DISSERTATION

ON

Use of Ga_2O_3 / ZnO heterostructure for fabricating enhanced UV photodetectors

under the guidance of

PROF. R. THANGAVEL

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Date: May 8, 2024.

CERTIFICATE

*Certified that the work presented in the dissertation entitled "**Use of Ga_2O_3 / ZnO heterostructure for fabricating enhanced UV photodetectors**" is an authenic record of the research work carried out by **ARCHIT AGARWAL** under my supervision in partial fulfilment of the requirement for the degree of* **B. TECH.** in **ENGINEERING PHYSICS** of the Indian Institute of Technology (ISM) Dhanbad during the Winter semester (July 2023 to May 2024). Further that no part of this dissertation has been presented previously for the award of any other degree.

Approved and Forwarded by

R. Thangavel.

PROF. R. THANGAVEL
(Supervisor)

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Archit Agarwal

Abstract

Photodetectors, including ultraviolet (UV) detectors, are one of the promising devices for efficient sensing and have gained quick momentum in recent demand with the intense research in the field of novel semiconductor materials and device architectures. In the present study, a heterostructure based on the physical properties of a hybrid of gallium oxide (Ga_2O_3) and zinc oxide (ZnO) is obtained to compare it with ZnO nanorods for possible use as a UV photodetector.

The Ga_2O_3/ZnO heterostructure is grown with the combination of hydrothermal growth and sol-gel method. The structural, optical, and electrical properties of the two materials are characterized in a systematic manner.

It was found that the heterostructure with Ga_2O_3/ZnO possessed great superiority in performance to the ZnO nanorods UV photodetection performance and featured much higher sensitivity to UV radiation. These features make a Ga_2O_3/ZnO heterostructure hold great potential in serving a new generation of UV photodetectors for many applications, including environmental monitoring, biomedical sensing, and optical communication systems.

Contents

Chapter 1

Overview on UV Photodetectors

1.1 Introduction

Modern UV photodetectors are highly sophisticated devices designed to measure and detect UV radiation within a wide range of UV wavelengths, usually extending from about 10 to 400 nanometers. They have wide applications in environmental monitoring, biomedical research, industrial processing, and defense systems.

The UV photodetectors work based on the phenomenon of the photoelectric effect, such that the incident photons from the UV light transfer energy to electrons within the semiconductor material. That engenders electron-hole pair creation, equivalent to a measurable electrical current. This current magnitude depends on the intensity of the incident UV radiation.

Semiconducting materials mainly used for photodetectors in UV applications include silicon carbide, gallium nitride, zinc oxide, and many compound semiconductors. A wide range of photodetectors can be used based on application requirements: photodiodes, phototransistors, and avalanche photodiodes.

This is due to the never-ending research in material sciences and improvements in device fabrication techniques and sensor integration, which enhance the sensitivity, response time, and reliability of UV photodetectors. All these developments have increased the scope of applications for UV photodetectors and made possible the development of UV-curing processes, monitoring water and air quality, flame detection, and UV spectroscopy.

Miniaturization and further integration of UV photodetectors into portable and wearable devices have enabled their use for the monitoring of personal UV exposure in such a way that one will be able to learn how to maintain the level of exposure from the sun and reduce the risk of skin damage and UV-induced cancers. Further development and research are forecasted to continue with UV photodetectors for better performance and the introduction of new applications using this technology in emerging systems.

1.2 Applications of UV Photodetectors

1.2.1 Deep Space Probes and Missions

Deep space probes include studying far-away planets, asteroids, or interstellar space, where UV photodetectors often form the very basis of communication with Earth-based control centers. Many onboard communication systems rely on these detectors to receive and decode signals from Earth, allowing transmission of scientific data, images, and telemetry over large distances. UV photodetectors form a part of laser communication systems implemented for deep space missions. Laser communications use UV lasers to send data between spacecraft and Earth stations. Onboard, UV photodetectors receive and decode the modulated laser signal, thus allowing high-bandwidth data transfer with much more efficiency and reliability than is possible with conventional radio-frequency communication methods.

UV photodetectors can be used in interstellar communication systems that intend to establish a line of communication with extraterrestrial civilizations or interstellar probes. UV radiation may have been a means of interstellar communication since it suffers little attenuation and interference in going through space.

Research into novel UV communication technologies, including quantum communication and entanglement-based communication for secure and ultra-long-distance communications in deep space missions and interstellar exploration undertakings.

1.2.2 High-Speed Data Transfer

In optical fiber communications, UV photodetectors are used to pick up the optical signals sent through digital data transmission as light pulses. The detectors in the system convert the incoming optical signal into electrical signals for further processing and decoding. Photodetectors working in the UV range can, therefore, work at high speed with high data transfer rates, very low latency, and only minor signal degradation.

The backbone infrastructure of high-speed internet networks relates to the UV photodetectors, including fiber optics networks deployed by telecommunication companies and internet service providers. This enables the transmission of a large amount of data over long distances, allowing for the deployment of bandwidth-intensive applications like video streaming, cloud computing, and online gaming.

1.2.3 Protien Analysis and DNA Sequencing

UV photodetectors find wide application in protein analysis approaches, including UV-visible spectrophotometry and chromatography. UV-VIS spectrophotometers determine the protein concentrations because proteins absorb UV light of peculiar wavelengths determined based on the presence of aromatic amino acids, such as tryptophan, tyrosine, and in lesser measure, phenylalanine. The UV photodetector in the spectrophotometer quantifies the absorbance of the sample protein at characteristic UV wavelengths, which helps elucidate the concentration of a protein component and protein impurity.

Automated DNA sequencers use UV photodetectors during DNA sequencing to monitor fluorescently LSD nucleotide bases, such as fluorescein. As the nucleotide base is incorporated into the DNA molecule during sequencing, it emits fluorescence stimulated by UV light, and the emitted fluorescence is recorded. The ability of the photodetector to capture fluorescence signals allows for monitoring and recording of the new DNA sequence being developed in the DNA sequencer. The photodetector systems are similarly used in nucleic acid labeling and detection applications, including Southern and Northern hybridization.

1.2.4 Sterlization and disinfection

UV radiation detectors are often incorporated in UV sterilizers applied in different fields of production, especially health care, food processing, drinking water decontamination, and air dehumidifying. They play a significant role in tracking the strength of UV radiation produced by ultraviolet lamps or UV-C LEDs,, thus guaranteeing the amount of ultraviolet light required to kill germs like bacteria and viruses ,in air, water bodies, objects, or even medical machines.

UV photodetectors are used in water treatment systems designed for UV radiation to regulate the amount of UV exposure necessary for infectious agent inactivation. Photodetectors are used in UV reactors where water flows so that they can measure the amount of UV light produced and time duration between exposures: by doing this, they help prevent any harm caused by pathogens like E.coli or Giardia inside unsafe drinking water.

1.2.5 Fire Alarms and Flame Sensing Systems

The UV photodetectors are very sensitive to the radiation of UV emitted from the flames during the combustion processes. They are mounted in critical locations and have a greater probability of fire starting locations, such as industrial facilities, chemical plants, and aircraft engines. In the presence of flame, these UV photodetectors detect characteristic UV emissions and trigger an alarm or activate fire suppression systems to prevent the spread and ensuing damage from fire.

UV photodetectors work in a fire alarm system by responding to a fire scenario early and generating an alarm signal to the occupants and proper authorities. For instance, a UV flame detector would be expected to work in conjunction with smoke detectors and heat detectors in a fire alarm system in buildings and facilities, especially those with high ceilings, open spaces, or using highly combustible materials.

UV flame detectors are installed in hazardous industries where the risk of an explosion is high due to flammable gases, vapors, or dust. UV flame detectors reduce the dangers to human lives and health, property, and critical infrastructure from disastrous explosions that may occur because of ignition sources by providing quick fire detection.

1.2.6 Air Pollution and Ozone Levels

Another application of UV photodetectors is their integration into air quality monitoring stations to measure particulate matter suspended in the atmosphere. Solar irradiation of airborne particles spreads the UV radiation, while airborne photodetectors can quantify it. Hence, their utilization enables the use of real-time data on the UV intensity of PM to determine the pollution sources. UV photodetectors are an essential part of ozone measurement tools such as ozone analyzers and ozone control sensors. In this case, the photodetectors are used to determine the UV dispersion by ozone molecules.These measurements are crucial for assessing air quality, understanding ozone formation and depletion processes, and implementing regulatory measures to protect human health and the environment.

1.2.7 Missile Plume Detection

UV photodetectors are a key components in early warning systems designed to detect the UV radiation emitted by missile plumes during launch. When a missile is launched, the rocket motor ignites, which produces intense UV emissions as a result of combustion. UV photodetectors, strategically positioned in surveillance networks or onboard defense platforms, swiftly detect these UV signatures, providing early warning of incoming missile threats.

They also play a crucial role in tracking the trajectory of missiles during flight by continuously monitoring their UV signatures. As missiles ascend into the atmosphere, their rocket plumes emit UV radiation that can be detected and tracked by these photodetectors. By analyzing the temporal and spatial evolution of UV emissions, photodetectors provide valuable data for predicting missile trajectories and assessing their threat potential.

1.3 Objectives

- Development of ZnO / Ga_2O_3 heterojunction
- To improve the sensitivity of currently existing UV photodetectors

Chapter 2

Experimental details

2.1 Device Fabrication

The hetrojunction between ZnO and Ga_2O_3 was formed using ZnO nanorods and Ga_2O_3 nanorods. Firstly a thin film of Zno was grown on clean glass substrates using sol gel spin coating method. Then using this ZnO seed layer, ZnO nanarod arrays were grown through hydrothermal growth method. Now to form a hetrojunction, the β -Ga_2O_3 nanorod arrays were grown on top of these ZnO nanorods using hydrothermal method. There are many reasons for using Ga_2O_3 and ZnO as UV photodetector. Ga_2O_3 has a direct bandgap of 4.9 eV which corresponds to an absorption wavelength of 254 nm. It has good transparency, radiation resistance, thermal and chemical stability. While ZnO has high exiton binding energy. The reason for using a hetrojunction is that hetrojunctioms can act as much better photodetectors as compared to other photodetectors due to the built in electric field in hetrojunctions.

2.2 Sol-Gel Method

The sol-gel process is a wet-chemical process for the fabrication of solid materials that generally have thin-film, fiber, or powder form. It refers to the transition of solution (sol) into a gellike state (gel) and finally into solid material after performing a series of controlled chemical reactions.

Below is a basic explanation of the sol-gel process :

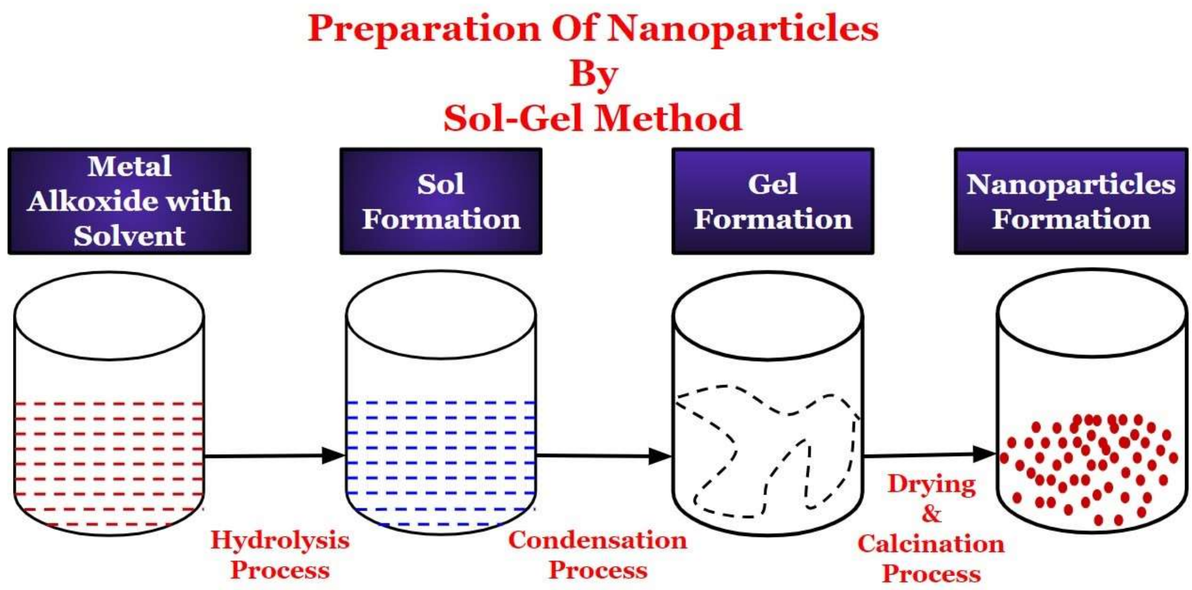

Figure 2.1: Schematic diagram of Sol-gel method

1. Sol Formation: The process begins with the preparation of a solution that contains one or more precursor compounds. Typically, these are metal alkoxides or metal salts which are dissolved in an appropriate solvent. Such a precursor molecule would contain those elements which are to compose the wanted solid material. Ordinarily, the solution is transparent and may appear colloidal due to the tiny particles that are suspended in it. These small particles are referred to as "sols".

2. Gelation: The next step is gelationâthe transformation of sol into three-dimensional network either of particles or polymers linked together. It is done by a number of chemical reactions, primarily hydrolysis and condensation, in which the particles of a sol are brought together to form a gel. Gelation can also be induced by varying the pH, temperature, or adding a catalyst to the sol.

3. Maturization After gelation, gel matures in which it goes further with chemical reactions and reformation of the structure. Aging process is one of the necessary steps for controlling the material properties of porosity, density, and mechanical strength at the end of the process. It can be performed at room temperatures or with controlled temperature and humidity conditions.

4. Drying: Upon proper aging of the gel, it is now ripe and dried so as to eliminate any sol-

vent or remaining water. This is done slowly to eliminate any cracking or structural damage to the material. The techniques for drying are many, from air drying, freeze drying, to supercritical drying, depending on the properties that the final material will take up.

5. Sintering (optional): Often, the dried gel is further sintered to achieve further densification and crystallization by high-temperature heating. Sintering usually enhances the mechanical, thermal, and electrical properties of the material.

6. Final Product: The final product of the sol-gel process would be a solid material that would have its properties specifically catered to the needs based on the choice of precursors, processing conditions, and post-treatment steps. Materials with such tailor-made properties are applied in ceramics, glass, coatings, catalysts, sensors, and biomedical devices with a unique combination of high surface area and porosity, not to speak of chemical reactivity. In general, sol-gel process offers a versatile and low-cost manner for obtaining materials in a broad range of composition, structure, and properties in a well-defined manner.

2.3 Hydrothermal Growth

Hydrothermal growth is a high-temperature and high-pressure synthesis process for the required material in the aqueous solution needed. It is normally used for crystals, ceramics, and materials with tuned properties by their growth. The general methodology of hydrothermal growth runs in the following way:

1. Preparation of Precursor Solution: A precursor solution containing desired chemical components is produced, which generally consists of water with dissolved salts, oxides, or other compounds that will react to produce the desired material.

2. Seal of the Reaction Vessel: The precursor solution is transferred to a sealed reaction vessel, usually made of a material able to withstand high pressure and temperature. The vessel is then sealed to prevent the escape of water or other volatile components.

3. Heating and Pressurizing: The sealed reactor is placed in an oven or a furnace, and heating is done to the desired temperature. At the same time, the pressure is maintained, ensuring that water is at a liquid state above its usual boiling temperature. By working at high pressure and temperature, this achieves the hydrothermal condition within the reaction vessel.

4. Crystal Growth: The compounds of precursors in the solution react to each other at hydrothermal conditions, for forming crystals or other solid state. This is done at a high pressure and temperature, in which dissolution of reactants, diffusion of ions, and nucleation of crystalline structures take place. Crystal growth can vary from a few hours to days, depending on specific conditions and desired crystal size.

5. Cooling and Decompression: The reactor is cooled and decompressed after achieving the growth period. This step is essential in order to prevent material from cracking or defects that can occur with a drastic change in temperature and pressure.

6. Product Recovery: After the reaction vessel reaches room temperature and atmospheric pressure, the vessel can be opened, and the synthesized material recovered. The recovered material might require washing or further processing for the removal of chemicals or any impurities that are left on it.

Advantages in synthesizing materials include the ability to control crystal size, shape, and composition, with the possibility of making high-quality single crystals. This technique finds wide use in the production of many materials, including but not limited to semiconductor crystals, piezoelectric ceramics, zeolites, and gemstones..

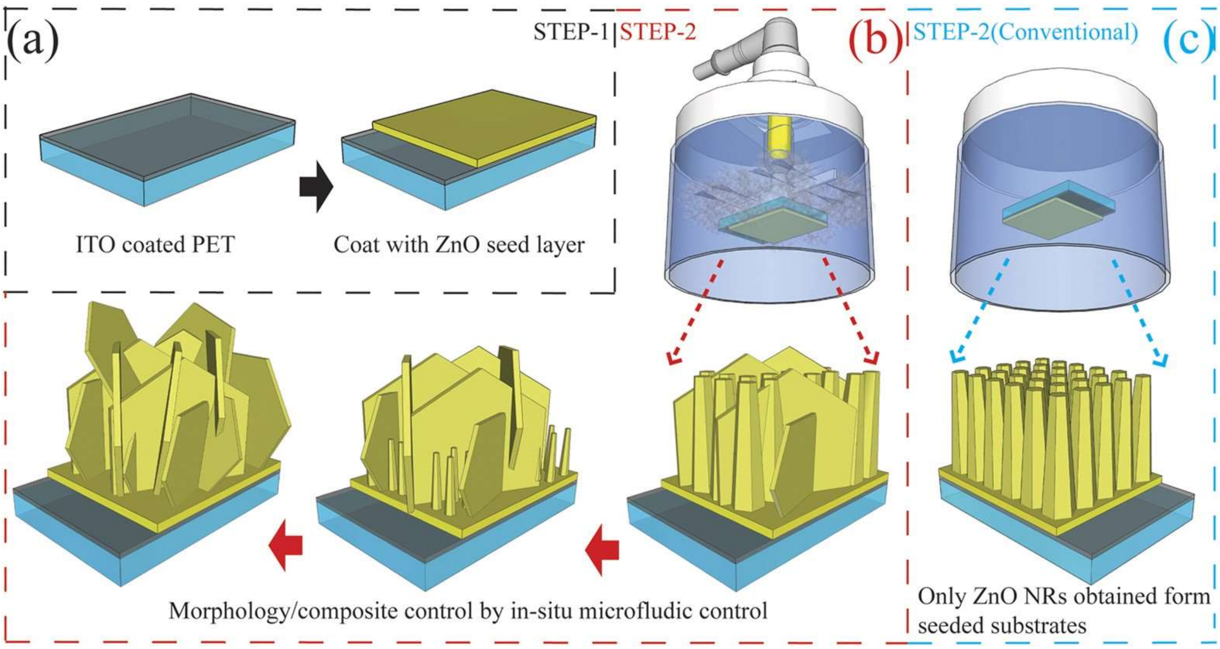

Figure 2.2: Schematic description of Hydrothermal growth

2.4 ZnO Thin Film

The growth of Zn0 nanorod can be done as follows. Firstly, the Zn0 thin films were deposited by sol-gel spin coating method onto clean glass substrates . Zinc acetate dihydrate, 2-methoxethanol and monoethanolamine (MEA) were used as solute, solvent and stabilizer, respectively. Zinc acetate ditydrate was first dissolved in the mixture of 2-methoxyethanol and monoethanolamine, The concentration of both zinc acetate and monoethanolamine was kept as 0.5 M. Then, the resulting mixture was stirred at 60 °C for 2h using a magnetic strirrer. Finally, a clear and transparent solution was formed. The solution was aged for at room temperature for 24 hrs. The glass substrate was cleaned in Piranha solution (H_2S0_4,:H_20_2 3:1) for 2 hrs in ultrasonic cleaner, then the substrate was washed with DI water, acetone, DI water, methanol and again with DI water each for 20 min by using ultrasonic cleaner and dried in an oven for 10 mins. The cleaned glass was kept at 120°C for 5min before applying the coating solution. The coating solution was rotated at 3000rpm for 30s by using a spin coater. After this the film was dried at 300C for 10 min on a hot plate to evaporate the solvent. This procedure was repeated five times for each substrate. The grown film was kept in a furnace for annealing in air at 550 °C for 1 hr. This resulted in a Zno seed layer having 100nm thickness approximately.

2.5 Growth of ZnO Nanorods

Growth of Zn0 nanorods was achieved using hydrothermal growth method. Zno seed layer is suspended upside-down in a glass beaker filled with the aqueous solution of zinc nitrate hexahydrate ($Zn(N0_3)_2.6H_20$) and hexamethylenetetramine (HMT) ($C_6H_{12}Na$) both having a concentration of 50 mM. During the growth, the glass beaker was heated at 90 °C for 10 hrs in a laboratory oven. At the end of the growth period, the substrates were removed from the solution, and then washed immediately with de-ionized water to remove any residual salt from the surface. These substrates were then dried in air.

Figure 2.3: ZnO nanorods grown on glass substrate

2.6 Growth of β-Ga_2O_3 nanorod arrays

The ZnO nanorod arrays were placed in $Ga(NO_3)_3.9H_2O$ and heated at 150 °C for 10 hrs to get GaOOH nanorod arrays. These GaOOH nanorod arrays were converted into the β -Ga2O3 through annealing at 700 °C for 30 min. After the growth, the sample was washed with DI water.

Figure 2.4: Ga_2O_3 / ZnO heterostructure grown on glass substrate

Chapter 3

Results & discussion

3.1 Introduction

Ga_2O_3 / ZnO heterostructure has been prepared, and its properties are tested using various characterization techniques. We used Feil Emission Scanning Electron Microscopy (FESEM) to check the formation of heterojunction, then UV Spectroscopy was used to determine the absorption band of the above formed heterojunction and finally we found the I-V curve of the heterojunction to understand its electrical properties.

3.2 FESEM

Fig 3.1 and 3.2 show the FESEM images of ZnO nanorods and Ga_2O_3 / ZnO heterostructure respectively. We can see that ZnO nanorods have been formed and later on there is also a formation of Ga_2O_3 / ZnO heterostructure between ZnO nanorod arrays and Ga_2O_3 nanorod arrays.

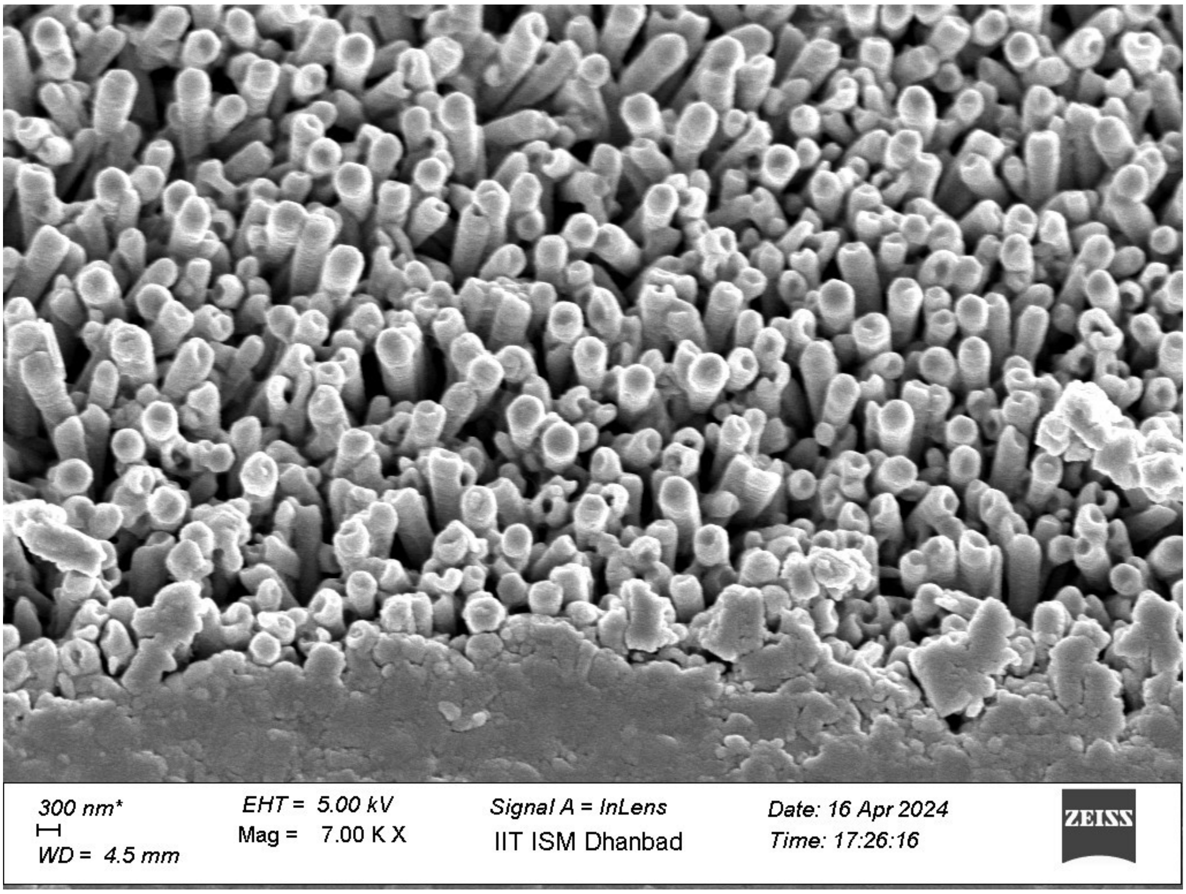

Figure 3.1: FESEM image of ZnO nanorods

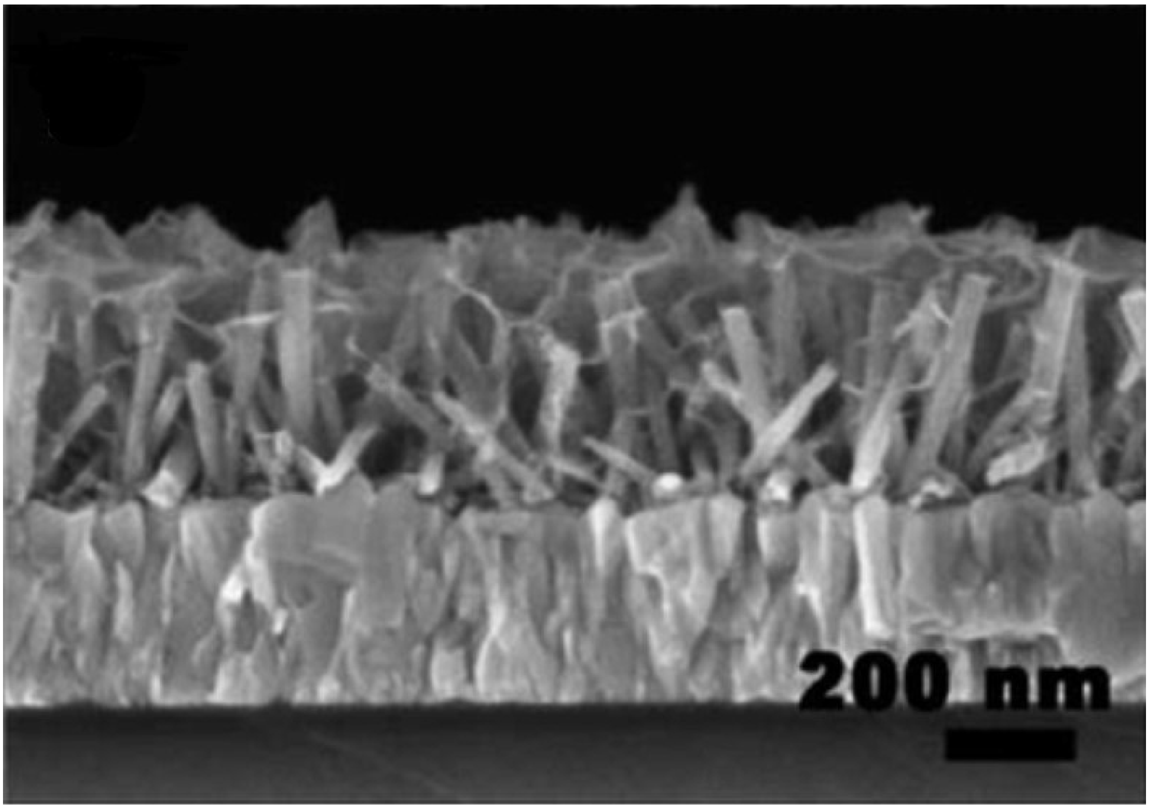

Figure 3.2: FESEM image of Ga_2O_3 / ZnO heterostructure

3.3 UV Spectroscopy

Fig 3.3 and 3.4 show the graphs for UV Spectroscopy of ZnO nanorods and Ga_2O_3 / ZnO heterostructure respectively. We can infer from these graphs that using a Ga_2O_3 / ZnO heterostructure has increased the absorption of UV radiation as compared to the absorption of UV radiation by ZnO nanorods.

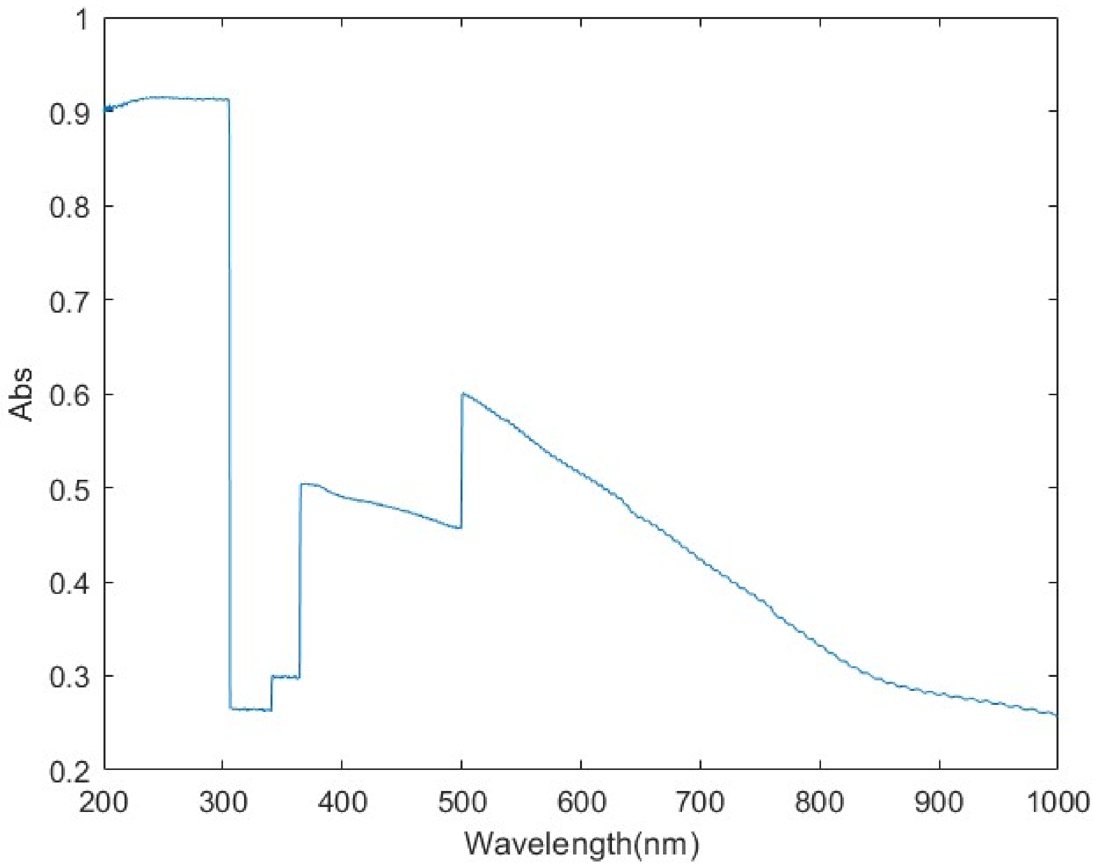

Figure 3.3: UV Spectroscopy of ZnO nanorods

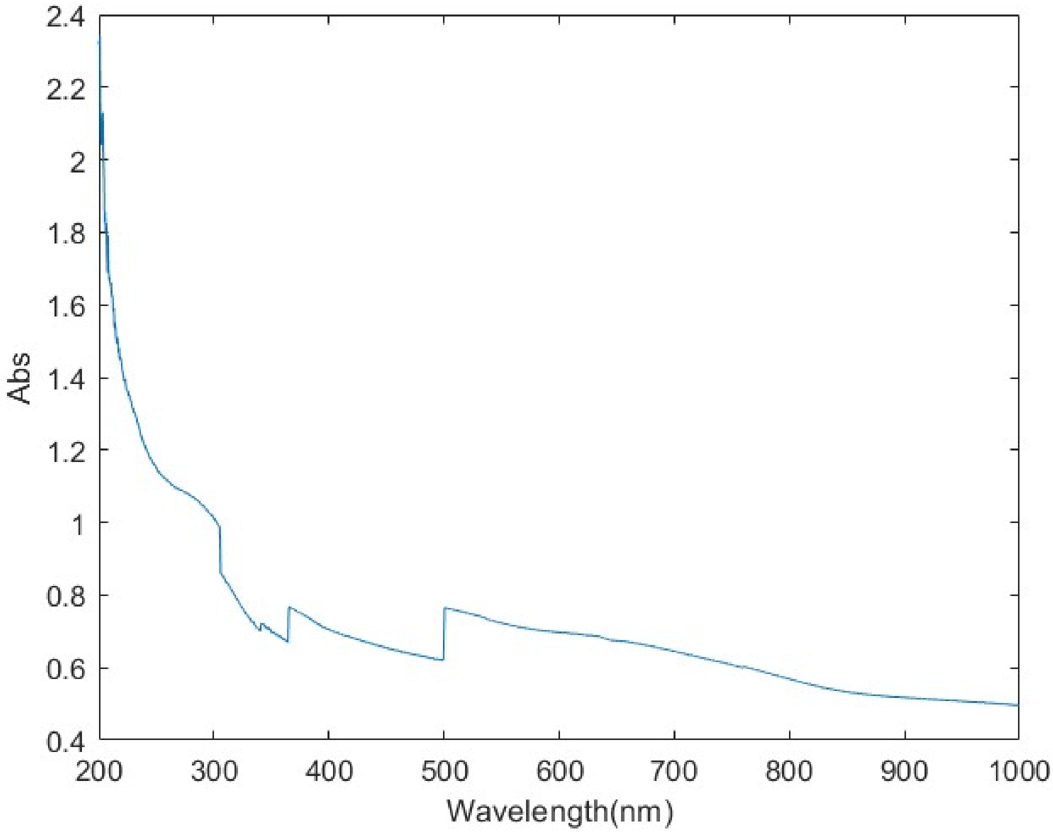

Figure 3.4: UV Spectroscopy of Ga_2O_3 / ZnO heterostructure

3.4 I-V Curves

Fig 3.5 and 3.6 represent the characteristic I-V curves for both ZnO nanorods and Ga_2O_3 / ZnO heterostructure, respectively. These curves show very low current, indicating that both ZnO nanorods and Ga_2O_3 / ZnO heterostructure have a large bandgap, corresponding to UV rays' absorption, making them suitable for use as UV photodetectors.

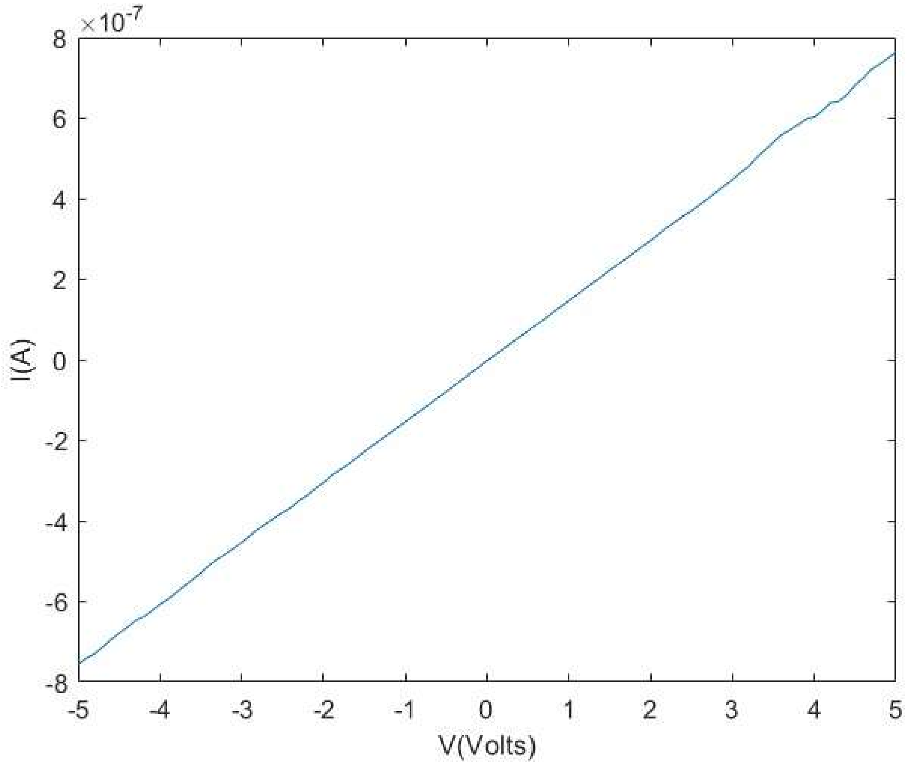

Figure 3.5: I-V Characteristic curve of ZnO nanorods

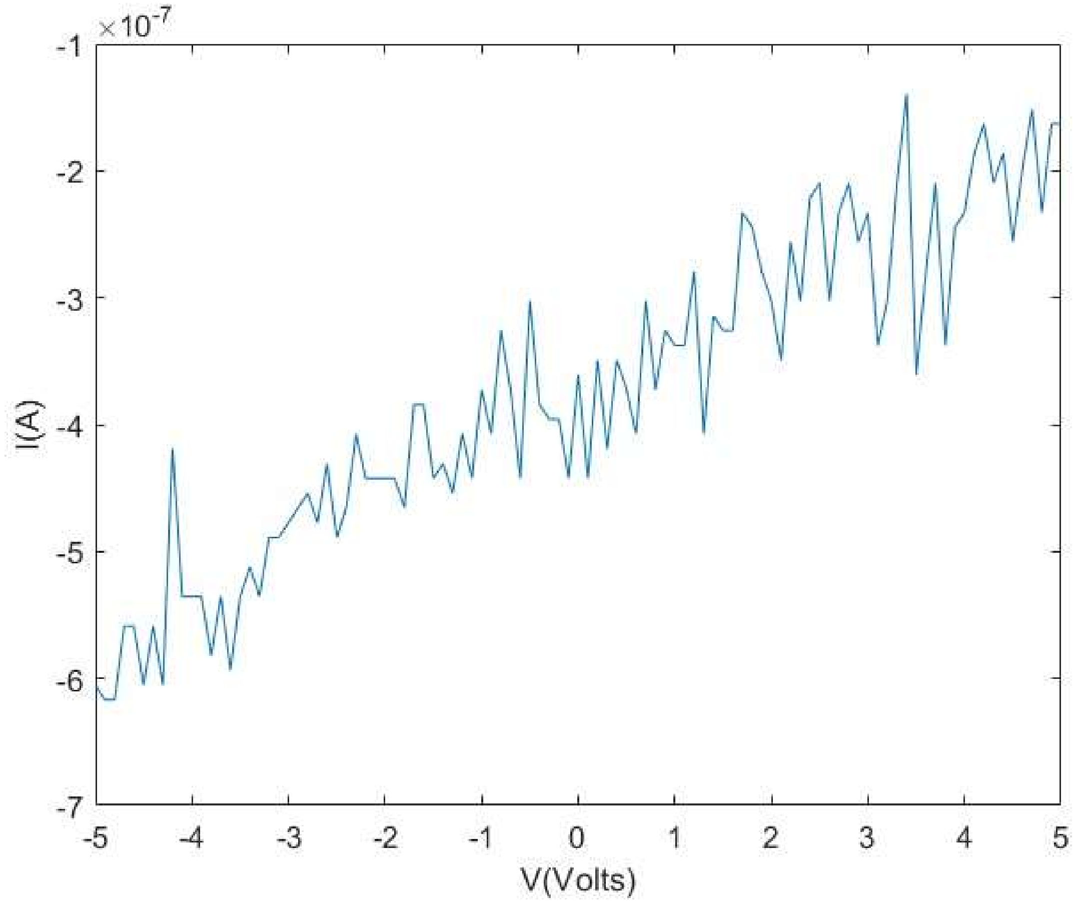

Figure 3.6: I-V Characteristic curve of Ga_2O_3 / ZnO heterostructure

Chapter 4

Conclusions & future scope

4.1 Conclusions

In summary, our comprehensive work involves the properties of a Ga_2O_3/ZnO heterostructure compared to ZnO nanorods to be suitable in UV photodetectors. The structural, optical, and electrical characteristics in our investigations will be able to provide valuable understanding about the performance of the said materials for UV detection.

The behaviors of both these compounds under UV radiation and their characteristic I-V curves are also studied. From the data we obtained we can infer that a heterostructure between Ga_2O_3 / ZnO is more sensitive towards UV radiation and can act as a better UV photodetector as compared to ZnO nanorods. The reason for this higher absorption of UV radiation by Ga_2O_3 / ZnO heterostructure can be attributed to the high exciton binding energy of ZnO and the in-built electric potential in the heterostructure which causing efficient separation of photogenerated election-hole pairs.

In conclusion, the overall study is very much in demand for the development of UV photodetection technology, the requirement of new materials, and device architectures. The heterostructure combining Ga_2O_3/ZnO presents a major leap towards increased performance and functionality beyond the capability of the present ZnO nanorod-based photo-detectors. As a result, future research effort might focus on further optimization in the heterostructure design and the fabrication technique in order to unlock its full potential for a wide range of practicalÂ applications.

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List of Figures

Ga2O3/ZnO

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