FABRICATION AND CHARACTERIZATION OF HIGH-

PHOTODETECTORS USING MOCVD-GROWN ZNGA2O4 UNDER HARSH ENVIRONMENTS

Taslim Khan

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY DELHI

June 2025

© Indian Institute of Technology Delhi (IITD), India, 2025

Fabrication and characterization of high-performance deep UV photodetectors using MOCVD-grown $ZnGa_2O_4$ epilayers for application under harsh environments

Taslim Khan

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY DELHI

June 2025

DEDICATION

This dissertation is dedicated to my family, whose unwavering financial support and encouragement have been the foundation of my academic journey. I also want to sincerely thank my teachers, whose counsel, insight, and encouragement have molded my career and stoked my curiosity. It would not have been feasible to accomplish this without your guidance and assistance.

CERTIFICATE

This is to certify that the thesis entitled **"Fabrication and characterization of high-performance deep UV photodetectors using MOCVD-grown $ZnGa_2O_4$ epilayers for application under harsh environments"** submitted by **Mr. Taslim Khan**, a Research Scholar in the *Department of Physics*, under *IIT Delhi-NYCU Taiwan Joint Doctoral Program, Indian Institute of Technology Delhi, New Delhi, India,* for the award of the joint degree of **Doctor of Philosophy,** is a record of original and Bonafide research work carried out by her under our supervision and guidance. The results contained in it have not been submitted in part or full to any other university or institute for the award of any degree/diploma.

Prof. Rajendra Singh
Department of Physics
IIT Delhi
New Delhi-110016, India

Prof. Ray-Hua Horng
International college of Semiconductor Technology
NYCU
Hsinchu-300093, Taiwan

Date: June 2025

ACKNOWLEDGEMENTS

The fruition of my doctoral thesis might have remained a cherished dream without the invaluable contributions and unwavering support of numerous remarkable individuals who fostered an environment conducive to my scholarly pursuits. Thus, I am deeply indebted to all those who played a pivotal role in nurturing the stimulating atmosphere that facilitated the successful culmination of my years of research.

Foremost, I wish to extend my heartfelt appreciation to my esteemed thesis supervisor, ***Prof. Rajendra Singh and Prof. Ray-Hua Horng,*** whose substantial influence profoundly shaped and guided the trajectory of my research. Their benevolent mentorship provided me with fertile ground in which I could glean wisdom, knowledge, and experience, ultimately enabling me to bring this study to fruition. Prof. Singh's boundless patience, profound expertise, and unwavering commitment to research have been a constant source of inspiration. His adept management of our extensive research group and his receptiveness to novel ideas and their implementation have been exceptionally motivating.

My profound gratitude extends to my co-supervisor at NYCU Taiwan, ***Prof. Ray-Hua Horng***, whose invaluable support, and insightful guidance during my visit to Taiwan significantly contributed to the consolidation and realization of this work.

In addition to my supervisors, I wish to convey my sincere thanks and admiration for the dedicated efforts of the members of the SRC, namely ***Prof. Shantanu Ghosh***, ***Prof. Pintu Das***, and ***Prof. Ankur Goswami***, whose consistently helpful demeanour and unwavering support were invaluable.

I am also thankful to Prof. Ratanmala Chatterjee and Prof. Pankaj Srivastava, the Heads of the Department of Physics at IIT Delhi, for providing essential research facilities.

I consider myself fortunate to be part of the Advanced Wide Bandgap Semiconductor Laboratory, which boasts a rich history of research and a tradition of dedication and innovation. My gratitude extends to ***Dr. Aditya Singh, Dr. Madan Sharma, Dr. Pallavi Agrawal, Dr. Hardhyan Sheoron, Dr. Nahid Chaudhary, Mr. Santanu Kandar, Mr. Kamlesh Bhatt, Mr. Anant Johari, and Dr. Kanika Arora*** from whom I gained valuable knowledge. It was joyful journey of PhD with lab mates namely ***Mr. Subodh Tyagi, Mr. Mudassir Hussain, Ms. Sonika Singh, Ms. Sakshi Garg, Mr. Ambuj Mishra, Mr. Shivansh Tiwari, Baby Asim Khan, Mr. Manish Singh Rautela*** *and* ***Ishtiyaq Ahmad*** in ASMD lab. I extend my appreciation to Mr. **Hemant Kumar** and **Rahul Sharma** for his assistance in both technical and non-technical aspects of research. The camaraderie and support I received from my colleagues in the laboratory have been invaluable.

I feel privileged to have collaborated with ***Prof. Ying-Hao Chu*** from NYCU/NTHU, Taiwan, where I stayed as a dual degree student and conducted experiments alongside me and provided invaluable insights for the development and understanding of various aspects of my research. I extend my gratitude for their meticulous and patient efforts in enhancing the quality of my research work.

I extend my heartfelt thanks to ***Ms. S D Malik, Mr. Sidharth Rana, Dr. Ahmed Shaban, Dr. Rekha Aggarwal, Dr. Surbhi Sharma, Ms. Fauqia Bilal, Dr. Arvid, Mr. Abu Bakar, Asif Ali, Mr. Faisal Khan, Dr. Sayeed Akhter, Adv. Raees Khan & Jaseem Raza Khan*** for standing by my side during the most challenging phases of my experimental work. Their friendship and unwavering support served as a wellspring of encouragement, making it one of the most enlightening periods of my research journey. I sincerely appreciate the constructive feedback and insightful discussions that guided me throughout my doctoral odyssey.

I am overjoyed to express my deep appreciation to my family for their unwavering love, support, and understanding, which allowed me to nurture my aspirations and look forward to further remarkable achievements in the future. I am profoundly grateful to my parents ***Mrs. Hushan Jahan*** and ***Mr. Shahid Khan,*** and my Uncle ***Mr. Tanveer Khan*** who offered encouragement and assistance at every juncture of my personal and academic journey.

I wish to acknowledge the council for scientific industry research (CSIR) for their invaluable funding support and Senior Research Fellowship, which enabled me to undertake this study.

Ultimately, I attribute the successful completion of this endeavour to the Almighty Allah, whose blessings bestowed upon me wisdom, health, and the resilience needed to fulfil this mission and bring it to fruition.

"So verily, with hardship, there is relief" – Al Quran (94:6)

Taslim Khan
Date: June-2025
New Delhi, India

ABSTRACT

This thesis investigates the advancement and development of high-performance deep ultraviolet photodetectors (DUV PDs) that are based on metalorganic chemical vapor deposition (MOCVD) grown zinc gallate ($ZnGa_2O_4$) thin coatings on c-plane sapphire. The applications of these devices are primarily focused on cosmic exploration and harsh environments. These devices achieve a photo-todark current ratio (PDCR) of over 10^8 at an applied bias of 10 V because they have an ultra-low dark current of 6.69 fA and a high photo-to-dark current ratio (PDCR) that exceeds 10^8 at 0.2 V. Additionally, the dark current of these devices is just 37 fA. In the presence of 245 nm illumination at room temperature (RT), the photodetectors exhibit remarkable responsiveness, achieving 185 A/W at 10 V and 3.53 A/W at 0.2 V. Additionally, they achieve a record detectivity of around 10^{17} Jones. Their resilience is demonstrated by the fact that there are small variations in dark current or reaction time, which highlights their dependability for high-temperature applications. It is noteworthy that the devices continue to operate in a stable manner over a broad temperature range that extends from 27 degrees Celsius to 125 degrees Celsius. In both lighted and dark settings, the ideality factor is close to unity, which further emphasizes the predominance of thermionic emission and demonstrates the effectiveness of these devices in environments that are difficult to maintain a constant temperature.

DUV photodetectors based on $ZnGa_2O_4$ exhibit remarkable resistance to γ-ray irradiation, a crucial characteristic for space-bound photodetectors which are essential for their functionality. Following the application of irradiation, the responsivity at zero bias increased from 0.98 to 1.94 mA/W, while the dark current increased from 0.11 to 5.6 pA, indicating that there was only a slight decline in performance. Additionally, the decay times improved from 220

milliseconds to 190 milliseconds, while the PDCR climbed from 3.2×10^3 to 3.1×10^4. An increase in surface oxygen defects was discovered by high-resolution X-ray photoelectron spectroscopy (HR-XPS). This was demonstrated by the shift in the core-level peak intensity of the O 1s atom, which went from 6.82% to 53.19% after being subjected to 200 kGy γ-irradiation. This suggests that there is a structural adaptation that plays a role in radiation hardness. Due to these features, $ZnGa_2O_4$ DUV photovoltaic detectors are able to maintain their effectiveness in zero-bias operation, which is essential for passive monitoring for extended periods of time in cosmic radiation conditions.

This thermally resilient DUV PD was produced by integrating a few-layer (FL)-MoS_2 van der Waals heterostructure on top of the $ZnGa_2O_4$ layer. The goal of this development was to further improve the stability and detectivity of the device. One can accomplish the creation of a type I heterointerface by employing a novel technique that involves selectively etching FL-MoS_2. With a detectivity of 4.9×10^{18} Jones and a response time of 77 milliseconds, this design can maintain temperature stability and exhibiting high sensitivity to low-UV radiation in the range of 200 to 280 nm. With a noise-equivalent power (NEP) of 1.2×10^{-20} $W/Hz^{1/2}$, the device exhibits exceptional performance, surpassing the capabilities of ordinary Si APDs when it comes to performance. Band alignment investigations that are more in-depth reveal that the valence band and the conduction band have offsets of 1.75 eV and 1.65 eV, respectively. These offsets make it possible for charge to be transported efficiently and to remain stable in high-temperature environments. Additional developments in photodetection are revealed by an investigation that is complimentary to the study of a solar-blind, self-powered heterojunction composed of NiO and $ZnGa_2O_4$. This device, which has a staggered type-II band alignment, makes use of the pyrophototronic effect (PPE), which is the combined effect of the photoelectric and pyroelectric phenomena that occur within the non-centrosymmetric structure of $ZnGa_2O_4$ to improve its responsivity and specific detectivity. This self-powered device can

achieve a very low dark current of 5.39 *f*A, a responsivity of 88 mA/W, and a specific detectivity of 2.03×10^{14} Jones when it is set to zero bias and subjected to irradiation at a wavelength of 246 nm. The pyrophototronic effect has the ability to dramatically enhance the transient response, with the responsivity reaching its highest point at 338 A/W and the detectivity reaching 7.1×10^{18} Jones when the light intensity is raised. As a result of its high-performance properties, the NiO/$ZnGa_2O_4$ heterostructure has the potential to be utilized in applications that need low power consumption, high sensitivity, and resistance in difficult operational situations.

After being manufactured at ambient temperature, the ZnO/$ZnGa_2O_4$ heterojunction photodetector can achieve outstanding selective UV-A and UV-C detection, which is useful for applications involving artificial optical synapses. The heterojunction in question demonstrates an exceptional spectrum selectivity, as evidenced by its responsivity of 142 milliamperes per watt and its detectivity of 6.5×10^{12} Jones. The responsivity of the device grows to 407 A/W when subjected to an external bias of -10 V, whereas the detectivity of the device is 2.6×10^{14} Jones. It is possible to achieve sub-nanosecond UV switching with this device thanks to its rapid response times (0.2 ns rise and 0.4 ns decay), which is necessary for applications involving artificial synapses. Taking advantage of the pyrophototronic effect, the device reacts selectively to ultraviolet A by accumulating heat in zinc oxide (ZnO) and having a limited thermal conductivity $ZnGa_2O_4$. This results in increased detection of ultraviolet A as opposed to ultraviolet C. This arrangement imitates biological synaptic activity by means of persistent photoconductivity under 380 nm (UV-A) irradiation. This is accomplished by reproducing synaptic plasticity. Thermally induced pyrophototronic effects provide additional support for synaptic processes, whereby synaptic weight updates are increased during the learning phase and decreased during the forgetting process. The utilization of ZnO/$ZnGa_2O_4$ heterostructures in artificial optoelectronic synapses that are controlled by temperature and band-bending

dynamics is highlighted by this selective response. $ZnGa_2O_4$-based photodetectors are presented in the thesis as candidates for DUV detection in severe conditions. These photodetectors are adaptable and resilient compared to other candidates. A convincing path towards the development of radiation-resistant, high-detectivity, and self-powered photodetectors is shown by the coupling of MOCVD-grown $ZnGa_2O_4$ with advanced heterostructures such as FL-MoS_2 and NiO. These devices not only illustrate fresh uses of artificial synapses by utilizing the pyrophototronic effect, but they also push the limits of photodetection under high-temperature and radiation exposure conditions. The findings establish $ZnGa_2O_4$ as a foundation for the development of next-generation optoelectronic devices for use in space exploration as well as artificial synapse systems that are efficient in terms of energy consumption.

Keywords: - Artificial Synapse, Deep Ultraviolet, MOCVD, Single Crystalline, and $ZnGa_2O_4$

सार

यह शोध प्रबंध उच्च प्रदर्शन वाले डीप अल्ट्रावायलेट फोटोडिटेक्टर (DUV PDs) के विकास और उन्नति की जांच करता है, जो कि मेटलऑर्गेनिक केमिकल वेपर डिपोजिशन (MOCVD) द्वारा उगाए गए जिंक गैलेट ($ZnGa_2O_4$) की पतली परतों पर आधारित हैं और इन्हें c-प्लेन सैफायर पर उगाया गया है। इन उपकरणों के मुख्य अनुप्रयोग कॉस्मिक अन्वेषण और कठोर वातावरण में किए गए कार्यों पर केंद्रित हैं। ये उपकरण 10 V पर लागू बायस पर 10^8 से अधिक के फोटो-डार्क करंट अनुपात (PDCR) को प्राप्त करते हैं क्योंकि इनमें अति-निम्न डार्क करंट (6.69 *f*A) और उच्च फोटो-टू-डार्क करंट अनुपात (PDCR) है जो कि 0.2 V पर 10^8 से अधिक है। इन उपकरणों का डार्क करंट केवल 37 fA है। 245 nm की रोशनी के तहत कमरे के तापमान (RT) पर इन फोटोडिटेक्टरों में उत्कृष्ट उत्तरदायित्व देखा गया है, जो कि 10 V पर 185 A/W और 0.2 V पर 3.53 A/W प्राप्त कर रहे हैं। इसके अलावा, ये उपकरण लगभग 10^{17} जोन्स का रिकॉर्ड डिटेक्टिविटी प्राप्त करते हैं। इनकी स्थायित्व का प्रदर्शन इस तथ्य से होता है कि उच्च तापमान अनुप्रयोगों के लिए इनकी डार्क करंट या प्रतिक्रिया समय में छोटे-छोटे परिवर्तन होते हैं। यह उल्लेखनीय है कि ये उपकरण 27 डिग्री सेल्सियस से 125 डिग्री सेल्सियस तक विस्तृत तापमान सीमा में स्थिरता से कार्य करते रहते हैं। रोशनी और अंधेरे दोनों स्थितियों में, आदर्शता गुणांक एकता के निकट होता है, जो थर्मियोनिक उत्सर्जन की प्रधानता को अधिकतम रूप से प्रदर्शित करता है और कठिन वातावरण में तापमान स्थिरता में भी इन उपकरणों की प्रभावशीलता को दर्शाता है।

$ZnGa_2O_4$ पर आधारित DUV फोटोडिटेक्टर γ-किरण विकिरण के प्रति अत्यधिक प्रतिरोधी होते हैं, जो कि अंतरिक्ष-आधारित फोटोडिटेक्टर के लिए एक महत्वपूर्ण विशेषता है। विकिरण के बाद, शून्य बायस पर उत्तरदायित्व 0.98 से बढ़कर 1.94 mA/W हो गया, जबकि डार्क करंट 0.11 से बढ़कर 5.6 pA हो गया, जो प्रदर्शन में मामूली गिरावट का संकेत देता है। इसके अतिरिक्त, डीके टाइम्स में सुधार हुआ, जो

220 मिलीसेकंड से घटकर 190 मिलीसेकंड हो गया, जबकि PDCR 3.2×10^3 से बढ़कर 3.1×10^4 हो गया। उच्च-रिज़ॉल्यूशन एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (HR-XPS) द्वारा सतही ऑक्सीजन दोषों में वृद्धि की खोज की गई थी। यह 200 kGy γ-विकिरण के अधीन होने के बाद O 1s परमाणु की कोर-स्तर पीक तीव्रता में 6.82% से 53.19% तक बदलाव द्वारा प्रदर्शित किया गया था। यह सुझाव देता है कि विकिरण कठोरता में एक संरचनात्मक अनुकूलन की भूमिका होती है। इन विशेषताओं के कारण, ZnGa2O4 DUV फोटोडिटेक्टर शून्य बायस ऑपरेशन में अपनी प्रभावशीलता बनाए रखने में सक्षम हैं, जो अंतरिक्ष विकिरण स्थितियों में विस्तारित समय के लिए निष्क्रिय निगरानी के लिए आवश्यक है।

यह थर्मल रूप से स्थिर DUV PD ZnGa2O4 पर एक वैन डेर वाल्स हेटरोस्ट्रक्चर की कुछ परतों वाले (FL)-MoS2 को एकीकृत करके उत्पादित किया गया था। इस विकास का उद्देश्य उपकरण की स्थिरता और डिटेक्टिविटी को और भी बेहतर बनाना था। FL-MoS2 को चुनिंदा रूप से उत्कीर्ण करने वाली एक नई तकनीक का उपयोग करके एक प्रकार I हेटरोइंटरफेस का निर्माण किया जा सकता है। 4.9×10^{18} जोन्स की डिटेक्टिविटी और 77 मिलीसेकंड की प्रतिक्रिया समय के साथ, यह डिजाइन तापमान स्थिरता को बनाए रख सकता है और 200 से 280 नैनोमीटर की सीमा में निम्न-UV विकिरण के प्रति उच्च संवेदनशीलता प्रदर्शित करता है। शोर-समतुल्य शक्ति (NEP) 1.2×10^{-20} A/Hz$^{1/2}$ के साथ, यह उपकरण असाधारण प्रदर्शन प्रदर्शित करता है, जो सामान्य Si APD की तुलना में श्रेष्ठ है। अधिक गहराई से किए गए बैंड संरेखण अनुसंधान से पता चलता है कि वेलेंस बैंड और कंडक्शन बैंड में 1.75 eV और 1.65 eV के क्रमिक ऑफसेट हैं। ये ऑफसेट उच्च तापमान वाले वातावरण में चार्ज परिवहन को कुशलतापूर्वक और स्थिर बनाए रखते हैं।

फोटोडिटेक्शन में अतिरिक्त प्रगति को NiO और $ZnGa_2O_4$ के यौगिक वाले एक सौर-अंध-आधारित, स्व-शक्ति संचालित हेटेरोजंक्शन का सहायक अनुसंधान द्वारा प्रकट किया गया है। यह उपकरण, जिसमें एक स्टैगर्ड प्रकार-II बैंड संरेखण है, $ZnGa_2O_4$ के गैर-सेंट्रोसिमेट्रिक संरचना में पायरोफोटोट्रॉनिक प्रभाव

(PPE) का उपयोग करता है, जिससे उसकी उत्तरदायित्व और विशिष्ट डिटेक्टिविटी में सुधार होता है। ZnO/ $ZnGa_2O_4$ हेटेरोजंक्शन फोटोडिटेक्टर कमरे के तापमान पर निर्मित होने के बाद उत्कृष्ट चयनात्मक UV-A और UV-C डिटेक्शन करने में सक्षम है, जो कि कृत्रिम ऑप्टिकल सिनैप्स से संबंधित अनुप्रयोगों के लिए उपयोगी है। $ZnGa_2O_4$ आधारित फोटोडिटेक्टरों को इस शोध प्रबंध में कठोर परिस्थितियों में डीप UV डिटेक्शन के लिए संभावित के रूप में प्रस्तुत किया गया है। इन उपकरणों में ऊर्जा कुशल कृत्रिम सिनैप्स प्रणालियों के साथ-साथ अंतरिक्ष अन्वेषण में उपयोग के लिए $ZnO/ZnGa_2O_4$ हेटेरोस्ट्रक्चर का उपयोग कर उन्हें आगे बढ़ाने का मार्ग दिखाया गया है।

TABLE OF CONTENTS

DEDICATION i

CERTIFICATE....... i

ACKNOWLEDGEMENTS....... iii

ABSTRACT....... vi

TABLE OF CONTENTS xiii

LIST OF FIGURES xv

ABBREVIATIONS....... xvi

Chapter 1: Introduction 1

1.1 Background 1

1.2 Fundamental of Photodetectors: Figure of Metris 2

1.2.1 Responsivity....... 2

1.2.2 Photo to dark current ratio (PDCR) 3

1.2.3 Switching Speed and response time....... 3

1.2.4 Noise Equivalent Power (NEP) 4

1.2.5 Specific detectivity....... 4

1.2.6 Technology advancement for the next generation Deep UV photodetector 5

1.2.7 Metal Semiconductor Metal (MSM)....... 6

1.2.8 Heterostructure based deep UV photodetector 7

1.3 Material selection for the Deep UV photodetectors 9

1.4 An Overview on $ZnGa_2O_4$ 11

1.5 Thesis overview 13

Chapter 2: Experimental Methods and Characterization Techniques 17

2.1 Growth of $ZnGa_2O_4$: MOCVD 18

2.2 Growth of NiO: PLD 19

2.3 Growth of ZnO: RF-Sputtering...20

2.4 Metal Electrode Deposition: Thermal and E-beam Evaporation 22

2.5 Characterization Techniques 24

2.5.1 X-ray diffraction (XRD) 24

2.5.2 UV-Visible spectroscopy...25

2.5.3 Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM) 26

2.5.4 X-ray photoelectron spectroscopy (XPS) 27

2.5.5 Transmission Electron Microscope (TEM)..28

2.5.6 Photoelectrical Measurements 30

2.5.7 Gamma Chamber 32

Chapter 3: Fabrication of MSM Type Deep Ultraviolet Photodetectors Based on MOCVD-Grown Epilayers on Sapphire for the High Temperature Functionality 33

3.1 Introduction...34

3.2 Experimental details...36

3.2.1 Growth of $ZnGa_2O_4$ using MOCVD...36

3.2.2 Material characterization techniques 36

3.2.3 Device fabrication and IV measurements 37

3.3 Results and discussion 37

3.3.1 Material characterization 37

3.3.2 Current Voltage (IV) characteristics 39

3.3.3 Temporal response and Temperature dependent characteristics 45

3.4. Conclusion 50

Chapter 4: Effect of γ-ray irradiation on MSM deep ultraviolet photodetector based on MOCVD-Grown $ZNGa_2O_4$ 53

4.1 Introduction 54

4.2 Experimental details 56

4.2.1 Growth of $ZnGa_2O_4$ and Device fabrication 56

4.2.2 Gamma Irradiation 56

4.2.3 Material characterization technique and photodetection measurements 56

4.3 Results and Discussion 57

4.3.1. AFM 57

4.3.2. XRD 58

4.3.3 UV-Vis spectra 58

4.3.4. Time resolved photoluminescence (TRPL) 59

4.3.5. Photoelectrical properties 61

4.3.6. X-ray photoelectron spectroscopy (XPS) Analysis 68

4.3.7. Temporal responses (IT) 70

4.4 Conclusion 73

Chapter 5: Utilizing the Ability of Few-Layer MoS_2 Integrated with MOCVD-Grown $ZnGa_2O_4$ for Thermally Stable Deep Ultraviolet Detection Performance 75

5.1 Introduction 76

5.2 Experimental details 78

5.2.1 Fabrication of the device 78

5.2.2 Material characterization and electrical measurements 79

5.3 Results and discussion 80

5.3.1 Synthesis of MoS_2 and Characterization of $MoS_2/ZnGa_2O_4$ 80

5.3.2. Material characterization 80

5.3.3 Photodetection performance 84

5.3.4. Energy band offsets 87

5.3.5 Temperature dependent photo response 89

5.4 Conclusion 93

Chapter 6: Unveiling Superior Solar-Blind Photodetection with a $NiO/ZnGa_2O_4$ Heterojunction Diode 95

6.1 Introduction 96

6.2 Experimental details 99

6.2.1 Growth of NiO on MOCVD-grown $ZnGa_2O_4$ 99

6.3 Results and discussion 100

6.3.1 Structural and optical properties analysis of $NiO/ZnGa_2O_4$ heterointerface 100

6.3.2 O 1s XPS spectra analysis of $NiO/ZnGa_2O_4$ 101

6.3.3 Cross-sectional transmission electron microscopy (XTEM) analysis of $NiO/ZnGa_2O_4$ heterointerface 103

6.3.4 Photoelectric characteristics of SB PDs of $NiO/ZnGa_2O_4$ heterointerface 104

6.3.5 Temporal response 108

6.3.6 Energy band Alignment of heterointerface 112

6.4 Conclusion 117

Chapter 7: Ultraviolet Sensor distinctive towards UV-A and UV-C Via Pyrophotronic Effect Based on $ZnO/ZnGa_2O_4$ Heterostructure 119

7.1 Introduction 120

7.2 Experimental section 123

7.2.1 Fabrication of $ZnO/ZnGa_2O_4$ heterojunction device 123

7.2.2 Characterization and photoelectrical measurements 123

7.3 Results and Discussion 124

7.3.1 Structural and optical investigations of $ZnO/ZnGa_2O_4$ heterostructure 124

7.3.2 XPS investigations of $ZnO/ZnGa_2O_4$ heterointerface 125

7.3.3 Self-powered deep UV photodetector 127

7.3.4 Mechanism of selective UVC and UVA responses 131

7.3.5 Pyro-phototropic effect modulated UVA artificial synapse 134

7.4 Conclusion 137

Chapter 8: Conclusion and Future Scope 139

8.1 Summary 140

8.2 Future scope 141

References 143-172

List of Publications 173-175

Appendices 176-188

Biodata 189

LIST OF FIGURES

Figure 1.1 Applications of the deep UV detectors 6

Figure 1.2 Energy band diagram of MSM structure under (a) thermal equilibrium (b) applied bias V in dark condition and (c) applied bias V upon optical illumination 7

Figure 1.3 Schematic of the heterostructure[32,32] 9

Figure 1.4 crystal lattice structure of $ZnGa_2O_4$ 12

Figure 2.1 Schematic of the MOCVD growth setup 19

Figure 2.2 (a) Image of the PLD setup system at IIT Delhi (b) ablation of the target creation of plasma plume of NiO target. 20

Figure 2.3 (a) Schematic of plasma and (b) depiction of the plasma creation of ZnO on bombardment of Ar+ ions. 22

Figure 2.4 Schematic of the thermal and the E-Gun Evaporation system 23

Figure 2.5 Schematic of UV-Visible spectroscopy setup. 26

Figure 2.6 Transmission electron microscopy setup and internal schematic of setup. 28

Figure 2.7 Block Diagram of the photoelectrical measurements 31

Figure 2.8 Keithley SCS4 200 setup 31

Figure 2.9 Image of the Gamma-ray chamber. 32

Figure 3.1 DUV PDs (a) Schematic of MSM device and (b) Scanning electron microscope (SEM) image of fabricated Pt/$ZnGa_2O_4$/Pt MSM structure. 36

Figure 3.2 (a) High-resolution GI-XRD pattern of $ZnGa_2O_4$ epilayer on sapphire, (b) Rocking curve of the (111) plan of the $ZnGa_2O_4$ epilayers, (c) absorbance spectra of $ZnGa_2O_4$ inset: corresponding tauc plot and (d) AFM image of surface topography of the $ZnGa_2O_4$. 38

Figure 3.3 (a) DUV PDs current-voltage characteristics with and without irradiated with UV light of peak wavelength of 245 nm, responsivity of the PD at 245 nm under UV irradiation, measured at (b) 0.2 bias and (c) biases of 2, 5, and 10 V, with a fixed power density, (d) variation of the detectivity and NEP with applied bias, (e) IV characteristics after a year and (f) spectral response after a year. 40

Figure 3.4 (a) Photocurrent as a function of power density in log axes. (b) Responsivity vs power density of PD irradiated at wavelength of 245 nm biased at 10 and 0.2 V. (c) Gain and responsivity variation with voltage at peak wavelength. (d) Plot of responsivity 42

Figure 3.5 (a) Energy-band diagram of metal-semiconductor-metal (MSM) structure in dark condition and (b) under deep ultraviolet light of 245 nm. 44

Figure 3.6 Temperature-dependent I-V properties of DUVPDs on the entire temperature range from 27 to 125 °C are shown in (a) dark, (b) exposure of 245 nm respectively and (c) variation of UV-Vis rejection ratio and PDCR at 245 nm with an applied voltage of 10, 5 and 0.2 V... 46

Figure 3.7 Temporal response of the DUV PD, semilog plots (a) Different bias at the RT (b) at 0.2 V on the various temperatures (c) semilog single cycle plot at the different applied bias (d) at 10 V on the various temperatures and (e) linear plot of single cycle at a different temperature on 10 V bias. 48

Figure 3.8 The plot of ln[$IexpqVKbT$] with respect to the voltage of MSM Pt/$ZnGa_2O_4$ in (a) dark conditions and (b) DUV exposure. 50

Figure 4.1 (a)-(d) AFM images of MOCVD grown $ZnGa_2O_4$ thin films after exposed to cumulative γ-ray doses of 50, 100, and 200 kGy, respectively. 58

Figure 4.2 γ-ray irradiated (a) GI-XRD of $ZnGa_2O_4$ thin film on sapphire, (b) omega scan of corresponding to (111) plan of $ZnGa_2O_4$, (c) UV -Vis Spectra absorption spectra and (d) Tauc plot corresponding to UV-Vis spectra. 59

Figure 4.3 (a)-(d) TRPL spectroscopy of $ZnGa_2O_4$ thin films Grown by MOCVD that were exposed to cumulative γ-ray dosages of 0, 50, 100, and 200 kGy. 61

Figure 4.4 Current-Voltage (IV) characteristics on the γ-Ray irradiation (a) dark current, (b) photoexcited current at 450 nm and (c) photoexcited current at peak wavelength of 245 nm. (d) Peak responsivity at 5 V bias, (e) spectral responsivity at zero bias and (f) detectivity and NEP variability with applied bias voltages. 64

Figure 4.5 (a) variation of PDCR on γ-ray irradiation doses, (b) rejection ratio variation with γ-ray irradiation, (c) dark current and SBH variation with γ-ray irradiation, (d) apparent barrier height variation on γ-ray irradiation with term e/kbT and (e) SEM image of pristine device and (f) SEM image γ-ray irradiated device after 200 kGy. 67

Figure 4.6 XPS analysis of O 1s peak of the $ZnGa_2O_4$ to understand the effect of γ-ray irradiation on the defect formation. 69

Figure 4.7 Temporal responses of γ-ray irradiated $ZnGa_2O_4$ DUV PDs (a) dynamic response at applied bias of 5 V, (b) single cycle response with normalized photocurrent, (c) dynamic response at without applied bias and (d) The compare graph between the reported DUV PDs and this work under γ-ray irradiation as responsivity is represented on the X-axis, while detectivity is plotted on the Y-axis. 71

Figure 4.8 Log-log axes (a) variation of photocurrent at applied bias of 5 V with energy density and (b) variation of photocurrent without applied bias. 72

Figure 5.1 Schematic of the Device 79

Figure 5.2 Scanning electron microscopic image (SEM). (b), (c), (d), (e), and (f) show the EPMA elemental mapping of the $MoS_2/ZnGa_2O_4$ heterostructure, illustrating the distribution of S, Zn, O, Ga, and Mo, respectively. This confirms that there is no deterioration in the $ZnGa_2O_4$ thin film on sapphire and that there is no MoS_2 present in the obtained channel. ... 79

Figure 5.3 (a) XTEM image of $ZnGa_2O_4$ hetroepitaxy on sapphire, (b) magnified XTEM image of $ZnGa_2O_4$ hetroepitaxy on sapphire, and (c)AFM image of as transferred image on $ZnGa_2O_4$ hetroepitaxy. 82

Figure 5.4 (a) GI-XRD of the heterointerface of the $MoS_2/ZnGa_2O_4$, (b) Omega scan corresponds to peak (111) of the single crystalline $ZnGa_2O_4$, (c) Raman spectra of as-grown-

MoS_2 (d) Raman spectra of the $MoS_2/ZnGa_2O_4$ heterostructure, (e) UV-Vis absorption Spectra of $MoS_2/ZnGa_2O_4$ and (f) Tauc plot corresponding to the absorption spectra of the $ZnGa_2O_4$. 83

Figure 5.5 Photo-electrical characteristics of the fabricated device (a) Current-Voltage (I-V) measurements in of FL 450 and 245 nm of wavelength radiation of FL-MoS2/ZnGa2O4, (b) Current-Voltage (I-V) measurements in dark, 450 and 245 nm of wavelength radiation of FL-$MoS_2/ZnGa_2O_4$/FL-MoS_2, (c) spectral response of the FL-$MoS_2/ZnGa_2O_4$ DUV PDs, (d) spectral response of the FL-$MoS_2/ZnGa_2O_4$/FL-MoS_2 DUV PDs, (e) single cycle response of FL-$MoS_2/ZnGa_2O_4$/FL-MoS_2 DUV PDs on fitted with bi-exponential equation and (f) Detectivity and NEP of FL-$MoS_2/ZnGa_2O_4$/FL-MoS_2 DUV PDs with applied bias............. 86

Figure 5.6 (a) Mo 3d and (b) 2p core-level of Ga and VB spectra of FL-MoS_2 and $ZnGa_2O_4$, (c) Ga 2p and Mo 3d core levels for FL-$MoS_2/ZnGa_2O_4$ heterointerface and (d) schematic of band offset of FL-$MoS_2/ZnGa_2O_4$ heterointerface.. 88

Figure 5.7 (a) temperature-dependent IV in presence of 245 nm and dark condition, (b) Dynamic temporal response at RT on 5 and 10 V of applied biases, (c) Temperature-dependent dynamic temporal response on the entire temperature range, (d) Temperature-dependent single cycle temporal response on the entire temperature range, (e) Log-log axes plot of photocurrent vs energy density at 10 V of fixed bias and (f) Log-log axes variation of responsivity vs applied bias. 92

Figure 6.1 Device fabrication steps: (a) MOCVD grown $ZnGa_2O_4$ epilayer on sapphire with physical mask for selected area deposition of cubic NiO (b) cubic NiO is deposited by PLD on $ZnGa_2O_4$ at RT (c) Metallization on the heterostructure of NiO/$ZnGa_2O_4$ and (d) Fabricated device annealed at 250 °C in presence of Ar for better adhesion. 99

Figure 6.2 (a) XRD of single crystalline NiO/$ZnGa_2O_4$ heterointerface (b) bitmap image of NiO/ $ZnGa_2O_4$ heterointerface on sapphire, (d) Omega scan of PLD grown NiO corresponding to (111) peak, (c) Omega scan of MOCVD grown $ZnGa_2O_4$ corresponding to (222) peak, € The core level XPS spectra of MOCVD grown $ZnGa_2O_4$ of O 1s, deconvoluted in two peaks termed as lattice oxygen and defect peak corresponds to oxygen vacancies and (f) The core

level XPS spectra of PLD grown NiO of O 1s, deconvoluted in two peaks termed as Ni^{+2} and $Ni(OH)_2$. 102

Figure 6.3 (a) Cross-sectional transmission electron microscopy (XTEM) images of $NiO/ZnGa_2O_4$ heterointerface on Sapphire substrate (b) magnified XTEM image of ZnGa2O4 and sapphire interface with their corresponding Selected area electron diffraction (SEAD) patterns and (c) magnified XTEM image of Cubic-$NiO/ZnGa_2O_4$ interface with their corresponding SAED patterns. 104

Figure 6.4 Photoelectric properties of SB PDs of $NiO/ZnGa_2O_4$ p-n heterointerface (a) Schematic of SB PDs of $NiO/ZnGa_2O_4$ p-n heterointerface (b) current-voltage (IV) characteristics of $ZnGa_2O_4$ and its heterointerface with NiO in dark condition, (c) IV of SB PDs of $NiO/ZnGa_2O_4$ p-n heterointerface in the dark and at peak wavelength of 246 nm, (d) bias dependent spectral response on -13, -10, and -7 volt respectively, (e) spectral response at zero bias and (f) variation of detectivity and NEP with applied bias. 107

Figure 6.5 Single cycle temporal response of SB PDs of $NiO/ZnGa_2O_4$ p-n heterointerface (a) at -13 V of applied bias, (b) without bias. Log-log axes plot of photocurrent with a varying energy density of peak wavelength of 246 nm (c) at -13 V of applied bias, and (d) without bias. 110

Figure 6.6 kelvin probe force microscopy (KPFM) images of (a) epitaxial $ZnGa_2O_4$ on sapphire, (b) epitaxial NiO on $ZnGa_2O_4$, (c) binding energy difference between Valence band (VB) of NiO and Ni 2p, and (d) binding energy difference between VB of $ZnGa_2O_4$ and Ga 3d. 111

Figure 6.7 (a) Core level binding energy difference between Ni 2p and Ga 3d b) Schematic of emerged heterointerface between $ZnGa_2O_4$ and NiO according to XPS and KPFM studies, (c) Mechanism depicting the p-type NiO photoresponse at 350 nm indicating restricting transport of electrons and holes due to the formation of Type-II band alignment (d) band diagram of $NiO/ZnGa_2O_4$ heterojunction after contact at 0 V bias under the irradiation of 246 nm light demonstrating the pyrophotoronic effect due dT/dt of non-centro symmetric nature of $ZnGa_2O_4$

with transient response showing various stages of mechanism with and without illumination. 114

Figure 7.1 (a) Gonio-XRD of $ZnO/ZnGa_2O_4$ heterostructure on sapphire, (b) GI-XRD of $ZnO/ZnGa_2O_4$ heterostructure to removing out the sapphire effect in XRD, (c) Reciprocal space mapping of $ZnO/ZnGa_2O_4$ heterostructure on sapphire, (d) absorbance spectra of $ZnGa_2O_4$ on sapphire and $ZnO/ZnGa_2O_4$ heterostructure with inset tauc plot corresponding the absorbance of $ZnGa_2O_4$, (e) absorbance of ZnO inset corresponding tauc plot. 125

Figure 7.2 HR-XPS of $ZnO/ZnGa_2O_4$ of heterostructure (a) survey spectra of surface and with different etching time, (b) Ga 2p spectra of surface and with different etching time, (c) Zn 2p spectra of surface and with different etching time (d) O 1s spectra of surface and with different etching time, (e) fitted O 1s peak spectra of surface and (f) fitted O 1s peak spectra of surface after 60 etching. 127

Figure 7.3 (a) dark current and photocurrent variation of -10 to 10 V applied voltage sweep of the heterostructure of the $ZnO/ZnGa_2O_4$ (b) spectral response on peak wavelength on applied -10 V and without applied bias and (c) detectivity variation for the UVC, UVA and visible region Temporal response of $ZnO/ZnGa_2O_4$ heterostructure device (d) self-powered dynamic response at peak wavelength of 230 nm (e) dynamic response at peak wavelength of 230 on applied bias of -10 V (f) dynamic response at 380 nm on-10 V applied bias (g) switching speed of the $ZnO/ZnGa_2O_4$ device: ultra-fast decay and rise time observed 0.2 ns and 0.4 ns respectively (h) dynamic temporal response over varying the energy density of peak wavelength of 230 nm and (i) performance comparison of reported self-powered UVC (230 nm) with $ZnO/ZnGa_2O_4$ heterostructure based UVC self-powered photodetector on basis of responsivity and detectivity 130

Figure 7.4(a) Dynamic temporal response in UVC without pyrophototronic current spikes (b) dynamic temporal response in UVA with pyrophototronic current spikes, making the device a selective for the UVA through pyrophotronic effect, (c) magnified view of the single cycle temporal response to better understanding of pyrophotronic effect in device, (d) a schematic of heterostructure,(e) UVC illumination on the $ZnO/ZnGa_2O_4$ heterostructure diode major absorption along $ZnGa_2O_4$, (f) no-Illumination of UVC on the $ZnO/ZnGa_2O_4$ heterostructure,

(g) UVA illumination on the $ZnO/ZnGa_2O_4$ heterostructure diode major absorption along ZnO, and (h) No UVA illumination on the $ZnO/ZnGa_2O_4$ resulted polarization of carriers occurring enhance the current, slows down the speed. 134

Figure 7.5 Schematic illustrating biological synaptic behaviour alongside a photonic synaptic device modulated by optical stimuli. 135

Figure 7.6 (a) Schematic depicting the memory process in the human brain, (b) I-T on the different, (c) I-T on different UVA light intensities on -10 V applied bias, (d) current modulation in the $ZnO/ZnGa_2O_4$ heterostructure caused by six successive light pulses (80 μW/cm², applied bias = -10 V), (e) A_1 and A_2 denote the amplitude of the current change during the initial and subsequent light pulses of the 5-second photonic paired pulse facilitation (PPF) index in relation to the time interval between consecutive pulses and (f) measured learning and relearning experience behaviour of the optical synaptic device just on 80 μW/cm² pulse intensity. 136

ABBREVIATIONS

PDs	Photodetectors
DUV	Deep Ultraviolet
SB PDs	Solar blind photodetectors
2DMs	Two dimensional materials
3D	Three dimensional
γ	Gamma
NEP	Noise equivalent power
TMDCs	Transition metal dichalcogenides
OM	Optical microscope
SEM	Scanning electron microscopy
AFM	Atomic force microscopy
KPFM	Kelvin probe force microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction
RSM	Reciprocal space mapping
B.E.	Binding energy
a.u.	Arbitrary unit
TEM	Transmission electron microscopy
XTEM	Cross-sectional transmission electron microscopy
HRTEM	High resolution transmission electron microscopy
PL	Photoluminescence
TRPL	Time-resolved photoluminescence
FESEM	Field emission scanning electron microscope
EPMA	Electron probe microanalyzer
EDA	Electron diffraction analysis
MOCVD	Metal organic chemical vapor deposition
PLD	Pulsed Laser Deposition
CVD	Chemical vapor Deposition