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To cite this article: J. O. Emegha *et al* 2021 *J. Phys.: Conf. Ser.* **1734** 012045

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Growth and characterization of copper cadmium sulphide thin films

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Abstract. Copper cadmium sulphide thin film was deposited onto glass (soda-lime) substrates using chemical bath deposition (CBD) technique at room temperature. Chemical, optical, structural, and microstructural features were examined via the Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), UV-Vis Spectroscopy, and High-resolution Transmission Electron Microscopy (HRTEM). FTIR revealed that the associated chemical bond was below the 900 cm⁻¹ marks. The optical band-gap of 2.36 eV was estimated from the absorption analysis. X-ray diffraction measurements reveal that the deposited material is polycrystalline with hexagonal and cubic structures typical of the binary constituents of and thin films. The grain sizes were randomly distributed and ranged between 35 and 60 nm as indicated by the HRTEM.

Keywords: Chemical bath deposition, *CuCdS*, Thin films, Band gap, X-ray diffraction

1. Introduction

Actually, the interest in cadmium sulphide (*CdS*) thin films is due to its unique properties and potential applications in optical and electronic equipment such as field effect transistors, LEDs, hetero-junction solar cells, photo-catalysis, semiconductor laser, piezo-electronics, NIR-detections and energy storage system [1-3]. Advances in nanocrystalline architecture reveal that *CdS* has a unique band-gap of 2.42 eV, low electrical resistivity as well as high transmittance in the ultraviolet and visible electromagnetic regions [2, 4]. Several physical and chemical deposition methods have been used to prepare *CdS* thin films such as metal organic chemical vapour deposition technique (MOCVD) [5], vacuum thermal evaporation [2], SILAR [3], chemical spray pyrolysis [6] electro-deposition [7] as well as chemical bath deposition (CBD) [1,8-10]. Chemical bath deposition technique has been widely used to fabricate high quality thin films owing to its several advantages over the other methods which include; low cost of deposition, simplicity, excellent film substrates adhesion, low growth temperature and uniformity of films [11]. Due to its high deposition rate, the properties of CBD deposited materials can be manipulated by varying the growth process such as deposition time, concentrations, precursors



and annealing. Besides the deposition process, another determining factor affecting the properties of CdS is doping with an appropriate elements.

Doping CdS films with elements like zinc, tin, aluminium, lead, boron, indium, sodium, silver, manganese, gallium and copper have been reported [12]. Copper doped cadmium sulphide ($Cu-Cd-S$) thin films preparation using CBD has been shown to influence the physiochemical properties of the material such as crystalline structure, band-gap, electrical conductivity, mobility, etc. Hussain et al., [13], have reported a reduction in optical band-gap of $Cu-Cd-S$ thin films from 2.50 eV to 2.21 eV due to the extrinsic properties of copper. Similar observations have been reported by Ganesh et al., (2014)[14] and Sharma et al., (2016)[15] using chemical bath deposition process. They attributed such observation to the effects of increase in structural crystallinity and the quantum confinement. Despite several researchers have worked on $Cu-Cd-S$ thin films using CBD technique, limited effort have been extended to using sodium sulphide Na_2S as the source of sulphur as well as potassium hydroxide (KOH) and ammonia nitrate (NH_4NO_3) as complexing agents. In this study, a $Cu-Cd-S$ thin film was synthesized via the CBD method using Na_2S as the source of the anion besides the complexing agents of KOH and NH_4NO_3 . The resultant films were investigated for its chemical, optical, structural and morphological properties.

2. Materials and Methods

2.1 Chemicals

The following analytical chemicals were used without further purification: copper (II) chloride dehydrate ($CuCl_2 \cdot 2H_2O$), cadmium chloride ($CdCl_2$), sodium sulphide (Na_2S), ammonia nitrate (NH_4NO_3), potassium hydroxide (KOH) and distilled water.

2.2 Deposition of $Cu-Cd-S$ thin films

$Cu-Cd-S$ thin films were prepared using the chemical bath deposition (CBD) technique. The reacting solution contains 10 ml of copper chloride dehydrate, 10 ml cadmium chloride, 20 ml sodium sulphide and distilled water. The bath pH was maintained using potassium hydroxide at 9.0. The solution was stirred thoroughly for some minutes and clean substrates were inserted vertically for about 12 hours. However, the substrates had earlier been cleaned using the procedure outline in Emegha et al.[16]. After deposition, the substrates coated with $Cu-Cd-S$ films were taken out, washed and dried at 24 °C.

Generally, the deposition of $Cu-Cd-S$ thin films via CBD process is based on the slow release of Cu^{2+} , Cd^{2+} and S^{2-} ions by the corresponding complexing agents and subsequently the nucleation of the films on the substrates. The chemical mechanism of the films formation and deposition is as follows: The dissociation of sodium sulphide to obtain sulphur ions (S^{2-}):



The NH_4NO_3 and KOH would react to release NH_4^+ and OH^- ions, therefore obtaining ammonia (NH_3) [17]:





When ammonia is added to the various salts solutions (Cu^{2+} and Cd^{2+}) their tetra-amine complexes are produced; thus:



When reaction (1), (5) and (6) is adequately slow, a heterogeneous nucleation of $CuCdS$ would occur on the inner walls of the beakers as well as on the immersed substrates, and the deposition of the material can be expected in each reaction.

2.3 Film Characterization

The chemical properties of the precursor and film were considered with the aid of Fourier transform infrared (FTIR) spectroscopy. The FTIR analyses were recorded using Shimadzu 8400S FTIR-Spectrometer under potassium bromide (KBr) background in the wavelength range of 4000 to 400 cm^{-1} . The optical characterization was obtained with UV-Vis Shimadzu 1800 spectrophotometer in the standard range of 300 to 1500 nm. The XRD was used for the crystallinity of the film. The observation was made using Bruker D8 Advanced X-ray diffractometer with a scanning rate of 1 degree per minute and a $CuK\alpha$ radiation of 1.5406 Å. TECNAI-F20 HRTEM was used to study the microstructure of the film.

3. Results and discussion

Figure 1 indicates the typical FTIR spectrum of $CuCdS$ precursor and the functional groups in KBr background. It indicated that the $CuCdS$ vibration is below the 900 cm^{-1} band. A broad band connected to the O-H group was also observed at 3444.98 and 3134.43 cm^{-1} . These bands were associated to the O-H and N-H vibrations of the spectrum. The occurrence of a broad OH band and two peaks indicated the existence of amino salt within the films [18]. The C-H stretching vibrations are responsible for the bands observed at 2970.48 and 2363.88 cm^{-1} . The bands between 1982.89 and 1637.62 cm^{-1} are related to the $C=C$. The vibration at 1560.46 cm^{-1} is attributed to $C=O$ stretching mode. Bonding within 1485.24 and 1111.03 cm^{-1} region consist of the C-H stretching vibrations. C-O stretching vibration is observed at 1026 to 900 cm^{-1} region of the spectrum. Figure 2 indicates the FTIR spectrum of $CuCdS$ film at room temperature. The spectrum exhibits no characteristic bands associated with the complex precursor. This observation is due to the complete breakdown of the precursor to yield $CuCdS$ films. A situation that is common to metal chalcogenides [19].

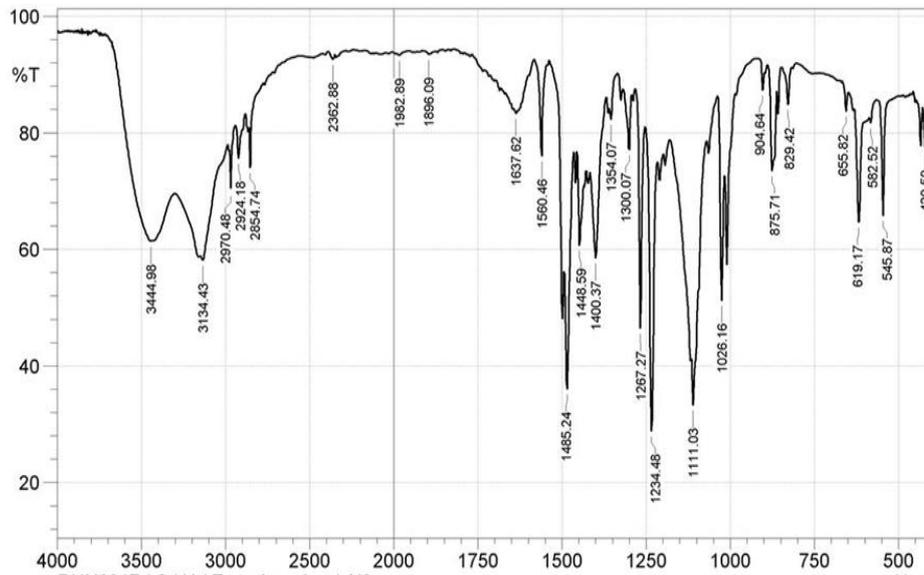


Figure 1: FTIR spectrum of *CuCdS* precursor

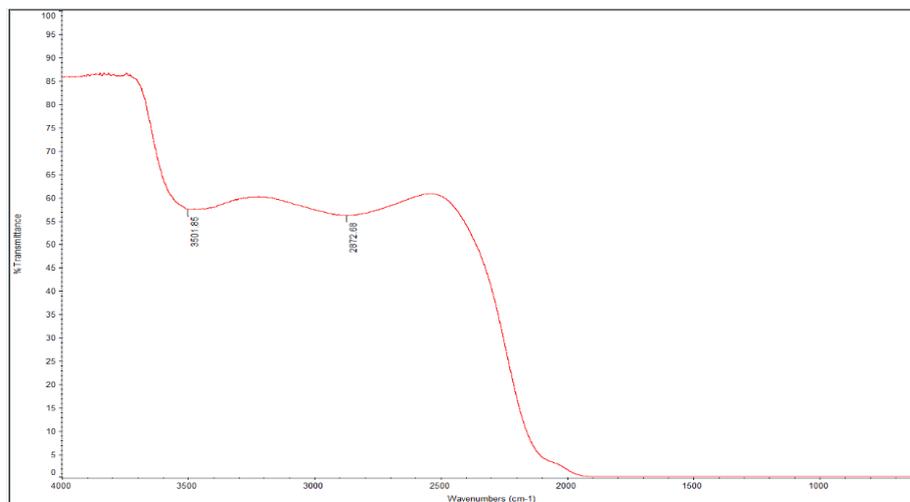


Figure 2: FTIR spectrum of the deposited *CuCdS* thin film

The optical absorption spectrum of *CuCdS* thin film is shown in Figure 3. It is clear from the graph that the optical absorption decreases with the increase in the electromagnetic wavelength which shows that the material is very absorbing in the UV and visible regions. Similar observations have been indicated in Damisa et al [20], and ascribed it to the presence of some impurities within the substrates as well as the deposited metal-sulphide films. This is possible as some elements from the substrates diffuse into the film during deposition process.

The (direct) band gap energy (E_g) of *CuCdS* film was calculated using the Tauc's relation [20] which depends on the incident photo energy and the absorption coefficient of the material. Thus the relation is given as:

$$\alpha = \left(\frac{A}{hv} \right) [hv - E_g]^n \quad (8)$$

where E_g is the band gap energy, α is the coefficient of absorption, and photon energy is given as hv . The transition probability depended constant is represented by A while n is taken as $1/2$. Figure 4 illustrates the graph of $(\alpha hv)^2$ against h . The graph of $(\alpha hv)^2$ against hv produced a straight line that is extrapolated to zero at the photo energy (hv) axis. The interception of the straight line at $h\nu$ -axis gives the optical band gap (E_g) value of *CuCdS* thin film. From Figure 4, the determined optical band-gap energy was found to be 2.36 eV. This value confirms that *CuCdS* film is a ternary material whose optical band-gap lies between *CdS* and *CuS* value of 2.44 eV and 1.70 eV respectively [9,21], hence, keeping the Vegard's rule of mixtures. The obtained value using chemical bath deposition is consistent with the values of other researchers using other routes for *CuCdS* thin films in literature.

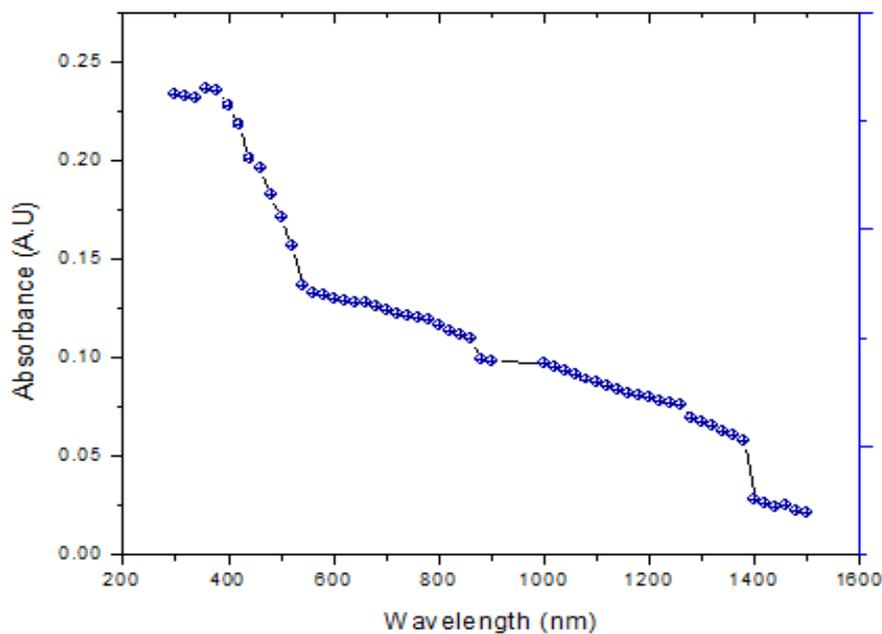


Figure 3: UV-visible absorption spectrum of *CuCdS* thin film

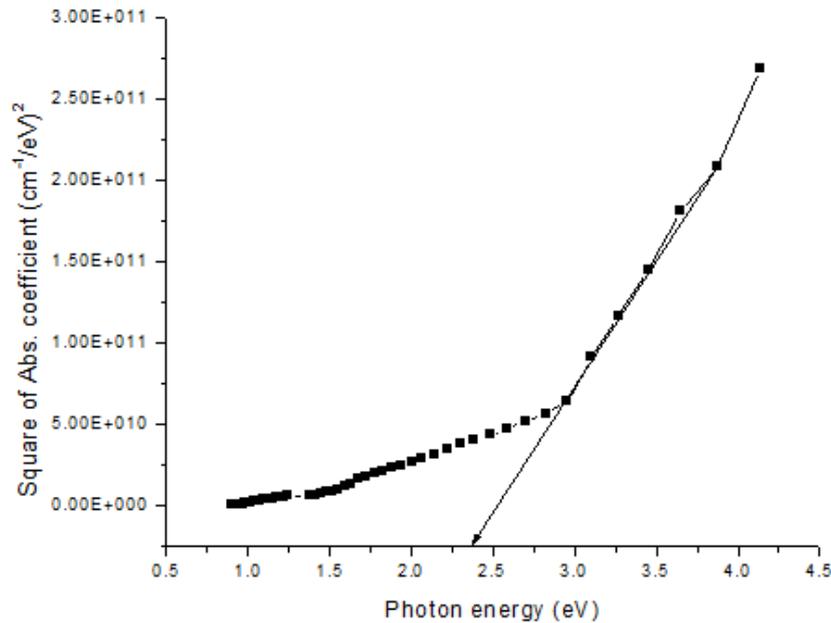


Figure 4: Absorption coefficient square vs photon energy for *CuCdS* thin film

Figure 5 shows the XRD measurement of the deposited *CuCdS* film in the range of angle 2θ from 10° to 45° . Peaks were observed at 13.83° (100), 21.03° (003), 29.58° (102), 32.61° (200), 34.84° (210), 36.07° (111) confirming the polycrystalline nature of CBD deposited film. As long as *CuCdS* films do not have a standard XRD pattern, the deposited material was compared against the peaks of *CuS* and *CdS*. Interestingly, the spectrum shows diffraction peaks of hexagonal *CdS* (card number 41-1049) at (101), (102) and (210). Cubic structured *CdS* (card number 78-0653) with corresponding peaks at (111) and (200) planes were also deduced. Additionally, the spectrum exhibits the hexagonal *CuS* (card number 78-0876) peaks at (101), (103) and (102) planes. From the XRD spectrum, it can be observed that the *Cu–Cd–S* film is a mixture of *CuS* and polymorphous *CdS* planes. This might be due to surface re-organization taking place within the films caused by the incorporation of copper into cadmium sulphide system. Similar observation have been reported in literature [22]. The average crystallite size of the most prominent peak (200) of the films was estimated using the Debye-scherrer's formula:

$$D = \frac{\lambda}{\beta \cos \theta} \quad (9)$$

where λ is the x-rays wavelength of, the Bragg angle is θ , and β is the full width at half maximum (FWHM) of the peak. Since the accuracy of Equation 9 is questionable for polycrystalline thin films [3], the estimated result was confirmed by analyzing the HRTEM picture of the film.

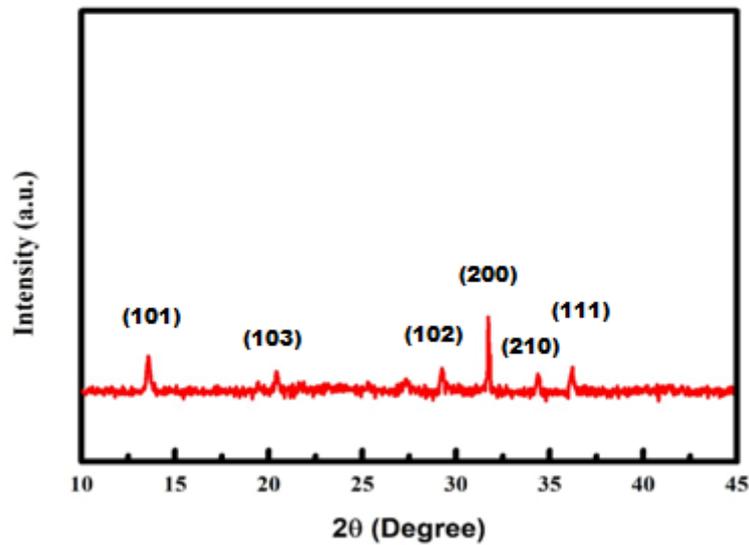


Figure 5: X-ray diffraction pattern of $CuCdS$ thin film

To obtain a better insight into the microstructural properties of $Cu-Cd-S$ thin film, the high-resolution transmission electron microscopy (HRTEM) measurement was employed. Figure 6(a) and 6(b) show the HRTEM micrographs of the film at various magnifications. The pictures indicated that the film consist of randomly distributed ellipsoidal grains with un-even sizes. The HRTEM revealed that the grains dimensions ranged between 35 and 60 nm with an average of about 47 nm. Figure 6(c) indicates that the substance deposited is polycrystalline from the associated selected area electron diffraction (SAED) pattern. The bright Debye Scherrer's rings confirmed that the chemically deposited $Cu-Cd-S$ thin film is consist of clusters of grains [19] A good correlation was found to exist between the grain sizes calculated from XRD and HRTEM studies.

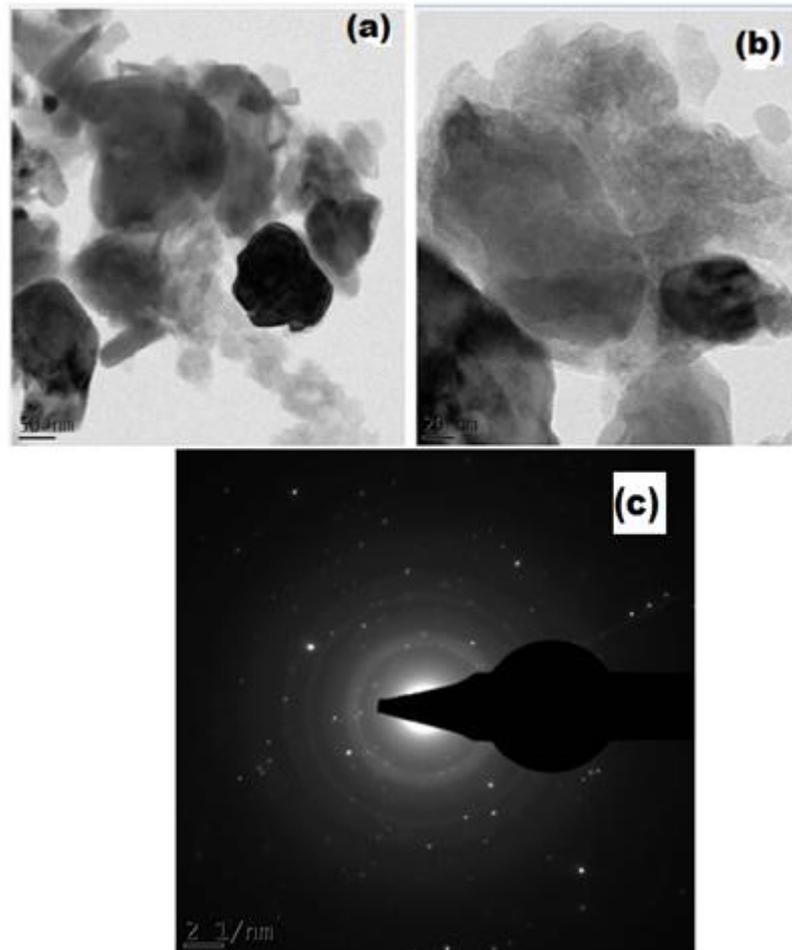


Figure 6: HR-TEM of *CuCdS* thin films (a) at 50 nm magnification (b) at 20 nm magnification (c) SAED pattern of *CuCdS* thin films

Conclusion

The spectra, crystalline and morphological properties confirmed that the CBD method is a reliable and useful technique in synthesizing copper cadmium sulphide (*CuCdS*) thin films. FTIR characterization indicated that the *Cu–Cd–S* band was below the 1000 cm^{-1} mark. The direct E_g was found to be 2.36 eV with absorption that decreases with the electromagnetic wavelength. The XRD and HRTEM analyses confirmed the polycrystalline nature of the deposited material with grains in the range of 47 nm.

Acknowledgement

The authors wish to appreciate the management of Covenant University for their financial support

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