding more flexibility to the Al foil (Figure 6.10(a)). The device piezo response under dark and UV illumination has been shown in figure 6.10(b). The device has demonstrated a maximum peak voltage of 36.78 mV on manually bending the film along the channel. Moreover, in order to check the UV response of the device, the sample was illuminated with a UV lamp and a significant suppression in the

Chapter 6: Synthesis of Al-doped ZnO nanowalls for ultra-low power, flexible UV photodetector



*Fig. 6.9:* Switching response of the AZO based UV photodetector



*Fig. 6.10:* (a) Image of the sample, (b) piezoresponse of AZO sample under dark and UV illumination, induced by bending the film along the channel

peak voltage to 1.5 mV has been observed. Therefore, obtained results have suggested that the prepared device can potentially also be used as a self-powered photodetector. Table 6.1 listed recently reported UV photodetectors. Comparing to previously reported works, our device has shown better performance in terms of responsivity and photo current to dark current ratio.

#### 6.4 Conclusions

In conclusion, we report a visible blind photodetector that can work on ultralow voltage and is sensitive to very low light intensity. Further, the device was fabricated over flexible Al foil to

Device	Applied bias	$\mathbf{I}_{photo}/\mathbf{I}_{dark}$	Responsivity	Reference
configuration	(V)		(mA. $W^{-1}$ )	
ZnO NWs/SiO <sub>2</sub>	5	4	500	[212]
SiC thin film	5	375	150	[213]
TiO <sub>2</sub> nanowires	5	54	0.00685	[214]
Au NPs coated	4	-	160	[215]
ZnO nanorods				
p-Si/n-ZnO	-2	31.93	0.013	[216]
In doped ZnO	1	740	$74 imes 10$ $^{-6}$	[203]
Al-doped	0.1	348	265	This
ZnO nanowalls				Work

*Table 6.1:* Comparison of recently reported UV photodetectors.

harvest the piezoelectric properties of ZnO towards the development of a self-sustaining UV photodetector. The proposed device could be a potential candidate for the application where UV light intensity is very low and/or available operating power is limited. Further, owing to piezoelectric characteristics, the device can also be utilized as a nano-generator to operate small power devices and to recharge the batteries.
# Chapter 7

### **Conclusions and future work**

#### 7.1 Conclusions

In summary, the high responsivity ZnO nanostructurebased broadband UV photodetector has been developed. The hydrothermal growth process has been used for the synthesis of ZnO nanostructure. The further, additives such as KMnO<sub>4</sub> and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> were used to create complex nanostructures with higher surface area comparing to basic nanostructures e.g. nanorods, nanocolumns etc. the growth mechanism to nanostructures were discussed in detail. Further, significant improvement has been observed in the thin film adhesion with the substrate. Moreover, the addition of KMnO<sub>4</sub> in the growth solution has significantly reduced the defect related emission in the sample. Additionally, incorporation of Zn interstitial defects in ZnO lattice has significantly improved the device response in the deep UV region. Further, drastic enhancement in the surface area has increased the surface-related defect states in the midgap of ZnO, the lower thickness of the ZnO nanoplates in the honeycomb nanostructures has significantly improved the device response in the visible and NIR region. Moreover, high charge transport efficiency of honeycomb nanostructures has drastically enhanced the device sensing response from deep UV to the NIR region. Further, for reliable operation of the UV photodetector, the sensing

material should be stable in the harsh conditions. Therefore, a systematic analysis of the device response in the UV illumination has been performed. The prolong UV illumination has resulted in the formation of oxygen vacancies over the ZnO surface which has initially improve the device responsivity and later start to decrease. Therefore, in order to improve the device stability ZnO nanostructures were coated with Pt nanoparticles which have not only eliminated the effect of UV radiation over the device performance but also improved the response speed of the device. Moreover, considering the increasing demand of high responsivity, wearable, and flexible UV photodetectors, Al-doped ZnO nanoplates were hydrothermally synthesized over the Al foil. The Al foil as the substrate has not only to provide flexibility to the substrate but also acts as a source of dopant (Al ions) during the growth of the ZnO nanostructure. Additionally, keeping in mind that the wearable photodetectors usually are batteryoperated, therefore lowering the power consumption could drastically lengthen the battery life. The device reported in this work has demonstrated high sensing response just at 0.1 V. Moreover, the effect of UV radiations over the piezoelectric response of the device has also been investigated where we have found significant suppression in the piezo voltage, thereby the device is a potential candidate for self-powered UV detector.

### 7.2 Future scope of the work

The research work presented in the dissertation has demonstrated hydrothermally synthesized ZnO nanostructures over the rigid glass and flexible Al foil substrates, for broadband and UV sensing applications. The proposed ZnO nanostructures could be potential candidates for future high responsivity photodetectors. However, the device has a lot of scopes to improve upon the device response speed. The intrinsic defects such as oxygen

vacancies act as trap states thereby reduce the response speed of the device. Therefore, the hydrothermal growth technique could be optimized for decreasing the defect concentration in the sample. Another possible way is to develop the heterostructures with some other p-type materials. The high built-in field at pn junction could accelerate the device speed. Further, from the nanostructure morphological point of view, different kinds of complex nanostructures can be synthesized with better charge transportation efficiency and larger surface area. Moreover, the device performance can be significantly improved by the incorporation of metal nanoparticles over the ZnO nanostructures surface, which could not only facilitate increased absorption in the UV and visible region but also could increase charge separation to improve the device response in the visible region of the electromagnetic Further, the as-synthesized nanostructures offered spectrum. larger surface area, therefore the nanostructures are the potential candidate for the other sensing applications where larger surface area is required such as gas sensor, ion sensors and glucose sensors.

# References

- [1] H. К. Liu, L. Hu, Chen, A.A. Al-Ghamdi, X. (2015), New concept ultraviolet pho-Fang 493-502 todetectors, Mater. Today, 18 (9), (doi: http://dx.doi.org/10.1016/j.mattod.2015.06.001)
- [2] M. Razeghi (2002), Short-wavelength solar-blind detectorsstatus, prospects, and markets, Proc. IEEE, 90 (6), 1006-1014 (doi: http://dx.doi.org/10.1109/jproc.2002.1021565)
- [3] L. Sang, M. Liao, M. Sumiya (2013), A comprehensive review of semiconductor ultraviolet photodetectors: from thin film to one-dimensional nanostructures, Sensors, 13 (8), 10482-518 (doi: http://dx.doi.org/10.3390/s130810482)
- [4] R.A. Yotter, D.M. Wilson (2003), A review of photodetectors for sensing light-emitting reporters in biological systems, IEEE Sensors J., 3 (3), 288-303 (doi: http://dx.doi.org/10.1109/jsen.2003.814651)
- [5] G. Konstantatos, E.H. Sargent (2010), Nanostructured materials for photon detection, Nat. nanotechnol., 5 (6), 391-400 (doi: http://dx.doi.org/10.1038/nnano.2010.78)
- [6] M. Razeghi, A. Rogalski (1996), Semiconductor ultraviolet detectors, J. Appl. Phys., 79 (10), 7433-7473 (doi: http://dx.doi.org/10.1063/1.362677)
- [7] Y. Qin, S. Long, H. Dong, Q. He, G. Jian, Y. Zhang, X. Hou, P. Tan, Z. Zhang, H. Lv, Q. Liu, M. Liu (2019), Review of deep ultraviolet photodetector based on gallium oxide, Chin. Phy. B, 28 (1), 018501 (doi: http://dx.doi.org/10.1088/1674-1056/28/1/018501)
- [8] W. Tian, T. Zhai, C. Zhang, S.L. Li, X. Wang, F. Liu, D. Liu, X. Cai, K. Tsukagoshi, D. Golberg, Y.

Bando (2013), Low-cost fully transparent ultraviolet photodetectors based on electrospun ZnO-SnO<sub>2</sub> heterojunction nanofibers, Adv. mater, 25 (33), 4625-30 (doi: http://dx.doi.org/10.1002/adma.201301828)

- [9] L. Hu, J. Yan, M. Liao, L. Wu, X. Fang (2011), Ultrahigh external quantum efficiency from thin SnO<sub>2</sub> nanowire ultraviolet photodetectors, Small, 7 (8), 1012-7 (doi: http://dx.doi.org/10.1002/smll.201002379)
- [10] M.-L. Lu, T.-M. Weng, J.-Y. Chen, Y.-F. Chen (2012), Ultrahigh-gain single SnO<sub>2</sub> nanowire photodetectors made with ferromagnetic nickel electrodes, NPG Asia Mater., 4 (9), e26-e26 (doi: http://dx.doi.org/10.1038/am.2012.48)
- [11] C.H. Lin, T.T. Chen, Y.F. Chen (2008), Photocurrent enhancement of SnO<sub>2</sub> nanowires through Au-nanoparticles decoration, Opt. Express, 16 (21), 16916-22 (doi: http://dx.doi.org/10.1364/oe.16.016916)
- [12] M.L. Lu, T.Y. Lin, T.M. Weng, Y.F. Chen (2011), Large enhancement of photocurrent gain based on the composite of a single n-type SnO<sub>2</sub> nanowire and p-type NiO nanoparticles, Opt. Express, 19 (17), 16266-72 (doi: http://dx.doi.org/10.1364/OE.19.016266)
- [13] S. Huang, H. Wu, K. Matsubara, J. Cheng, W. Pan (2014), Facile assembly of n-SnO<sub>2</sub> nanobelts-p-NiO heterojunctions with enhanced ultraviolet photoresponse, Chem. Commun. (Camb), 50 (22), 2847-50 (doi: http://dx.doi.org/10.1039/c3cc47860b)
- [14] L. Li, E. Auer, M. Liao, X. Fang, T. Zhai, U.K. Gautam, A. Lugstein, Y. Koide, Y. Bando, D. Golberg (2011), Deep-ultraviolet solar-blind photoconductivity of individual gallium oxide nanobelts, Nanoscale, 3 (3), 1120-6 (doi: http://dx.doi.org/10.1039/c0nr00702a)
- [15] Y. Li, T. Tokizono, M. Liao, M. Zhong, Y. Koide, I. Yamada, J.-J. Delaunay (2010), Efficient Assembly of Bridged β-Ga<sub>2</sub>O<sub>3</sub> Nanowires for Solar-Blind Photodetection, Adv. Funct. Mater., 20 (22), 3972-3978 (doi: http://dx.doi.org/10.1002/adfm.201001140)

- [16] X. Fang, L. Hu, K. Huo, B. Gao, L. Zhao, M. Liao, P.K. Chu, Y. Bando, D. Golberg (2011), New Ultraviolet Photodetector Based on Individual Nb<sub>2</sub>O<sub>5</sub> Nanobelts, Adv. Funct. Mater., 21 (20), 3907-3915 (doi: http://dx.doi.org/10.1002/adfm.201100743)
- [17] R. Tamang, B. Varghese, S.G. Mhaisalkar, E.S. Tok, C.H. Sow (2011), Probing the photoresponse of individual Nb<sub>2</sub>O<sub>5</sub> nanowires with global and localized laser beam irradiation, Nanotechnology, 22 (11), 115202 (doi: http://dx.doi.org/10.1088/0957-4484/22/11/115202)
- [18] L. Li, Y. Zhang, X. Fang, T. Zhai, M. Liao, X. Sun, Y. Koide, Y. Bando, D. Golberg (2011), WO<sub>3</sub> nanowires on carbon papers: electronic transport, improved ultraviolet-light photodetectors and excellent field emitters, J. Mater. Chem., 21 (18), 6525 (doi: http://dx.doi.org/10.1039/c0jm04557h)
- [19] K. Huang, Q. Zhang, F. Yang, D. He (2010), Ultraviolet photoconductance of a single hexagonal WO<sub>3</sub> nanowire, Nano Res., 3 (4), 281-287 (doi: http://dx.doi.org/10.1007/s12274-010-1031-3)
- [20] N.W. Emanetoglu, C. Gorla, Y. Liu, S. Liang, Y. Lu (1999), Epitaxial ZnO piezoelectric thin films for saw filters, Mat. Sci. Semicon. Proc., 2 (3), 247-252 (doi: http://dx.doi.org/10.1016/s1369-8001(99)00022-0)
- [21] Y. Chen, D. Bagnall, T. Yao (2000), ZnO as a novel photonic material for the UV region, Mater. Sci. Eng. B, 75 (2-3), 190-198 (doi: http://dx.doi.org/10.1016/s0921-5107(00)00372-x)
- [22] S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu, H. Shen (2001), ZnO Schottky ultraviolet photodetectors, J. Cryst. Growth, 225 (2-4), 110-113 (doi: http://dx.doi.org/10.1016/s0022-0248(01)00830-2)
- [23] J.Y. Lee, Y.S. Choi, J.H. Kim, M.O. Park, S. Im (2002), Optimizing n-ZnO/p-Si heterojunctions for photodiode applications, Thin Solid Films, 403-404 553-557 (doi: http://dx.doi.org/10.1016/s0040-6090(01)01550-4)

- [24] N. Padmavathy, R. Vijayaraghavan (2008), Enhanced bioactivity of ZnO nanoparticles - an antimicrobial study, Sci. Technol. Adv. Mater., 9 (3), 035004 (doi: http://dx.doi.org/10.1088/1468-6996/9/3/035004)
- [25] J.B. Baxter, A.M. Walker, K.v. Ommering, E.S. Aydil (2006), Synthesis and characterization of ZnO nanowires and their integration into dye-sensitized solar cells, Nanotechnology, 17 (11), S304-S312 (doi: http://dx.doi.org/10.1088/0957-4484/17/11/s13)
- [26] M.H. Koch, P.Y. Timbrell, R.N. Lamb (1995), The influence of film crystallinity on the coupling efficiency of ZnO optical modulator waveguides, Semicond. Sci. Technol., 10 (11), 1523-1527 (doi: http://dx.doi.org/10.1088/0268-1242/10/11/015)
- [27] P. Mitra, A.P. Chatterjee, H.S. Maiti (1998), ZnO thin film sensor, Mater. Lett., 35 (1-2), 33-38 (doi: http://dx.doi.org/10.1016/s0167-577x(97)00215-2)
- [28] Z.L. Wang (2004), Zinc oxide nanostructures: growth, properties and applications, J. Condens. Matter Phys., 16 (25), R829-R858 (doi: http://dx.doi.org/10.1088/0953-8984/16/25/r01)
- [29] A. Kuoni, R.I. Holzherr, M. Boillat, N.F.d. Rooij (2003), Polyimide membrane with ZnO piezoelectric thin film pressure transducers as a differential pressure liquid flow sensor, J. Micromech. Microeng., 13 (4), S103-S107 (doi: http://dx.doi.org/10.1088/0960-1317/13/4/317)
- [30] F.R. Blom, D.J. Yntema, F.C.M. Van De Pol, M. Elwenspoek, J.H.J. Fluitman, T.H.J.A. Popma (1990), Thinfilm ZnO as micromechanical actuator at low frequencies, Sens. Actuator A Phys., 21 (1-3), 226-228 (doi: http://dx.doi.org/10.1016/0924-4247(90)85044-5)
- [31] A. Janotti, C.G. Van de Walle (2009), Fundamentals of zinc oxide as a semiconductor, Rep. Prog. Phys., 72 (12), 126501 (doi: http://dx.doi.org/Artn 126501 10.1088/0034-4885/72/12/126501)

- [32] C. Woll (2007), The chemistry and physics of zinc oxide surfaces, Prog. Surf. Sci., 82 (2-3), 55-120 (doi: http://dx.doi.org/10.1016/j.progsurf.2006.12.002)
- [33] J. Wang, L. Gao (2004), Hydrothermal synthesis and photoluminescence properties of ZnO nanowires, Solid State Commun., 132 (3-4), 269-271 (doi: http://dx.doi.org/10.1016/j.ssc.2004.07.052)
- [34] S. Baruah, J. Dutta (2009), Hydrothermal growth of ZnO nanostructures, Sci. Technol. Adv. Mater., 10 (1), 013001 (doi: http://dx.doi.org/10.1088/1468-6996/10/1/013001)
- [35] K. Keem, H. Kim, G.-T. Kim, J.S. Lee, B. Min, K. Cho, M.-Y. Sung, S. Kim (2004), Photocurrent in ZnO nanowires grown from Au electrodes, Appl. Phys. Lett., 84 (22), 4376-4378 (doi: http://dx.doi.org/10.1063/1.1756205)
- [36] C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P. Aplin, J. Park, X.Y. Bao, Y.H. Lo, D. Wang (2007), ZnO nanowire UV photodetectors with high internal gain, Nano lett., 7 (4), 1003-9 (doi: http://dx.doi.org/10.1021/nl070111x)
- [37] Q. Yang, X. Guo, W. Wang, Y. Zhang, S. Xu, D.H. Lien, Z.L. Wang (2010), Enhancing sensitivity of a single ZnO micro-/nanowire photodetector by piezophototronic effect, ACS nano, 4 (10), 6285-91 (doi: http://dx.doi.org/10.1021/nn1022878)
- [38] Z.L. Wang (2004), Nanostructures of zinc oxide, Mater. Today, 7 (6), 26-33 (doi: http://dx.doi.org/10.1016/s1369-7021(04)00286-x)
- [39] Z.L. Wang (2009), ZnO nanowire and nanobelt platform for nanotechnology, Mater. Sci. Eng. R Rep., 64 (3-4), 33-71 (doi: http://dx.doi.org/10.1016/j.mser.2009.02.001)
- [40] K. Liu, M. Sakurai, M. Aono (2010), ZnO-based ultraviolet photodetectors, Sensors, 10 (9), 8604-34 (doi: http://dx.doi.org/10.3390/s100908604)
- [41] Y.K. Su, S.M. Peng, L.W. Ji, C.Z. Wu, W.B. Cheng, C.H. Liu (2010), Ultraviolet ZnO nanorod photosensors, Langmuir, 26 (1), 603-6 (doi: http://dx.doi.org/10.1021/la902171j)

- [42] R. Triboulet, V. Munoz-Sanjosé, R. Tena-Zaera, M.C. Martinez-Tomas, S. Hassani (2005), The Scope of Zinc Oxide Bulk Growth, 194 3-14 (doi: http://dx.doi.org/10.1007/1-4020-3475-x\_1)
- [43] U. Ozgur, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, H. Morkoc (2005), A comprehensive review of ZnO materials and devices, J. Appl. Phys., 98 (4), 041301 (doi: http://dx.doi.org/10.1063/1.1992666)
- [44] J. Agrawal, T. Dixit, A.I. Palani, M.S.R. Rao, V. Singh (2018), Zinc Interstitial Rich ZnO Honeycomb Nanostructures for Deep UV Photodetection, Phys. Status Solidi Rapid Res. Lett., 12 (10), 1800241 (doi: http://dx.doi.org/10.1002/pssr.201800241)
- [45] S.-W. Kim, S. Fujita, H.-K. Park, B. Yang, H.-K. Kim, D.H. Yoon (2006), Growth of ZnO nanostructures in a chemical vapor deposition process, J. Cryst. Growth, 292 (2), 306-310 (doi: http://dx.doi.org/10.1016/j.jcrysgro.2006.04.026)
- [46] I. Udom, M.K. Ram, E.K. Stefanakos, A.F. Hepp, D.Y. Goswami (2013), One dimensional-ZnO nanostructures: Synthesis, properties and environmental applications, Mat. Sci. Semicon. Proc., 16 (6), 2070-2083 (doi: http://dx.doi.org/10.1016/j.mssp.2013.06.017)
- [47] A.B. Djurisic, X.Y. Chen, Y.H. Leung (2012), Recent progress in hydrothermal synthesis of zinc oxide nanomaterials, Recent Pat. Nanotechnol., 6 (2), 124-34 (doi: http://dx.doi.org/10.2174/187221012800270180)
- [48] S. Xu, Z.L. Wang (2011), One-dimensional ZnO nanostructures: Solution growth and functional properties, Nano Res., 4 (11), 1013-1098 (doi: http://dx.doi.org/10.1007/s12274-011-0160-7)
- [49] J. Liu, X. Huang, Y. Li, X. Ji, Z. Li, X. He, F. Sun (2007), Vertically Aligned 1D ZnO Nanostructures on Bulk Alloy Substrates: Direct Solution Synthesis, Photoluminescence, and Field Emission, J. Phys. Chem. C, 111 (13), 4990-4997 (doi: http://dx.doi.org/10.1021/jp0677820)

- [50] Y. Sheng, Y. Jiang, X. Lan, C. Wang, S. Li, X. Liu, H. Zhong (2011), Mechanism and Growth of Flexible ZnO Nanostructure Arrays in a Facile Controlled Way, J. Nanomater., 2011 1-12 (doi: http://dx.doi.org/10.1155/2011/473629)
- [51] H. Wang, C. Xie, D. Zeng, Z. Yang (2006), Controlled organization of ZnO building blocks into complex nanostructures, J. Colloid Interface Sci., 297 (2), 570-7 (doi: http://dx.doi.org/10.1016/j.jcis.2005.10.059)
- [52] D. Vernardou, G. Kenanakis, S. Couris, A.C. Manikas, G.A. Voyiatzis, M.E. Pemble, E. Koudoumas, N. Katsarakis (2007), The effect of growth time on the morphology of ZnO structures deposited on Si (100) by the aqueous chemical growth technique, J. Cryst. Growth, 308 (1), 105-109 (doi: http://dx.doi.org/10.1016/j.jcrysgro.2007.07.032)
- [53] Y. Sun, N. George Ndifor-Angwafor, D. Jason Riley, M.N.R. Ashfold (2006), Synthesis and photoluminescence of ultrathin ZnO nanowire/nanotube arrays formed by hydrothermal growth, Chem. Phys. Lett., 431 (4-6), 352-357 (doi: http://dx.doi.org/10.1016/j.cplett.2006.09.100)
- [54] H. Zhang, D. Yang, S. Li, X. Ma, Y. Ji, J. Xu, D. Que (2005), Controllable growth of ZnO nanostructures by citric acid assisted hydrothermal process, Mater. Lett., 59 (13), 1696-1700 (doi: http://dx.doi.org/10.1016/j.matlet.2005.01.056)
- [55] Y. Tong, Y. Liu, L. Dong, D. Zhao, J. Zhang, Y. Lu, D. Shen, X. Fan (2006), Growth of ZnO nanostructures with different morphologies by using hydrothermal technique, J. Phys. Chem. B, 110 (41), 20263-7 (doi: http://dx.doi.org/10.1021/jp063312i)
- [56] W.L. Z.L. Wang (2005), Hughes, Controlled syn-ZnO manipulation of thesis and nanorings and nanobows, Appl. Phys. Lett., 86 (4), 043106 (doi: http://dx.doi.org/10.1063/1.1853514)
- [57] X.Y. Kong, Z.L. Wang (2003), Spontaneous Polarization-Induced Nanohelixes, Nanosprings, and Nanorings of Piezoelectric Nanobelts, Nano Lett., 3 (12), 1625-1631 (doi: http://dx.doi.org/10.1021/nl034463p)

- [58] T. Sun, J. Qiu, C. Liang (2008), Controllable Fabrication and Photocatalytic Activity of ZnO Nanobelt Arrays, J. Phys. Chem. C, 112 (3), 715-721 (doi: http://dx.doi.org/10.1021/jp710071f)
- [59] M. Snure, A. Tiwari (2007), Synthesis, characterization, and green luminescence in ZnO nanocages, J. Nanosci. Nanotechnol., 7 (2), 481-5 (doi: http://dx.doi.org/10.1166/jnn.2007.139)
- [60] W.L. Hughes, Z.L. Wang (2004), Formation of piezoelectric single-crystal nanorings and nanobows, J. Am. Chem. Soc., 126 (21), 6703-9 (doi: http://dx.doi.org/10.1021/ja049266m)
- [61] M. Chen, Z. Wang, D. Han, F. Gu, G. Guo (2011), Highsensitivity NO<sub>2</sub> gas sensors based on flower-like and tubelike ZnO nanomaterials, Sens. Actuators B Chem., 157 (2), 565-574 (doi: http://dx.doi.org/10.1016/j.snb.2011.05.023)
- [62] T. Dixit, A. Bilgaiyan, I.A. Palani, D. Nakamura, T. Okada, V. Singh (2015), Influence of potassium permanganate on the anisotropic growth and enhanced UV emission of ZnO nanostructures using hydrothermal process for optoelectronic applications, J. Sol-Gel Sci. Techn., 75 (3), 693-702 (doi: http://dx.doi.org/10.1007/s10971-015-3741-1)
- [63] S. Chen, C. Teng, M. Zhang, Y. Li, D. Xie, G. UV-Vis-NIR Shi А (2016),Flexible Photodetector based Perovskite/Conjugated-Polymer on а Composite, Adv. mater., (28),5969-74 28 (doi: http://dx.doi.org/10.1002/adma.201600468)
- [64] Y. Cao, J. Zhu, J. Xu, J. He, J.L. Sun, Y. Wang, Z. Zhao (2014), Ultra-broadband photodetector for the visible to terahertz range by self-assembling reduced graphene oxidesilicon nanowire array heterojunctions, Small, 10 (12), 2345-51 (doi: http://dx.doi.org/10.1002/smll.201303339)
- [65] Q. Hong, Y. Cao, J. Xu, H. Lu, J. He, J.L. Sun (Nov. 2014), Self-powered ultrafast broadband photodetector based on p-n heterojunctions of CuO/Si nanowire array, ACS Appl. Mater. Interfaces, 6 (23), 20887-20894 (doi: http://dx.doi.org/10.1021/am5054338)

- [66] L. Hu, L. Zhu, H. He, Y. Guo, G. Pan, J. Jiang, Y. Jin, L. Sun, Z. Ye (2013), Colloidal chemically fabricated ZnO : Cu-based photodetector with extended UVvisible detection waveband, Nanoscale, 5 (20), 9577-81 (doi: http://dx.doi.org/10.1039/c3nr01979a)
- [67] J. Yao, J. Shao, Y. Wang, Z. Zhao, G. Yang (2015), Ultrabroadband and high response of the Bi<sub>2</sub>Te<sub>3</sub>-Si heterojunction and its application as a photodetector at room temperature in harsh working environments, Nanoscale, 7 (29), 12535-41 (doi: http://dx.doi.org/10.1039/c5nr02953h)
- [68] G. Chen, B. Liang, X. Liu, Z. Liu, G. Yu, X. Xie, T. Luo, D. Chen, M. Zhu, G. Shen, Z. Fan (2014), High-performance hybrid phenyl-C61-butyric acid methyl ester/Cd<sub>3</sub>P<sub>2</sub> nanowire ultraviolet-visible-near infrared photodetectors, ACS nano, 8 (1), 787-96 (doi: http://dx.doi.org/10.1021/nn405442z)
- [69] C.-C. Cheng, J.-Y. Zhan, Y.-M. Liao, T.-Y. Lin, Y.-P. Hsieh, Y.-F. Chen (Aug. 2016), Self-powered and broadband photodetectors based on graphene/ZnO/silicon triple junctions, Appl. Phys. Lett., 109 (5), 053501 (doi: http://dx.doi.org/10.1063/1.4960357)
- [70] P. Ghamgosar, F. Rigoni, M.G. Kohan, S. You, E.A. Morales, R. Mazzaro, V. Morandi, N. Almqvist, I. Concina, A. Vomiero (2019), Self-Powered Photodetectors Based on Core-Shell ZnO-Co<sub>3</sub>O<sub>4</sub> Nanowire Heterojunctions, ACS Appl. Mater. Interfaces, 11 (26), 23454-23462 (doi: http://dx.doi.org/10.1021/acsami.9b04838)
- [71] M. Peng, Y. Wang, Q. Shen, X. Xie, H. Zheng, W. Ma, Z. Wen, X. Sun (2018), High-performance flexible and broadband photodetectors based on PbS quantum dots/ZnO nanoparticles heterostructure, Sci. China Mater., 62 (2), 225-235 (doi: http://dx.doi.org/10.1007/s40843-018-9311-9)
- [72] J. Yu, X. Chen, Y. Wang, H. Zhou, M. Xue, Y. Xu, Z. Li, C. Ye, J. Zhang, P.A. van Aken, P.D. Lund, H. Wang (2016), A high-performance self-powered broadband photodetector based on a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite/ZnO nanorod ar-

ray heterostructure, J. Mater. Chem. C, 4 (30), 7302-7308 (doi: http://dx.doi.org/10.1039/c6tc02097f)

- [73] Y. Zhu, Z. Song, H. Zhou, D. Wu, R. Lu, R. Wang, H. Wang (2018), Self-powered, broadband perovskite photodetector based on ZnO microspheres as scaffold layer, Appl. Surf. Sci., 448 23-29 (doi: http://dx.doi.org/10.1016/j.apsusc.2018.04.047)
- [74] R. Khokhra, B. Bharti, H.N. Lee, R. Kumar (2017), Visible and UV photo-detection in ZnO nanostructured thin films via simple tuning of solution method, Sci. Rep., 7 (1), 15032 (doi: http://dx.doi.org/10.1038/s41598-017-15125-x)
- S. [75] Z. Alaie, Mohammad Yousefi Nejad, M.H. advances (2015),Recent in ultraviolet photode-Mat. Sci. Semicon. Proc., 29 16-55 tectors, (doi: http://dx.doi.org/10.1016/j.mssp.2014.02.054)
- [76] U. Pal, J.G. Serrano, P. Santiago, G. Xiong, K.B. Ucer, R.T. Williams (2006),Synthesis and opti-ZnO cal properties of nanostructures with different morphologies, Opt. Mater., 29 (1), 65-69 (doi: http://dx.doi.org/10.1016/j.optmat.2006.03.015)
- [77] M. Guo, P. Diao, S. Cai (2005), Hydrothermal growth of perpendicularly oriented ZnO nanorod array film and its photoelectrochemical properties, Appl. Surf. Sci., 249 (1-4), 71-75 (doi: http://dx.doi.org/10.1016/j.apsusc.2004.11.053)
- [78] G. Kortüm (1969), Reflectance Spectroscopy: Principles, Methods, Applications, (doi: http://dx.doi.org/10.1007/978-3-642-88071-1)
- [79] P. Kubelka, F. Munk, (1931) Ein Beitrag Zur Optik Der Farbanstriche, Z. Techn. Phys., 12, 593 -601.
- [80] A.E. Morales, E.S. Mora, U. Pal (2007), Use of diffuse reflectance spectroscopy for optical characterization of unsupported nanostructures, Rev. Mex. F´ıs. S, 53 (5), 18-22 (doi:

- [81] T.H. Gfroerer (2006), Photoluminescence in Analysis of Surfaces and Interfaces, (doi: http://dx.doi.org/10.1002/9780470027318.a2510)
- [82] N. Bhardwaj, S. Kuriakose, A. Pandey, R.C. Sharma, D.K. Avasthi, S. Mohapatra (2014), Effects of MeV ion irradiation on structural and optical properties of SnO<sub>2</sub>–ZnO nanocomposites prepared by carbothermal evaporation, J. Alloys Compd., 617 734-739 (doi: http://dx.doi.org/10.1016/j.jallcom.2014.08.066)
- [83] A. Mandal, S. Erramilli, L.D. Ziegler (2016), Origin of Dispersive Line Shapes in Plasmonically Enhanced Femtosecond Stimulated Raman Spectra, J. Phys. Chem. C, 120 (37), 20998-21006 (doi: http://dx.doi.org/10.1021/acs.jpcc.6b03303)
- [84] K.A. Alim, V.A. Fonoberov, M. Shamsa, A.A. Balandin (2005), Micro-Raman investigation of optical phonons in ZnO nanocrystals, J. Appl. Phys., 97 (12), 124313 (doi: http://dx.doi.org/10.1063/1.1944222)
- [85] G. Memisoglu, C. Varlikli (Jan. 2015), Conventional and Inverted UV-PDs Based on Solution Processed PFE:ZnO Active Layer, IEEE Photon. Technol. Lett., 27 (5), 537-540 (doi: http://dx.doi.org/10.1109/lpt.2014.2384532)
- [86] B. Hanna, K.P. Surendran, K.N.N. Unni (Oct. 2018), thin films for Low temperature-processed ZnO junction-based visible-blind phoultraviolet p–n 37365-37374 (doi: todetectors, RSC Adv., 8 (65), http://dx.doi.org/10.1039/c8ra07312k)
- [87] J. Yao, Z. Zheng, G. Yang (May 2016), Promoting the Performance of Layered-Material Photodetectors by Alloy Engineering, ACS Appl. Mater. Interfaces, 8 (20), 12915-24 (doi: http://dx.doi.org/10.1021/acsami.6b03691)
- [88] L. Dou, Y.M. Yang, J. You, Z. Hong, W.H. Chang, G. Li, Y. Yang (Nov. 2014), Solution-processed hybrid perovskite photodetectors with high detectivity, Nat. Commun., 5 5404 (doi: http://dx.doi.org/10.1038/ncomms6404)

- [89] X. Gong, M. Tong, Y. Xia, W. Cai, J.S. Moon, Y. Cao, G. Yu, C.L. Shieh, B. Nilsson, A.J. Heeger (Aug. 2009), Highdetectivity polymer photodetectors with spectral response from 300 nm to 1450 nm, Science, 325 (5948), 1665-7 (doi: http://dx.doi.org/10.1126/science.1176706)
- [90] J.F. Muth, R.M. Kolbas, A.K. Sharma, S. Oktyabrsky, J. Narayan (1999), Excitonic structure and absorption coefficient measurements of ZnO single crystal epitaxial films deposited by pulsed laser deposition, J. Appl. Phys., 85 (11), 7884-7887 (doi: http://dx.doi.org/10.1063/1.370601)
- [91] P.F. Carcia, R.S. McLean, M.H. Reilly, G. Nunes (2003), Transparent ZnO thin-film transistor fabricated by RF magnetron sputtering, Appl. Phys. Lett., 82 (7), 1117-1119 (doi: http://dx.doi.org/10.1063/1.1553997)
- [92] H. Wan, H.E. Ruda (2010), A study of the growth mechanism of CVD-grown ZnO nanowires, J. Mater. Sci.: Mater. Electron., 21 (10), 1014-1019 (doi: http://dx.doi.org/10.1007/s10854-010-0118-7)
- [93] B.D. Yao, Y.F. Chan, N. Wang (2002), Formation of ZnO nanostructures by a simple way of thermal evaporation, Appl. Phys. Lett., 81 (4), 757-759 (doi: http://dx.doi.org/10.1063/1.1495878)
- [94] L. Shi, A.J. Naik, J.B. Goodall, C. Tighe, R. Gruar, R. Binions, I. Parkin, J. Darr (2013), Highly sensitive ZnO nanorod- and nanoprism-based NO<sub>2</sub> gas sensors: size and shape control using a continuous hydrothermal pilot plant, Langmuir, 29 (33), 10603-9 (doi: http://dx.doi.org/10.1021/la402339m)
- [95] T. Wang, B. Jin, Z. Jiao, G. Lu, J. Ye, Y. Bi (2014), Photo-directed growth of Au nanowires on ZnO arrays for enhancing photoelectrochemical performances, J. Mater. Chem. A, 2 (37), 15553-15559 (doi: http://dx.doi.org/10.1039/c4ta02960g)
- [96] M.F. Elkady, H. Shokry Hassan, E.E. Hafez, A. Fouad (2015), Construction of Zinc Oxide into Different Morphological Structures to Be Utilized as Antimicrobial Agent against

Multidrug Resistant Bacteria, Bioinorg. Chem. Appl., 2015 536854 (doi: http://dx.doi.org/10.1155/2015/536854)

- [97] S. Das, K. Dutta, A. Pramanik (2013), Morphology control of ZnO with citrate: a time and concentration dependent mechanistic insight, CrystEngComm, 15 (32), 6349 (doi: http://dx.doi.org/10.1039/c3ce40822a)
- [98] K.H. Kim, K. Utashiro, Y. Abe, M. Kawamura (2014), Growth of Zinc Oxide Nanorods Using Various Seed Layer Annealing Temperatures and Substrate Materials, Int. J. Electrochem. Sci., 9 2080-2089 (doi:
- [99] Y. Zhang, M.K. Ram, E.K. Stefanakos, D.Y. Goswami (2012), Synthesis, Characterization, and Applications of ZnO Nanowires, J. Nanomater., 2012 1-22 (doi: http://dx.doi.org/10.1155/2012/624520)
- [100] M. Kokotov, G. Hodes (2009), Reliable chemical bath deposition of ZnO films with controllable morphology from ethanolamine-based solutions using KMnO<sub>4</sub> substrate activation, J. Mater. Chem., 19 (23), 3847 (doi: http://dx.doi.org/10.1039/b821242b)
- [101] A.B. Djurišić, A.M.C. Ng, X.Y. Chen (2010), ZnO nanostructures for optoelectronics: Material properties and device applications, Prog. Quantum. Electron., 34 (4), 191-259 (doi: http://dx.doi.org/10.1016/j.pquantelec.2010.04.001)
- [102] C.Y. Liu, H.Y. Xu, J.G. Ma, X.H. Li, X.T. Zhang, Y.C. Liu, R. Mu (2011), Electrically pumped near-ultraviolet lasing from ZnO/MgO core/shell nanowires, Appl. Phys. Lett., 99 (6), 063115 (doi: http://dx.doi.org/10.1063/1.3625925)
- [103] A. Dev, R. Niepelt, J.P. Richters, C. Ronning, T. Voss (2010), Stable enhancement of near-band-edge emission of ZnO nanowires by hydrogen incorporation, Nanotechnology, 21 (6), 065709 (doi: http://dx.doi.org/10.1088/0957-4484/21/6/065709)
- [104] J.P. Richters, T. Voss, D.S. Kim, R. Scholz, M. Zacharias (2008), Enhanced surface-excitonic emission in ZnO/Al<sub>2</sub>O<sub>3</sub>

core-shell nanowires, Nanotechnology, 19 (30), 305202 (doi: http://dx.doi.org/10.1088/0957-4484/19/30/305202)

- [105] J. Agrawal, T. Dixit, I.A. Palani, M.S. Ramachandra Rao, V. Singh (2018), Fabrication of high responsivity deep UV photo-detector based on Na doped ZnO nanocolumns, J. Phys. D, 51 (18), 185106 (doi: http://dx.doi.org/10.1088/1361-6463/aab8d3)
- [106] T.M. Khan, M. Irfan (2014), Studies on the complex behavior of optical phonon modes in wurtzite  $(ZnO)_{1-X}$   $(Cr_2O_3)_X$ , Appl. Phys. A, 117 (3), 1275-1282 (doi: http://dx.doi.org/10.1007/s00339-014-8518-9)
- [107] F. Decremps, J. Pellicer-Porres, A.M. Saitta, J.-C. Chervin, A. Polian (2002), High-pressure Raman spectroscopy study of wurtzite ZnO, Phys. Rev. B, 65 (9), (doi: http://dx.doi.org/10.1103/PhysRevB.65.092101)
- [108] M.A. Gluba, N.H. Nickel, N. Karpensky (2013), Interstitial zinc clusters in zinc oxide, Phys. Rev. B, 88 (24), (doi: http://dx.doi.org/10.1103/PhysRevB.88.245201)
- [109] A.-J. Cheng, Y. Tzeng, H. Xu, S. Alur, Y. Wang, M. Park, T.-h. Wu, C. Shannon, D.-J. Kim, D. Wang (2009), Raman analysis of longitudinal optical phonon-plasmon coupled modes of aligned ZnO nanorods, J. Appl. Phys., 105 (7), 073104 (doi: http://dx.doi.org/10.1063/1.3093877)
- [110] A.B. Djurišić, Y.H. Leung, K.H. Tam, L. Ding, W.K. Ge, H.Y. Chen, S. Gwo (2006), Green, yellow, and orange defect emission from ZnO nanostructures: Influence of excitation wavelength, Appl. Phys. Lett., 88 (10), 103107 (doi: http://dx.doi.org/10.1063/1.2182096)
- [111] K.-F. Lin, H.-M. Cheng, H.-C. Hsu, L.-J. Lin, W.-F. Hsieh (2005), Band gap variation of sizecontrolled ZnO quantum dots synthesized by sol–gel method, Chem. Phys. Lett., 409 (4-6), 208-211 (doi: http://dx.doi.org/10.1016/j.cplett.2005.05.027)
- [112] C. Bouvy, W. Marine, R. Sporken, B.L. Su (2006), Photoluminescence properties and quantum size effect of

ZnO nanoparticles confined inside a faujasite X zeolite matrix, Chem. Phys. Lett., 428 (4-6), 312-316 (doi: http://dx.doi.org/10.1016/j.cplett.2006.06.106)

- [113] H. Zeng, W. Cai, Y. Li, J. Hu, P. Liu (Sep. 2005), Composition/structural evolution and optical properties of ZnO/Zn nanoparticles by laser ablation in liquid media, J. Phys. Chem. B, 109 (39), 18260-18266 (doi: http://dx.doi.org/10.1021/jp052258n)
- [114] T.L. Sounart, J. Liu, J.A. Voigt, J.W.P. Hsu, E.D. Spoerke, Z. Tian, Y.B. Jiang (2006), Sequential Nucleation and Growth of Complex Nanostructured Films, Adv. Funct. Mater., 16 (3), 335-344 (doi: http://dx.doi.org/10.1002/adfm.200500468)
- [115] Z.R. Tian, J.A. Voigt, J. Liu, B. McKenzie, M.J. McDermott, M.A. Rodriguez, H. Konishi, H. Xu (2003), Complex and oriented ZnO nanostructures, Nat. Mater., 2 (12), 821-6 (doi: http://dx.doi.org/10.1038/nmat1014)
- [116] R. Yogamalar, R. Srinivasan, A. Vinu, K. Ariga, A.C. Bose (2009), X-ray peak broadening analysis in ZnO nanoparticles, Solid State Commun., 149 (43-44), 1919-1923 (doi: http://dx.doi.org/10.1016/j.ssc.2009.07.043)
- [117] P. Bindu, S. Thomas (2014), Estimation of lattice strain in ZnO nanoparticles: X-ray peak profile analysis, J. Theor. Appl. Phys., 8 (4), 123-134 (doi: http://dx.doi.org/10.1007/s40094-014-0141-9)
- [118] E. Amani, K. Khojier, N. Zare (2012), Nano-structural Characterization of Post-annealed ZnO Thin Films by Xray Diffraction and Field Emission Scanning Electron Microscopy, Int. J. Bio-Inorg. Hybrid Nanomater., 1 (4), 265-270 (doi:
- [119] S.Y. Ma, X.H. Yang, X.L. Huang, A.M. Sun, H.S. Song, H.B. Zhu (2013), Effect of post-annealing treatment on the microstructure and optical properties of ZnO/PS nanocomposite films, J. Alloys Compd., 566 9-15 (doi: http://dx.doi.org/10.1016/j.jallcom.2013.02.179)

- [120] X.Q. Wei, Z.G. Zhang, M. Liu, C.S. Chen, G. Sun, C.S. Xue, H.Z. Zhuang, B.Y. Man (2007), Annealing effect on the microstructure and photoluminescence of ZnO thin films, Mater. Chem. Phys., 101 (2-3), 285-290 (doi: http://dx.doi.org/10.1016/j.matchemphys.2006.05.005)
- [121] S. Cimitan, S. Albonetti, L. Forni, F. Peri, D. Lazzari (2009), Solvothermal synthesis and properties control of doped ZnO nanoparticles, J. Colloid Interface Sci., 329 (1), 73-80 (doi: http://dx.doi.org/10.1016/j.jcis.2008.09.060)
- [122] M.I. Khalil, M.M. Al-Qunaibit, A.M. Al-zahem, J.P. Labis (2014), Synthesis and characterization of ZnO nanoparticles by thermal decomposition of a curcumin zinc complex, Arab. J. Chem., 7 (6), 1178-1184 (doi: http://dx.doi.org/10.1016/j.arabjc.2013.10.025)
- [123] R. Sharma, F. Alam, A.K. Sharma, V. Dutta, S.K. Dhawan (2014), ZnO anchored graphene hydrophobic nanocomposite-based bulk heterojunction solar cells showing enhanced short-circuit current, J. Mater. Chem. C, 2 (38), 8142-8151 (doi: http://dx.doi.org/10.1039/c4tc01056f)
- [124] Z. Wu, Y. Li, L. Gao, S. Wang, G. Fu (2016), Synthesis of Na-doped ZnO hollow spheres with improved photocatalytic activity for hydrogen production, Dalton Trans, 45 (27), 11145-9 (doi: http://dx.doi.org/10.1039/c6dt02155g)
- [125] V. Džimbeg-Malčić, Ž. Barbarić-Mikočević, K. Itrić (2011), Kubelka-Munk theory in describing optical properties of paper (I), Teh. Vjesn., 18 (1), 117-124 (doi:
- [126] C.-J. Huang, H.-C. Yao, M.-C. Chiu, R.-S. Yu, F.-S. Shieu (2007), Characteristics of ZnO Thin Films Prepared by Acidic Sol Method, Jpn. J. Appl. Phys., 46 (8A), 5264-5268 (doi: http://dx.doi.org/10.1143/jjap.46.5264)
- [127] L.R. Valério, N.C. Mamani, A.O. de Zevallos, A. Mesquita, M.I.B. Bernardi, A.C. Doriguetto, H.B. de Carvalho (2017), Preparation and structural-optical characterization of dipcoated nanostructured Co-doped ZnO dilute magnetic oxide thin films, RSC Adv., 7 (33), 20611-20619 (doi: http://dx.doi.org/10.1039/c7ra01200d)

- [128] R.M. Sheetz, I. Ponomareva, E. Richter, A.N. Andriotis, M. Menon (2009), Defect-induced optical absorption in the visible range in ZnO nanowires, Phys. Rev. B, 80 (19), (doi: http://dx.doi.org/10.1103/PhysRevB.80.195314)
- [129] X. Ma, B. Lu, D. Li, R. Shi, C. Pan, Y. Zhu (2011), Origin of Photocatalytic Activation of Silver Orthophosphate from First-Principles, J. Phys. Chem. C, 115 (11), 4680-4687 (doi: http://dx.doi.org/10.1021/jp111167u)
- [130] K. Bandopadhyay, J. Mitra (2015), Zn interstitials and O vacancies responsible for n-type ZnO: what do the emission spectra reveal?, RSC Adv., 5 (30), 23540-23547 (doi: http://dx.doi.org/10.1039/c5ra00355e)
- [131] T. Dixit, M. Shukla, I.A. Palani, V. Singh (2016), Insight of dipole surface plasmon mediated optoelectronic property tuning of ZnO thin films using Au, Opt. Mater., 62 673-679 (doi: http://dx.doi.org/10.1016/j.optmat.2016.10.053)
- [132] J. Tauc, R. Grigorovici, A. Vancu (1966), Optical Properties and Electronic Structure of Amorphous Germanium, Phys. Status Solidi B, 15 (2), 627-637 (doi: http://dx.doi.org/10.1002/pssb.19660150224)
- [133] E.A. Davis, N.F. Mott (1970), Conduction in nonsystems V. Conductivity, crystalline optical absorpphotoconductivity tion and in amorphous semiconductors, Philos. Mag., 22 (179), 0903-0922 (doi: http://dx.doi.org/10.1080/14786437008221061)
- [134] S.T. Tan, B.J. Chen, X.W. Sun, W.J. Fan, H.S. Kwok, X.H. Zhang, S.J. Chua (2005), Blueshift of optical band gap in ZnO thin films grown by metal-organic chemicalvapor deposition, J. Appl. Phys., 98 (1), 013505 (doi: http://dx.doi.org/10.1063/1.1940137)
- [135] R.C. Rai (2013), Analysis of the Urbach tails in absorption spectra of undoped ZnO thin films, J. Appl. Phys., 113 (15), 153508 (doi: http://dx.doi.org/10.1063/1.4801900)

- [136] J.I. Pankove (1965), Absorption Edge of Impure Gallium Arsenide, Phys. Rev., 140 (6A), A2059-A2065 (doi: http://dx.doi.org/10.1103/PhysRev.140.A2059)
- [137] A.S. Hassanien, A.A. Akl (2015), Influence of composition on optical and dispersion parameters of thermally evaporated non-crystalline Cd<sub>50</sub>S<sub>50-X</sub>Se<sub>X</sub> thin films, J. Alloys Compd., 648 280-290 (doi: http://dx.doi.org/10.1016/j.jallcom.2015.06.231)
- [138] M. Caglar, S. Ilican, Y. Caglar, F. Yakuphanoglu (2009), Electrical conductivity and optical properties of ZnO nanostructured thin film, Appl. Surf. Sci., 255 (8), 4491-4496 (doi: http://dx.doi.org/10.1016/j.apsusc.2008.11.055)
- [139] Q. Tang, W. Zhou, J. Shen, W. Zhang, L. Kong, Y. Qian (2004), A template-free aqueous route to ZnO nanorod arrays with high optical property, Chem. Commun. (Camb), (6), 712-3 (doi: http://dx.doi.org/10.1039/b313387g)
- [140] T. Dixit, I.A. Palani, V. Singh (2016), Selective tuning of enhancement in near band edge emission in hydrothermally grown ZnO nanorods coated with gold, J. Lumin., 170 180-186 (doi: http://dx.doi.org/10.1016/j.jlumin.2015.10.003)
- [141] W. Tang, D. Huang, L. Wu, C. Zhao, L. Xu, H. Gao, X. Zhang, W. Wang (2011), Surface plasmon enhanced ultraviolet emission and observation of random lasing from selfassembly Zn/ZnO composite nanowires, CrystEngComm, 13 (7), 2336 (doi: http://dx.doi.org/10.1039/c0ce00710b)
- [142] B. Roul, R. Pant, A.M. Chowdhury, G. Chandan, D.K. Singh, S. Chirakkara, K.K. Nanda, S.B. Krupanidhi (Jan. 2019), Highly Responsive ZnO/AlN/Si Heterostructure-Based Infrared- and Visible-Blind Ultraviolet Photodetectors With High Rejection Ratio, IEEE Trans. Electron Devices, 1-8 (doi: http://dx.doi.org/10.1109/ted.2019.2892133)
- [143] M. Dolatyari, A. Rostami, S. Mathur, A. Klein (May 2018), UV/IR Dual-Wavelength Photodetector Design Based on ZnO/PMMA/PbSe Nanocomposites, IEEE Trans. Nanotechnol., 17 (3), 574-581 (doi: http://dx.doi.org/10.1109/tnano.2018.2827201)

- [144] Z. Liu, D. Zhang, S. Han, C. Li, T. Tang, W. Jin, X. Liu, B. Lei, C. Zhou (2003), Laser Ablation Synthesis and Electron Transport Studies of Tin Oxide Nanowires, Adv. Mater., 15 (20), 1754-1757 (doi: http://dx.doi.org/10.1002/adma.200305439)
- [145] Y.R. Ryu, T.S. Lee, J.A. Lubguban, A.B. Corman, H.W. White, J.H. Leem, M.S. Han, Y.S. Park, C.J. Youn, W.J. Kim (2006), Wide-band gap oxide alloy: BeZnO, Appl. Phys. Lett., 88 (5), 052103 (doi: http://dx.doi.org/10.1063/1.2168040)
- [146] S. Han, W. Jin, D. Zhang, T. Tang, C. Li, X. Liu, Z. Liu, B. Lei, C. Zhou (2004), Photoconduction studies on GaN nanowire transistors under UV and polarized UV illumination, Chem. Phys. Lett., 389 (1-3), 176-180 (doi: http://dx.doi.org/10.1016/j.cplett.2004.03.083)
- [147] X. Fang, Y. Bando, M. Liao, U.K. Gautam, C. Zhi, B. Dierre, B. Liu, T. Zhai, T. Sekiguchi, Y. Koide, D. Golberg (2009), Single-Crystalline ZnS Nanobelts as Ultraviolet-Light Sensors, Adv. Mater., 21 (20), 2034-2039 (doi: http://dx.doi.org/10.1002/adma.200802441)
- [148] S.-J. Young, Y.-H. Liu (Sep. 2017), High Response of Ultraviolet Photodetector Based on Al-Doped ZnO Nanosheet Structures, IEEE J. Sel. Topics Quantum Electron., 23 (5), 1-5 (doi: http://dx.doi.org/10.1109/jstqe.2017.2684540)
- [149] T. Dixit, I.A. Palani, V. Singh (Jun. 2016), Hot holes behind the improvement in ultraviolet photoresponse of Au coated ZnO nanorods, Mater. Lett., 181 183-186 (doi: http://dx.doi.org/10.1016/j.matlet.2016.06.038)
- [150] H. Cheng-Liang, C. Kuan-Chao, H. Ting-Jen (Apr. 2014), UV Photodetector of a Homojunction Based On p-Type Sb-Doped ZnO Nanoparticles and n-Type ZnO Nanowires, IEEE Trans. Electron Devices, 61 (5), 1347-1353 (doi: http://dx.doi.org/10.1109/ted.2014.2312253)
- [151] Y.K. Mishra, R. Adelung (2018), ZnO tetrapod materials for functional applications, Mater. Today, 21 (6), 631-651 (doi: http://dx.doi.org/10.1016/j.mattod.2017.11.003)

- [152] L. Su, H. Chen, X. Xu, X. Fang (Aug. 2017), Novel BeZnO Based Self-Powered Dual-Color UV Photodetector Realized via a One-Step Fabrication Method, Laser Photonics Rev., 11 (6), 1700222 (doi: http://dx.doi.org/10.1002/lpor.201700222)
- [153] C. Xie, X.-T. Lu, X.-W. Tong, Z.-X. Zhang, F.-X. Liang, L. Liang, L.-B. Luo, Y.-C. Wu (Jan. 2019), Recent Progress in Solar-Blind Deep-Ultraviolet Photodetectors Based on Inorganic Ultrawide Bandgap Semiconductors, Adv. Funct. Mater., 29 (9), 1806006 (doi: http://dx.doi.org/10.1002/adfm.201806006)
- [154] S. Maity, T. Thomas (Mar. 2019), Hybrid-Organic-Photodetector Containing Chemically Treated Zn-Promising MgO Layer With and Reliable Detec-Responsivity and Low Dark Current, IEEE tivity, Trans. Device Mater. Rel., 19 (1), 193-200 (doi: http://dx.doi.org/10.1109/tdmr.2019.2895668)
- [155] S.H. Tsai, S. Basu, C.Y. Huang, L.C. Hsu, Y.G. Lin, R.H. Horng (sept. 2018), Deep-Ultraviolet Photodetectors Based on Epitaxial ZnGa<sub>2</sub>O<sub>4</sub> Thin Films, Sci. Rep., 8 (1), 14056 (doi: http://dx.doi.org/10.1038/s41598-018-32412-3)
- [156] C. Yan, N. Singh, P.S. Lee (Feb. 2010), Wide-bandgap  $Zn_2GeO_4$  nanowire networks as efficient ultraviolet photodetectors with fast response and recovery time, Appl. Phys. Lett., 96 (5), 053108 (doi: http://dx.doi.org/10.1063/1.3297905)
- [157] J. Zúñiga-Pérez, V. Muñoz-Sanjosé, M. Lorenz, G. Benndorf, S. Heitsch, D. Spemann, M. Grundmann (2006), Structural characterization of a-plane  $Zn_{1-X}Cd_XO$  ( $0 \le X \le 0.085$ ) thin films grown by metal-organic vapor phase epitaxy, J. Appl. Phys., 99 (2), 023514 (doi: http://dx.doi.org/10.1063/1.2163014)
- [158] C.S. Olson, H. Liu, O. Ledyaev, B. Hertog, A. Osinsky,
  W.V. Schoenfeld (2015), High-gain Zn<sub>1-x</sub>Mg<sub>x</sub>O-based ultraviolet photodetectors on Al<sub>2</sub>O<sub>3</sub> and LiGaO<sub>2</sub> substrates,

Phys. Status Solidi Rapid Res. Lett., 9 (1), 82-86 (doi: http://dx.doi.org/10.1002/pssr.201409311)

- [159] C. Li, Y. Bando, M. Liao, Y. Koide, D. Golberg (2010), Visible-blind deep-ultraviolet Schottky photodetector with a photocurrent gain based on individual Zn<sub>2</sub>GeO<sub>4</sub> nanowire, Appl. Phys. Lett., 97 (16), 161102 (doi: http://dx.doi.org/10.1063/1.3491212)
- [160] B.C. Iheanacho, C.-H. Lee, W.S. Wong (Dec. 2017), ZnO Core–a-Si:H Shell Infrared Photode-Hybrid With Thin-Film IEEE tectors Integrated Transistors, Electron Device Lett., 38 (12),1688-1691 (doi: http://dx.doi.org/10.1109/led.2017.2759230)
- [161] S.-B. Wang, C.-H. Hsiao, S.-J. Chang, Z.Y. Jiao, S.-J. Young, S.-C. Hung, B.-R. Huang (Mar. 2013), ZnO Branched Nanowires and the p-CuO/n-ZnO Heterojunction Nanostructured Photodetector, IEEE Trans. Nanotechnol., 12 (2), 263-269 (doi: http://dx.doi.org/10.1109/tnano.2013.2243916)
- [162] J. Jeong, S. Nam, H. Kim, Y. Kim (Sep. 2014), Inverted Organic Photodetectors With ZnO Electron-Collecting Buffer Layers and Polymer Bulk Heterojunction Active Layers, IEEE J. Sel. Topics Quantum Electron., 20 (6), 130-136 (doi: http://dx.doi.org/10.1109/jstqe.2014.2354649)
- [163] H. Liu, Q. Sun, J. Xing, Z. Zheng, Z. Zhang, Z. Lu, K. Zhao (Mar. 2015), Fast and enhanced broadband photoresponse of a ZnO nanowire array/reduced graphene oxide film hybrid photodetector from the visible to the nearinfrared range, ACS Appl. Mater. Interfaces, 7 (12), 6645-6651 (doi: http://dx.doi.org/10.1021/am509084r)
- [164] H.E. Farnsworth, R.P. Winch (1940), Photoelectric Work Functions of (100) and (111) Faces of Silver Single Crystals and Their Contact Potential Difference, Phys. Rev., 58 (9), 812-819 (doi: http://dx.doi.org/10.1103/PhysRev.58.812)
- [165] A.W. Dweydari, C.H.B. Mee (1975), Work function measurements on (100) and (110) surfaces of

silver, Phys. Status Solidi A, 27 (1), 223-230 (doi: http://dx.doi.org/10.1002/pssa.2210270126)

- [166] H. Sheng, S. Muthukumar, N.W. Emanetoglu, Y. Lu (2002), Schottky diode with Ag on (1120) epitaxial ZnO film, Appl. Phys. Lett., 80 (12), 2132-2134 (doi: http://dx.doi.org/10.1063/1.1463700)
- [167] J. Agrawal, T. Dixit, I.A. Palani, V. Singh (Apr. 2019), Systematic investigations on the effect of prolong UV illumination on optoelectronic properties of ZnO honeycomb nanostructures, Scr. Mater., 163 1-4 (doi: http://dx.doi.org/10.1016/j.scriptamat.2018.12.029)
- [168] A. Bilgaiyan, T. Dixit, I.A. Palani, V. Singh (2017), Performance improvement of ZnO/P3HT hybrid UV photodetector by interfacial Au nanolayer, Physica E, 86 136-141 (doi: http://dx.doi.org/10.1016/j.physe.2016.07.010)
- [169] L.W. Ji, S.M. Peng, Y.K. Su, S.J. Young, C.Z. Wu, W.B. Cheng (2009), Ultraviolet photodetectors based on selectively grown ZnO nanorod arrays, Appl. Phys. Lett., 94 (20), 203106 (doi: http://dx.doi.org/10.1063/1.3141447)
- [170] D. Gedamu, I. Paulowicz, S. Kaps, O. Lupan, S. Wille, G. Haidarschin, Y.K. Mishra, R. Adelung (2014), Rapid fabrication technique for interpenetrated ZnO nanotetrapod networks for fast UV sensors, Adv. Mater., 26 (10), 1541-50 (doi: http://dx.doi.org/10.1002/adma.201304363)
- [171] X. Wang, Z. Tian, T. Yu, H. Tian, J. Zhang, S. Yuan, X. Zhang, Z. Li, Z. Zou (Feb. 2010), Effective electron collection in highly (110)-oriented ZnO porous nanosheet framework photoanode, Nanotechnology, 21 (6), 065703 (doi: http://dx.doi.org/10.1088/0957-4484/21/6/065703)
- [172] C.-Y. Lu, S.-P. Chang, S.-J. Chang, Y.-Z. Chiou, C.-F. Kuo, H.-M. Chang, C.-L. Hsu, I.C. Chen (Jul. 2007), Noise Characteristics of ZnO-Nanowire Photodetectors Prepared on ZnO:Ga/Glass Templates, IEEE Sensors J., 7 (7), 1020-1024 (doi: http://dx.doi.org/10.1109/jsen.2007.896567)

- [173] T.-Y. Tsai, S.-J. Chang, W.-Y. Weng, S.-H. Wang, C.-J. Chiu, C.-L. Hsu, T.-J. Hsueh (Sep. 2012), TiO<sub>2</sub> Nanowires UV Photodetectors With Ir Schottky Contacts, IEEE Photon. Technol. Lett., 24 (18), 1584-1586 (doi: http://dx.doi.org/10.1109/lpt.2012.2209412)
- [174] R. Dong, C. Bi, Q. Dong, F. Guo, Y. Yuan, Y. Fang, Z. Xiao, J. Huang (Mar. 2014), An Ultraviolet-to-NIR Broad Spectral Nanocomposite Photodetector with Gain, Adv. Opt. Mater., 2 (6), 549-554 (doi: http://dx.doi.org/10.1002/adom.201400023)
- [175] T. Rauch, M. Böberl, S.F. Tedde, J. Fürst, M.V. Kovalenko, G. Hesser, U. Lemmer, W. Heiss, O. Hayden (May 2009), Near-infrared imaging with quantum-dot-sensitized organic photodiodes, Nat. Photonics, 3 (6), 332-336 (doi: http://dx.doi.org/10.1038/nphoton.2009.72)
- [176] Z.Q. Bai, Z.W. Liu (Sep. 2017), A broadband photodetector based on Rhodamine B-sensitized ZnO nanowires film, Sci. Rep., 7 (1), 11384 (doi: http://dx.doi.org/10.1038/s41598-017-11154-8)
- [177] N. Alwadai, M.A. Haque, S. Mitra, T. Flemban, Y. Pak, T. Wu, I. Roqan (Nov. 2017), High-Performance Ultraviolet-to-Infrared Broadband Perovskite Photodetectors Achieved via Inter-/Intraband Transitions, ACS Appl. Mater. Interfaces, 9 (43), 37832-37838 (doi: http://dx.doi.org/10.1021/acsami.7b09705)
- [178] H. Liu, X. Zhang, L. Zhang, Z. Yin, D. Wang, J. Meng, Q. Jiang, Y. Wang, J. You (Jun. 2017), A high-performance photodetector based on an inorganic perovskite–ZnO heterostructure, J. Mater. Chem. C, 5 (25), 6115-6122 (doi: http://dx.doi.org/10.1039/c7tc01998j)
- [179] A.R. Md Foisal, T. Dinh, P. Tanner, H.-P. Phan, T.-K. Nguyen, E.W. Streed, D.V. Dao (Aug. 2018), Photoresponse of a Highly-Rectifying 3C-SiC/Si Heterostructure Under UV and Visible Illuminations, IEEE Electron Device Lett., 39 (8), 1219-1222 (doi: http://dx.doi.org/10.1109/led.2018.2850757)

- [180] H. Zhou, P. Gui, Q. Yu, J. Mei, H. Wang, G. Fang (Nov. 2015), Self-powered, visible-blind ultraviolet photodetector based on n-ZnO nanorods/i-MgO/p-GaN structure lightemitting diodes, J. Mater. Chem. C, 3 (5), 990-994 (doi: http://dx.doi.org/10.1039/c4tc02390k)
- [181] Z. Song, H. Zhou, P. Gui, X. Yang, R. Liu, G. Ma, H. Wang, G. Fang (Apr. 2018), All-inorganic perovskite CsPbBr<sub>3</sub>-based self-powered light-emitting photodetectors with ZnO hollow balls as an ultraviolet response center, J. Mater. Chem. C, 6 (19), 5113-5121 (doi: http://dx.doi.org/10.1039/c8tc00978c)
- [182] H. Zhou, Y. Zhu, H. Wang, X. Chen, G. Fang (Mar. 2013), Electroluminescence Transition From Visible- to Ultraviolet-Dominant Mode in n-Mn<sub>0.04</sub>Zn<sub>0.96</sub>O/i-ZnGa<sub>2</sub>O<sub>4</sub>/p-GaN Structure With Highly Ultraviolet Detection Performance, IEEE Electron Device Lett., 34 (3), 423-425 (doi: http://dx.doi.org/10.1109/led.2012.2236295)
- [183] A.K. Srivastava, Praveen, M. Arora, S.K. Gupta, B.R. Chakraborty, S. Chandra, S. Toyoda, H. Bahadur (2010), Nanostructural Features and Optical Performance of RF Magnetron Sputtered ZnO Thin Films, J. Mater. Sci. Technol., 26 (11), 986-990 (doi: http://dx.doi.org/10.1016/s1005-0302(10)60161-2)
- [184] T. Dixit, I.A. Palani, V. Singh (2017), Role of Surface Plasmon Decay Mediated Hot Carriers toward the Photoluminescence Tuning of Metal-Coated ZnO Nanorods, J. Phys. Chem. C, 121 (6), 3540-3548 (doi: http://dx.doi.org/10.1021/acs.jpcc.6b11526)
- [185] R.-D. Sun, A. Nakajima, A. Fujishima, T. Watanabe, K. Hashimoto (2001), Photoinduced Surface Wettability Conversion of ZnO and TiO<sub>2</sub> Thin Films, J. Phys. Chem. B, 105 (10), 1984-1990 (doi: http://dx.doi.org/10.1021/jp002525j)
- [186] H.P. Chang, E.D. Chu, Y.T. Yeh, Y.C. Wu, F.Y. Lo, W.H. Wang, M.Y. Chern, H.C. Chiu (2017), Influence of Oxygen Vacancies on the Frictional Properties

of Nanocrystalline Zinc Oxide Thin Films in Ambient Conditions, Langmuir, 33 (34), 8362-8371 (doi: http://dx.doi.org/10.1021/acs.langmuir.7b01242)

- [187] S. Lany, A. Zunger (2005), Anion vacancies as a source of persistent photoconductivity in II-VI and chalcopyrite semiconductors, Phys. Rev. B, 72 (3), (doi: http://dx.doi.org/10.1103/PhysRevB.72.035215)
- [188] M.-P. Lu, C.-W. Chen, M.-Y. Lu (2016), Charge-Separation Kinetics of Photoexcited Oxygen Vacancies in ZnO Nanowire Field-Effect Transistors, Phys. Rev. Appl., 6 (5), (doi: http://dx.doi.org/10.1103/PhysRevApplied.6.054018)
- [189] C.E. Kim, P. Moon, S. Kim, J.-M. Myoung, H.W. Jang, J. Bang, I. Yun (2010), Effect of carrier concentration on optical bandgap shift in ZnO:Ga thin films, Thin Solid Films, 518 (22), 6304-6307 (doi: http://dx.doi.org/10.1016/j.tsf.2010.03.042)
- [190] C. Drouilly, J.M. Krafft, F. Averseng, S. Casale, D. Bazer-Bachi, C. Chizallet, V. Lecocq, H. Vezin, H. Lauron-Pernot, G. Costentin (2012), ZnO Oxygen Vacancies Formation and Filling Followed by in Situ Photoluminescence and in Situ EPR, J. Phys. Chem. C, 116 (40), 21297-21307 (doi: http://dx.doi.org/10.1021/jp307693y)
- [191] S.M. Evans, N.C. Giles, L.E. Halliburton, L.A. Kappers (2008), Further characterization of oxygen vacancies and zinc vacancies in electron-irradiated ZnO, J. Appl. Phys., 103 (4), 043710 (doi: http://dx.doi.org/Artn 043710 10.1063/1.2833432)
- [192] H. Kaftelen, K. Ocakoglu, R. Thomann, S. Tu, S. Weber, E. Erdem (2012), EPR and photoluminescence spectroscopy studies on the defect structure of ZnO nanocrystals, Phys. Rev. B, 86 (1), (doi: http://dx.doi.org/10.1103/PhysRevB.86.014113)
- [193] L. Zhang, L. Yin, C. Wang, N. lun, Y. Qi, D. Xiang (2010), Origin of Visible Photoluminescence of

ZnO Quantum Dots: Defect-Dependent and Size-Dependent, J. Phys. Chem. C, 114 (21), 9651-9658 (doi: http://dx.doi.org/10.1021/jp101324a)

- [194] L. Jing, Z. Xu, J. Shang, X. Sun, W. Cai, H. Guo (2002), The preparation and characterization of ZnO ultrafine particles, Mater. Sci. Eng. A, 332 (1-2), 356-361 (doi: http://dx.doi.org/10.1016/s0921-5093(01)01801-9)
- [195] N.G. Kakazey, T.V. Sreckovic, M.M. Ristic (1997), Electronic paramagnetic resonance investigation of the evolution of defects in zinc oxide during tribophysical activation, J. Mater. Sci., 32 (17), 4619-4622 (doi: http://dx.doi.org/10.1023/a:1018689721667)
- [196] M. Zhang, D. Zhang, F. Jing (Aug. 2016), Hybrid Photodetector Based on ZnO Nanofiber Polymers With High Spectrum Selectivity, IEEE Photon. Technol. Lett., 28 (15), 1677-1679 (doi: http://dx.doi.org/10.1109/lpt.2016.2566444)
- [197] L. Yu-Ren, W. Chung-Yun, C. Chia-Tsung, H. Yu-Chih, T. Wan-Lin, I.C. Lee, C. Huang-Chung (Aug. 2015), Sensitivity Enhancement of Ultraviolet Photodetectors With the Structure of p-NiO/Insulator-SiO<sub>2</sub>/n-ZnO Nanowires,IEEE Electron Device Lett., 36 (8), 850-852 (doi: http://dx.doi.org/10.1109/led.2015.2448721)
- [198] Z. Haifeng, R. Shengping, X. Tianjiao, F. Caihui, Q. Pengfei, C. Weiyou, D. Wei (May 2011), Zr<sub>0.27</sub>Ti<sub>0.73</sub>O<sub>2</sub>-Based MSM Ultraviolet Detectors With Pt Electrodes, IEEE Electron Device Lett., 32 (5), 653-655 (doi: http://dx.doi.org/10.1109/led.2011.2110633)
- [199] T. Dixit, A. Tripathi, K.L. Ganapathi, I.A. Palani, M.S.R. Rao, V. Singh (Feb. 2019), Solution processed transparent CuO thin films for solar blind photodetection, IEEE Electron Device Lett., 40 (2), 255-258 (doi: http://dx.doi.org/10.1109/led.2018.2886928)
- [200] M. Shukla, Pramila, J. Agrawal, T. Dixit, I.A. Palani, V. Singh (May 2018), Facile hydrothermal synthesis of Mn doped ZnO nanopencils for development of amperometric

glucose biosensors, Mater. Res. Express, 5 (5), 055031 (doi: http://dx.doi.org/10.1088/2053-1591/aac339)

- [201] C.-T. Lee, T.-S. Lin, H.-Y. Lee (Aug. 2010), Mechanisms of Low Noise and High Detectivity of p-GaN/i-ZnO/n-ZnO: Al-Heterostructured Ultraviolet Photodetectors, IEEE Photon. Technol. Lett., 22 (15), 1117-1119 (doi: http://dx.doi.org/10.1109/lpt.2010.2050473)
- [202] S.-J. Young, Y.-H. Liu (Aug. 2016), Ultraviolet Photodetectors With 2-D Indium-Doped ZnO Nanostructures, IEEE Trans. Electron Devices, 63 (8), 3160-3164 (doi: http://dx.doi.org/10.1109/TED.2016.2582506)
- [203] B.P. Nabar, Z. Celik-Butler, D.P. Butler (Jan. 2015), Self-Powered Tactile Pressure Sensors Using Ordered Crystalline ZnO Nanorods on Flexible Substrates Toward Robotic Skin and Garments, IEEE Sensors J., 15 (1), 63-70 (doi: http://dx.doi.org/10.1109/jsen.2014.2337115)
- [204] X. Li, Y.-H. Wang, A. Lu, X. Liu (Nov. 2015), Controllable Hydrothermal Growth of ZnO Nanowires on Cellulose Paper for Flexible Sensors and Electronics, IEEE Sensors J., 15 (11), 6100-6107 (doi: http://dx.doi.org/10.1109/jsen.2015.2450179)
- [205] J.B. Shim, J.W. Grant, W.R. Harrell, H. Chang, S.-O. Kim (Mar. 2011), Electrical properties of rapid hydrothermal synthesised Al-doped zinc oxide nanowires in flexible electronics, Micro. Nano Lett., 6 (3), 147 (doi: http://dx.doi.org/10.1049/mnl.2010.0226)
- [206] E.S.P. Leong, S.F. Yu, S.P. Lau, A.P. Abiyasa (Nov. 2007), Edge-Emitting Vertically Aligned ZnO Nanorods Random Laser on Plastic Substrate, IEEE Technol. Lett., 19 (22),1792-1794 (doi: Photon. http://dx.doi.org/10.1109/lpt.2007.906835)
- [207] A.P. Nayak, A.M. Katzenmeyer, Y. Gosho, B. Tekin, M.S. Islam (Apr. 2012), Sonochemical approach for rapid growth of zinc oxide nanowalls, Appl. Phys. A, 107 (3), 661-667 (doi: http://dx.doi.org/10.1007/s00339-012-6823-8)

- [208] M. Hjiri, L. El Mir, S.G. Leonardi, A. Pistone, L. Mavilia, G. Neri (Feb. 2014), Al-doped ZnO for highly sensitive CO gas sensors, Sens. and Actuators B: Chem., 196 413-420 (doi: http://dx.doi.org/10.1016/j.snb.2014.01.068)
- [209] J. Wang, Z. Wang, B. Huang, Y. Ma, Y. Liu, X. Qin, X. Zhang, Y. Dai (Jul. 2012), Oxygen Vacancy Induced Band-Gap Narrowing and Enhanced Visible Light Photocatalytic Activity of ZnO, ACS Appl. Mater. Interfaces, 4 (8), 4024-4030 (doi: http://dx.doi.org/10.1021/am300835p)
- [210] S.A. Ansari, M.M. Khan, S. Kalathil, A. Nisar, J. Lee, M.H. Cho (Oct. 2013), Oxygen vacancy induced band gap narrowing of ZnO nanostructures by an electrochemically active biofilm, Nanoscale, 5 (19), 9238-46 (doi: http://dx.doi.org/10.1039/c3nr02678g)
- [211] Y. Kumar, H. Kumar, B. Mukherjee, G. Rawat, C. Kumar, B.N. Pal, S. Jit (Jul. 2017), Visible-Blind Au/ZnO Quantum Dots-Based Highly Sensitive and Spectrum Selective Schottky Photodiode, IEEE Trans. Electron Devices, 64 (7), 2874-2880 (doi: http://dx.doi.org/10.1109/ted.2017.2705067)
- [212] L. Xu, X. Li, Z. Zhan, L. Wang, S. Feng, X. Chai, W. Lu, J. Shen, Z. Weng, J. Sun (Aug. 2015), Catalyst-Free, Selective Growth of ZnO Nanowires on SiO<sub>2</sub> by Chemical Vapor Deposition for Transfer-Free Fabrication of UV Photodetectors, ACS Appl. Mater. Interfaces, 7 (36), 20264-71 (doi: http://dx.doi.org/10.1021/acsami.5b05811)
- [213] A. Aldalbahi, E. Li, M. Rivera, R. Velazquez, T. Altalhi, X. Peng, P.X. Feng (Mar. 2016), A new approach for fabrications of SiC based photodetectors, Sci. rep., 6 23457 (doi: http://dx.doi.org/10.1038/srep23457)
- [214] T.-Y. Tsai, S.-J. Chang, W.-Y. Weng, C.-L. Hsu, S.-H. Wang, C.-J. Chiu, T.-J. Hsueh, S.-P. Chang (Feb. 2012), A Visible-Blind TiO<sub>2</sub> Nanowire Photodetector, J. Electrochem. Soc., 159 (4), J132-J135 (doi: http://dx.doi.org/10.1149/2.008205jes)
- [215] J.D. Hwang, F.H. Wang, C.Y. Kung, M.C. Chan (Jan. 2015), Using the Surface Plasmon Resonance of Au

Nanoparticles to Enhance Ultraviolet Response of ZnO Nanorods-Based Schottky-Barrier Photodetectors, IEEE Trans. Nanotechnol., 14 (2), 318-321 (doi: http://dx.doi.org/10.1109/tnano.2015.2393877)

[216] Z. Wang, R. Yu, X. Wang, W. Wu, Z.L. Wang (Aug. 2016), Ultrafast Response p-Si/n-ZnO Heterojunction Ultraviolet Detector Based on Pyro-Phototronic Effect, Adv. mater., 28 (32), 6880-6 (doi: http://dx.doi.org/10.1002/adma.201600884)