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Preparation and Physical Properties of $Cu_xZn_{1-x}S$ Thin Films Deposited by Metal Organic Chemical Vapour Deposition Technique

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Copper Zinc Sulphide ($Cu_xZn_{1-x}S$) thin films were prepared and deposited using metal organic chemical vapour deposition (MOCVD) technique. The films were studied using Rutherford backscattering (RBS) spectroscopy for elemental composition and thickness, X-ray diffraction (XRD) for crystallographic structure, Scanning electron microscopy (SEM) for surface morphology and Ultraviolet-Visible spectroscopy analysis for optical characterization. Experimental results showed that all the films were polycrystalline with good adherent with the substrate. The direct optical band gap changes from 2.20 eV to 3.42 eV for different values of x with an average transmittance of above 80%. SEM analysis showed that the deposited films are dense in nature with well defined grains of different sizes. The study demonstrates that the properties of the deposited films were strongly influenced by the copper / zinc concentrations in $Cu_xZn_{1-x}S$ matrix.

Keywords: Dithiocarbamate; MOCVD; precursor; thin films; RBS.

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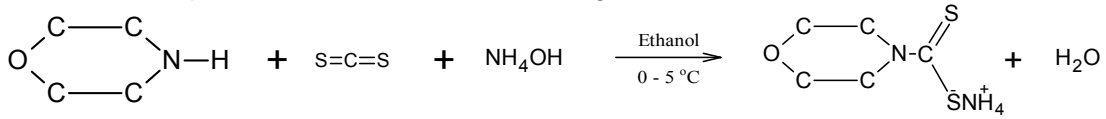
1. INTRODUCTION

In solid state technology, ternary semiconducting thin films have very important role in modern electronics and photonic devices due to their diverse structural and elemental properties. $Cu_xZn_{1-x}S$ as a ternary semiconductor is on high demand due to its wide band gap and high coefficient of absorption [1]. It has found applications in absorber and window materials in solar cell fabrication [2,3], in light emitting diodes (LEDs), plasma display devices, lasers and sensors [4,5]. Up to now, different techniques have been reported to deposited $Cu_xZn_{1-x}S$ thin films, such as SILAR[1], Chemical spray pyrolysis [2-3,6], chemical bath deposition [7,8], solution growth technique[5], electron beam evaporation [4] and electrochemical atomic layer deposition [9]. Most of these methods have their various deficiencies ranging from lack of reproducibility in composition of films to non-uniformity of films due to the use of two or more precursors with different aerosol properties [10,11].

In the present study, metal organic chemical vapour deposition (MOCVD) technique is used to produce $Cu_xZn_{1-x}S$ crystalline thin films. MOCVD as a relatively new deposition technique is used to produce high quality films for industrial applications [12]. It is an improvement over liquid phase epitaxy and vapour phase epitaxy. The attraction of this technique is in its adaptability to large area deposition, cost effectiveness, simple apparatus and low deposition temperature range [13-15]. It is also attractive in its use of single solid source precursor with the ability to modify the process for better reproducibility of the film with desired properties [16]. The preparation of copper dithiocarbamate and zinc dithiocarbamate as a single solid source precursors and the deposition of $Cu_xZn_{1-x}S$ thin films on glass (soda lime) substrates at a deposition temperature of 400^0C is reported. Elemental, structural and optical properties of the deposited films are discussed.

2. EXPERIMENT DETAILS

The synthesis of the intermediate precursor of ammonium morpholino-dithiocarbamate was achieved by the method reported by Ajayi et al. [17] according to the reaction scheme 1.



Scheme 1.

The single solid source precursors of copper dithiocarbamate and zinc dithiocarbamate were prepared from ammonium morpholino-dithiocarbamate, copper (11) chloride, zinc chloride, ethanol, acetone and water.

Copper dithiocarbamate was prepared by dissolving 18.75g of ammonium morpholino-dithiocarbamate in a solvent of acetone and water in a beaker. 8.869g of copper (II) chloride was also completely dissolved in $60cm^3$ of ethanol separately. The solution of copper (II) chloride in ethanol was added gradually to the solution of ammonium morpholino-dithiocarbamate on a hot plate and stirred continually. The formation of dark-brown precipitate typical of copper dithiocarbamate was formed. The precipitate formed was oven dried for several hours at 50ºC.

Similarly, zinc dithiocarbamate was prepared by dissolving 18.499g of ammonium morpholino-dithiocarbamate in a solvent of acetone and water. 6.997g of zinc chloride dissolved separately in 60 cm^3 of water was gradually added to the solution of ammonium morpholino-dithiocarbamate on a hot plate and vigorously stirred. There was a spontaneous formation of white precipitate as the addition proceeds. The solution was filtered under gravity and allowed to dry in air for hours. The product, zinc dithiocarbamate had a mass of 11.65g.

Samples of the corresponding precursors were weighted and the different proportion of the precursors according to their atomic mass ratio in quantities is presented in Table 1. The precursors were properly mixed to a fine powder before being poured into an unheated receptacle and nitrogen gas was passed through the precursors at a rate of $2.0dm^3$/min. The nitrogen borne precursors were moved into the working chamber maintained at 400ºC by an electrically heated furnace. At the chamber, the precursors sublime first before thermal decomposition which resulted in the $Cu_xZn_{1-x}S$ thin films. Each deposition process was maintained for 2 hours. The MOCVD experimental setup is illustrated in Fig. 1.

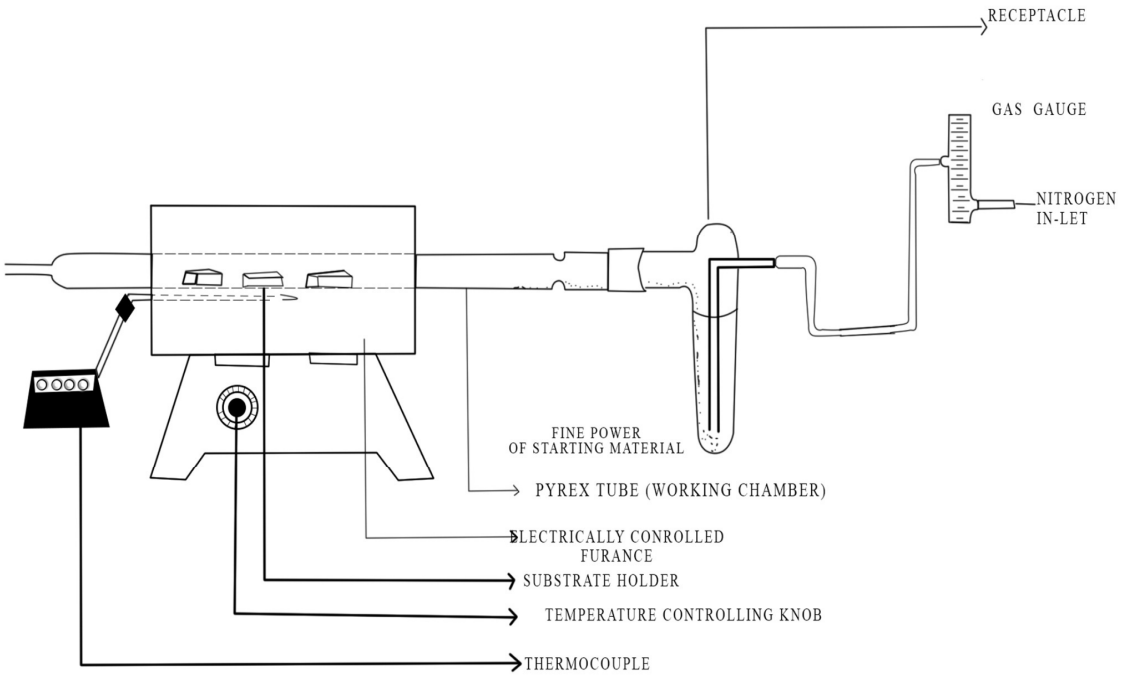


Fig. 1. Experimental set-up of the MOCVD Pyrolysis of the precursors

Table 1. Composition by weight (g) of the constituent elements in the various samples of $Cu_xZn_{1-x}S$ thin films

Samples	Value of x in $Cu_xZn_{1-x}S$	% by weight of copper dithiocarbamate	% by weight of zinc dithiocarbamate	Deposition temperature (^0C)
B_1	0.9	45	5	400
B_2	0.7	35	15	400
B_3	0.3	15	35	400
B_4	0.1	5	45	400

RBS was employed to determine the thickness and the elemental composition of the films. The X-ray diffraction pattern was tested by D8-High resolution x-ray diffractometer with radiation of 1.5406Å

The surface morphology was observed by scanning electron microscope of model JEOL JSM-7600F while the optical properties of the films was investigated using Double beam UV-1800 Shimadzu spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Compositional Studies

The elemental composition, thickness and stoichiometry of the deposited $Cu_xZn_{1-x}S$ thin films were determined using RBS techniques. Fig.2. displays the typical spectra obtained for Sample B_1. The other films at different concentrations show similar display. From all the spectra, the presence of Copper, Zinc and Sulphur were clearly shown. Also, the presence of nitrogen (N) impurity which may be from the carrier gas was also observed in small quantity in some of the films. This result suggests a complete decomposition of the precursors to produce Cu-Zn-S stable compound. Further examination revealed that the ratio of the Cu:Zn:S in the precursors are not preserved in the thin films. This effect had been reported in literature by other authors [18,19]. The confirmation that the stoichiometry of the elements in the precursor is not same as that of the deposited films can be credited to the possible breaking of the metal-metal bond of the precursor in the vapour phase at the deposited temperature and further reconstitution of the bonds resulting in different stoichiometry of the

film [20]. This indicates that the stoichiometry of the deposited films is not only controlled by concentration of the films but also the deposition temperature.

The film thickness was estimated using the knowledge of the material density given in Equation (1) [18]. The thickness and composition obtained are summarized in Table 2. From the table, it was revealed that the film composition has been altered as copper concentration was seemingly decreased from x = 0.90 to 0.10 which, therefore, implies that MOCVD is a convenient technique for producing desired films from the precursors. The film thickness obtained does not follow a regular pattern as it varies from 25.85 nm to 57.56 nm over the ranges. Sample B_2 has the highest thickness while Sample B_4 recorded the lowest with the rest films having values between the two extremes.

Thickness = atom per unit area / atom per unit volume (1)

3.2 Structural Examination

The x-ray diffraction patterns of $Cu_xZn_{1-x}S$ thin films is presented here. The diffraction angle of 2θ was scanned in the range of 5^o to 90^o. Fig.3. shows the diffraction pattern of Sample B_1. It is seen from the figure that peaks appear at 7.00^o, 9.78^o, 13.50^o, 29.00^o, 31.50^o and 38.49^o. Furthermore, there are other peaks that appear in relatively low intensities. Apart from these characteristic peaks, no peak that corresponds to either copper sulphide, zinc sulphide or their complex oxides could be seen within the detection limit of the XRD, indicating that the film does not have a secondary phase formation. The XRD spectra of the other Samples are similar. All the films have sharp peaks indicating that they are polycrystalline in nature [21]. Also, the films show an intense peak at 2θ =7.00 which decreases with copper concentration. This observation is consistent with that reported by Ortiz-Ramos et al. [22] which they attributed to the effect of copper concentration within the film matrix.

Fig.4. Shows the SEM micrographs of $Cu_xZn_{1-x}S$ thin films for various concentrations. The SEM micrographs revealed a crystalline film that has good adhesion with the substrates. Nearly all the films are composed of dense and well defined shaped grains of different sizes that are uniformly distributed. Most of the grains are interconnected to each other without cracks or pinholes. Careful observation showed that there is a critical difference in the morphological structure within the films as the concentration of copper is decreased. This may be attributed to the different expansion coefficients present within the films. A similar copper/zinc concentration dependent grains sizes were reported by Rahman et al. [23]. The SEM results confirmed that decreasing copper (or increasing zinc) concentration had great effect in controlling the surface morphology of the MOCVD deposited films.

3.3 Optical Characterization

A plot of the optical transmittance spectra against wavelength is shown in Fig. 5. It was observed that the films had a very high transmittance of above 80% in the visible and near infrared regions. Sample B_2 had the least transmittance in the infrared region and Sample B_3 had the highest in same region. Also, copper concentrations were found to decrease with transmittance. This observation agrees well with Ezenwa and Okoli [8] who reported a transmittance of above 80% in the visible and infra-red regions. A somewhat lower transmittance was reported by Uhuegbu and Babatunde [5]. They attributed the high transmittance to the enhanced crystalinity of the films, which in turn, reduces the defects in the grain boundaries. Films of such high transmittance could serve as transparent conducting materials in LEDs and solar cells.

Table 2. Film compositional analysis and thickness investigated by Rutherford backscattering spectroscopy of $Cu_xZn_{1-x}S$

Samples	Nature	% Composition			RBS thickness ($Atoms/cm^2$)	Linear thickness (nm)
		Cu	Zn	S		
B_1	$Cu_{0.9}Zn_{0.1}S$	31.5	31.4	37.1	274.96×10^{15}	44.49
B_2	$Cu_{0.7}Zn_{0.3}S$	30.3	30.5	39.2	351.19×10^{15}	57.56
B_3	$Cu_{0.3}Zn_{0.7}S$	27.7	34.6	38.1	318.96×10^{15}	52.29
B_4	$Cu_{0.1}Zn_{0.9}S$	28.7	35.0	36.3	158.96×10^{15}	25.85

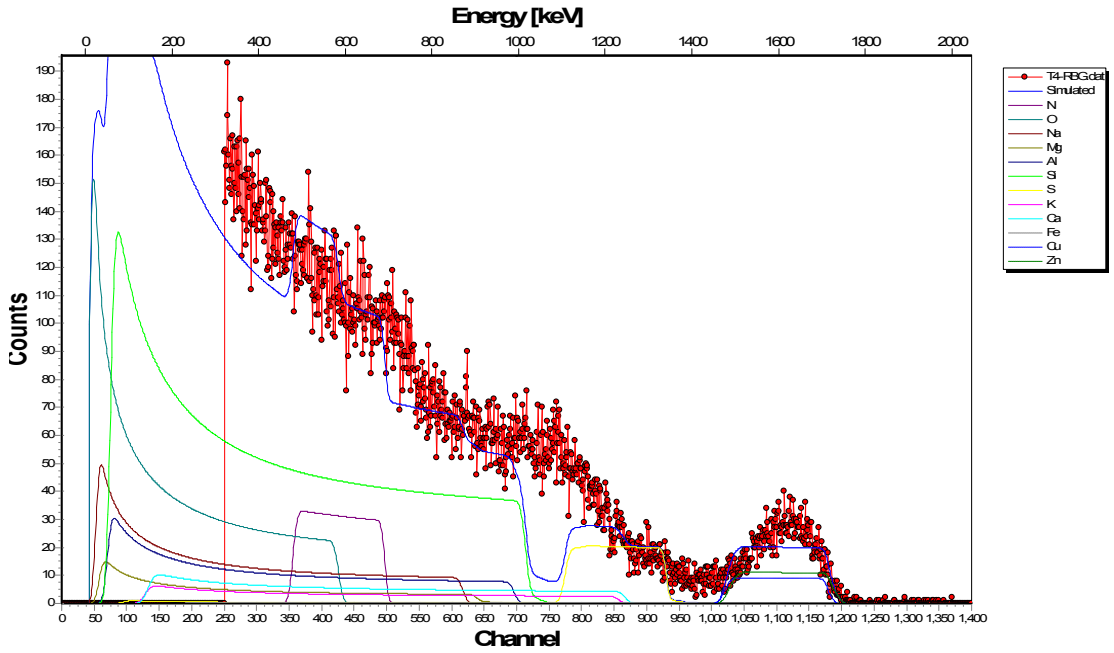


Fig. 2. Rutherford backscattering spectrum of $Cu_xZn_{1-x}S$ thin film (Sample B_1)

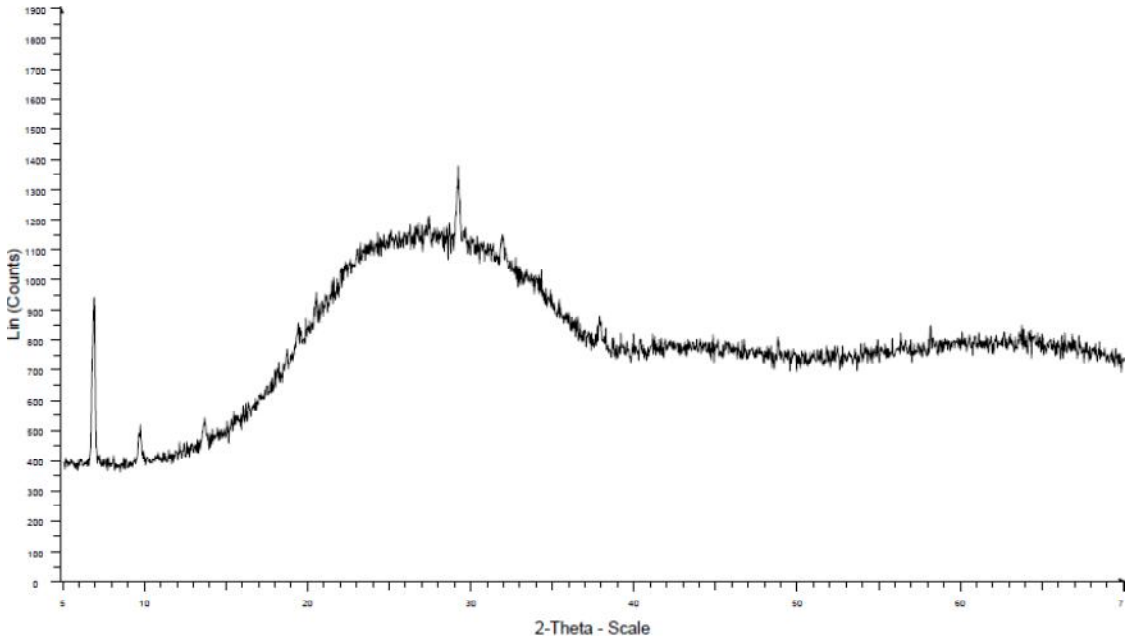


Fig. 3. X-ray diffraction pattern of of $Cu_xZn_{1-x}S$ thin film (Sample B_1)

The direct optical band gap (E_g) of the deposited films was estimated by plotting $(\propto h\nu)^2$ against photon energy ($h\nu$). The estimated values of the direct optical band gaps are 2.20 eV (Sample B_1), 2.25eV (Sample B_2), 3.35 eV (sample B_3) and 3.42 eV (Sample B_4) as shown in Fig. 6. For all compositions, the direct optical band gap increases with zinc concentrations. The variation in the direct band gap energy with zinc or copper concentration was found to be somewhat linear which is due to the fact that the band gap energy of ZnS thin films is greater than that of CuS thin

films. This increase toward higher energy side is in accordance with the trend reported in literature. Sreejith et al. [24] reported that the direct optical band gap of the films varies from 1.8 eV to 3.40 eV on increasing zinc (or decreasing copper) concentration in the films. Direct optical band gap of 1.8eV to 3.50eV was also estimated by Noriyuki et al. [3] on decreasing copper concentration in $Cu_xZn_{1-x}S$ matrix. The increase in direct optical band gap energy is indicative of the increase in grain size and reduction in structural defects [24]. It can also be as a result of the famous Burstein-Moss effect. Another possibility for the direct optical band gap increase can be attributed to quantum size effects [25].

Furthermore, such films can find application in solar cell fabrication since the film will allows more short wavelength photons to reach the absorber layer and generate more photocurrent than binary CuS thin films [26,27].

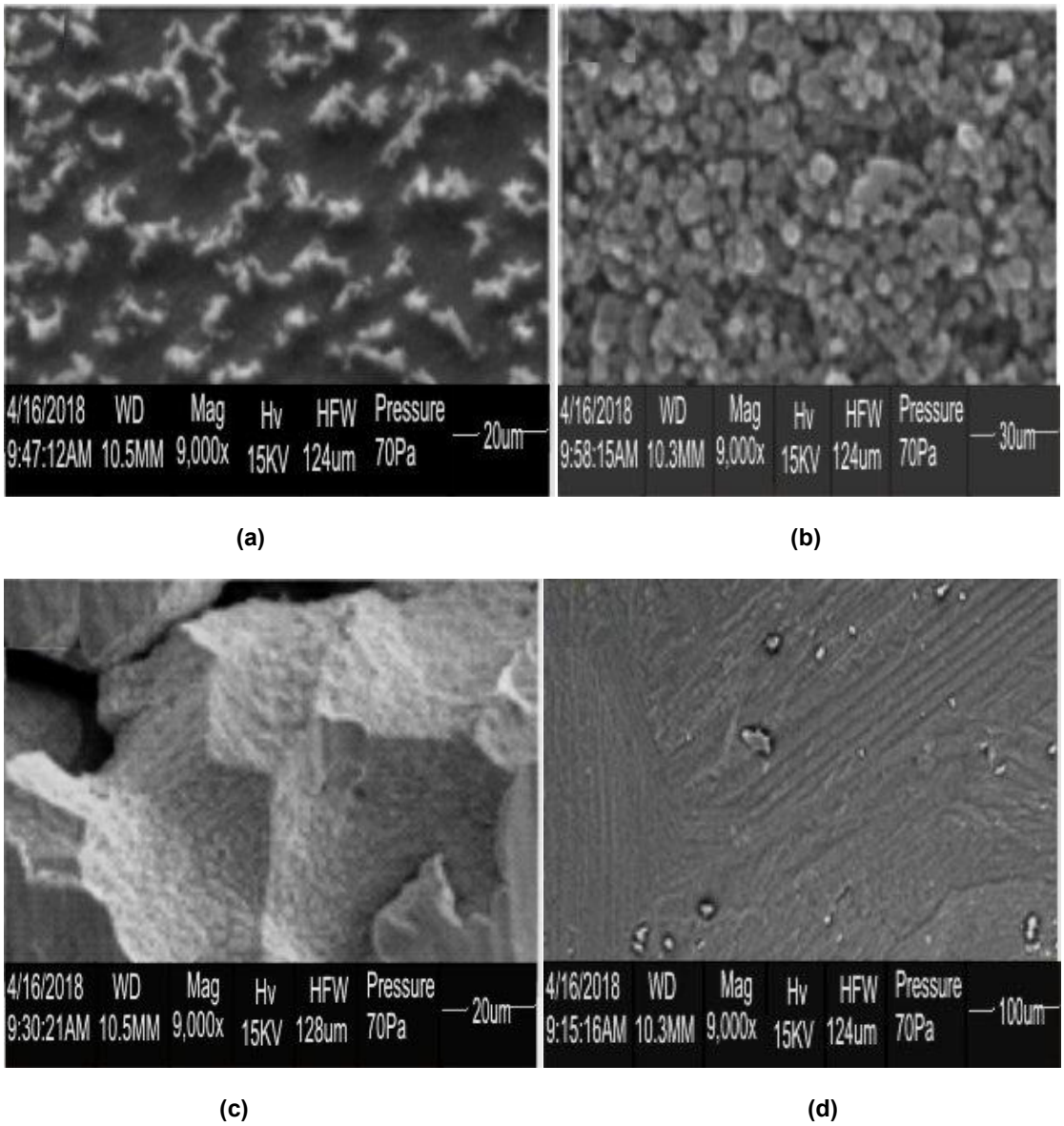


Fig. 4. The SEM micrograph of deposited thin films of $Cu_xZn_{1-x}S$: (a) sample B_1, (b) sample B_2, (c) sample B_3 and (d) sample B_4

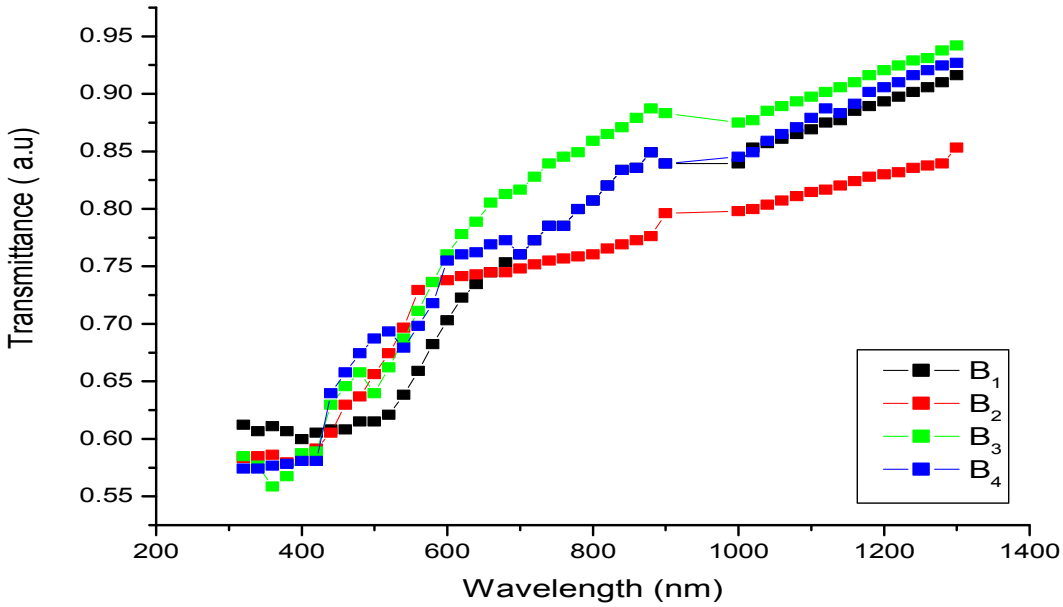


Fig. 5. Transmittance versus wavelength of the deposited $Cu_xZn_{1-x}S$

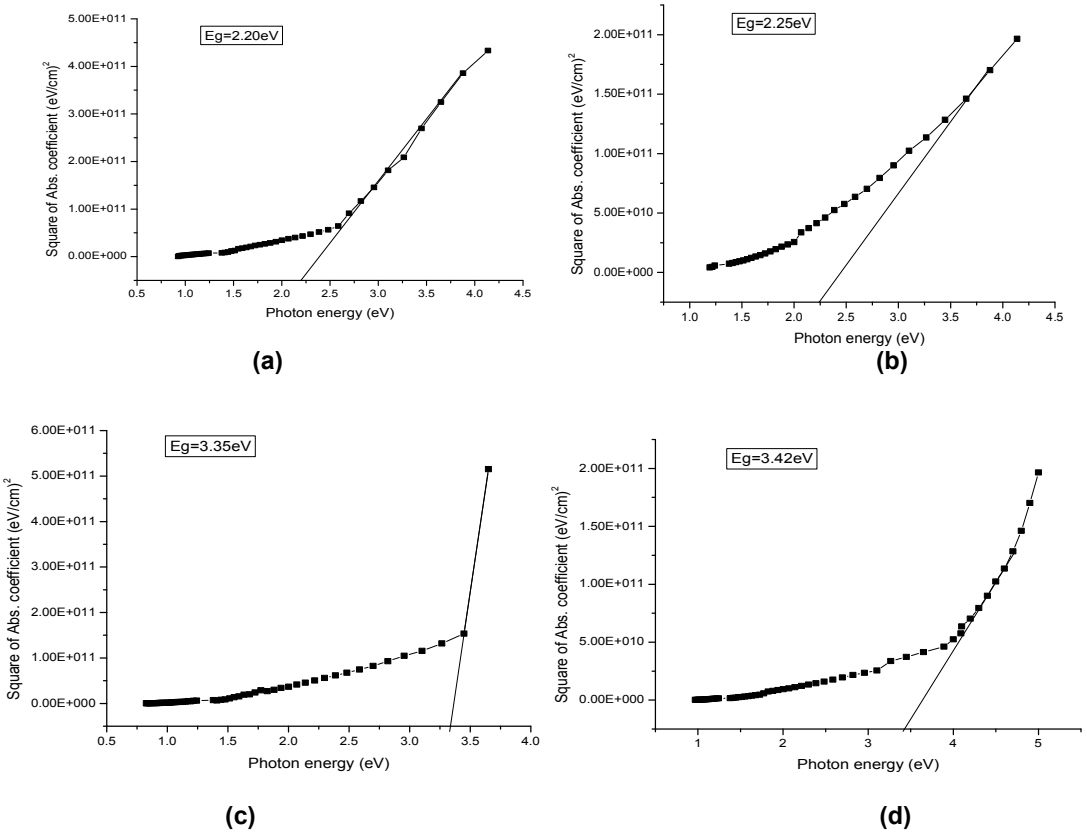


Fig. 6. The plot of $(\propto h\nu)^2$ versus photon energy ($h\nu$). for $Cu_xZn_{1-x}S$: (a) sample B_1, (b) sample B_2, (c) sample B_3 and (d) sample B_4

4. CONCLUSION

The films of $Cu_xZn_{1-x}S$ were deposited on soda lime substrates by MOCVD technique at 400ºC for a period of 2 hours. The effect of concentration on the elemental composition, thickness and structural as well as the optical and electrical properties of the films were also studied. RBS experiment revealed changes in the stoichiometry and thickness. This shows that the stoichiometry depend strongly on the concentrations of the films. The structural studies as observed by XRD and SEM showed that the films are polycrystalline with grains that are dense and uniformly distributed within the substrates. Optical characterization revealed that the films are highly transmitting in the Ultraviolet regions of the spectrum with a band gap energy that varies from 2.20 to 3.42 eV as Zn content changes from 0.1 to 0.9. The obtained results indicate the suitability of using the deposited films in various optoelectronics applications such as thermal control window coatings for cold climates, antireflection coatings, light emitting devices as well as hetero-junction in solar cells. In particular, this study have provided another method of depositing copper zinc sulphide thin films for industral applications.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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