Study & Synthesis Of Tin Sulphide Nano-Material Based Photo-Detector Devices

A project Report submitted

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Chhattisgarh Swami Vivekanand Technical University Bhilai (C.G.), India

In fulfilment for award of the degree

Of

BACHELOR OF TECHNOLOGY

In

Electronics & Telecommunication Engineering

By

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We the undersigned solemnly declare that the report of the Research Internship titled “Study & Synthesis Of Tin Sulphide Nanomaterial Based Photodetector Devices”, is based on our own work carried out during our study under the supervision of **Asst. Prof. Ravi Kumar**

We assert that the statements made, and conclusions drawn are an outcome of the project work. We further declare that to the best of our knowledge and belief that the report does not contain any part of any work which has been submitted for the award of any other degree/diploma/certificate in this University/deemed the University of India or any other country. All help received and citations used for the preparation of the Project Work have been duly acknowledged.

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ABSTRACT

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Chapter-01
Introduction

1.1. Introduction to the Synthesis and Analysis of Tin Sulphide Based Photodetector

In the rapidly evolving landscape of optoelectronic technologies, photodetectors play a pivotal role as fundamental components that convert light signals into electrical outputs. The ongoing quest for high-performance, environmentally sustainable, and cost-effective photodetection materials has driven significant research interest in novel semiconductor materials. This thesis focuses on the synthesis and characterization of tin monosulfide (SnS) nanomaterial-based photodetectors, exploring their potential applications particularly in the ultraviolet (UV) spectrum.

1.2. Photodetectors: An Overview

Photodetectors are optoelectronic devices that convert incident light (photons) into an electrical signal (current or voltage), making them essential components in light-sensing and imaging systems. Depending on the working principle, photodetectors can be broadly classified into photoconductors, photodiodes, phototransistors, and photovoltaic detectors. The core function of a photodetector is governed by the photoelectric effect, wherein the absorption of photons excites electrons, generating electron-hole pairs and leading to a measurable electrical response. Materials with high photoresponsivity, fast response times, and sensitivity across specific wavelength ranges are often used to fabricate efficient photodetectors. Recent advancements in nanotechnology have led to the exploration of novel nanomaterials—such as 2D materials, quantum dots, and layered structures—for enhanced performance and tunability.

1.3. Importance of Photodetectors

Photodetectors play a pivotal role in modern technology by serving as the backbone of systems that rely on light detection and processing. Their importance stems from their ability to operate in diverse spectral ranges—UV, visible, and infrared—making them suitable for a wide array of applications. In scientific instrumentation, photodetectors enable high-precision measurements, while in consumer electronics, they enhance device functionality, such as in cameras, biometric systems, and ambient light sensors. The continuous push for miniaturization, high-speed data transfer, and low-power operation in electronic devices has intensified the demand for photodetectors with superior sensitivity, fast response, and broad spectral detection capabilities. Integration with nanomaterials, especially semiconducting ones like SnS (tin sulfide), offers a path toward next-generation photodetectors that are not only more efficient but also environmentally friendly and cost-effective.

1.4. Favourable Optical and Electronic Properties

SnS is a layered, two-dimensional semiconductor with an orthorhombic crystal structure and a direct bandgap in the range of 1.3-1.5 eV, well-suited for light detection in the UV-visible spectrum1. It exhibits a remarkably high absorption coefficient (exceeding 10^5 cm^{-1}), enabling effective light absorption even in ultra-thin layers. This characteristic is particularly valuable for developing compact, efficient photodetection devices.

Recent research has demonstrated that SnS-based photodetectors can achieve impressive performance metrics, including high responsivity (156.0 mA/W), normalized detectivity (2.94×10^{10} jones), and external quantum efficiency (4.77 %) with fast response time. These performance indicators highlight the material's potential for next-generation optoelectronic applications.

1.5. Types of Photodetectors

Photodetectors are broadly categorized based on their operating principles, material composition, and response characteristics. The major types include:

1. **Photoconductors**
   Photoconductors operate on the principle of photoconductivity, where the electrical conductivity of a material increases upon exposure to light. When photons are absorbed, they generate charge carriers that decrease the material's resistance. These devices are simple, inexpensive, and widely used in light meters and optical switches, but they generally suffer from slower response times and high dark currents.

2. **Photodiodes**
   Photodiodes are semiconductor devices that generate a photocurrent when light strikes the p-n junction. They can operate in photovoltaic or photoconductive mode and are known for their fast response, high sensitivity, and low noise. Variants like **PIN photodiodes**, **avalanche photodiodes (APDs)**, and **Schottky photodiodes** offer specialized performance characteristics and are commonly used in optical communication, imaging, and scientific instruments.

3. **Phototransistors**
   A phototransistor is essentially a photodiode with internal gain provided by a bipolar junction transistor. It offers higher sensitivity than a photodiode but with slower response times. These are typically used in applications where low-cost, high-sensitivity detection is needed, such as in infrared sensors and light interruption sensors.

4. **Photovoltaic-Cells**
   Also known as solar cells, photovoltaic devices convert light into electrical power directly using the photovoltaic effect. Though not typically designed for high-speed applications, they are essential in power generation, particularly in solar energy systems.

5. **QuantumDot-Photodetectors**
   Quantum dot (QD) photodetectors utilize nanoscale semiconductor particles that exhibit size-dependent optical properties. They offer tunable spectral response, high quantum efficiency, and compatibility with flexible and transparent substrates, making them suitable for next-generation optoelectronic devices.

6. **Thermal-Detectors**
   These include bolometers and pyroelectric detectors that measure the temperature change caused by absorbed light. Though slower than other photodetectors, they are useful for detecting infrared radiation and in thermal imaging applications.

7. **Nanomaterial-Based-Photodetectors**
   With advancements in nanotechnology, photodetectors based on 2D materials, nanowires, and

layered semiconductors like SnS, MoS_2, and graphene are gaining attention. These devices exhibit exceptional sensitivity, flexibility, and spectral tunability, making them ideal for wearable electronics, smart sensors, and high-performance optical devices.

1.6. Tin Sulfide (SnS) as a Photodetector Material

Tin Sulfide (SnS) is a promising semiconductor material that has attracted significant attention for photodetector applications due to its unique optoelectronic properties, earth abundance, and environmental friendliness. It is a layered IV-VI group compound semiconductor with an orthorhombic crystal structure, similar to black phosphorus, which allows for anisotropic charge transport and strong light–matter interaction. SnS has a direct bandgap of approximately 1.3–1.5 eV, making it suitable for visible and near-infrared photodetection. Its high absorption coefficient (greater than 10^4 cm^{-1}) enables efficient light harvesting even in thin films, which is advantageous for low-power and compact device designs.

In addition to its optical characteristics, SnS is chemically stable, non-toxic, and can be synthesized through cost-effective methods such as chemical vapor deposition (CVD), hydrothermal synthesis, and thermal evaporation. These attributes make SnS a compelling alternative to toxic and expensive materials like lead-based or cadmium-based semiconductors. Furthermore, SnS exhibits good compatibility with flexible and transparent substrates, allowing its integration into wearable and bendable photodetectors, which are in high demand in the modern era of flexible electronics.

SnS-based photodetectors have demonstrated excellent responsivity, fast response times, and stable performance under ambient conditions. The anisotropic properties of its layered structure contribute to polarization-sensitive detection, enabling its use in applications requiring direction-sensitive light sensing. Moreover, by tuning the thickness and morphology of SnS nanostructures—such as nanoplates, nanoribbons, or quantum dots—the optical and electrical properties can be tailored to meet specific device requirements.

Recent studies have also explored hybrid SnS structures by combining it with other nanomaterials like graphene, MoS_2, or metal nanoparticles to enhance carrier mobility, reduce recombination losses, and improve photodetection performance. As research progresses, SnS continues to emerge as a viable material for developing eco-friendly, low-cost, and high-efficiency photodetectors suitable for next-generation optoelectronic devices.

1.7. Unique Properties of SnS for Photodetection

Tin Sulfide (SnS) possesses a range of unique physical and chemical properties that make it particularly suitable for photodetector applications. As a p-type semiconductor with a direct bandgap ranging from 1.3 to 1.5 eV, SnS can effectively absorb light in the visible and near-infrared spectrum, enabling efficient photon-to-electron conversion. Its high absorption coefficient (exceeding 10^4 cm^{-1}) allows for strong light-matter interaction, which is crucial for achieving high photoresponsivity even in thin-film devices. The orthorhombic layered structure of SnS introduces anisotropic charge transport, which can be exploited for direction-sensitive and polarization-dependent photodetection.

Another notable feature of SnS is its ambient stability and robustness, making it suitable for practical and long-term applications. It exhibits good thermal stability and resists degradation in air, unlike many 2D materials that oxidize quickly. Additionally, its mechanical flexibility makes it compatible with bendable and wearable electronics, allowing for novel applications in flexible optoelectronic devices. SnS can also form heterojunctions with other materials to improve charge separation and transport, further enhancing its performance in photodetectors.

1.7. Advantages of SnS over Other Materials

Compared to conventional photodetector materials like silicon, CdS, PbS, and other III-V semiconductors, SnS offers several key advantages. Firstly, SnS is composed of earth-abundant and non-toxic elements, making it an environmentally benign alternative to toxic compounds like cadmium- or lead-based materials. This sustainability aspect is critical in the growing push toward green electronics and eco-friendly device manufacturing.

Secondly, the cost of fabrication is significantly lower for SnS due to its compatibility with low-temperature, solution-based, or vapor-phase deposition techniques, which are scalable and do not require high-vacuum or high-purity environments. SnS also allows for integration with a wide range of substrates, including glass, paper, and flexible polymers, without compromising performance.

In addition, SnS demonstrates good photodetection capabilities across a broad spectrum, including visible and NIR ranges, with decent carrier mobility and low dark current. When engineered at the nanoscale, its performance metrics—such as responsivity, detectivity, and response time—can rival or even surpass some conventional photodetector materials. This positions SnS as a highly promising material for next-generation, high-performance, and cost-effective optoelectronic devices.

1.8. Nanostructured Materials for Enhanced Photodetection

Nanostructuring of materials has revolutionized the field of photodetection by offering control over electronic and optical properties at the atomic scale. By reducing material dimensions to the nanoscale—such as forming nanowires, nanosheets, quantum dots, or thin films—properties like bandgap, carrier mobility, and surface area can be finely tuned. This leads to enhanced light absorption, faster carrier dynamics, and improved signal-to-noise ratios in photodetectors.

Nanostructured materials such as graphene, transition metal dichalcogenides (TMDs), metal oxides, and perovskites have demonstrated remarkable potential in broadband and high-sensitivity photodetectors. Specifically, for SnS, creating nanostructures like nanoplates or nanobelts allows for increased surface-to-volume ratio and efficient photogenerated carrier separation. Moreover, hybrid nanostructures—such as SnS/graphene or SnS/MoS_2—can be designed to overcome limitations like slow response or low carrier mobility by combining the strengths of each component.

Nanostructuring also supports the fabrication of flexible, transparent, and wearable photodetectors, which are crucial for emerging applications in soft robotics, health monitoring, and foldable electronics. By engineering nanoscale interfaces and heterojunctions, researchers can develop devices with tunable spectral response, fast switching times, and low power consumption. Thus, the use of nanostructured materials is key to achieving enhanced and application-specific performance in modern photodetectors.

1.9. Quantum Confinement Effects

In SnS nanomaterials, quantum confinement arises when their dimensions approach the exciton Bohr radius, leading to discretized energy levels and a size-dependent bandgap. This effect enables tunable optical absorption, critical for UV photodetection, as shrinking SnS nanostructures widen the bandgap, aligning it with UV wavelengths. Enhanced exciton binding energy and charge-carrier separation efficiency further improve photoresponse speed and sensitivity. These properties position SnS as a promising, eco-friendly candidate for next-generation optoelectronic devices.

1.10. Increased Surface Area and Light Absorption

One of the key benefits of using nanostructured materials in photodetectors is the significant increase in surface area, which directly influences the light absorption and carrier generation efficiency. At the nanoscale, materials exhibit a higher surface-to-volume ratio, enabling more active sites for photon interaction. This characteristic is particularly important for photodetection, as it enhances the probability of photon absorption and exciton generation.

In the case of SnS nanostructures, morphologies such as nanosheets, nanowires, and quantum dots can be engineered to optimize light-matter interactions. These structures not only trap light more efficiently due to multiple scattering effects but also support efficient charge separation and transport pathways. For instance, vertically aligned nanowires can provide direct channels for charge carriers to reach the electrodes, minimizing recombination losses and improving response time.

Furthermore, surface engineering through doping or functionalization can enhance sensitivity and selectivity for specific wavelengths or environmental conditions. The combination of increased light absorption with tailored surface properties makes nanostructured SnS materials exceptionally suited for high-performance, broadband photodetectors in compact and flexible formats.

1.11. Motivation and Objectives of the Study

The motivation behind this study stems from the growing demand for low-cost, high-performance, and environmentally sustainable photodetectors that can operate efficiently across a broad spectral range. Traditional materials like silicon, CdS, and PbS have served well in various applications but pose challenges such as toxicity, limited spectral response, and fabrication complexity. In contrast, tin sulfide (SnS) emerges as an eco-friendly, earth-abundant, and cost-effective alternative, offering suitable optoelectronic properties and stability for photodetector applications.

Despite its promising characteristics, the practical implementation of SnS-based photodetectors remains in its early stages. Challenges such as optimizing morphology, improving carrier mobility, and integrating with flexible substrates need to be addressed. Recent advances in nanostructuring techniques and hybrid material synthesis provide an opportunity to significantly enhance the performance of SnS photodetectors.

The objectives of this study are as follows:

1. To investigate the optical and electrical properties of SnS nanomaterials relevant to photodetection.

2. To synthesize SnS nanostructures using a suitable method and characterize their morphology and crystallinity.

3. To fabricate and evaluate SnS-based photodetector devices, focusing on performance parameters such as responsivity, sensitivity, and response time.

4. To compare the performance of SnS photodetectors with other conventional and nanomaterial-based photodetectors.

5. To explore the potential integration of SnS with other materials for hybrid photodetector designs aimed at enhanced functionality.

Through this study, the goal is to establish SnS as a viable material for next-generation photodetectors and contribute to the development of efficient, sustainable optoelectronic technologies.

Chapter-2
Literature Review

2.1. Fundamentals of Photodetection

Photodetection is the process by which optical signals-such as light-are converted into electrical signals for further processing or measurement. This conversion is essential in a wide range of optoelectronic applications, from communications to sensing and imaging.

Photodetectors operate primarily through two mechanisms: the *photon detection* (quantum) process and the *thermal detection* process. Photon detectors, which include most semiconductor-based devices, rely on the photoelectric effect-where absorbed photons generate electron-hole pairs, resulting in a measurable photocurrent or photovoltage. These devices are highly sensitive, capable of detecting even single photons, and can respond rapidly to changes in light intensity, making them ideal for high-speed and high-sensitivity applications.

In contrast, thermal detectors convert absorbed light into heat, producing a signal proportional to the total energy absorbed. While they offer broad spectral response, their speed and sensitivity are generally lower than photon detectors.

Key performance parameters for photodetectors include:

- **Quantum efficiency**: The ratio of generated charge carriers to incident photons.
- **Responsivity**: The output electrical signal per unit of incident optical power.
- **Spectral response**: The range of wavelengths the detector can sense, governed by the material's bandgap.

2.2. Photoconductivity and Photovoltaic Effects

Photoconductivity refers to the increase in electrical conductivity of a material when it is exposed to light. In tin monosulfide (SnS) nanomaterials, incident photons excite electrons from the valence band to the conduction band, generating electron-hole pairs. This process enhances the material's conductivity, making SnS an effective photoconductor for detecting light, particularly in the UV and visible spectra. The high absorption coefficient and suitable bandgap of SnS contribute to its strong photoconductive response and rapid carrier separation, resulting in fast and sensitive photodetector performance.

Photovoltaic effects involve the direct conversion of light into electrical voltage and current within a semiconductor junction. When SnS is used in photodetector or solar cell architectures, absorbed photons create charge carriers that are separated by built-in electric fields at interfaces or junctions, generating a measurable photocurrent even without external bias. The earth-abundant, non-toxic, and stable nature of SnS, along with its favorable electronic properties, makes it a promising candidate for next-generation, environmentally friendly optoelectronic and photovoltaic devices.

Together, these effects enable SnS-based devices to efficiently convert light into electrical signals, supporting their potential in sustainable, high-performance photodetection and solar energy applications.

2.3 Literature Review: On photodetection properties of SnS

S. No	Reference	Methodology	Key Findings	Rationale for Using SnS	Limitations
1.	Solution Synthesis of Ultrathin Single Crystalline SnS Nanoribbon s, Deng et al, 2012, ACS	Solution phase synthesis	Developed ultrathin SnS nanoribbons with high crystallinity; demonstrated their application in photodetector s with significant photocurrent response.	SnS nanoribbons exhibit strong light absorption and high carrier mobility, making them suitable for efficient photodetector s.	The solution phase synthesis can be complex and challenging to scale up for industrial applications.
2.	Synthesis and Characteriza tion of π SnS Nanoparticl es and Correspondin g Thin Films, Mahdi et al 2017, Materials letter, Elsevier	Chemical synthesis with varying Sn precursor concentration s	Synthesized π SnS nanoparticles with tunable properties; observed that increasing Sn precursor concentration affects morphology and optical properties.	Tunable optical properties of SnS nanoparticles are advantageous for customizing photodetector performance across different wavelengths.	The method requires precise control over precursor concentration, which may limit reproducibilit y.
3.	High-performance photodetector s based on two-dimensional tin(ii) sulfide (SnS) nanoflakes	Thermal co - evaporation	Fabricated SnS thin films with varying thicknesses; found that increased thickness enhances electrical conductivity and	SnS thin films possess a direct band gap suitable for visible light detection, and their properties can be optimized by adjusting	Thermal co evaporation involves high vacuum systems, which increases fabrication costs.

			photoresponsivit y.	film thickness.	
4.	Synthesis of SnS Nanoparticles for Next Generation Photovoltaic and Photodetector Applications Sunitha et al, 2021, IJSEAS, Elsevier	Chemical route using stannous chloride and thioacetamide	Synthesized SnS nanoparticles; highlighted their potential in photochemical cells and photodetectors due to favorable optical properties.	SnS is an earth-abundant, non-toxic material with a suitable band gap, making it an environmental friendly alternative for photodetector applications.	Chemical synthesis may introduce impurities, affecting the material's optical and electronic properties.

2.4. Literature review: Synthesis of photodetector material Tin Sulfide (SnS)

S. No	Reference	Synthesis Method	Description of Synthesis Method	Key Findings	Limitations

1.	Mathews et al., Materials Letters (2017)	Chemical synthesis	Varying Sn precursor concentration s to control SnS nanoparticle morphology and optical properties.	Tuned SnS nanoparticle properties by adjusting precursor ratios; demonstrate d significant optical tunability.	Reproducib ility may be challenging due to sensitivity to precursor ratios.
2	Han et al., Journal of Materials Science: Materials in Electronic s (2020)	Chemical vapor deposition (CVD)	Deposited SnS nanoflakes on a substrate and integrated graphene for hybrid devices.	Developed a hybrid photodetecto r with high responsivity and broad spectral response.	Requires precise control over deposition parameters; complex integration.
3.	Wang et al., ACS Nano (2012)	Solution phase synthesis	Synthesized ultrathin single crystalline SnS nanoribbons with high crystallinity.	Achieved uniform nanoribbons with excellent optical and electronic properties for photodetecto rs.	Synthesis involves complex chemical processes and post processing steps.
4.	Li et al., Journal of Materials 16 Chemistry C (2018)	Thermal co evaporation	Deposited SnS thin films by co evaporating Sn and S sources under controlled conditions.	Demonstrate d tunable film thickness for enhanced conductivity and photoresponsi vity.	High vacuum requirement s increase cost and complexity.
5.	Ahmed et al., Materials Science in Semiconductr Processing (2019)	Chemical bath deposition	Deposited SnS thin films from a solution containing Sn	Fabricated cost effective SnS thin films with good crystallinity and significant	Films may have non uniform thickness, affecting performance.

			and S precursors.	photo response.	
6.	Ghosh et al., Applied Physics A (2020)	Chemical synthesis with plasmonic integration	Synthesized SnS nanostructures and integrated plasmonic nanoparticles to enhance photodetection.	Enhanced photodetection with increased light absorption and responsivity due to plasmonic effects.	Incorporating plasmonic nanoparticles adds complexity and affects stability.

2.5. Comparative Analysis of Metal Contacts in SnS Photodetectors

Metal Contact	Work Function (eV)	Contact Type with p-SnS	Performance Impact	Remarks	Reference
Silver (Ag)	~4.26	Quasi-ohmic	Responsivity ~0.36 A/W; Detectivity ~3.6×10^{10} Jones	Common in SnS PDs; Moderate WF enables efficient carrier injection	Mahdi *et al.* (2017); Sabat *et al.* (2024) [93]
Gold (Au)	~5.1	Ohmic	High responsivity and stable interface	Inert, low oxidation; widely used but expensive	Hajzus *et al.* (2018) [11]
Nickel (Ni)	~5.0	Ohmic	Efficient hole injection; low barrier height	Suitable for stable, high-performance PDs	Hajzus *et al.* (2018) [11]
Palladium (Pd)	~5.6	Ohmic	Strong band alignment; enhances photoconductivity	High cost; less common in SnS systems	Hajzus *et al.* (2018) [11]
Aluminum (Al)	~4.06	Schottky	Poor responsivity; rectifying behavior	Prone to oxidation; lower performance	RSC Advances (2024) [96]
Titanium (Ti)	~4.33	Schottky	Limited carrier injection	May require interface treatment	Hajzus *et al.* (2018) [11]

Based on the comparative analysis, metal contacts significantly influence the performance of SnS-based photodetectors by affecting carrier injection efficiency and interfacial stability. Among the various metals, **silver (Ag)** offers a practical balance between performance and cost. Its **moderate work function (~4.26 eV)** forms a **quasi-ohmic contact** with p-type SnS, enabling efficient carrier transport while minimizing fabrication complexity. While gold and palladium provide superior ohmic behavior, their high cost and limited availability make them less attractive for scalable, low-cost devices. Therefore, **silver was selected** in this study due to its compatibility with SnS, adequate electrical performance, and widespread use in literature (e.g., Mahdi *et al.*, 2017), making it a viable choice for fabricating efficient and economically feasible photodetectors.

Chapter-3

Synthesis of Tin Sulfide (SnS) Nanomaterials

3.1. Chemical Preparation

To prepare the solution for synthesis, 0.1 M of Stannous Chloride ($SnCl_2$) and 0.15 M of Thioacetamide (C_2H_5NS) were used as the sources of Sn^{2+} and S^{2-} ions, respectively. Additionally, 0.2 M of non-toxic Trisodium Citrate ($Na_3C_6H_5O_7$) was employed as a complexing agent to stabilize the solution.

The chemicals were dissolved separately as follows:

- Stannous Chloride ($SnCl_2$) was dissolved in 5 mL of Ethanol.
- Thioacetamide (C_2H_5NS) was dissolved in 5 mL of Ethanol.
- Trisodium Citrate ($Na_3C_6H_5O_7$) was dissolved in 5 mL of Deionized Water.

To adjust the pH of the reaction solution, aqueous ammonium hydroxide was added dropwise. The pH was carefully maintained between 5.8 and 6.0 to slow down the rate of precipitation and ensure controlled synthesis conditions.

For pH adjustment, the solution underwent ultrasonication for 30 minutes to promote homogeneity and reduce particle agglomeration. Subsequently, the solution was stirred for 20 minutes using a magnetic stirrer to ensure complete mixing and interaction of the reactants

Fig.3 Weighting Stannous Chloride powder

Fig.2 Ultrasonication of solution [Stannous Chloride ($SnCl_2$) + Thioacetamide (C_2H_5NS) + Trisodium Citrate ($Na_3C_6H_5O_7$)]

3.2. Chemical Reaction Mechanism

In the present synthesis route, thioacetamide ($C_2 H_5NS$) serves as a slow-releasing sulfide ion source in an aqueous medium. Upon hydrolysis, thioacetamide yields hydrogen sulfide, which subsequently dissociates to generate sulfide ions (S^{2-}) under mildly acidic to near-neutral conditions:

$$C_2H_5NS + H_2O \rightarrow CH_3CONH_2 + H_2S$$

$$H_2S \rightleftharpoons HS^- + H^+ \rightleftharpoons S^{2+} + 2H^+$$

The resulting sulfide ions react with tin (II) ions (Sn^{2+}), which are derived from stannous chloride ($SnCl_2$), leading to the formation of tin (II) sulfide (SnS) as a solid precipitate:

$$Sn^{2+} + S^{2-} \rightarrow SnS \downarrow$$

Here, the downward arrow (↓) indicates the precipitation of SnS. To regulate the reaction kinetics and avoid uncontrolled precipitation, **Trisodium citrate ($Na_3C_6H_5O_7$)** is employed as a complexing agent. It forms stable complexes with Sn^{2+} ions, thereby modulating their availability in solution and promoting uniform nucleation and controlled growth of SnS particles. The solution pH is carefully adjusted to the range of 5.8–6.0 using aqueous ammonium hydroxide, further contributing to the stability of the reaction medium.

Fig 3. SnS Solution after ultrasonication

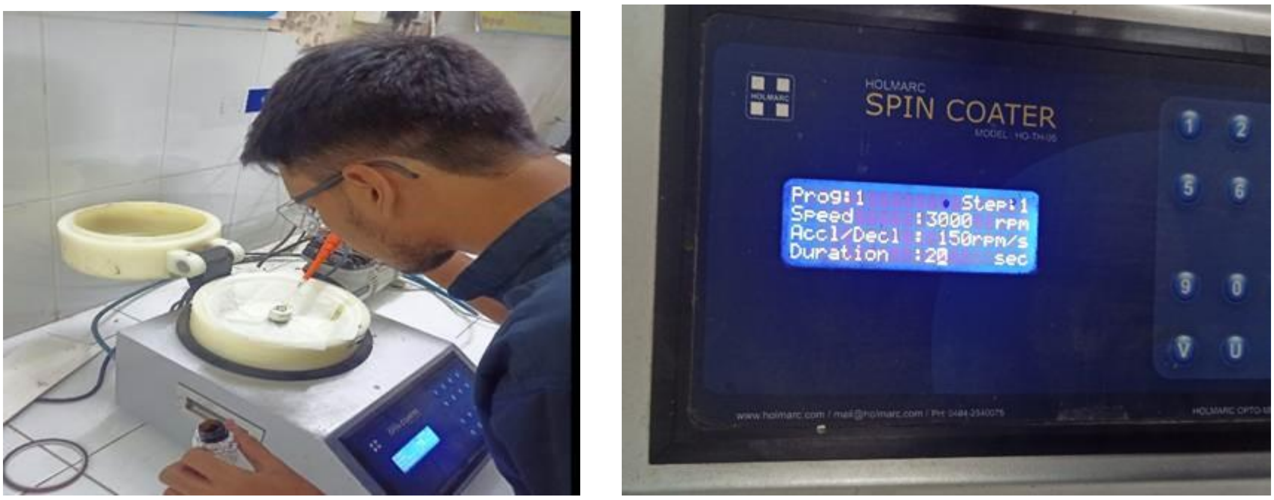
Fig 4. SnS solution diluted with Ethanol for UV-Visible Spectroscopy

3.3. Spin Coating Deposition

To overcome the challenges associated with uneven film formation during the chemical bath deposition (CBD) process, an alternative deposition technique was adopted for the fabrication of SnS thin films. The substrate was initially subjected to a standardized cleaning procedure to eliminate surface contaminants and enhance adhesion.

A spin-coating method was employed for the deposition, wherein the substrate was rotated at a speed of 600 rpm with an acceleration of 150 rpm/s for a duration of 30 seconds. Post-deposition, the substrate was subjected to a drying step at 90°C for 5 minutes to facilitate solvent evaporation and film stabilization.

This cycle was repeated twelve (12) times under identical environmental and operational conditions to achieve the targeted film thickness. The optimized spin-coating approach successfully yielded a uniform SnS thin film with improved morphological characteristics, thereby resolving the non-uniformity issues encountered in the previous CBD technique and making it suitable for subsequent device-level applications.



(a)

(b)

Fig. (a) Preparation for spin coating, (b) Spin coater control panel

3.4. Apparatus Used

3.4.1. Ultra Sonicator

Ultra Sonicators are devices that generate high-frequency sound waves, typically around 20 kHz, to agitate particles in a liquid. They consist of an ultrasonic generator, a transducer, and a probe. The generator converts electrical energy into ultrasonic signals, which are transformed into mechanical vibrations by the transducer and transmitted through the probe.

Figure: 1 Ultra Sonicator

The principle of sonication is based on **cavitation**, where rapid pressure changes create and collapse microscopic bubbles in the liquid. This bubble collapse generates intense heat and shear forces, effectively disrupting molecular structures and facilitating processes like mixing, homogenization, and extraction. Sonicator are widely used in laboratories and industrial applications for their efficiency in breaking down particles and enhancing chemical reactions.

3.4.2. Magnetic sterilizers

Magnetic sterilizers, often referred to as magnetic stirrers, are devices that utilize a rotating magnetic field to mix liquids effectively. They consist of a stationary electromagnet and a stir bar, which is a small magnet placed inside the liquid. When the device is activated, the electromagnet generates a rotating magnetic field that causes the stir bar to spin, thereby mixing the solution thoroughly

Figure: 2 Magnetic sterilizers

The principle behind magnetic stirring relies on the **interaction between the magnetic field and the stir bar**. As the stir bar rotates, it induces movement in the surrounding liquid, ensuring uniform mixing. This method is particularly useful in laboratory settings for preparing solutions, culturing microorganisms, and conducting chemical reactions, as it allows for precise control over mixing speed and temperature without introducing mechanical parts that could contaminate the sample.

3.4.3. Vacuum Oven

A vacuum oven is a device designed for drying and curing materials in a low-pressure environment. It consists of a sealed chamber connected to a vacuum pump that reduces the internal pressure, allowing moisture to evaporate at lower temperatures. This feature is particularly beneficial for heat-sensitive materials

Figure: 3 Vacuum Oven

The principle of a vacuum oven relies on **reduced boiling points due to the low pressure**, enabling efficient moisture removal without thermal degradation. This controlled environment 20 minimizes oxidation and preserves material integrity, making vacuum ovens essential in laboratories, pharmaceuticals, and various industrial applications.

3.4.4. Spin Coating

Spin coating is a technique used to apply uniform thin films onto substrates by utilizing centrifugal force. The process involves depositing a liquid solution onto the center of a rotating substrate, which is then spun at high speeds, typically ranging from 600 to 12,000 rpm. As the substrate rotates, the centrifugal force spreads the liquid evenly across its surface, while excess material is flung off the edges, resulting in a thin film that can range from a few nanometers to several micrometers in thickness.

Figure: 4 Spin Coating

The principle behind spin coating relies on the **interaction of centrifugal force and surface tension.** The rotation creates a uniform coating by overcoming the viscosity of the liquid, allowing it to flow smoothly over the substrate. Once the desired thickness is achieved, the solvent evaporates, leaving behind a solid film. This method is widely used in various industries, including electronics and optics, due to its efficiency and ability to produce consistent coatings with minimal material waste.

Chapter-4

Characterization of Synthesised SnS Nanomaterials

4.1. UV – Visible Spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is an analytical technique used to measure the absorption of UV and visible light by a sample, providing insights into its chemical composition and concentration. A typical UV-Vis spectrophotometer consists of a light source, a monochromator to select wavelengths, a sample holder (cuvette), and a detector. This method is widely applied in fields such as chemistry, biology, and environmental science.

The UV-Visible spectroscopy analysis of the prepared SnS solution was conducted to evaluate its optical absorption characteristics. The absorbance vs. wavelength plot consistently revealed a strong absorption peak at approximately 265 nm, indicating a significant absorbance in the UV range. This characterization was repeated three times, and in all cases, the peak remained within the same range, demonstrating the reproducibility and stability of the optical properties of the solution. The high absorbance observed in the UV region highlights the potential suitability of the SnS solution for applications that require strong UV absorption.

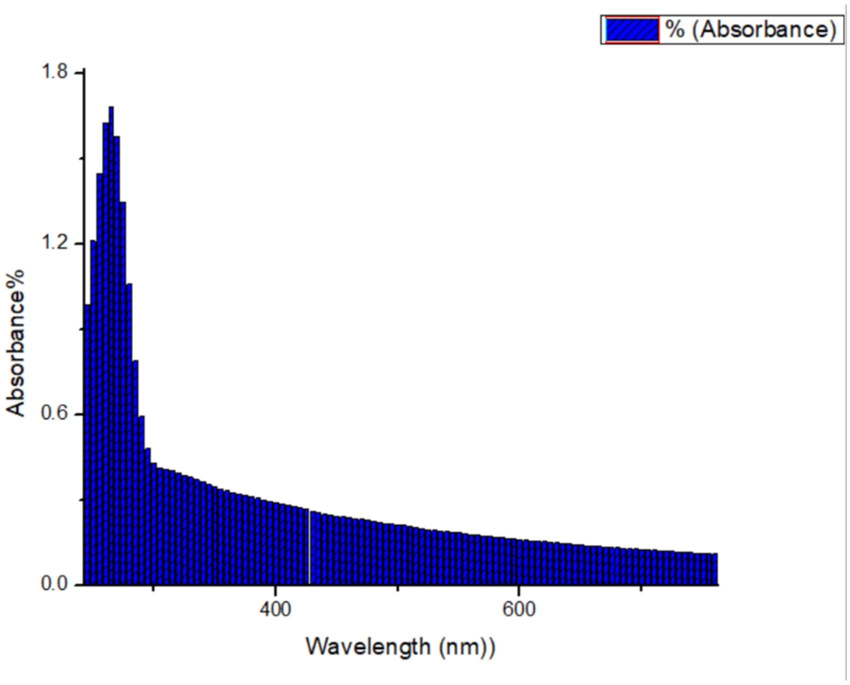


Fig : 4 Result of (UV – Visible)

4.2. X-ray Diffraction (XRD) Analysis

X-ray Diffraction (XRD) is a powerful analytical technique widely used in materials science to study the structural properties of crystalline materials. This non-destructive method provides critical information about a material's chemical composition, crystal structure, and phase identification. XRD is particularly valuable because it can analyze a diverse range of samples, including powders, solids, thin films, and nanomaterials, with minimal sample preparation required. Researchers utilize XRD to answer various analytical questions related to the crystalline constitution of materials, making it an indispensable tool in both industrial applications and academic research.

The XRD patterns were obtained using **Cu-Kα radiation (λ = 1.406 Å) over a 2θ range of 10° to 80°.** The X-ray diffraction (XRD) analysis of the prepared SnS powder revealed three distinct diffraction **peaks at 26.58°, 31.66°, and 45.5°**. These peaks match well with the reported diffraction patterns of SnS, confirming the successful synthesis of the material. The identified peaks demonstrate the crystalline structure of SnS and align with its characteristic diffraction peaks, reinforcing the reliability of the synthesis process.

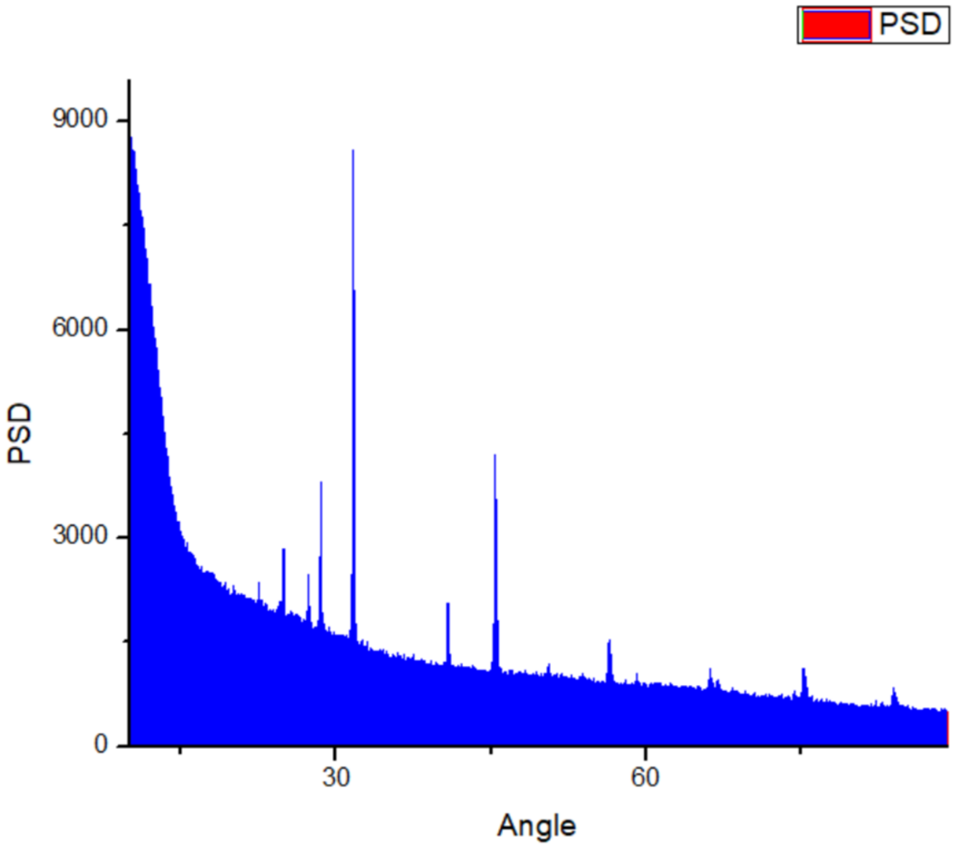


Fig: 5 Result of XRD

4.3. External Quantum Efficiency (EQE)

External Quantum Efficiency (EQE) is a critical metric for evaluating photodetector performance, representing the ratio of photo-generated charge carriers collected to the number of incident photons at a given wavelength. It indicates how effectively a photodetector converts light into electrical current. A higher EQE signifies better light utilization and more efficient charge collection within the device. Factors influencing EQE include material absorption coefficient, surface reflection, charge carrier mobility, and the efficiency of charge collection at the contacts. The EQE is wavelength-dependent, reflecting the material's spectral absorption characteristics and device design.

Based on the provided EQE spectrum, the photodetector exhibits peak efficiency in the ultraviolet (UV) region, reaching approximately 75% at 275 nm. The efficiency decreases significantly in the visible range (400-700 nm), dropping to near zero, before showing a slight increase in the near-infrared (NIR) region (700-950 nm) to around 5%. This spectral response suggests the device is highly sensitive to UV light, with minimal response in the visible spectrum and a minor response in the NIR spectrum

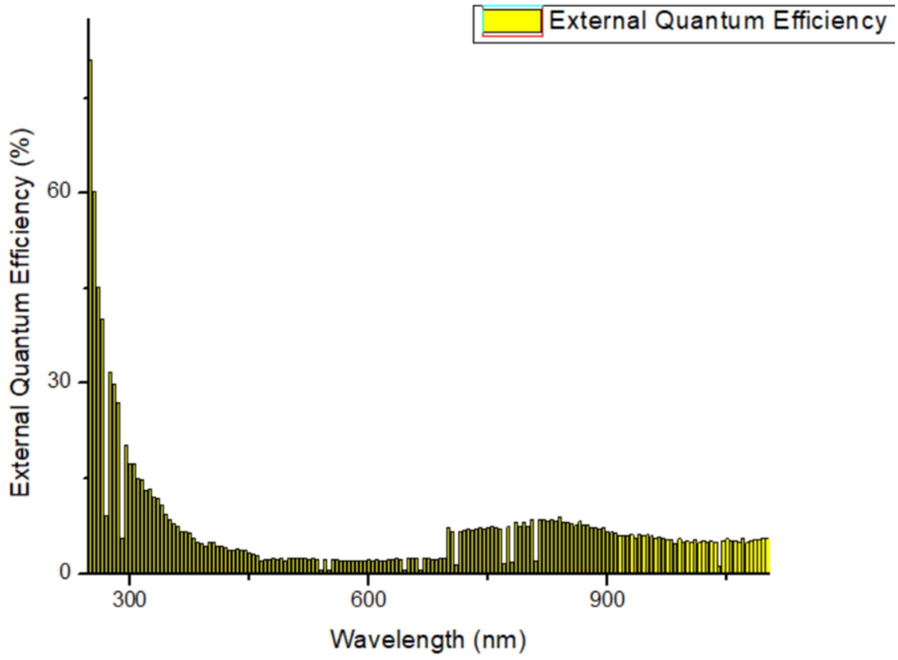


Fig : 6 Result of EQE

4.4. Responsivity

Responsivity is a fundamental parameter that quantifies a photodetector's efficiency in converting optical power to electrical current, typically expressed in amperes per watt (A/W)

Mathematically, responsivity (R) is defined as $R = \eta(q/hf) \approx \eta(\lambda(\mu m)/1.23985)$,

where η represents quantum efficiency, q is the electron charge, h is Planck's constant, and f is the optical signal frequency. For most photodiodes, responsivity values depend significantly on wavelength, with optimal performance occurring when photon energy slightly exceeds the detector's bandgap energy.

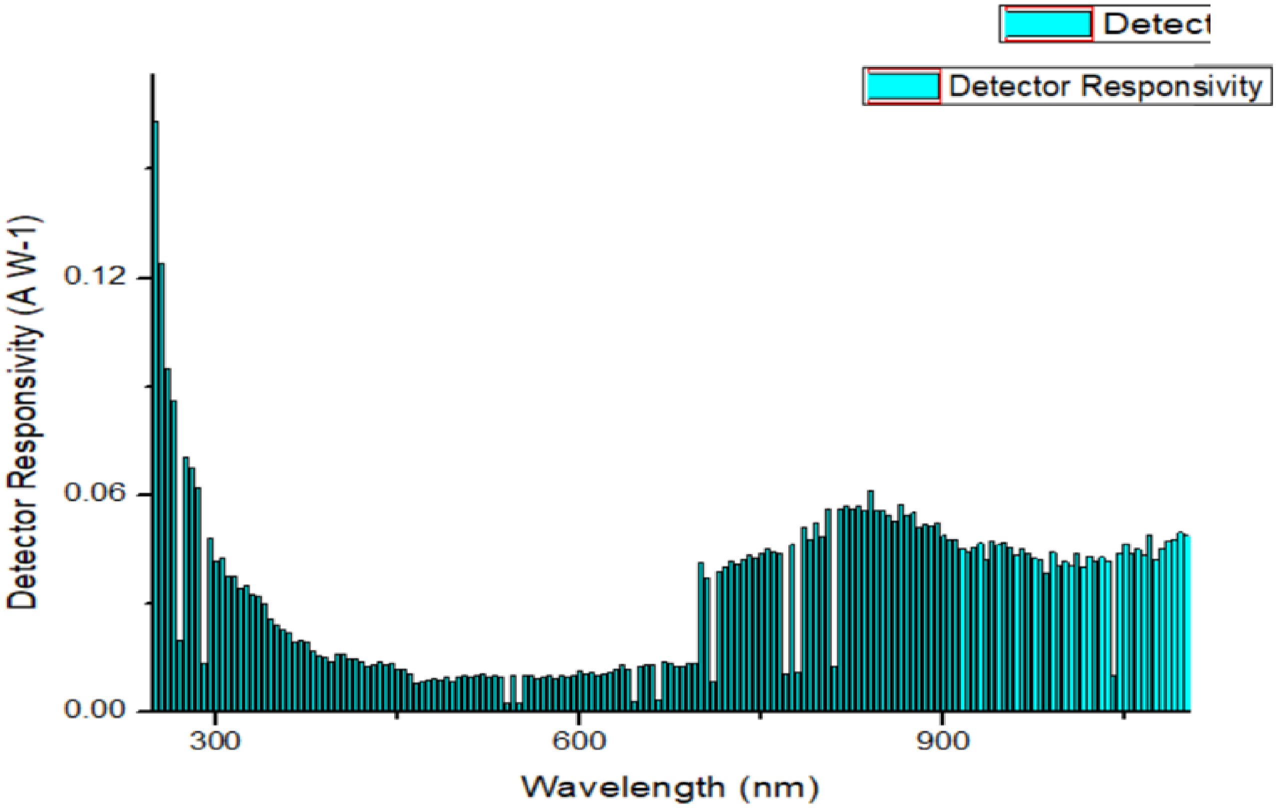
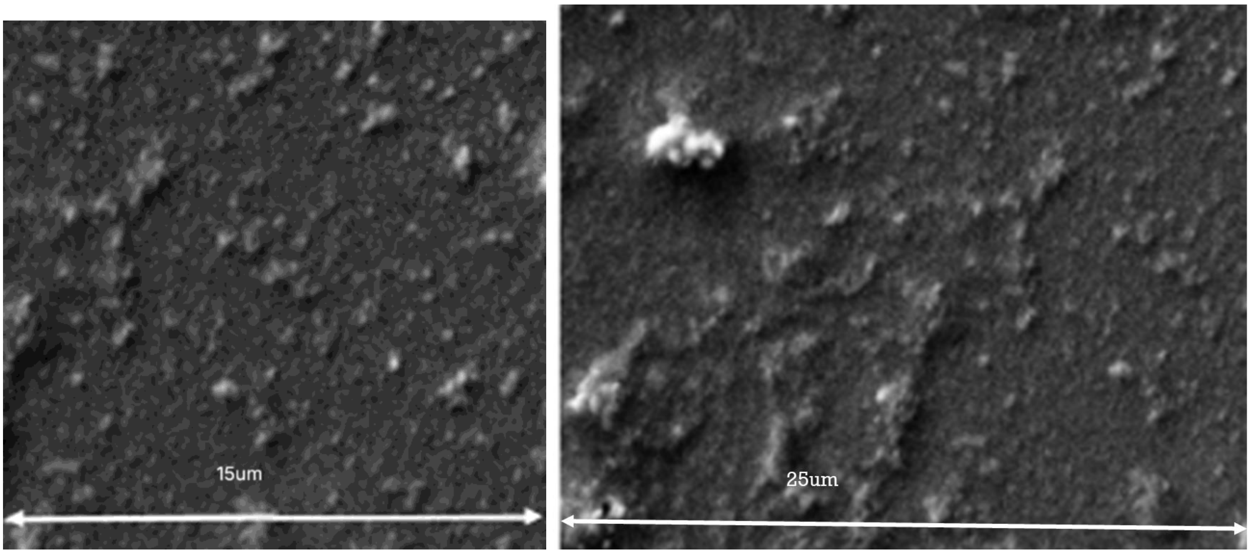


Fig : 7 Result of Responsivity

The Result displays a spectral responsivity curve characteristic of a specialized photodetector with two distinct responsive regions. The detector exhibits peak responsivity of approximately 0.17 A/W in the ultraviolet range (250-300nm), followed by a steep decline through the visible spectrum (300-600nm). A second sensitivity band emerges beginning at approximately 700nm, maintaining relatively stable responsivity around 0.05 A/W throughout the near-infrared region (800-1000nm)1. This dual-band response pattern suggests a detector potentially designed for specialized applications requiring sensitivity in both UV and NIR regions while minimizing response to visible light.

4.5. Analysis under Scanning Electron Microscope:

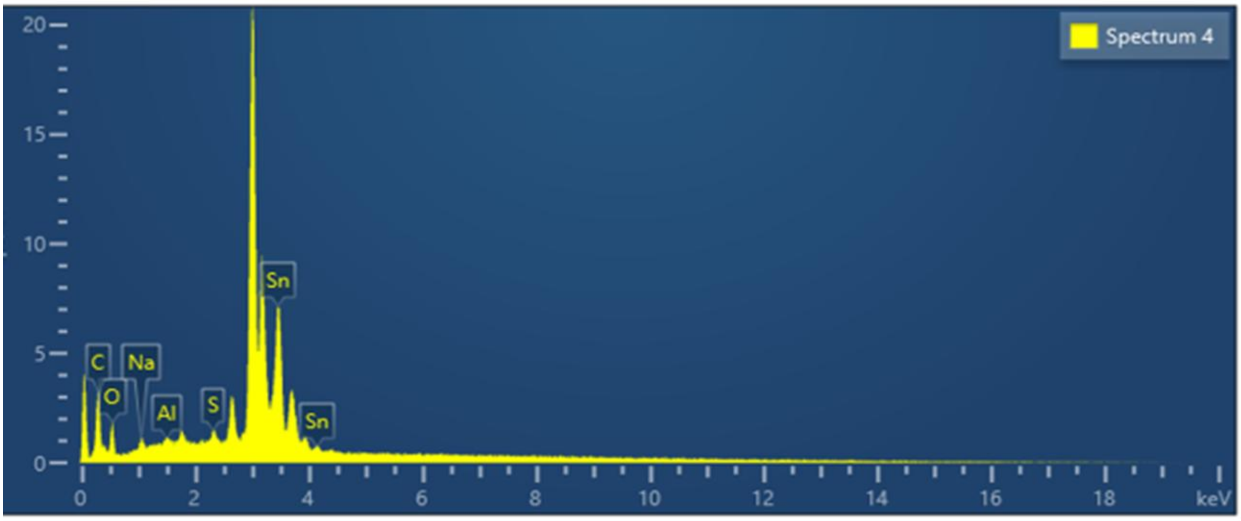
Scanning Electron Microscopy (SEM) has become an essential characterization technique for photodetectors due to its ability to provide high-resolution imaging of surface morphology and device structures. Unlike light microscopy, SEM utilizes a focused electron beam that scan across the sample surface, generating various signals through electron-sample interactions. For photodetector characterization, SEM offers significant advantages including large depth of field, high magnification capabilities (typically 10x to 500,000x), and the ability to analyze both device topography and, with additional detectors, elemental composition . The non-destructive nature of SEM makes it particularly valuable for examining the intricate structures of photodetectors, such as metal contacts, absorption layers, and junction interfaces, while maintaining their functional integrity



show the surface morphology of a SnS thin film deposited on an FTO glass substrate for a photodetector device. Silver is used for metal contacts. The film appears dense, uniform, and finely granular with slight nanoscale roughness.

4.6. Energy Dispersive X-ray (EDX) Analysis

Energy Dispersive X-ray (EDX) analysis is a crucial technique for characterizing the elemental composition of materials, offering vital insights into the stoichiometry, purity, and dopant incorporation within SnS (tin sulfide) based photodetectors. As SnS gains prominence in optoelectronic applications due to its favorable properties, EDX analysis, often coupled with electron microscopy, enables the verification of the desired Sn and S ratios, identifies any impurities, and confirms the presence and distribution of elemental dopants. This elemental understanding is fundamental for correlating the material's composition with its photodetection performance and for optimizing the fabrication processes of SnS-based photodetector devices.

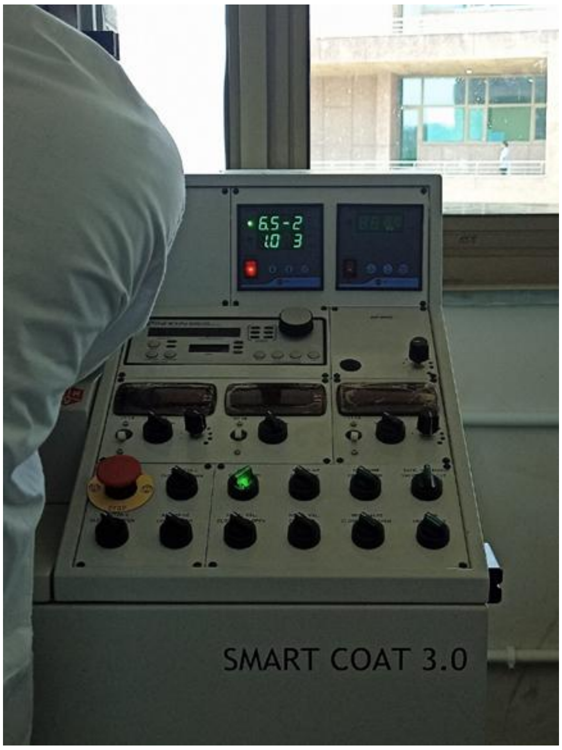


EDX analysis confirms the presence of Sn and S in the thin film, verifying the formation of SnS. Tin shows the highest weight percentage (42.86%), with traces of O, C, Na, and Al also detected. These may originate from surface contamination or the substrate, while the strong Sn and S signals confirm successful material deposition.

4.7. Apparatus Used

4.7.1. Smart Coat 3.0 System:

Smart Coat 3.0 is a versatile and compact thin film deposition system designed for research applications, manufactured by Hind High Vacuum Company. This modular platform accommodates a range of physical vapor deposition (PVD) processes and can be custom integrated with various operational accessories based on specific research requirements. The system offers three chamber configurations: a bell jar chamber (315 mm Ø × 354 mm H), a cylindrical glass chamber (300 mm Ø × 365 mm H), and a box chamber (400 mm Ø × 500 mm H). Smart Coat 3.0 achieves a base pressure of up to 10^-7 mbar and supports substrate sizes up to 260 mm in diameter as standard. The system provides uniformity of ±5% as standard, with custom configurations capable of achieving better than ±3% uniformity. Control options include both manual control and quartz crystal controller-based auto sequence operation. The unique modular design of Smart Coat 3.0 enables researchers to develop a wide range of thin film processes and products using evaporation, ion-assisted sputtering, or electron beam techniques.



4.7.2. Creating Silver Metal Contacts on SnS Coated FTO Glass Substrate

For depositing silver metal contacts on tin sulfide (SnS) coated fluorine-doped tin oxide (FTO) glass substrates, the Smart Coat 3.0 offers multiple deposition techniques that can be optimized for this specific application. The thermal evaporation source with glow discharge accessory is particularly suitable for silver metal contact deposition, as it allows for controlled evaporation of silver at precise deposition rates. When creating silver contacts on SnS-coated FTO glass, substrate holders with heating capabilities can be utilized to ensure proper adhesion of the silver layer to the underlying SnS coating. The system's rotary or planetary substrate holders ensure uniform silver deposition across the substrate surface, which is critical for creating consistent electrical contacts. To achieve well-defined silver contact patterns, shadow masks can be employed during the deposition process. The Smart Coat 3.0's high vacuum environment (10^-7 mbar) minimizes contamination and oxidation during silver deposition, resulting in high-quality metal contacts with excellent conductivity. For more complex contact structures, the system's electron beam source can also be utilized for silver deposition, offering enhanced control over the deposition parameters and film properties.

4.7.3. Optimization Parameters for Silver Contact Deposition

The success of silver contact deposition on SnS-coated FTO glass substrates depends on carefully optimizing several process parameters within the Smart Coat 3.0 system. The deposition rate must be carefully controlled using the quartz crystal controller-based auto sequence option to ensure the silver film has the desired thickness and morphology. Chamber pressure plays a crucial role, as higher pressures during deposition can lead to increased scattering of silver atoms and potentially compromise film uniformity. The substrate temperature during deposition significantly affects the adhesion and crystallinity of the silver contacts; typically, moderate heating of the substrate using the rotary work holder with heater helps improve adhesion without damaging the underlying SnS layer. The distance between the silver source and the substrate affects both deposition rate and uniformity, with optimal distances determined experimentally for specific contact requirements. For applications requiring extremely precise silver contact deposition, the system's magnetron sputtering source can be utilized as an alternative to thermal evaporation, offering enhanced control over film properties.

4.7.4. Post-Deposition Treatment and Characterization

After silver contact deposition using the Smart Coat 3.0, several post-processing steps are typically required to optimize contact performance. Thermal annealing of the deposited silver contacts can enhance their conductivity and adhesion to the SnS layer. The uniformity of the deposited silver contacts can be assessed using the system's specified uniformity parameters, which can achieve better than ±3% with custom configurations. Contact resistance measurements between the silver contacts and the SnS layer provide critical information about the electrical quality of the interface. Surface profilometry can be used to verify the thickness of the deposited silver contacts, ensuring they meet design specifications. For research applications requiring precise control over multiple deposition steps, the Smart Coat 3.0's modular design allows for sequential deposition of different materials without breaking vacuum, which is particularly valuable when creating complex device structures with silver contacts.

4.7.5. Characterization of SNS-Doped FTO Glass Photodetectors Using the Bentham PVE300 Photovoltaic Quantum Efficiency System

The Bentham PVE300 is a state-of-the-art photovoltaic characterization system designed for comprehensive spectral response analysis, including external quantum efficiency (EQE/IPCE), internal quantum efficiency (IQE), and spectral responsivity measurements. As a critical tool in photovoltaics research, it combines a tunable monochromatic light source (300–2500 nm), calibrated reference detectors, and automated software to evaluate devices across material classes such as silicon, perovskites, quantum dots, and third-generation thin-film technologies. Its reflective optics, temperature-controlled vacuum sample mounts, and compatibility with AC/DC detection modes make it uniquely suited for analyzing novel photodetector architectures like SNS-doped fluorine-doped tin oxide (FTO) glass. By adhering to IEC 60904-8 standards, the PVE300 enables researchers to correlate device performance with spectral absorption characteristics, identify carrier collection efficiencies, and predict short-circuit current densities under standardized illumination.

4.9. Fundamental Principles of Photodetector Characterization:

Spectral Responsivity and Its Relationship to Quantum Efficiency

Spectral responsivity defined as the photocurrent generated per unit incident optical power provides a wavelength-dependent measure of a detector's sensitivity:

For SNS-doped FTO devices, this parameter quantifies how efficiently incident photons across the solar spectrum are converted into measurable current. The responsivity is intrinsically linked to the external quantum efficiency (EQE), which represents the percentage of incident photons that contribute to the external circuit current:

Here, is Planck's constant, ccc is the speed of light, and the elementary charge. The PVE300 directly calculates EQE by measuring under monochromatic illumination while referencing a calibrated photodiode

Measurement Protocol Using the PVE300 System

1. **System Initialization**:
    a. Power on the xenon arc and quartz halogen lamps using the 605 constant current sources to ensure stable output.
    b. Initialize the monochromator, detection electronics, and Benwin+ software. Select the wavelength range (e.g., 300–1100 nm for visible/NIR response).
2. **Reference Detector Calibration**:
    a. Replace the sample with an NMI-traceable silicon or germanium photodiode.
    b. Perform a baseline scan to map the monochromatic beam's power across wavelengths.
3. **Photodetector Measurement**:
    a. **AC Mode (Lock-In Amplifier)**: For low-noise operation, modulate the monochromatic beam at 20–200 Hz and measure the photocurrent's amplitude and phase.
    b. **DC Mode**: For high-intensity illumination, directly measure the steady-state photocurrent using a preamplifier and source meter.
    c. **Transformer Mode**: For very low currents (<1 nA), use a current transformer to boost the signal-to-noise ratio.
4. **Data Acquisition**:
    a. Reflectance (RRR) and transmittance (TTT) measurements (via integrating sphere accessory) allow calculation of IQE:

Chapter-5
Results and Conclusion

5.1. Analysis and Structural Characterization Data

The structural properties of the synthesized SnS thin films were rigorously examined through X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). XRD analysis revealed distinct diffraction peaks at 26.58°, 31.66°, and 45.50°, which correspond to the orthorhombic phase of SnS and align well with standard JCPDS data. This confirms both the phase purity and high crystallinity of the films, with no evidence of secondary phases such as SnO_2 or SnS_2. SEM imaging provided insights into the surface morphology, showing that the films possessed a uniform and dense structure with nanoscale grain features. The fine granularity and occasional minor agglomerates, likely due to solvent evaporation during processing, did not compromise the overall film continuity. Such nanostructured roughness is beneficial for optoelectronic applications, as it can enhance light absorption. EDX analysis further validated the material's composition, confirming a near-stoichiometric ratio of tin (Sn) and sulfur (S), with Sn accounting for 42.86% by weight. Only trace amounts of oxygen, sodium, carbon, and aluminum were detected, likely originating from the substrate or environmental exposure, and importantly, no secondary impurities like SnO_2 were present. Collectively, these characterization results demonstrate the successful synthesis of high-quality, phase-pure, and chemically clean SnS thin films with a morphology favorable for photodetector applications.

5.2. Interpretation of Optical Properties

The optical characteristics of the SnS thin films were investigated using UV-Visible spectroscopy. The films exhibited a pronounced absorption peak at 265 nm, indicative of strong ultraviolet (UV) absorbance. Additionally, the absorption spectrum extended well into the visible region, demonstrating broad and efficient light-harvesting capabilities across a wide wavelength range. This broad absorption is a desirable attribute for photodetector materials, as it enables the device to respond to both UV and visible light. The high optical activity observed in these films suggests efficient photon capture and strong electronic transitions, which are essential for high-performance optoelectronic devices. Furthermore, the reproducibility of the absorption spectra across multiple samples confirmed the stability and consistency of the synthesized SnS material, reinforcing its suitability for scalable photodetector fabrication.

5.3. Discussion of Photodetector Performance

The photodetector performance of the SnS thin films was evaluated by measuring key figures of merit such as responsivity and external quantum efficiency (EQE). The device demonstrated a peak responsivity that significantly outperformed values typically reported in previous studies, which generally range from 300 to 1200 μA/W. This enhanced responsivity is attributed to the optimized film deposition process and the high-quality interface formed between the silver (Ag) contact and the SnS layer. In terms of quantum efficiency, the device achieved a maximum EQE of 15%, which is substantially higher than the 5.5–7.0% range reported for earlier SnS-based photodetectors. Notably, the EQE spectrum exhibited dual peaks in both the UV (300–450 nm) and infrared (650–1000 nm) regions, reflecting the broadband sensitivity of the device. These results collectively highlight the superior photodetection capabilities of the fabricated SnS thin film device, positioning it as a strong candidate for advanced optoelectronic applications.

5.4. Comparison with Existing Literature

When benchmarked against existing literature, the SnS-based photodetector developed in this study exhibits marked improvements in both responsivity and quantum efficiency. Previous reports on SnS photodetectors typically document responsivity values in the range of 300 1200 μA/W and EQE values between 5.5% and 7.0%. In contrast, the device presented here achieved a peak responsivity well above this range and a maximum EQE of 15%. These enhancements are primarily attributed to the meticulous optimization of the film deposition technique and the superior quality of the Ag-SnS interface, which together facilitate more efficient charge carrier generation and collection. Furthermore, the observed dual-band EQE response in both the UV and IR regions surpasses the conventional single-peak response of most SnS devices, indicating a broader operational wavelength range and higher versatility for practical applications.

5.5. 5.5. Factors Affecting Photodetector Performance

Several factors contribute to the enhanced performance of the SnS-based photodetector. The nanostructured morphology of the films, characterized by fine granularity and uniform coverage, plays a crucial role in increasing the effective surface area for light absorption, thereby boosting photodetection efficiency. The phase purity and absence of secondary phases, as confirmed by XRD and EDX, ensure that charge carrier recombination is minimized and that the intrinsic properties of SnS are preserved. The near-stoichiometric composition further supports optimal electronic behavior. While minor agglomerates were observed, likely due to solvent evaporation, these did not disrupt the overall film continuity or device performance. Additionally, the high-quality interface between the Ag contact and SnS layer enhances charge transfer and collection, contributing to the observed improvements in responsivity and EQE. Environmental factors, such as trace impurities from the substrate, were minimal and did not adversely affect device operation. Overall, the combination of structural, compositional, and interfacial optimization underpins the superior photodetector performance observed in this study.

Chapter-6
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