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Synthesis and Characterization of CdS/Cu_2ZnSnS_4 (CZTS) Heterojunction Thin Film for Solar Cell Applications

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The CdS/Cu_2ZnSnS_4 (CZTS) heterojunction thin films successfully synthesized using Successive Ionic Layer Adsorption And Reaction (SILAR) method at room temperature over the glass substrate with the motive to characterize for solar cell applications. These as deposited thin films have been characterized for structural, compositional, morphological, optical and I-V characteristics. The X-ray diffraction (XRD) pattern analysis confirms formation of kesterite structure with tetragonal geometry; high intensity of pronounced peak associated with dominated growth oriented along (112) direction. Peaks obtained at 800 cm^{-1}, 950 cm^{-1} and 1100 cm^{-1} as observed from Raman spectrum also confirms kesterite CZTS structure. Surface morphology as observed shows uniform distribution of grains over the substrate surface, the optical transmittance spectrum used to calculate energy band gap, which is observed to be 2.79 eV corresponding to the exciton induced grain boundary charge transfer phenomenon. I–V characteristic shows semiconducting nature, however an increase in current voltage response is noted upon illumination to light of 100 mW/cm^2 (AM1.5) resulted into obtaining of 1.78% of conversion efficiency.

1. Introduction

Copper Zinc Tin Sulphide (CZTS) is one of promising material for photovoltaic applications due to potential optical and electronic properties [1,2]. It is composed of abundant, non-toxic elements, and serves as an excellent absorber material for solar cells, with high absorption coefficient exceeding 10^4 cm^{-1} and a direct band gap ranging from 0.90 to 1.45 eV [3,4]. Despite their potential properties conversion efficiency of CZTS based solar cells has yet to achieve efficiency range of thin-film technologies such as CdTe and CIGS. Several attempts have been made by various scientist to resolve these issues like by introducing window materials as an interfacial, which aim to improve band alignment and reduce recombination losses [5,6]. Certain other parameters also make effect on photo conversion efficiency such as defect density, thickness etc which collectively impacts on open-circuit voltage (Voc), short-circuit current density (Jsc) etc [7]. Hence by preparing CdS based heterojunction thin films electron affinity in such configuration may play crucial role in reducing the recombination current and enhancing the carrier flow. This approach demonstrates the potential for improved charge separation and collection, ultimately contributing to an enhanced conversion efficiency. Even it has been observed that the synthesis methods play important role in surface-based applications of the thin films by virtue of interface optimization between window and absorber layers, a centre for reducing the defects, and minimizing the interfacial strain caused by the window layer [8]. This interface formation may lead on incorporating higher carrier concentration which could demonstrate advantages and challenges in enhancing the solar cell efficiency [9]. This approach could form an increased open-circuit voltage (Voc), it also results in higher carrier recombination rates. The formation of heterojunction structure would highlight the complex interplay between the carrier concentration, interface quality, and device performance in CZTS-based solar cells.

In recent past, various methods have been used for preparation of CZTS thin films such as physical and chemical, one amongst them being Successive Ionic Layer Adsorption and Reaction (SILAR) which has gained attention due to its numerous advantages like surface morphology, large area deposition, user friendly and cost effectiveness. The present work focuses on utilizing the SILAR for synthesis of CdS/CZTS thin films, with the motive to test the solar cell property of the materials. These as deposited heterojunction thin films have been characterized for physicochemical and optoelectronic properties using X-Ray diffraction pattern, Raman spectroscopy, Fourier transform infra-red spectroscopy, Energy dispersive X-ray absorption spectrum, surface morphology using Scanning electron microscopy, UV-Vis spectrum and I-V under dark and light illumination conditions.

2. Experimental Methods

CdS/CZTS thin films synthesized over the glass substrate surface using the successive ionic layer adsorption and reaction (SILAR) method at room temperature in step wise systematic manner. This technique involves sequential immersion of the substrate in cationic and anionic precursor solutions, allowing for controlled layer-by-layer growth of the thin film. The precursor solutions were carefully prepared using analytical grade chemicals. Copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$), zinc chloride ($ZnCl_2$), tin chloride dihydrate ($SnCl_2{\cdot}2H_2O$), thiourea, and cadmium chloride ($CdCl_2$) were selected as CZTS and CdS sources, respectively. Each precursor was meticulously dissolved in ultrapure distilled water to create 0.1 M solutions, with the exception of $ZnCl_2$ and $SnCl_2{\cdot}2H_2O$, which were prepared at lower 0.05 M concentrations to maintain the desired stoichiometry in the final film [10]. To optimize the reaction conditions and enhance film quality, sodium hydroxide (NaOH) and ammonia (NH_4) were added to the cationic solutions. These additives served dual purposes: as pH monitor and as complexing agents to control the release of metal ions during the deposition process. The deposition process involved a series of precisely timed immersions and each step was carefully calibrated to ensure optimal film growth. The thoroughly cleaned glass substrate was first dipped in a cationic solution (a meticulously prepared mixture of Cu, Zn, and Sn precursors) for exactly 10 s. This step allows the adsorption of metal ions onto the substrate surface. Subsequently, the substrate underwent a brief 2-second rinse in distilled water to remove any loosely bound or excess ions, preventing unwanted precipitation [11]. Subsequently, the substrate was immersed in an anionic solution (containing thiourea and $CdCl_2$) for a longer duration of 20 s. During this step, the adsorbed metal ions react with sulphur and cadmium ions in the solution, forming the desired CdS and CZTS compounds. Another 2-second rinse in distilled water was used to

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terminate the reaction and prepare the surface for the next deposition cycle. This intricate cycle was meticulously repeated 60 times to obtain the desired film thickness, with each cycle contributing to the gradual growth of the thin film.

These thin film solar cells characterized for structural, compositional, optical and illumination characteristics. The structural analysis was made using X-ray diffraction (XRD) patterns of the solar cell recorded on Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20–80° (2θ) using CuKα radiations with wavelength 1.5405 Å. The Raman spectrum is measured using Raman spectrometer Renishaw model In-via Raman microscope using Argon ion LASER excitation of 514 nm (5 mW power). Fourier Transform Infra-Red Radiation (FTIR) spectra obtained on Nexus B-70 provided by Thermo Nicolet Company. Surface morphology using scanning electron microscopy (SEM) recorded on JOEL-JSM-5600. The electronic transitions were monitored from the optical absorbance spectra of the films recorded in the 400–1100 nm range using UV-Vis Photo-spectrometer Perkin Elmer Lamda-25. The energy conversion efficiency experiments were recorded by illuminating the heterojunction thin films with 100 mW/cm^2 light source.

3. Results and Discussion

3.1 Characterization Studies

The X-ray diffraction (XRD) pattern of CdS/Cu_2ZnSnS_4 (CZTS) provides valuable insights into its crystallographic properties as shown in Fig. 1. In addition to the primary peaks at 28.5°, 47.3°, and 56.2° corresponding to the (112), (220) and (312) planes, respectively, several secondary peaks may also be observed [10-12]. These include peaks at approximately 33.0, 37.0, and 69.2°, which are associated with the (200), (211) and (008) planes, respectively. The relative intensities of these peaks can provide information on the preferential orientation of crystallites within the sample. The XRD pattern of CdS/CZTS can also be used to distinguish it from other related compounds such as secondary phases or impurities that may form during synthesis. For example, the presence of peaks corresponding to Cu_2S, ZnS, or SnS_2 indicates incomplete reaction or phase segregation. Furthermore, the width and shape of the XRD peaks provide information on the crystallite size and strain within the material. Broader peaks generally indicate smaller crystallite sizes or higher levels of structural disorder, whereas sharper peaks indicate larger crystallites and higher crystallinity [12-14]. This information is crucial for optimizing the synthesis conditions and understanding the relationship between the structure of a material and its optoelectronic properties in photovoltaic applications. The average crystallite size is observed to be 39 nm for the heterojunction thin films.

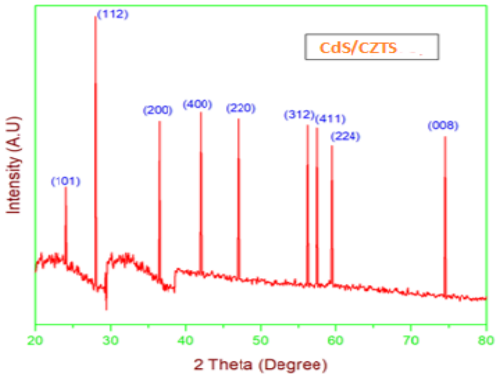

Fig. 1 XRD pattern obtained from CdS/CZTS thin film

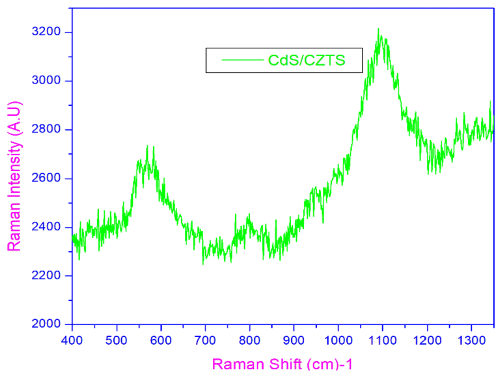

Fig. 2 Raman spectrum of CdS/CZTS Thin film

Fig. 2 represents the Raman spectrum obtained from the CdS/CZTS heterojunction thin films, it particularly useful for assessing the quality of the interface between two materials, identifying potential impurities or secondary phases, and monitoring the effects of various synthesis parameters on the final product [13-15]. The peaks at 600 cm^{-1} may corresponds to first-order longitudinal optical (LO) phonon mode and its second-order harmonic, respectively. Peaks at 800 cm^{-1}, 950 cm^{-1}, and 1100 cm^{-1} infer with different vibrational modes of the crystal lattice, including the A1 and E symmetry modes. No separate peaks corresponding to any impurity is observed into the domain [16].

Fig. 3 shows the FTIR spectrum of the CdS/CZTS sample revealed several characteristic peaks that provided insights into its molecular structure and composition. The broad absorption band observed at approximately 3500 cm^{-1} attributed to the stretching vibrations of Sn-S groups, likely due to surface-adsorbed molecules. Deep at 1000 cm^{-1} may correspond to the stretching modes of metal-sulfur bonds, specifically Cd-S and Cu-Zn-Sn-S, confirming the presence of both CdS and CZTS components in the sample [16-18].

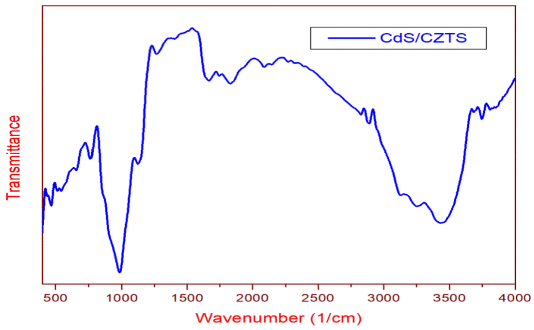

Fig. 3 FTIR Spectrum of CdS/ CZTS thin film

UV-Visible absorbance data obtained have been used for calculations of energy band gap of the materials by extrapolating the energy as shown in Fig. 4, the energy band gap is observed to be 2.79 eV which may correspond to exciton induced charge transfer and grain boundary interactions between and grain growth [19]. More detailed examination of the absorption spectrum can yield insights into the nature of the electronic transitions within the CdS/CZTS material. This information is particularly relevant for optimizing the performance of materials in photovoltaic devices, where efficient light absorption and charge separation are essential. Additionally, the spectrum may reveal any defects or impurities present in the material, which can significantly affect its optoelectronic properties. The grain boundaries of these materials are electrically benign and do not form high recombination sites [20,21]. Another possible explanation is attributed to compositional differences at the grain growth and boundaries as compared to the gain interior that leads to the formation of a larger hole barrier that repels holes and reduces recombination.

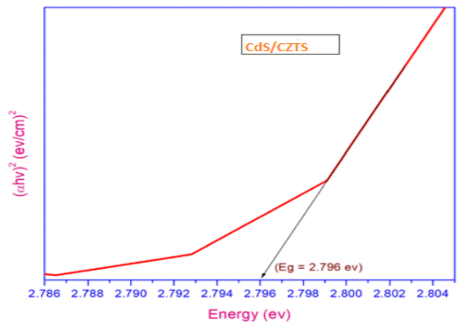

Fig. 4 Energy band gap calculated from the data of UV-Vis absorption of CdS/CZTS

3.2 Surface Morphology Study

Fig. 5 represents SEM analysis of the thin films revealed a complex surface morphology characterized by porous and granular crystallites. This structure is particularly advantageous for surface sensing applications due to its high surface area-to-volume ratio, which enhances the interaction between the incident light and surface molecules. The average grain size of approximately 50 nm, determined through image analysis software. Nanoscale grains typically exhibit enhanced reactivity and sensitivity compared to their bulk counterparts, owing to quantum confinement effects and increased surface energy [22]. The interconnected network of grains observed in the SEM images is a crucial feature for the film's electrical properties and overall performance.

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This interconnectivity facilitates efficient charge transport throughout the film, which is essential for translating the chemical interactions between the molecules.

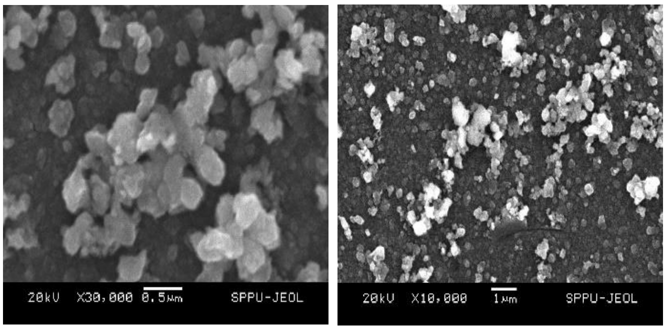

Fig. 5 Scanning electron microsopy images observed for CdS/CZTS thin films

3.3 I-V Study

The I-V study of these heterojunctions thin film has been studied under dark and illumination conditions. Fig. 6 shows the typical I-V spectrum obtained from the heterojunction thin films. The CdS have good compactness, uniform morphology and also good interface with CZTS materials [23-25]. The CdS works as a window layer and CZTS as an absorber layer in the present heterojunction solar cell. Window layer has an important role to play in the heterojunction solar cell as it produces inbuilt electric field required for separation of photo-charge carriers by forming a junction with the absorber layer. Also, window layer should have wide band gap to admit the maximum solar spectrum radiations which should be transferred to absorber layer [26]. The conversion efficiency is observed to be 1.78%.

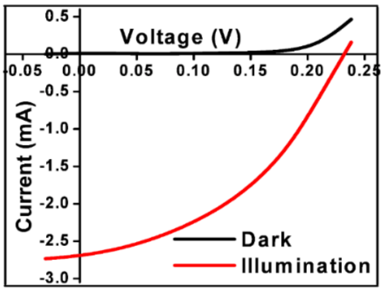

Fig. 6 I-V graph obtained under dark and illumination condition from CdS/CZTS

4. Conclusion

The X-ray diffraction (XRD) analysis provided crucial evidence for the successful synthesis of CdS / CZTS (copper zinc tin sulphide) thin films with the desired kesterite crystal structure. The presence of distinct peaks corresponding to the (112), (220), and (312) planes was characteristic of high-quality CdS/CZTS. These peaks indicate the formation of a well-ordered crystal lattice, which is essential for the efficient charge transport in photovoltaic devices. The absence of secondary phases or impurities in the XRD pattern further confirms the purity of the synthesized CdS/CZTS thin films. Raman spectrum and FTIR have also confirmed the elemental composition and chemical ingredients as expected and used during the synthesis method. Furthermore, scanning electron microscopy (SEM) shows granular distribution over the substrate surface, which may be more useful for surface-based phenomenon. The optical properties of the CdS/CZTS thin films, as determined by UV-Vis spectroscopy, revealed an optical band gap of approximately 2.79 eV. This value falls within the optimal range for solar cell applications because it allows for the efficient absorption of a broad spectrum of solar radiation. The conversion efficiency is observed to be 1.78% upon exposure to sun lights.

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