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Comparative studies on pinhole free CBD-CdZnS thin films on ITO and FTO substrate

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The development of CdZnS thin films using the chemical bath deposition process in non-aqueous media is a technological challenge. In this work, 75 millilitres of ethylene glycol and ethanol (1:2 ratios) were used to develop a CdZnS thin film on ITO and FTO glass substrates using cadmium acetate, zinc sulphate, and thiourea. The ideal bath temperature was kept at 130^0C and the anneal temperature of the film that had been deposited in the air was maintained at 350^0C. The films have been examined using FTIR, WCA, FESEM, and XRD. XRD studies reveal that CdZnS films have a hexagonal crystal structure with a preference for orientation (002) during the deposition and annealing processes and the assessment of the various attributes have been done, such as dislocation density, micro strain, and grain size. FESEM study indicates that as deposited film on ITO glass have smooth surface and grains appear in the form of small needle shape of equal sizes where as FTO substrate reveals the grains of equal size throughout the entire surface in cluster form. It is also confirmed that both the CdZnS films formed on ITO and FTO substrates have hydrophilic quality. The presence of chemical bonds and functional groups was confirmed by FTIR analysis.

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1. Introduction

Because of its special chemical and physical characteristics, the creation of nanocrystalline materials has attracted a lot of attention in the field of materials research. Due to their unique qualities, semiconducting materials have drawn a lot of interest recently. They can be employed in photovoltaic systems as solar cells, alongside cadmium telluride (CdTe), copper indium diselenide/sulfuride, and copper indium gallium diselenide/sulfuride (CIGS) [1]. Semiconductors from the "III-V and II-VI group" are particularly sought after because of their possible uses in optoelectronic devices, photoconductors, detectors, and other applications [2-4]. Chalcogenide-based semiconducting materials, which are widely employed in photovoltaic systems and photodetectors, have garnered more attention in recent times. Due to their large number of surface atoms, simple synthesis in the required size, and potential applications in a variety of technical fields such as photoluminescence, solar cells, and photovoltaic applications, nanocrystalline binary and ternary semiconductors of groups II–VI are gaining more attention [5-7]. Chalcogenide CdZnS films are of great interest because they could be used in solar cells [8] and photoconductive devices. As the Zn concentration increases in CdS material, CdZnS semiconductors are formed, which have characteristics that lay between ZnS and CdS [9], optical bandgap of CdZnS likewise varies from 2.4 eV to 3.7 eV, depending upon the ratio of Cd:Zn [10]. Several methods, including spray pyrolysis [11], ion beam deposition [12], molecular beam epitaxial growth [13, 14], chemical vapour deposition, and chemical bath deposition, can be used to produce CdZnS

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nanocrystalline structure. Among these techniques, chemical bath deposition in a nonaqueous solution is easy to use, affordable, and suitable for large-scale deposition without the need for a vacuum apparatus, among other advantages. Using the chemical bath deposition approach in a nonaqueous medium, high-quality CdZnS films can be produced. Higher operating temperature ranges, more freedom in selecting the deposition source, and absence of the common hydrogen evolution reaction which frequently causes stress and pinhole-free deposits, are all benefits of non-aqueous bath technology [15].

This work reports the growth of CdZnS films grown on ITO and FTO glass substrates in a non-aqueous solution by chemical bath deposition, which were then annealed at 350^0c. This work describes the structural, morphological, water contact angle, and Fourier transform infrared spectroscopy features of these films that were examined using XRD, FESEM, W.C.A. measurement, and FTIR techniques.

2. Experimental

2.1. Preparation technique of CdZnS thin films

Analytical grade, high purity (>99%) chemicals such as Cd $(CH_3CO_2)_2$, $ZnSO_4$, and NH_2-CS-NH_2 are employed as source materials of Cd^{+2}, Zn^{+2} and S^{2-} ions respectively, in the production of CdZnS thin films. AR grade 0.40M Cd $(CH_3CO_2)_2$, 0.15M $ZnSO_4$ mixed in 75ml (1:2 ratio) of ethylene glycol and ethanol were used to make the electrolyte. A magnetic stirrer was used to continuously swirl the electrolyte as it was aged for an hour at a temperature of 130^0c. For the purpose of depositing CdZnS films, well cleaned ITO and FTO glasses were used as a substrate, and they were vertically placed into the electrolyte bath with the assistance of a rigid support. At time t=0, the electrolyte was mixed moderately at 220 rpm with 0.27M NH_2-CS-NH_2. The electrolyte was white at first, but as the deposition time increased, it turned yellowish, and after 20 minutes, film was finally deposited on the substrate. To get rid of organic contaminants and counter ions, films were rinsed with pure water for 25 seconds after they were deposited. The CdZnS films that were deposited on FTO and ITO glass substrates showed good adhesion and were physically stable. The CdZnS thin films that had been produced and placed on the two glasses were annealed in air at 350^0C.

Fig. 1.Experimental arrangement of CdZnS films by CBD method.

2.2. Characterization techniques

Powder X-ray diffraction (XRD) is used to characterise the crystal structure of CdZnS as deposited and annealed thin films placed on ITO and FTO glass substrate. CuKα radiation (λ=1.54Å) is used to record XRD patterns on a RigaKuC/max-2500 diffractometer at 40 kV and 30 mA between $2\theta = 20^0$ to 80^0. The surface morphology or particle distribution on the surface of CdZnS as deposited and annealed thin films has been observed using a field emission scanning electron microscope (Model: FESEM, Philip XL 30). Wettability study of CdZnS as deposited and

annealed thin films on both substrates have been done by water contact angle measuring apparatus (OCA Make-Dataphysics, Germany). The occurrence of chemical bonding in CdZnS as deposited and annealed thin films have been investigated using an FTIR spectrometer operating in the range 500–4000 cm^{-1} (Model: Perkin Elmer, Make: Spectrum RX I).

3. Results and discussion

3.1. Structural study

An essential method for characterising materials, X-ray diffraction (XRD) is used to determine their orientation, structure, nature, and other characteristics as well as their lattice parameters, flaws, stress, and strain. The XRD patterns of CdZnS as deposited and annealed thin films on (a) FTO and (b) ITO glass substrates are shown in Figure 2. Every peak in the spectrum has a label and identification. It is evident that upon depositing CdZnS films on ITO glass and annealing them at 350^0c, the film displays peaks on the spectrum at $2\theta=26.72^0$, 29^0, and 34.6^0. These peaks correspond to the (002), (101), and (102) diffraction planes of the crystalline hexagonal structure. The ITO substrate's reflections are responsible for the following peaks, which are a result of the (110) and (200) planes scattering. The availability of a significant number of defects is one of the main reasons because it is noticed that after annealing, there is no change in the crystal phase but that the intensities corresponding to the (002) and (102) diffraction peaks become sharper and more widened [16]. Nonetheless, once CdZnS films were applied to FTO glass and heated to 350^0c, the film displayed peaks on the spectrum at $2\theta=25^0$, 27^0, 34.6^0, and 58^0. These peaks correspond to the (100), (002), (101), and (202) diffraction planes. The peaks that follow are thought to be the result of scattering from the (102), (200), (104), and (203) planes, reflecting light from the FTO substrate. It is observed that peak intensities are sharper following annealing. The subsequently produced CdZnS thin films adhere well and are homogeneous. The structural characteristics of CdZnS, such as crystallite size (D), micro-strain (ε), and dislocation density (δ), were measured for both as deposited and annealed thin films on ITO and FTO glass substrates.

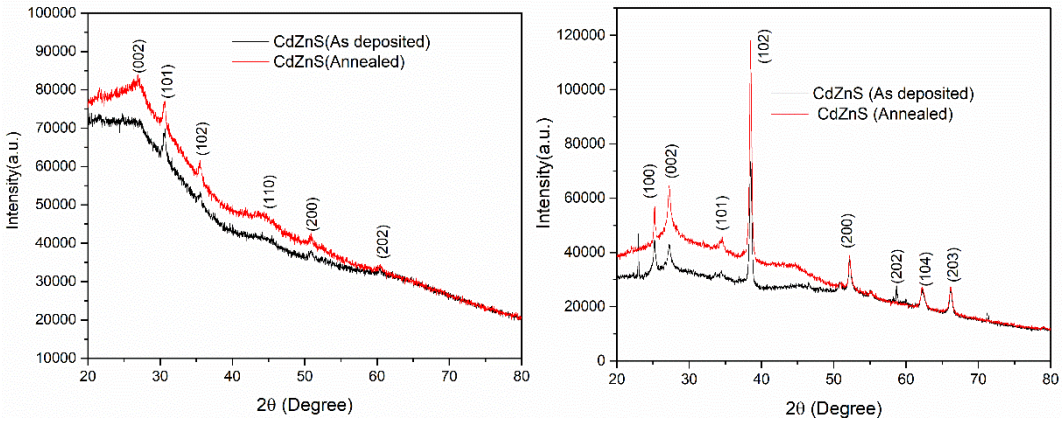

Fig. 2. XRD spectra of CdZnS as deposited and annealed films on (a) ITO and (b) FTO glasses.

The scherrer's formula [17] was used to determine the average grain size (D) of the CdZnS as deposited and annealed films placed on both glass substrates:

$$D = \frac{0.94\lambda}{\beta \mathrm{Cos}\theta} \qquad \text{(i)}$$

where λ is the wavelength of the X-rays (1.54Å), β is the full-width at half maxima(FWHM), and θ is the angle of diffraction.

The microstrain (ε) [18] of CdZnS as deposited and annealed films placed on both glass substrates can be calculated using the following equation:

$$\varepsilon = \frac{\beta \mathrm{Cos}\theta}{4} \quad \text{(ii)}$$

The equation [19] that follows can be used to compute the dislocation density (δ) of CdZnS as deposited and annealed films on both glass substrates:

$$\delta = \frac{1}{D^2} \quad \text{(iii)}$$

For CdZnS thin films that have been deposited and annealed on ITO substrate, have grain size 15.42 nm and 19.16 nm, respectively and the film on FTO substrate, they are 25 nm and 41.54 nm respectively. The improvement in crystallinity is evident from the annealing-induced rise in average grain size. The recombination centre at the grain borders is lowered as a result of the average grain size increases [15].

Table 1 below displays the crystallite size, FWHM, Micro-strain (Ɛ) and dislocation density of the CdZnS films deposited on FTO and ITO glass substrates. It suggests that after annealing, micro-strain and dislocation density decreases as grain size increases.

Table 1. Crystallite size, FWHM, Micro-strain and dislocation density of CdZnS as deposited and annealed thin films on ITO and FTO substrates.

Substrate used	Name of Sample	2θ	hkl plane	FWHM	Grain Size (D) (nm)	Micro strain (Ɛ)	Dislocation density (δ)(nm^{-2})
ITO	CdZnS as deposited	26.79^0	002	0.552	15.42	0.234×10^{-3}	0.0042057
	CdZnS Annealed	26.80^0	002	0.433	19.16	0.188×10^{-3}	0.0027241
FTO	CdZnS as deposited	26^0	002	0.340	25	0.144×10^{-3}	0.0016
	CdZnS Annealed	26^0	002	0.205	41.54	0.0871×10^{-3}	0.0005795

3.2. Field emission scanning electron microscope (FESEM)-surface morphology study

FESEM is a technique which is used to study the topography of the materials and it provides the crucial details about the particles grow and take their shape. Figure 3 (a), (b) show the surface morphology of CdZnS as deposited and annealed thin films deposited on ITO and fig 4(a), (b) indicates the films deposited on FTO glass substrates which has been studied using FESEM with magnification taken at 10.00KX. From figure 3 (a) it is observed that microstructure of the as deposited film on ITO substrate reveals that film surface was smooth, composed of tightly packed cloud of grains appear in the form of small needle shape of equal sizes with sharp and clear edges are evinced in cluster forms and interconnected with each other throughout the analysed area however annealed films shows small shaped spherical grains distributed in both single and cluster form throughout the studied area. Figure 4(a), CdZnS as deposited film coated on FTO substrate indicates that the surface are covered with grains of equal size throughout the entire surface in cluster forms whereas annealed film big spherical shaped grains are attached in fibres like structure on the whole analysed surface.

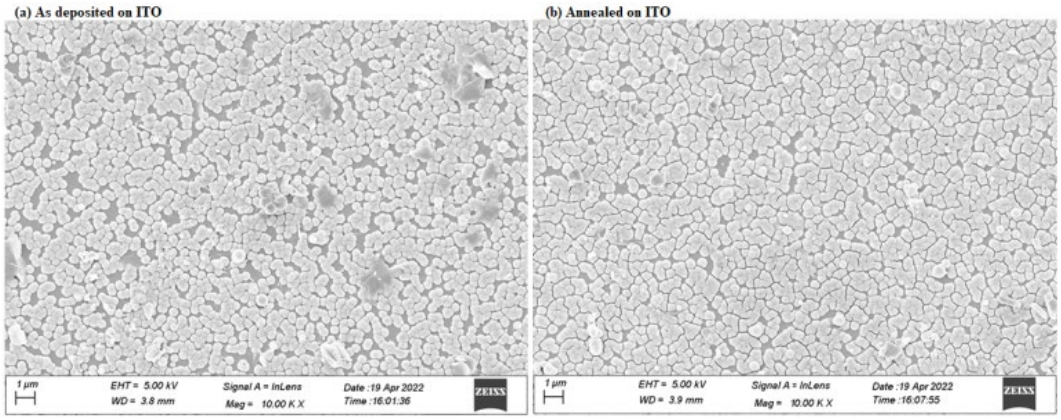

Fig. 3. FESEM micrograph of CdZnS as deposited (a) and annealed (b) thin films on ITO substrate.

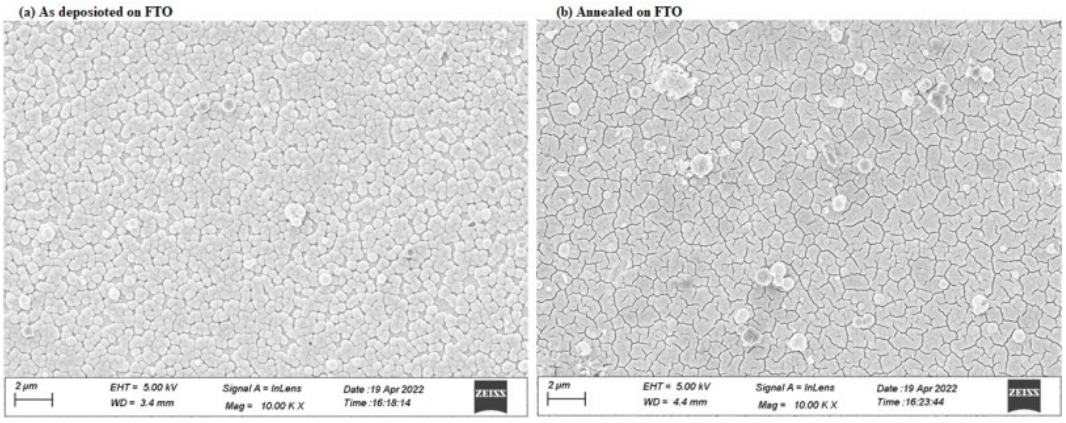

Fig. 4. FESEM micrograph of CdZnS as deposited (a) and annealed (b) thin films on FTO substrate.

3.3. Wettability study

For making the thin layer of CdS/ZnCdS deposited on ITO and FTO glass substrates beneficial for solar cell or smart window applications, wettability investigations is one of the crucial factors that must be taken under consideration. The measurement of the water contact angle (θ) is used to assess the wetness of the surface. A solid surface's hydrophobicity and hydrophilicity are key characteristics that determine whether water droplets interact with the surface of the material. When wettability is high, the surface is hydrophilic (contact angle $\theta<90^0$) and hydrophobic (contact angle $\theta>90^0$) [20, 21]. On the contrary, when wettability is low, the surface is hydrophobic. Figures 5 (a) and (b) depict the contact angle for CdZnS as deposited and annealed films on ITO glass substrate. It is noted that the WCA of the deposited film is 54.710, but the annealed film has a WCA of 67.700. The same investigation has been carried out when the synthesised material mentioned above is coated on the FTO glass substrate, as seen in figures 5(a) and (b). WCA is given as 83.410 for the as deposited film and 59.670 for the annealed film for this substrate. It may be concluded that both CdZnS films formed on ITO substrates have a hydrophilic quality, but that annealed CdZnS film on FTO substrates makes the surface more hydrophilic [22].

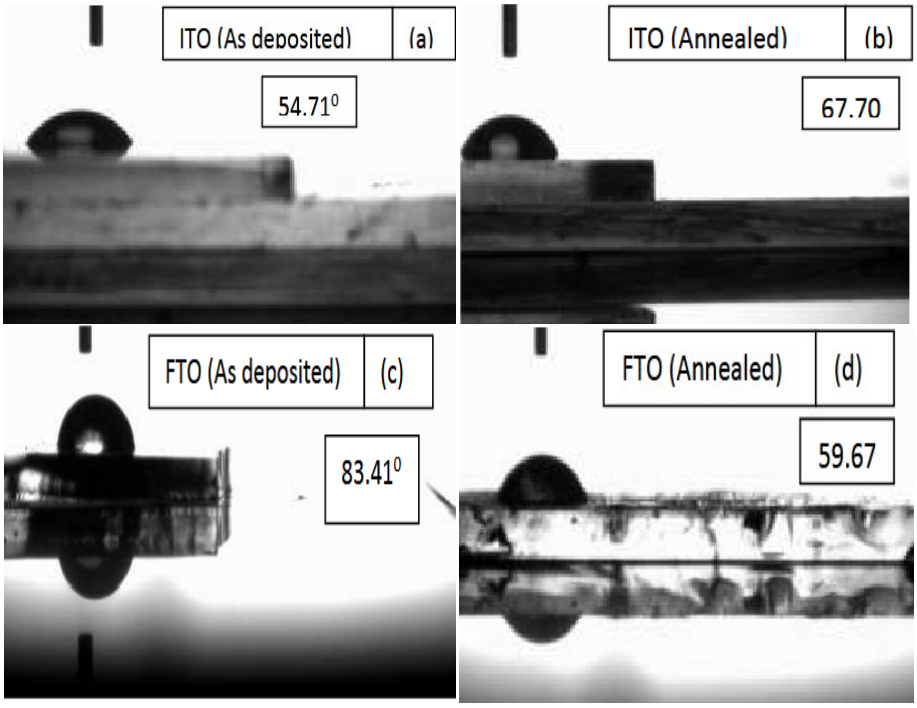

Fig. 5. (a,b) WCA image of as deposited and annealed CdZnS thin film on ITO and (c,d) as deposited and annealed CdZnS thin film on FTO

3.4.FTIR studies

One method for learning more about the chemical bonding that exists in a material is FTIR spectroscopy. It can be used to identify and explain the organic species and/or contents of the material. Figure 6 (a) and (b) depict the results of the FTIR analysis of CdZnS as deposited and annealed thin films developed at room temperature on ITO and FTO glass substrates using the chemical bath deposition method. The wave number range has been taken from 500cm^{-1} to 4000cm^{-1}. The features of their chemical bonding are revealed by the spectra's peaks. Regarding the two CdZnS films on the ITO substrate, graph 6(a) shows that the peak that appears at 3246 cm^{-1} can be attributed to the availability of –OH stretching as a result of air pressure [23]. Peak at 1660 cm^{-1} is ascribed to the O-H bending vibrational mode [24]. Because of ethylene glycol and ethanol, the absorption peak at 1434 cm^{-1} and 1136 cm^{-1} can be attributed to the C-O stretching vibration [25].

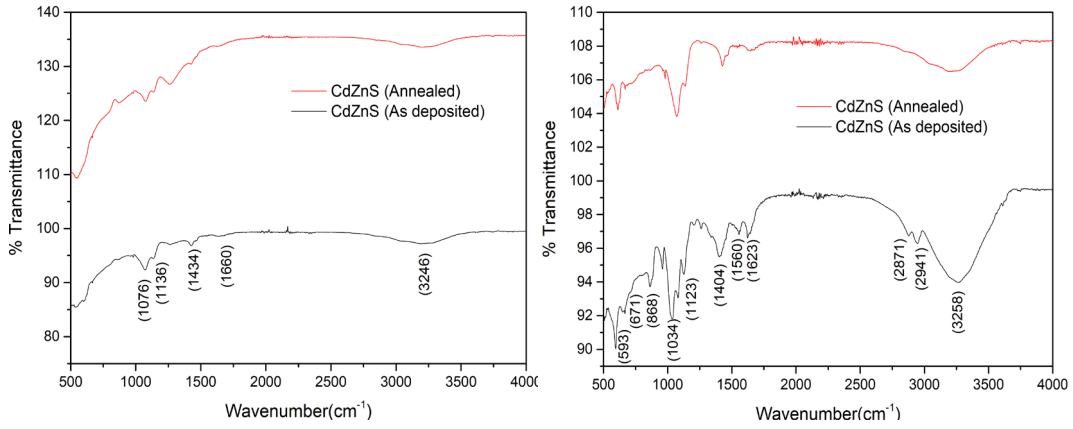

Fig. 6. FTIR spectra of CdZnS as deposited and annealed thin films on (a) ITO and (b) FTO glasses.

In the similar way, the interpretation on figure 6(b) have been discussed, which shows that the material deposited on the FTO substrate has a peak that appears at 3258 cm^{-1}, which can be attributed to the availability of –OH stretching. The peak that was seen at 2941 cm^{-1} and 2871 cm^{-1} is ascribed to the C-H stretching vibration, which indicates the species are present on the nanocrystal's surface [26]. The O-H bending vibrational mode can be accountable for the peak values at 1560 cm^{-1} and 1623 cm^{-1}. Because of ethylene glycol and ethanol, the absorption peak at 1404 cm^{-1} and 1123 cm^{-1} can be ascribed to the C-O stretching vibration. Peak was observed at 868 cm^{-1} with 671 cm^{-1} attributed to stretching vibrations of ZnS and CdS [25].

4. Conclusions

Cadmium acetate, $ZnSO_4$, and NH_2-CS-NH_2 are used to develop CdZnS thin films on FTO and ITO glass substrates using chemical bath deposition in a non-aqueous solution. The films exhibit good adhesion and are found physically stable. XRD, FESEM, WCA, and FTIR have been used to characterise the films as deposited and annealed. According to the XRD results, the nucleation of the reaction deposition is connected to the hexagonal structure of the CdZnS thin films, which have a (002) plane. Both the CdZnS films formed on ITO and FTO substrates have a hydrophilic quality; however, the annealed CdZnS film on FTO substrates makes the surface more hydrophilic. Various chemical bonds present in the films have been identified by FTIR study. The Peaks at 868 cm^{-1} and 671 cm^{-1} attributed to stretching vibrations of ZnS and CdS. The aforementioned feature suggests that it may be appropriate for window layers in solar cells application.

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