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Electrodeposition-based synthesis and characterization of ZnS nanostructure thin films for optoelectronics devices

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Abstract
Zinc sulphide (ZnS) nanostructure thin films were effectively deposited on ITO substrate in the current investigation using the electrodeposition method. The structural and geometric properties of the developed thin films were analysed using XRD and SEM. XRD investigation revealed a wurtzite hexagonal crystal structure, and the estimated crystal size for the favoured orientation was around 63 nm. The visual characteristics were ascertained by analyzing UV-visible spectra, and the direct bandgap of ZnS is calculated to be ~ 3.93 eV using Tauc's plot. Since the developed nanostructure thin film comprises defect states, the band gap energy is lower than bulk material. The current-voltage aspects of the developed thin film were measured in the dark and the presence of 20 W LED light and 100 W tungsten filament light, respectively. Compared to dark mode, there was a discernible difference in the current for both LED and conventional light. These findings suggest that low-cost ZnS may be used as a substitute for solar cells, which are environment-friendly and Cd-free window layers for optoelectronic devices.

Keywords: Electrodeposition, thin film, optical properties, electrical resistivity, illumination

1. Introduction
Recently, there has been significant excitement and focus in material science and nanotechnology regarding the development and characterization of inorganic structures with nanoscale dimensions and innovative shapes. Renewable energy sources such as hydropower, solar electricity, and wind have recently gained interest as potential substitutes for fossil fuels. Due to remarkable photovoltaic performances, inorganic material-based solar cells have received a lot of attention during the past 20 to 25 years. Metal oxide nanostructures are expected to be incorporated into various nanodevices as nanotechnology continues to advance to perform at a high level in applications. Chalcogenide materials such as cadmium sulphide (CdS), zinc oxide (ZnO) and zinc sulphide (ZnS) are appropriate buffer layers for solar cells [1-3]. Zinc sulphide is II-VI, n-type semiconductor material that is non-toxic, cheap and abundant in nature with wide band gap 3.68 to 3.94 eV which is greater than CdS (2.42 eV) and ZnO (3.42 eV) nanostructures so it provides a better option for visible and ultraviolet (UV) light-based devices such as sensors/photo detectors [4-6]. ZnS exhibits enhanced optical, electrical, and catalytic properties in nanostructured thin film form due to its high surface-to-volume ratio, quantum confinement effects, and the ability to adjust the morphology of nanoparticles, nanowires, and nanosheets. ZnS is a plausible option to displace CdS as a cushion layer in Cu (In, Ga) (S, Se)$_2$ (CIGS) solar cells because of low toxicity and enhanced efficiency [7-8]. ZnS nanostructures can be utilized in transparent conductive coatings, electroluminescent devices, UV and visible light photodetectors, and display panels (as phosphor layers). A shift in conductivity and surface adsorption makes ZnS nanostructures sensitive to gases such as H_2S, CH_4, and NO_2. ZnS nanoparticles also have antibacterial properties, which makes thin films beneficial for packaging and medical applications. Recent studies have explored various applications of ZnS, including fluorescent nanoparticles based on the CdSe/ZnS system for diagnosing oncological diseases [9], light emitting devices [10], gas and chemical sensors [11], optoelectronic, luminescence and heterojunction devices [12], infrared windows and lasers [13]. As a result, various efforts have been made to synthesise ZnS nanostructures in variety of sizes and forms, which offer. Special features for electrical and optoelectronic applications. The electronic and crystalline makeup, surface energy, and electrical features of nanostructures can

all be modified by adjusting their surface morphologies. Numerous methods have been suggested for synthesizing ZnS nanostructures with varied morphologies at the nanoscale. Such Physical and chemical methods include chemical vapor deposition (CVD) [16], hydrothermal [17], vacuum evaporation [18], spray pyrolysis [19], sol-gel process [20], magnetron sputtering [21], electrochemical deposition [1, 5, 12, 22-25].

To realise large-scale homoepitaxial growth of metal oxide nanostructures, it is desirable to investigate a straight forward procedure. It is possible to create metal oxide nanostructures using several physical, chemical, and biological processes. Electro-deposition is an inexpensive, solution-based hybrid technique for the creation of thin films with nanostructures. In a comparison study between pulsed and regular electrochemical deposition (ECD), Fathy *et al.* [26] demonstrated that electrodeposition is a very appealing and practical method for producing ZnS thin films for a variety of applications. Due to the low material consumption processes, electrochemical deposition of ZnS thin films from aqueous solutions has great promise for the large-scale manufacture of solar cells. It doesn't require expensive vacuum equipment, high temperature and has a simple technological design. The method under consideration has the critical benefit of producing almost no harmful gaseous products, which are often formed when using techniques like pyrolysis and chemical bath deposition. In this paper, we discuss the electrochemical deposition of zinc sulphide thin films from a sulphate bath. By using this technique, films may be deposited at relatively low temperatures, which is beneficial for producing materials with fewer imperfections.

2. Experiments

2.1 Materials and Method

A classic homemade three-electrode electrochemical bath was adopted to develop ZnS thin film at ambient temperature. In this bath zinc sulphate ($ZnSO_4$) of 0.4 M and sodium thiosulphate ($Na_2S_2O_3$) of 0.1 M are employed as sources of zinc and sulphur during the synthesis. The pH of the solution was 4.4 before adding several drops of H_2SO_4, and it was adjusted to 2.4 after that. The setup involved a saturated calomel electrode (SCE) as the reference, a platinum wire serving as the counter electrode, and a glass substrate implanted with indium tin oxide (ITO) as the working electrode. The ITO substrate was thoroughly sanitized in an ultrasonic bath, then washed in highly purified water before implantation to eliminate surface impurities. A thin ZnS layer was created by applying a 2 V potential for 30 minutes with an HTC DC 3002 power source.

2.2 Characterization of the Nanostructure

The constitutional features of ZnS thin film were characterized using X-ray diffraction (XRD) on a Siemens D-5000 diffractometer with Cu Kα radiation (λ = 1.54 Å). Surface morphology and microstructure were examined utilizing scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) for elemental mapping (Jeol JSM-7610F Plus). Optical properties were measured with a Shimadzu UV-2600 spectrophotometer, and bonding characteristics were analysed using a Bruker Alpha FTIR spectrometer in the 4000-500 cm^{-1} range. The electrical characteristics, including current-voltage behaviour, were assessed in both dark conditions and when illuminated by a standard tungsten filament bulb and 20 W LED using a Keithley 6517A electrometer.

3. Results and Discussion

The following equations (i to iii) illustrate the general chemical mechanism for the growth of ZnS thin films on ITO sheet in an aqueous solution through electrodeposition [4, 12].

$$S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S+3H_2O \quad \text{(i)}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \quad \text{(ii)}$$

$$Zn + S \rightarrow ZnS \quad \text{(iii)}$$

3.1 Structural Characteristics

The diffraction pattern of the deposited ZnS nanostructure, scanned from 10° to 80°, is shown in Figure 1, indicating the material's structural nature and purity. The (111) and (200) planes, which are associated with the zinc blende structure, are shown by the strong peaks in the spectrum of deposited ZnS thin films. The observable acute peak patterns demonstrate the good crystalline quality of the developed thin film. The crystallite dimension (D) was computed with the Debye-Scherrer equation.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{..... (iv)}$$

In this context, λ denotes the wavelength of the incoming X-ray radiation, 2θ signifies the Bragg diffraction angle of the preferred orientation, and β represents the full width at half maximum (FWHM). Using equation (IV), the average crystalline dimension (D) of the produced thin film was estimated to be 63.28 nm for a diffraction angle of 32.95°.

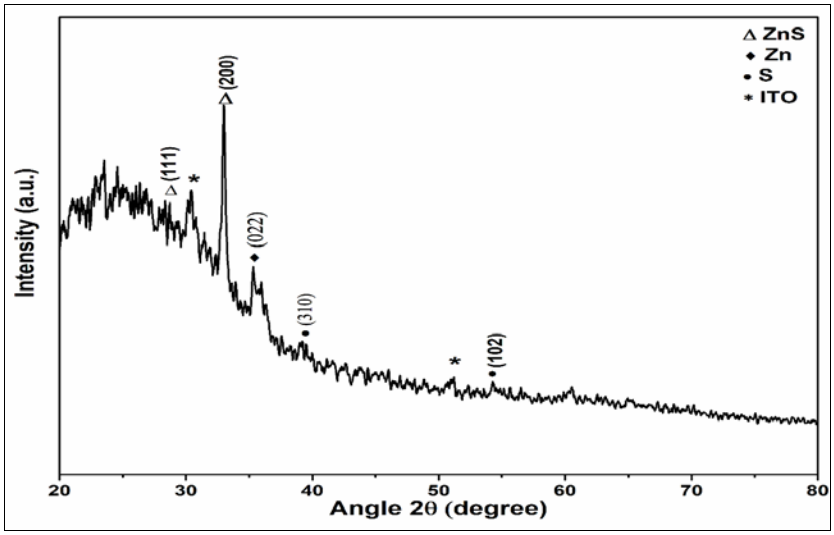

Fig 1: Diffraction spectrum of synthesized ZnS thin films.

3.2 Scanning Electron Micrograph (SEM) with EDX Analysis

The shape and dimensions of the produced thin film were examined with a field emission scanning electron microscope (FESEM). SEM microscopic image and the elemental composition of the generated ZnS thin film are demonstrates by Figure 2. Additionally, an EDX detector attached to the SEM was applied to determine the chemical makeup of the developed thin film. Based on the surface form of the created thin film, the electrodeposition technique was used to precisely deposit the film.

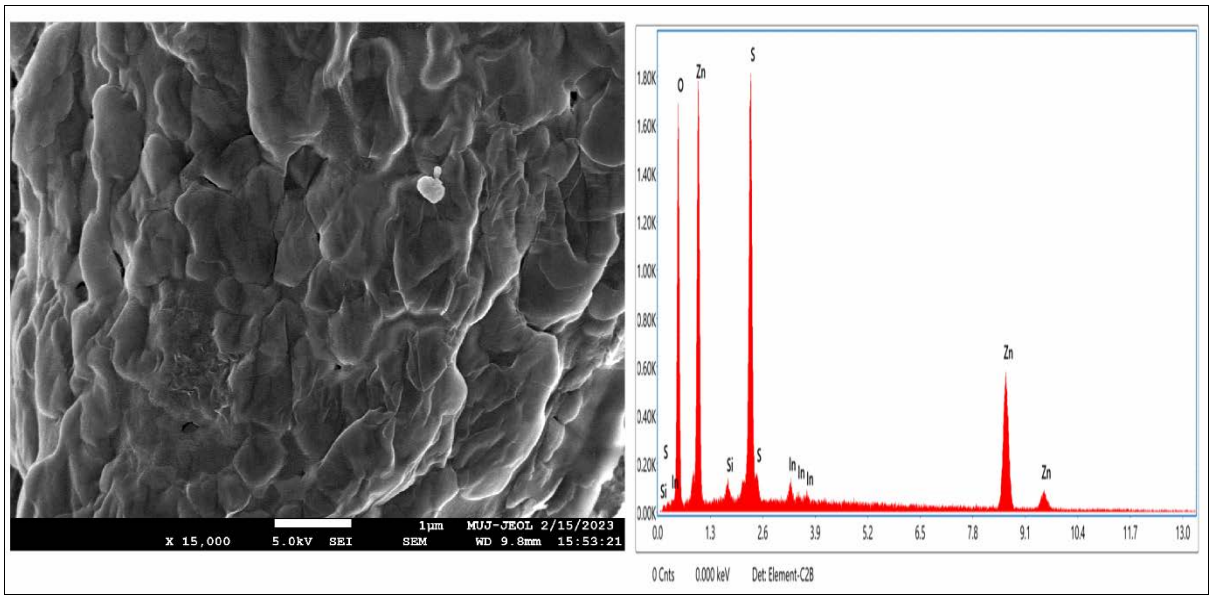

Fig 2: SEM micrograph with corresponding elemental mapping of synthesized ZnS thin film.

The diameters of the grains and their arrangement in the composite were evaluated through Image J software with particles from the deposited thin film that had identical dimensions in the range of nanometers. The developed thin film comprises by components ranging from 95 to 685 nm, with an average size of 315 nm and a standard deviation of 131 nm, as shown in Figure 3.

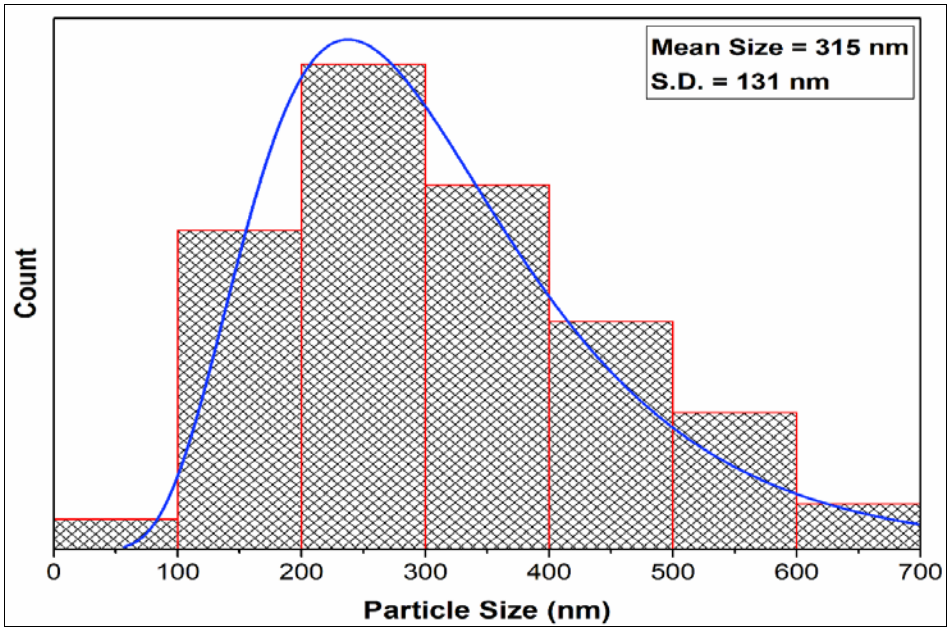

Fig 3: Particle size distribution diagram.

3.3 UV-Visible Analysis

Figure 4 demonstrates the UV-vis spectra of the deposited ZnS thin film between 300 and 800 nm. Figure (a) displays the absorbance spectrum and (b) displays the Tauc's plot of $(\alpha h\nu)^2$ against photon energy. This suggests that the ZnS nanostructure undergoes direct transitions because the profile is straight across a broad spectrum of photon energy. The optical band gap was estimated with Tauc's formula equation (v) [27]

$$(\alpha h\nu)^2 = C\,(h\nu - E_g) \quad \text{(v)}$$

Where C denotes a constant, $h\nu$ denotes the incident photon's energy, E_g denotes the transition band gap, and α denotes the absorption coefficient. By expanding the linear portion of the Tauc's curve, the gap in the visual band was found to be 3.93 eV, as seen in Figure 4(b). This obtained value is comparable to several authors who also reported the band gap between 3.6 to 3.95 eV [12, 23, 28].

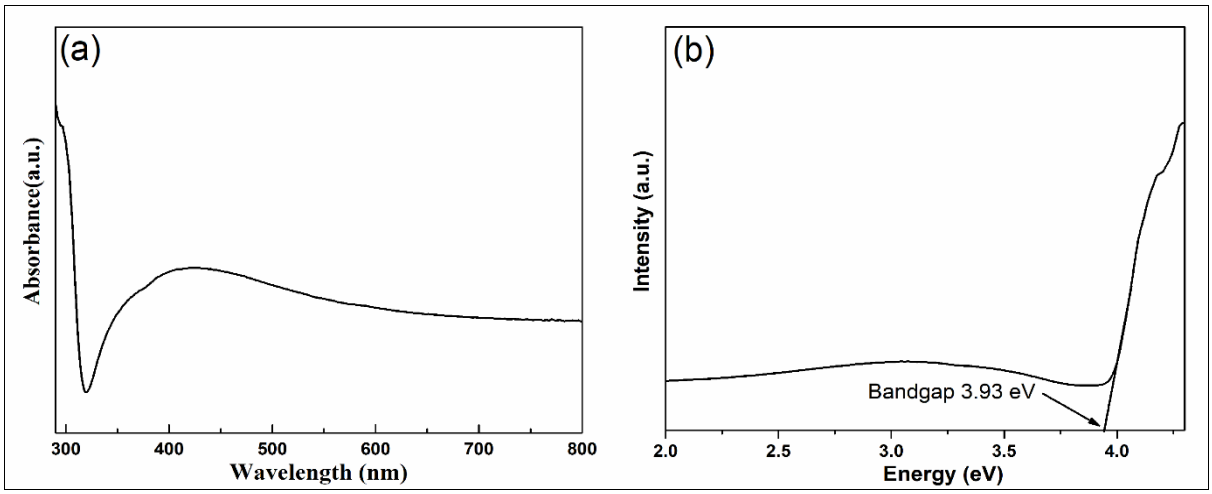

Fig 4: (a) Absorbance spectrum of developed ZnS thin film (b) Tauc's plot.

3.4 FTIR Analysis

Considering the association of separate functional groups with distinct absorbance peaks in the spectra, FTIR spectroscopy was applied to judge whether the produced nanostructure contained organic or inorganic components. Figure 5 displays the FTIR spectra of the developed ZnS nanostructure thin film, which exhibits transmission spikes between 500 and 4000 cm^{-1}. The stretching vibration of ZnS is suggested by the peak at 522 cm^{-1}. The other functional groups present in the synthesized nanostructure such as CO_2, CO, C-H and OH also shown in the figure at different peaks.

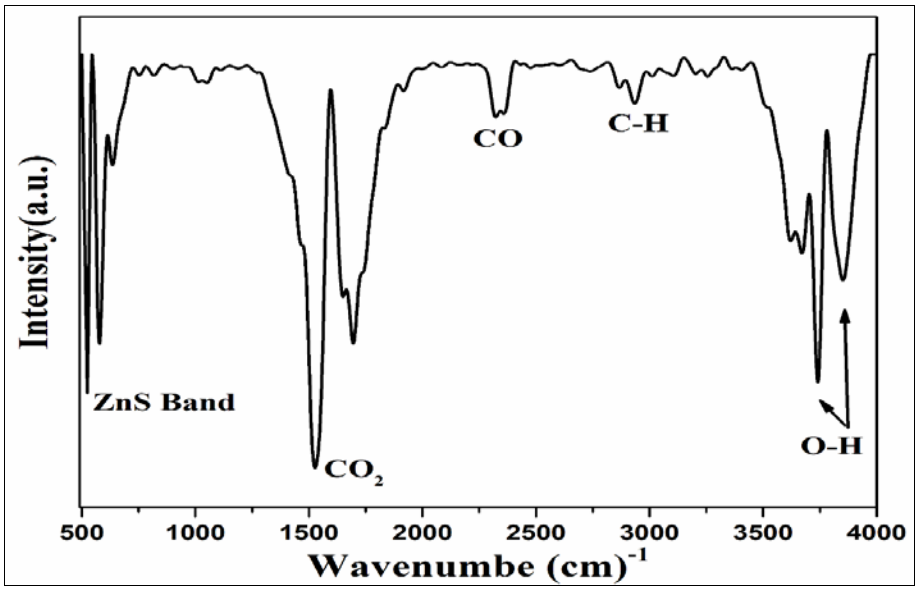

Fig 5: FTIR spectrum of synthesized ZnS nanostructure.

3.5 Electrical Properties

The current-voltage (I-V) attributes of the developed thin film were examined at room temperature between -2.5 V and 2.5 V under darkness, tungsten bulb light (100W), and LED light (20W). Zinc sulphide (ZnS) with zinc having the electronic configuration [Ar] $3d^{10}4s^2$ and sulphur [Ne] $3s^23p^4$, is a direct band gap semiconductor that exhibits n-type behaviour due to native defects or doping, making it useful in optoelectronic applications as the current flow is influenced by the concentration of Zn^{2+} ions. The Zn^{2+} concentration determined the current flowing through a thin film, while charge mobility and carrier concentration determined the conductivity of the deposited thin film. Equation (v) represents a relation for the "conductivity σ and mobility μ of charge carriers" of a material.

$$\sigma = nq\mu \quad \text{(v)}$$

In this context, q denotes the charge of the electron, and n represents the charge carrier density in the conduction band. These results indicate an Ohmic contact between the electrodes and the ZnS thin film, as the current-voltage characteristics remain linear in both bias directions up to 2.5 V. For both LED and regular tungsten filament bulb, the current-voltage profile appears nearly identical, with similar outcomes also reported by Ali *et al.* and Faithy *et al.* [29, 30]. Reduced grain boundary zones and grain displacement can lead to either increased conductivity or decreased resistivity.

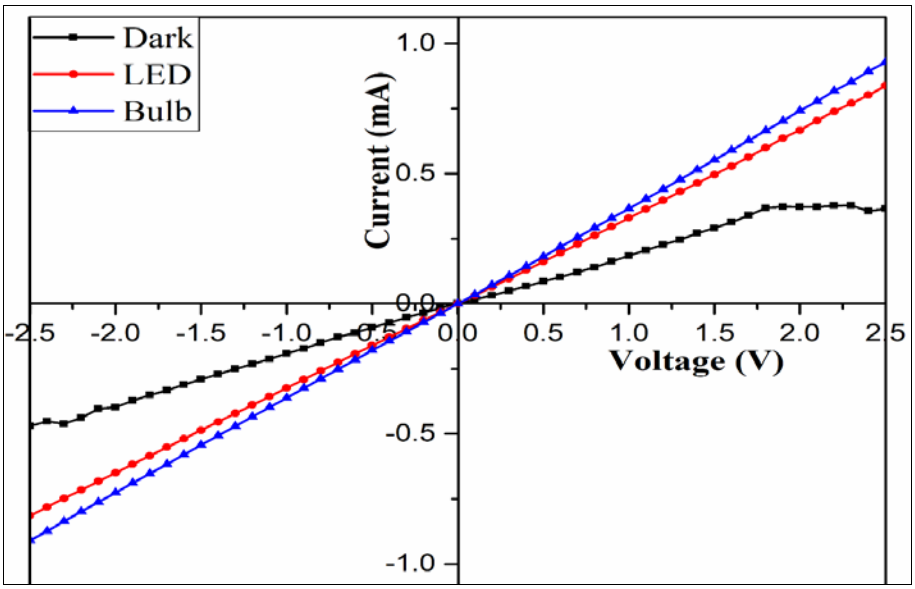

Fig 6: Current-voltage characteristics of synthesized ZnS nanostructure thin film.

4. Conclusion

Zinc sulfide (ZnS) nanostructure thin film was created making use of a three-electrochemical deposition setup in an inorganic electrolyte solution over a glass substrate plated with indium doped tin oxide (ITO). The structural, optical, and electrical characteristics of the produced ZnS thin film were evaluated through advanced characterization techniques. X-ray diffraction (XRD) observations confirmed that the ZnS film has crystalline nature with hexagonal wurtzite phase, predominantly oriented along the (111) plane, with mean crystallite size about 63.28 nm. A uniform surface morphology of the structure and adhesion of the ZnS layer with the substrate were revealed by the SEM results. The optical band gap of the developed ZnS film was calculated to be around 3.93 eV, slightly narrower than that of bulk ZnS because of the existence of defect states within the material. These films also exhibited excellent conductivity and a high degree of visible light absorption, making them promising for optoelectronic applications. Ghezali *et al.* [12] demonstrated that the electrochemical behaviour and growth rate of ZnS films are significantly influenced y the applied deposition potential. Ricardez *et al.* [22] also reported that the elemental composition of ZnS thin film varies with changes in the applied voltage, further affecting their physical properties. ZnS thin films possess unique optical and electronic properties that make them suitable for a variety of advanced technologies such as buffer layers in solar cells, photo-detectors, light-emitting diodes and optical coatings. Their ability to absorb visible light and their compatibility with flexible substrates also open possibilities for integration into next-generation flexible electronics and wearable energy-harvesting systems.

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