

PREPARATION AND CHARACTERIZATION OF METAL ORGANIC CHEMICAL VAPOUR DEPOSITED COPPER ZINC SULPHIDE THIN FILMS USING SINGLE SOLID SOURCE PRECURSORS

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Abstract

Metal organic chemical vapour deposition (MOCVD) was used with a mixed single solid source precursors of copper dithiocarbamate ($CuC_{10}H_{16}N_2O_2S_4$) and zinc dithiocarbamate ($ZnC_{10}H_{16}N_2O_2S_4$) to prepare pyrolysed copper zinc sulphide thin films. The precursors were analysed by Fourier Transform Infrared Spectroscopy (FTIR), to determine the structures present. The films were deposited on glass substrates at a temperature of 420 °C. Experimental results showed that the compositional studies were found to be complementary. The structural analyses revealed that the film is crystalline with an average grain size of approximately 2 μm . An optical energy of 2.50 eV was obtained with an absorbance that decreases with wavelength. The electrical characterization gave values of sheet resistance, resistivity and conductivity of the film as $5.13 \times 10^{-6} \Omega/Sq$, $2.27 \times 10^{-1} \Omega.cm$ and $3.61 \times 10^{-2} (\Omega.cm)^{-1}$ respectively. The findings confirmed that the synthesized precursor is a potential material for depositing high quality copper zinc sulphide thin films.

Keywords: precursor; substrate; MOCVD; copper zinc sulphide; dithiocarbamate.

Introduction

Copper Zinc sulphide or CZS has gained much interest due to its versatility and potential applications in electronics and Optoelectronics. The CZS thin films have properties in between its binary chalcogenide constituents of CuS and ZnS with a lattice structure that may be very unstoichiometric [1]. The vacancies and interstitials control the conductivity type as an excess of copper or zinc leads to either p-type or n-type conductivity. It presents some unexpected physical properties such as anomalous band gap energy values, high dielectric constants and high carrier mobility, that makes the material attractive in the fabrication of solar cells, LEDs, sensors and so on [2, 3].

Diverse methods of deposition have been used to prepare CZS thin films such as chemical spray pyrolysis [1-2, 4]. Chemical bath deposition [5-7], SILAR [8, 9], solution growth technique [10] and Election beam evaporation [11]. In the case of CZS preparation using these chemical methods, it is difficult to avoid the undesired side reactions and incorporation of impurities within the precursors, which may cause diffusion of layers and affect the quality of the films. This is probably due to the use of two or more precursors of different properties [12]. Other limitations are non uniformity of the deposited films and the use of unusually high temperature. For physical method of electron beam evaporation, the plasma-induced defect associated with the films due to the bombardment of energetic ions taking place within the surface of the films is a case of disturbance [13]. To overcome these limitations, the development of alternative single solid source precursor has been pursued. A single solid source

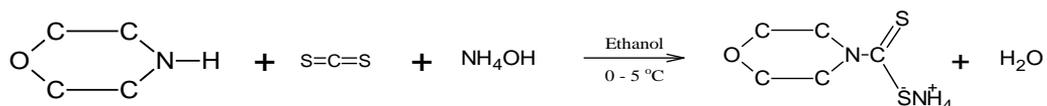
precursor is a metal-organic molecule which contains all the desired elements for the growth of a compound material, likely with its stoichiometry [14, 15]. The use of a single solid source precursor has potential advantages over the conventional precursors. First, it offers the unique advantage of mildness, safety and simplified preparation procedure and delivers exact control over stoichiometry of the film [14]. Another important attraction of this route is seen in the unusual crystal growth or metastable phase formation of the resultant products which are sometimes not possible using the other technique. For these reasons, the single solid source precursor technique has proven to be a precise route to prepare films of high quality [15, 16].

This study reports on the preparation of copper dithiocarbamate and zinc dithiocarbamate (50:50) as a single solid source precursors used in the deposition of CZS thin films with MOCVD. Thus, the synthesis using MOCVD is simple and reduced the preparation cost, therefore making it more viable economically when compared with other deposition methods [17]. Therefore, the aim of this study is to demonstrate the feasibility of using dithiocarbamate as a single solid source material for the production of CZS films and to study their physical properties.

Experimental

Preparation of Precursor

The preparation of ammonium morpholino-dithiocarbamate (intermediate complex) is achieved by modifying the experimental procedure reported by Ajayi et al. [18], according to the reaction scheme below.



A 250 ml round-bottom beaker with a thermometer was immersed in an ice bath due to the nature of the reaction and to achieve the desired temperature of between 0 to 5 °C. Ethanol of 100 cm³ was poured into a beaker containing morpholine (9.66 cm³, 9.66 g, 0.10 mol) which was kept stirring over a period of 30 minute to ensure that the temperature was kept below 5 °C. Carbon disulphide (6.7 cm³, 8.44 g, 0.10 mol) was added while stirring vigorously. Ammonia solution of 75 cm³ was gently added to the reaction to obtain a pale yellow solution which was then put in a freezer to obtain the crude product of ammonium morpholino-dithiocarbamate crystal as a white to yellow solid. The product was filtered under gravity and let to dry completely at room temperature. The dried product, ammonium morpholino dithiocarbamate, was found to be 13.46 g (67.3 % yield).

For copper dithiocarbamate, the prepared intermediate precursor of ammonium morpholino-dithiocarbamate (18.752 g, 0.104 mol) was dissolved in a solvent with a 2:1 ratio of acetone and water in a 500 cm³ beaker. Copper (II) chloride (8.869 g, 0.052 mol) was also completely dissolved in 60 cm³ of ethanol separately. The solution of copper (II) chloride in ethanol was gradually added to the solution of ammonium morpholino-dithiocarbamate on a hot plate, vigorously stirred at 60 °C. There was a spontaneous formation of dark-brown precipitate as the addition proceeds. The precipitate formed was heated for another 30 minutes before cooled at room temperature and filtered under gravity. After 24 hours, the product was oven dried for another 72 hours at 50 °C to yield copper dithiocarbamate (CuC₁₀H₁₆N₂O₂S₄) with a percentage yield of 78.15 % (15.63 g). The reaction is represented below :

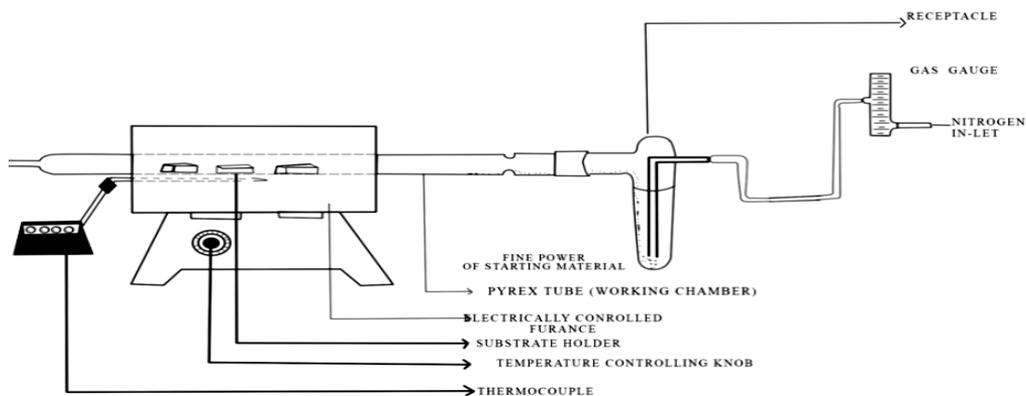


Fig. 1. Experimental setup for CZS deposition

Results and Discussion

Infrared (IR) Spectrophotometry

The IR spectrum in Fig. 2. shows the different functional groups present in the mixed copper and zinc dithiocarbamate precursors. The measurement was done at room temperature range of 4000 and 500 cm^{-1} in KBr background. A close examination showed a broad peak attributed to O-H stretching vibration at 3448.84 cm^{-1} [21], N-H stretching at 3122.86 cm^{-1} , C-H stretching vibration is between 2966.62 and 2852.81 cm^{-1} . However, a series of weak bands appear between 2300 and 1700 cm^{-1} reflecting the substitutional pattern of the organic compound in the precursor [22]. There are also C=O vibration at 1627.97 cm^{-1} , C-C stretching at 1489.10, 1265.35, 1234.46, 1114.89, 1026.16 and 997.23 cm^{-1} , out of plane C-H bending 875.71 cm^{-1} , Cu-S and Zn-S bands are below 829.42 cm^{-1} . This indicates that the ligand was attached to CZS.

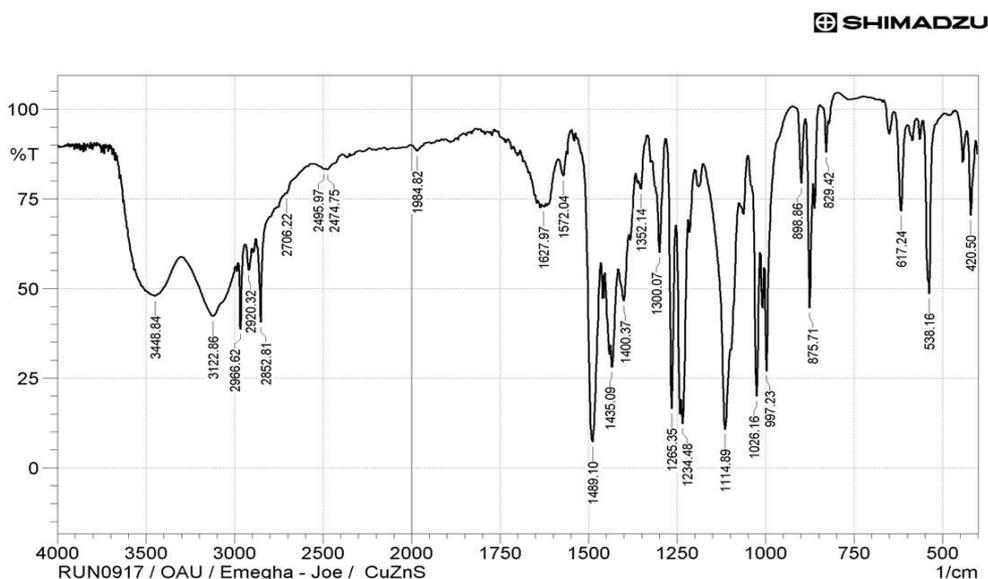


Fig. 2. Infrared spectrum of the precursor

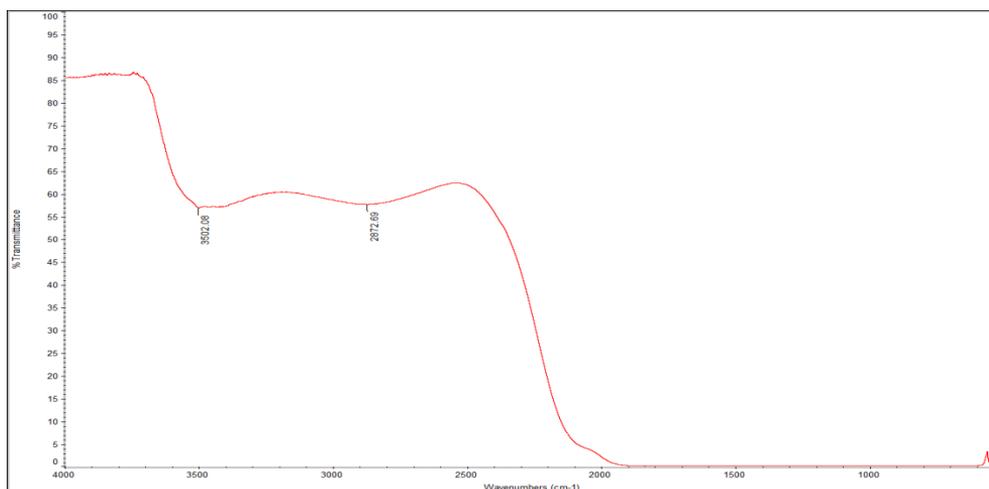


Fig. 3. Infrared spectrum of deposited CZS on soda lime substrate

Fig. 3 shows the IR spectra of the deposited films at 420 °C. The signals when compared to that of Fig. 2, showed that the characteristic bands associated with organic ligands were missing, suggesting a complete decomposition of the precursor to produce copper zinc sulphide. An observation that is consistent with the decomposition of metal sulphides [18, 23].

Compositional Studied of CZS Thin Film

The EDX spectrum of the deposited films is shown in Fig. 4. The signals confirmed the presence of copper, zinc and sulphur as the major elements present within the film. The other feature elements evident in the spectrum is due to the nature of the substrate (soda lime) used [24]. The RBS spectrum of the deposited film is exhibited in Fig. 6. The elemental analysis measured are copper (31.6 %), zinc (31.5 %) and sulphur (30.5 %). This observation shows that the decomposition of the precursors in nitrogen gas produced CZS thin film [12]. The thickness was found to be 54.00 nm using the relation below [25].

$$Thickness(nm) = \frac{Atoms\ per\ unit\ area\ (cm^{-2})}{atomic\ density\ (cm^{-3})} \tag{1}$$

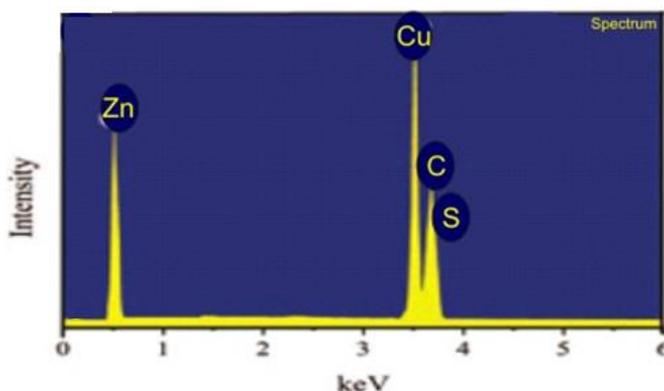


Fig. 4. EDX spectrum of CZS thin film

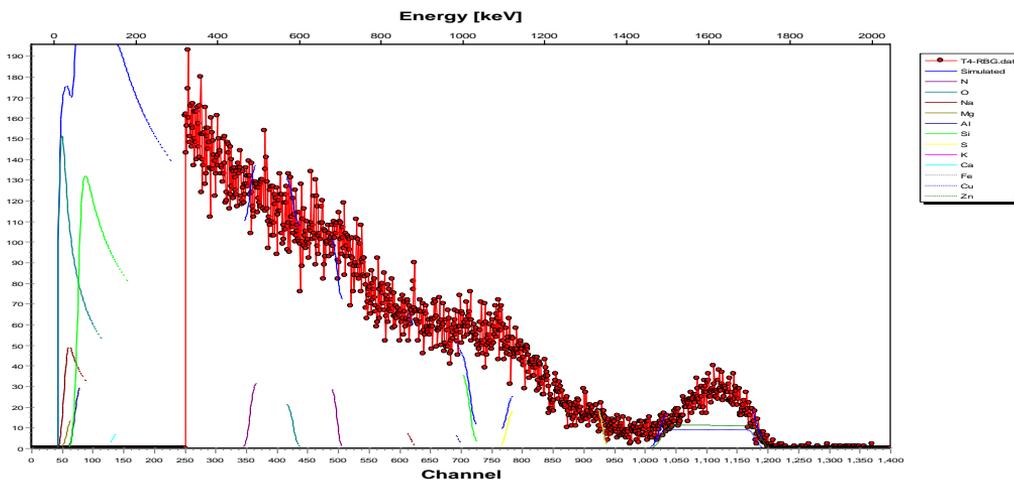


Fig. 5. RBS spectrum of CZS thin film

Optical Characterization

To establish the suitability of the MOCVD deposited thin film for device applications, the absorbance in the range of 300 nm to 1400 nm was investigated in a step size of 20. Measurements were taken with a clean blank substrate before the deposited substrate was introduced. The optical absorbance A, was estimated from the relation.

Absorbance:

$$(A) = 10 \log \frac{1}{T} \tag{2}$$

Where T is the transmittance. The variation of the optical absorbance with wavelength for CZS thin film is displayed in Fig. 6. As seen, it is observed that the optical absorbance decreased with increase in wavelength. Also, we noticed that that value of the optical absorbance is high in ultra violet region and low in the visible and near infrared regions. This, therefore, means an improvement in the transmittance of the film [26]. The nature of the film having an enhanced absorbance in the ultra violet (UV) region makes the film a good window layer in solar cells fabrication.

The energy gap (E_g) has been observed to follow the form [11]:

$$\alpha hr = k(hr - E_g)^n \tag{3}$$

Where K is a constant, r is frequency, h is the plank’s constant while E_g is the energy gap. In equation (3), there is another constant n, known as the power factor of the electronic transition mode [28]. It relates to the nature of the material. For CZS film, the value of n is 0.5, being a direct allowed band gap semiconductor [21, 29]. Experimentally, the energy gap is determined by a graph of $(\alpha hr)^2$ versus hr. The energy gap value is obtained by extending the linear portion to intercept (hr)-axis at $(\alpha hr)^2$ equal to zero. Fig. 7 shows that the energy gap obtained for CZS film is equal to 2.50 eV. The optical energy gap shows that CZS film is a ternary material whose band gap falls between the binary constituents of 1.38 eV for CuS [20] and 3.67 eV for ZnS [23] thus, conserving the Vegard’s rule of mixture. Also, the value obtained is in agreement with the range of 1.8 to 3.52 eV determined by Noriyuki et al. [4] and 2.4 to 2.7 eV obtained by Ezenwa and Okoli [5] using other routes.

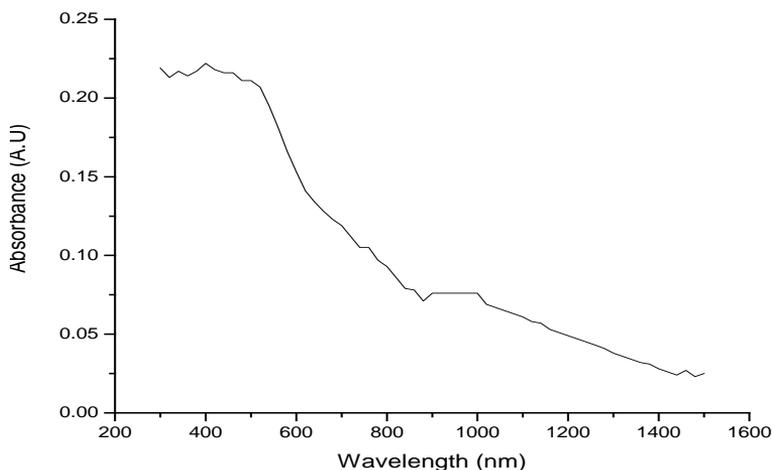


Fig. 6. Absorbance against wavelength of CZS thin film

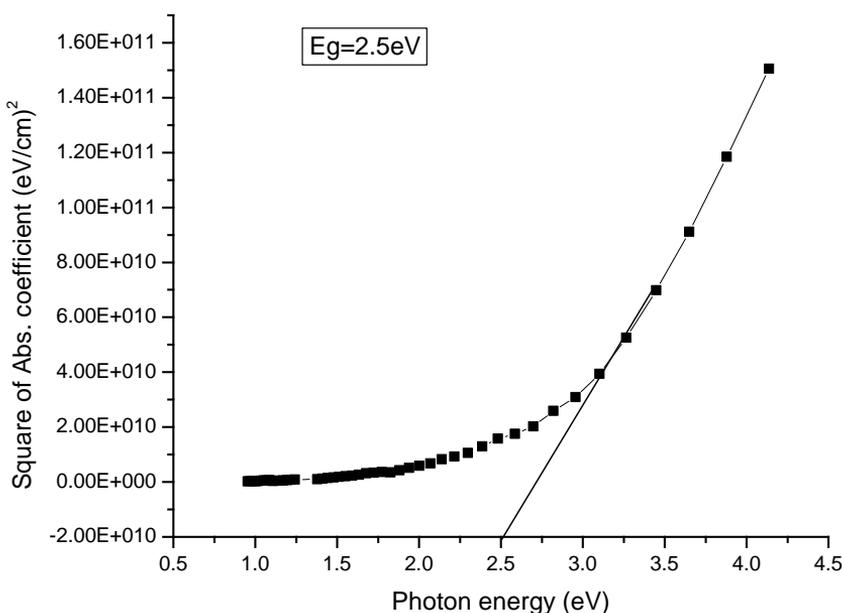


Fig. 7. Square of absorption coefficient against photon energy for CZS thin film

Electrical Characterization

The electrical properties of the film was determined through the four point probe method. Errors were minimized in the current-voltage measurements by taking the reading several times and average values of the voltage and current were recorded. The resistivity (ρ), of the film was calculated by multiplying the thickness (W) and the sheet resistance (R_s) as follows:

$$\text{Resistivity} = R_s \times W \tag{4}$$

Where w is the thickness from RBS study. The reciprocal of the resistivity was taken as the conductivity value.

The average voltage and current generated in the study were determined as 1.74×10^{-2} V and 15.38×10^{-9} A respectively. The sheet resistance was calculated to be $5.13 \times 10^6 \Omega/\text{square}$, the resistivity was found to be $27.70 \Omega \cdot \text{cm}$ and the conductivity was also calculated to be $3.61 \times 10^{-2} (\Omega \cdot \text{cm})^{-1}$. The electrical conductivity falls within the range of 10^{-13} to 10^2 reported for semiconductor thin films [30], suggesting that the deposited film is conductive. The rather high resistive properties of the deposited films indicate that CZS film could find application as semiconductor sensors either as gas or touch sensor [31]. The observed high resistivity may be a result of the high impurity content within the film.

Surface Morphology

The surface morphology of the deposited film was observed by HRTEM. The HRTEM image of the deposited film is shown in Fig. 8. From the image, it can be observed that the film consists of grains that are ellipsoidal in nature and are randomly distributed throughout the substrate. The size of the grains ranges from $2.5 \mu\text{m}$ to about $6.0 \mu\text{m}$ with an average of approximately $4.0 \mu\text{m}$. It is evident from the corresponding SAED pattern in Fig. 9 that the film is polycrystalline in nature. The presence of Debye-Scherrer ring shows that the deposited CZS film is composed of cluster of grains [4, 32].

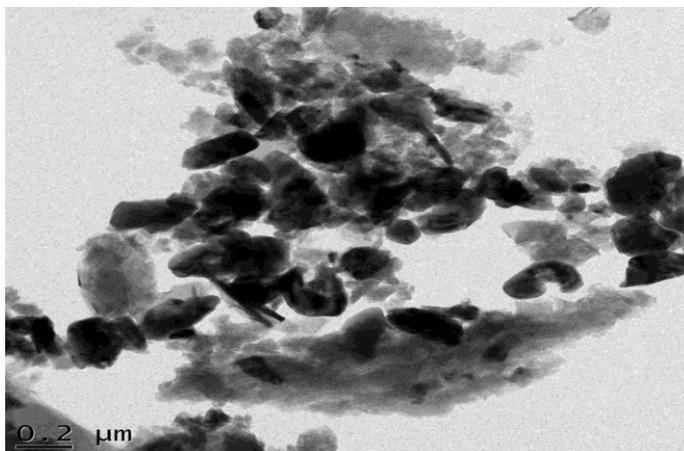


Fig. 8. HRTEM image of the deposited film

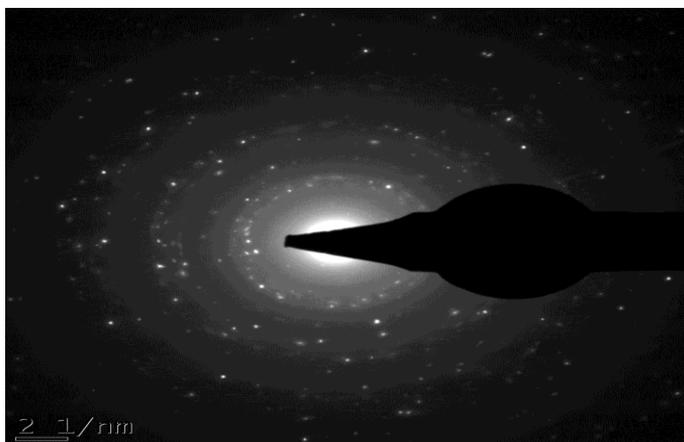


Fig. 9. SAED Pattern of the deposited film

X-ray Diffraction Studies

The x-ray diffraction pattern of the film is shown in Fig. 10. Sharp peaks occur at angle $2\theta = 28.50^\circ, 33.01^\circ, 47.50^\circ, 56.50^\circ, 69.5^\circ, 77.00^\circ$ and 78.50° . Corresponding to diffraction line of (111), (200), (220), (311), (222), (400), (332) and (420) plane from the shalerite ZnS diffraction data file of 005-0566.

As seen, it can be inferred that there was a phase separation from the deposited copper zinc sulphide to binary zinc sulphide, which is in agreement with reported literature on ternary thin film materials [33 – 35]. Also, it is clear that the deposited film is polycrystalline [36]. This measurement collaborated with the SAED studies. Furthermore, the broad hump observed in the spectrum within the range $19^\circ \leq 2\theta \leq 38^\circ$ is due to the amorphous nature of the substrate (soda line) used in the deposition [33, 34].

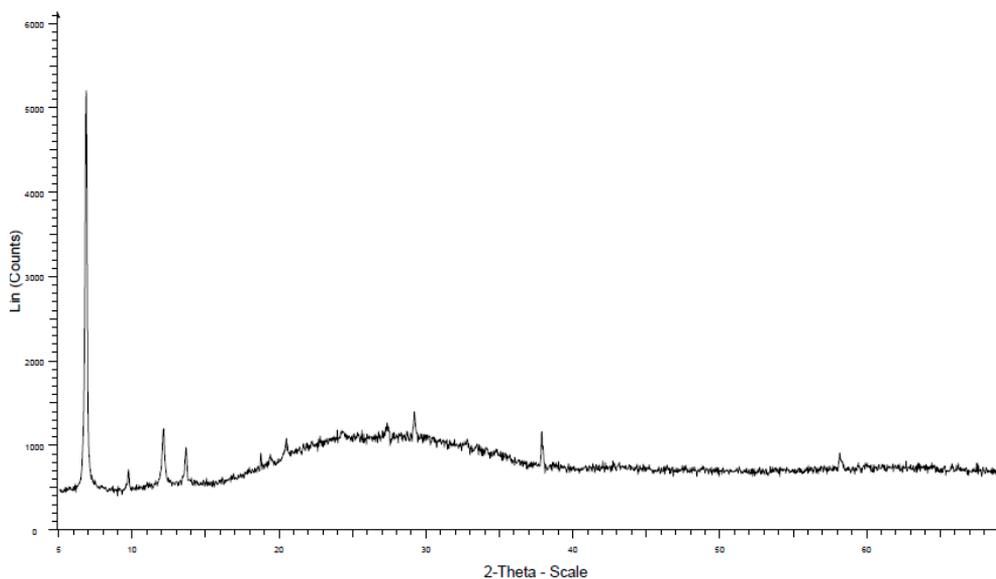


Fig. 10. XRD Spectrum of CZS thin film

Conclusion

Copper zinc sulphide(CZS) thin films have been prepared and deposited at 420°C on soda lime substrate by the pyrolysis of a mixture of copper dithiocarbamate and Zinc dithiocarbonate (50:50) using MOCVD technique. Thus, providing a new and cheap method of depositing CZS films. Characterization confirmed that the film is crystalline with a direct optical band gap of 2.50 eV and an average thickness of $54.00\ \mu\text{m}$. In this case, the elemental analyses showed a film that consist of copper, zinc and sulphur in various proportion that has good adhesion with the substrate. The electrical conductivity determined with four-point method was $3.61 \times 10^{-2} (\Omega \cdot \text{cm})^{-1}$ with a high resistivity of $27.70 (\Omega \cdot \text{cm})$.

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