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EFFECT OF MOLAR CONCENTRATION OF PRECURSOR ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CuAlS₂ THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION TECHNIQUE

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Abstract

CuAlS₂ thin films have been prepared on glass substrates by Chemical bath deposition (CBD) technique at a substrate temperature (T_s) 75°C, pH value 10.5. The Effect of three different molar concentration (0.05, 0.025, 0.1), (0.075, 0.0375, 0.15), and (0.1, 0.05, 0.2) M of precursors of (CuSO₄·5H₂O, Al₂(SO₄)₃·16H₂O, and (NH₂)₂CS), respectively on the structural, optical and electrical properties of deposit thin films was studied. The X-ray diffraction (XRD) patterns showed that the films have an amorphous structure with simple enhancement in the structure of the films with the higher molar concentration. Field emission scanning electron microscopy (FESEM) analysis of thin films showed that the deposited films were a good surface morphology, homogenous and uniform spherical nanoparticles over the substrate surface with very little agglomerated particles with average grain size in the range (45 to 72 nm) increase with increasing molar concentration of precursors. Atomic force microscopy (AFM) showed the topography of deposited films has nanoparticles with structures like conical and lobes shape, with the average grain sizes, root mean square (rms) roughness, and surface roughness increase with increasing molar concentration of precursors. The optical analysis by UV-Vis Spectrophotometer showed high absorption in the ultraviolet region, with absorption edge and direct energy gaps (3.5 to 4eV) varied at different molar concentrations of precursors. The electrical results from Hall effect measurements showed that the values of resistivity, conductivity, mobility, and carrier concentration were varied in range (0.046 to 0.594 ohm.cm), (1.86 to 21.7 (ohm.cm)⁻¹), (301 to 1510 cm²/V.S), and (3.29×10¹⁶ to 1.46×10¹⁷ cm⁻³), respectively. Also, n-type conductivity was investigated for all prepared film at different molar concentration of

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precursors. The obtained results of the prepared CuAlS₂ thin films can be suitable in many optoelectronics applications.

Keywords: CuAlS₂ Thin Films, Effect of Precursor Concentration, Optical Properties, Electrical Properties, Chemical Bath Deposition Technique, Structural Properties, Morphological.

Introduction

The chalcopyrite semiconductor that belongs to I-III-VI compound has substantial interest in recent years (Naveena & Bose, 2019). The CuAlS₂ is the one of the family of the ternary chalcopyrite having direct optical band gap of 3.5 eV, and this value highest among those of all the chalcopyrite compound semiconductors, also having major advantage such as low cost, non-toxic and earth abundant, which making it an interesting material for many technological applications, in solar cells, photovoltaic, light emitting devices in blue region of spectrum, as window layers of solar cells (Naveena & Bose, 2019) (Chaki, Mahato, Malek, & Deshpande, 2017), as oxygen gas sensor (Abaab, Bouazzi, & Rezig, 2000), and as UV detectors (Perng, Kao, & Chang, 2014).

There are many techniques used to prepare ternary CuAlS₂ thin films, such as chemical spray pyrolysis (Caglar, Ilican, & Caglar, 2008), thermal evaporation (Abaab et al., 2000), sulfurization of metallic precursors in a vacuum (Bhandari, Hashimoto, & Ito, 2004), spark plasma sintering (Liu, Wang, Huang, Chen, & Wang, 2007), direct polyol methods (Yue, Wang, Wang, Wang, & Peng, 2008), wet chemical method (Harichandran & Lalla, 2008), simple colloidal route (Poulose et al., 2012), chemical vapour transport (CVT) technique (Chaki, Mahato, & Deshpande, 2014), hydrothermal method (HT) (Sugan, Baskar, & Dhanasekaran, 2015), metal organic chemical vapour deposition (MOCVD) (Damisa, Olofinjana, Ebomwonyi, Bakare, & Azi, 2017), and atomic layer deposition (Schneider et al., 2018), and chemical bath deposition technique (CBD).

There are many advantages to use CBD technique comparing with other techniques such as low cost, available and inexpensive, environmentally friendly, deposition temperature is low and safe to use, simply controlling with deposition parameters, deposition with large area of thin films, chemical precursors are available and dissolved in distilled water, nontoxic for using, and simplicity for the preparation of films on various substrates (Ho, 2015).

CBD technique of prepared CuAlS₂ thin films were used by many researchers, where Tariq J. et al. prepared CuAlS₂ thin films by CBD technique on glass substrates, where all films were amorphous structure. Optical properties showed direct energy gap 2.81 and 2.4 eV as deposited and annealing, respectively, and with thickness 118±5 nm (Alwan & Jabbar, 2010).

S.M. Ahmad prepared CuAlS₂ thin films by SPS and CBD technique, and showed the prepared films by CPS has polycrystalline while amorphous structure for CBD, optical properties showed direct energy gap with 3.00 eV by CPS and 2.8 eV by CBD technique (Ahmad, 2017).

In this study CuAlS₂ thin films were deposited at 75°C in alkaline medium with pH 10.5, and deposition time 40 minute. Effect of different molar concentration of precursors was studied. The aim of this study to find the best prepared conditions for getting on high quality of deposited thin films, and using its in different optoelectronic devices.

2. Experimental details

Solution of CuAlS₂ was prepared with three different molarity concentrations of precursors (0.05, 0.025, 0.1), (0.075, 0.0375, 0.15), and (0.1, 0.05, 0.2) M from copper (II) sulfate pentahydrate [CuSO₄·5H₂O] (Honeywell Fluka, Germany), Aluminum sulphate [Al₂(SO₄)₃·16H₂O] (Thomas Baker, India), and Thiourea [(NH₂)₂CS] (Merck, Germany), which used as a sources of Cu, Al, and S ions, respectively. EDTA disodium salt dihydrate [Na₂EDTA·2H₂O] (Glenthams, UK) with 0.04M was used as a complex agent in all prepared solutions.

Before the solutions were mixed, the glass substrates were cleaned by the following procedure, in the first the glass substrates were cleaned by distilled water and shampoo, followed by distilled water only at 100°C on hotplate, and dried in air before immersed in nitric acid for 48 h, after that washed by distilled water before its immersed in HCl for 24 h, and after cleaned by distilled water before its immersed in ethanol, followed in acetone for 30 min., and finally washed by distilled water and lifted to dry in air. The advantage of cleaned procedure to enhanced the nucleation and adherent thin films on glass substrates.

For the first concentration of precursor was done by mixing 10ml of copper sulfate CuSO₄·5H₂O (0.05M) added into beaker 100 ml, and stirred on hotplate heater at 40°C by magnetic dipole for

five min., added to it 10ml of Na₂EDTA (0.04M), and stirred for 5 min., 5 ml of Al₂(SO₄)₃.16H₂O (0.05M) added to solution and stirred for 5 min., after that ammonia solution added to solution to adjust pH value to 10.5, and finally 10 ml of (NH₂)₂CS (0.1M) added slowly to solution, after that, the magnetic dipole was left from the beaker, and two glass substrate face to face was immersed vertically in beaker after cleaned procedure, and the beaker was putted directly in water bath which was adjusted at temperature 75±0.2 °C. The deposition time was calculated at the time of lifting the beaker from the water bath, and the substrates were carried out from the beaker, and were washed by distilled water and lifted to dry in air. The process was repeated in the same way for the second and third concentration of precursors which are shown in the Table 1. Table 1. Different molar concentrations of precursors of CuAlS₂ thin films.

sample	a		b		c	
concentrations (M)/volume (ml)	M	V(ml)	M	V(ml)	M	V(ml)
CuSO ₄ .5H ₂ O	0.05M	10ml	0.075M	15ml	0.1M	20ml
Al ₂ (SO ₄) ₃ .16H ₂ O	0.025M	5ml	0.037M	7.5ml	0.05M	10ml
(NH ₂) ₂ CS	0.1M	10ml	0.15M	15ml	0.2M	20ml

Different molar concentration of precursors (0.05, 0.025, 0.1), (0.075, 0.0375, 0.15), and (0.1, 0.05, 0.2) M were symbolized by 1, 1.5, and 2M, respectively.

The following changes were observed after the beaker was kept in a water bath, where, when ammonia solution were added to the solution, The color of the solution in the first threemin., changed from light sky to lightblue, after threemin., changed to bold blue. While, when the thiourea was added after that the solution, the color changed to light green after threemin., and to a deep yellowish after twomin., and after fourmin., the solution gradually changed to bold orange or brown color (Bhattacharyya, Pandit, Rajasekar, & Pandey, 2018), and finally after threemin., the solution became black color (Yue et al., 2008).

Color changing for the solution was affected mainly by molar concentration of precursors, where the interval of color changing of solution was increased with increasing the molar concentration of precursors, and this may be due to decrease the homogenous process in the solution. Some of these observations of color changing were reported (Mohammed, Ahmed, & Mohammed, 2020) (Alwan & Jabbar, 2010) (Ahmad, 2017).

The XRD patterns of deposit CuAlS₂ thin films were taken by the Phillips X-pert High Score

PANalytical X-ray diffractometer with CuK α ($\lambda = 1.5406 \text{ \AA}$) radiation as a source, with the range of 2θ degree from 10.35° to 80.00° , with a step size $(2\theta) 0.05^\circ$, and scan step time 1s.

Optical measurements of deposit films were obtained by using a UV-Vis spectrophotometer model Cary 60 Agilent, with a wavelength range of 190-1200 nm at room temperature. Electrical measurements of deposit films were done at room temperature by using Hall Effect measurements, model IRASOL/HSR-24 AC Hall Effect. The Surface morphology and cross section of deposit films were tested by field emission scanning electron microscopy (FESEM) model ZEISS Supra 35 VP with high resolution mode, and with magnification 100 KX. Topography of thin films were tested by atomic force microscopy (AFM), model JPK Nanowizard, Germany, where the physical size of surface topography of films are observed approximately from (1000,1000) to (2500,2500) nm.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction patterns of deposit CuAlS₂ thin films onto the amorphous glass substrate for different molar concentrations of precursors are shown in Fig.1. The amorphous structure of all prepared thin films was observed, where no peaks in all films. This behavior has been mentioned by other researchers (Alias et al., 2019) (Kawaguchi, Ishigaki, Adachi, Oshima, & Ohmi, 2015). The amorphous nature of deposited films may be due to the low thickness, nanoparticles, which have a small grain size, and the amorphous of glass substrate, which cause weakness in the intensity of X-ray diffraction patterns (Naji, Alias, Taher, & Al-Douri, 2018). The enhancement of patterns intensity was observed at higher molar concentration of precursors due to the increasing of

thickness from 45 nm to 250 nm with increasing the molar concentrations of precursors from 1 to 2 M.

Fig.1. XRD patterns for CuAlS2 thin films for molar concentrations of precursors (a) 1, (b) 1.5, and (c) 2 M.

3.2. Thickness measurements

The average thickness of CuAlS2 thin films was done by cross section analysis of deposit films which are shown in Fig.2. The values of thickness average were 40, 46, and 250 nm for molar concentrations of precursors 1, 1.5, and 2 M, respectively. The thickness increases with increasing the molar concentrations of precursors, and this may be due to increase the heterogeneous processes compared with homogeneous processes on the surface of the films. The values of thickness average were used to calculate the parameters of optical properties of deposit thin films.

c)
Fig.2. Cross section images of CuAlS₂ thin films for molar concentrations of precursors (a) 1, (b) 1.5, and (c) 2 M.

3.3. Optical properties measurements

Fig.3 shows the UV-Vis absorption spectra of CuAlS₂ thin films with various deposition times in the wavelength range of 200 to 1100 nm.

Fig.3. Absorbance spectrum of CuAlS₂ thin films for molar concentrations of precursors 1, 1.5, and 2 M.

The spectrum shows high absorption in the ultraviolet region with an absorption edge at 350 to 360 nm. The absorption edge increases with increasing the molar concentrations from 1 to 2 M, respectively.

A sharper absorption edge means fewer impurities and defects in the deposited films, (Najm et al., 2020).

Fig.4 shows the direct energy gap was calculated by plotting $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$ of the films. The optical energy gap values are obtained by extrapolating the linear portion of the plots to intercept the photon energy axis which were shown in our previous work (Alias et al., 2019). The variation of energy gaps with the molar concentrations of precursors is tabulated in Table 2.

Fig.4. Energy gap of CuAlS₂ thin films for molar concentrations of precursors 1, 1.5, and 2 M.

Table 2. Values of direct energy gap for depositing CuAlS₂ thin films.

Molar concentrations of precursors (M)	E _g (eV)
1	3.6
1.5	3.5
2	4.0

The direct band gap E_g values were found to vary between 3.5 to 4.0 eV depending on the molar concentrations of precursors. It is clear from Table 2 that energy band gap is affected by molar concentrations of precursors, where the energy gap decreases with increasing molar concentration of precursors from 1 to 1.5 M, and after that increases at 2 M which are shown in Fig.5. The variation in the energy values may be variation in grain size, which are observed from FESEM and AFM results, where the energy gap decreases with the increasing grain size due to size effect (Najm et al., 2020). The energy gap values for CuAlS₂ thin films which were prepared in this work are greater than with that found by Alwan et al ($E_g = 2.81$ eV) (Alwan & Jabbar, 2010), Ahmad (E_g

= 3.00 eV)(Ahmad, 2017), Naveena and Chadra ($E_g = 3.26$ eV) (Naveena & Bose, 2019), and the value of energy gap at 1.5 M agreement with that found by Bhandari et al. ($E_g = 3.5$ eV)(Bhandari et al., 2004).

Fig.5. Energy gap of CuAlS2 thin films as a function for molar concentrations of precursors 1, 1.5, and 2 M.

Fig.6 shows the transmittance (T%) and the reflectance (R%) spectra as a function of wavelength from 350 to 1200 nm for CuAlS2 thin films for different molar concentrations of precursors 1, 1.5, and 2 M. At wavelength 650 nm, the maximum transmittance decreases from 80% to 70% with increasing the concentration of precursors from 1 to 1.5 M, after that the transmittance increase to 75% at concentration 2 M. where the maximum transmittance for deposited films is observed at wavelength 650 nm for all molar concentrations of precursors. This variation of transmittance due to the variation in energy gaps of deposited films.

The transmittance increases at wavelengths from 350 to 650 nm gradually at concentrations 1 and 1.5 M, while it increases quickly at concentration 2 M. In the wavelength range from 700 to 1200 nm, the transmittance slightly reduces and arrived to 70% for concentration 1M, 60% for 1.5 M, and 65% for 2 M. Therefore these materials can be used as a window layer in solar cell and infrared devices. The reflectance behavior of deposit films is reciprocal the transmittance.

Fig.6. Transmittance and Reflectance spectrum of CuAlS2 thin films for molar concentrations of precursors 1, 1.5, and 2 M.

3.4. Electrical properties analysis

The electrical properties of CuAlS2 thin films measured by Hall Effect measurement at room temperature. Table 3 shows the Hall parameters of deposit CuAlS2 thin films for different molar concentrations of precursors 1, 1.5, and 2 M. The conductivity (σ) of prepared films increases with increasing the molar concentration of precursors. The behavior of resistivity (ρ) inversely compares with that observed for conductivity which are shown in Fig.7 (a). Values of resistivity and conductivity were in the range (0.594 to 0.046 ohm.cm) and (1.68 to 21.7 (ohm.cm)⁻¹), respectively which are a good agreement with that found by (Kawaguchi et al., 2015).

The charge carrier concentration (n) of prepared films increases with increasing the molar concentration of precursors. This behavior is same as of that of the thickness of prepared films. This behavior due to the film with high thickness has more carrier concentration, and the verse versa. Values of carrier concentration were varied in the range (3.49×10^{16} to 1.46×10^{17} cm⁻³)

which are a good agreement and greater than found by Chaki et al ($\sim 1016 \text{ cm}^{-3}$)(Chaki et al., 2017).

The mobility of charge carriers (μ) for prepared films increases with increasing the molar concentration from 1 to 1.5 M, and after that it decreases with increasing the molar concentration from 1.5 to 2 M. The maximum value of mobility was found at molar concentration 1.5 M, but decreases at molar concentration 2 M. the behavior of mobility is inversely compared with that observed for carrier concentrations which are shown in Fig.7(b).

The prepared films with low carrier concentration have high mobility, due to the movement of charge carriers are free, and vice versa. Values of mobility were varied in the range (301 to 1510 ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)) which are greater than found by Min et al (1.1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)(Liu et al., 2007).

The type of conductivity of prepared films was n-type at all molar concentrations of precursors 1, 1.5, and 2 M., this type of conductivity was found by (Chaki et al., 2014).

Table 3. Hall parameters of as deposited CuAlS₂ thin films for different molar concentrations of precursors.

Sample	n (cm^{-3})	ρ (ohm.cm)	σ (ohm.cm) ⁻¹	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Type of conductivity
CuAlS ₂ at 1 M	3.49×10^{16}	0.594	1.68	301	n
CuAlS ₂ at 1.5 M	3.62×10^{16}	0.114	8.77	1510	n
CuAlS ₂ at 2 M	1.46×10^{17}	0.046	21.7	930	n

Fig.7. (a) Resistivity and conductivity, (b) carrier concentration and mobility of CuAlS₂ thin films as a function of molar concentrations of precursors.

3.5. Surface morphological analysis

3.5.1. FESEM characterization

Morphological properties of CuAlS₂ thin films were done by field emission scanning electron microscopy (FESEM). FESEM images of prepared films at different molar concentrations of precursors 1, 1.5, and 2 M were shown in Fig.8. The prepared film at 1 M shows homogenous and uniform spherical nanoparticles with a good surface morphology over the substrate surface and some agglomerated particles were observed. The average grain size was about 45 nm. At molar concentration 1.5 M, the prepared film shows spherical nanoparticles with an average grain size about 52 nm, and some agglomerated particles like nanotube shape were observed, with diameter about 57 nm and length about 950 nm. The prepared film at molar concentration 2 M shows spherical nanoparticles covering large areas of total film with an average grain size about 72 nm, and some of agglomerated particles were found. The morphological properties at molar concentration 2 M showed enhancement in the microstructure of prepared film. The grain sizes of deposit films increase with the increasing the molar concentrations of precursors, which are shown in Table 4, and this may be due to the increasing the growth process in the deposited films.

The values of G.S in this work are smaller than with that found (380 nm and 150 nm) by Ahmad (Ahmad, 2017), and greater than with that found (19.09 nm) by Moataz et al (Ata, Abdellateef, & Elrouby, 2020).

Fig.8.FESEM images of prepared CuAlS₂ thin films for molar concentrations of precursors (a)1 M, (b)1.5 M, and (c)2 M.

3.5.2. AFM characterization

Topography properties of prepared CuAlS₂ thin films were taken by atomic force microscopy (AFM). AFM images for prepared CuAlS₂ thin films on glass substrate at different molar concentrations of precursors 1, 1.5, and 2 M were shown in Fig.9. Values of average grain size (G.S), surface roughness, and root mean square (rms) roughness for prepared films were tabulated in Table 4.

Prepared film at all molar concentrations were smooth, good adhesion to the substrate. The films at concentration 1 M and 1.5 M showed structures like conical shape, but at 2 M the structure like lobes shape covering all surface of film. The increasing in the molar concentrations of precursors leads to increase the nanoparticles to the large crystals due to the increasing the growth process (ismail, Al-Samarai, & Ahmed, 2020).

Fig.9.AFM images of prepared CuAlS₂ thin films for molar concentrations of precursors (a) 1 M, (b) 1.5 M, and (c) 2 M.

Table 4, shows values of the average grain size (G.S), root mean square (rms) roughness, and surface roughness increase in the range (45 to 72 nm), (0.467 to 4.33 nm), (0.304 to 3.36 nm), respectively with the increasing the molar concentrations of precursors from 1 to 2 M.

Table 4. Values of (G.S from FESEM and AFM, surface roughness, rms roughness) of deposit CuAlS₂ thin film for different molar concentrations of precursors.

concentrations of precursors	Average G.S (nm) by FESEM	by AFM measurements		
		Average G.S (nm)	surface roughness (nm)	rms roughness (nm)
1 M	45	62	0.304	0.467
1.5 M	52	130	0.963	1.7
2 M	72	-	3.36	4.33

The same manner was observed for average grain sizes which were found by FESEM and AFM results which are shown in the Table 3.

4. Conclusions

In this study, CuAlS₂ thin films on amorphous glass substrates were prepared by using the CBD technique at substrate temperature 75°C and pH value 10.5, with different molar concentrations of precursors 1, 1.5, and 2 M. The highlight above results is following:

The prepared films showed the amorphous structure. Increasing the molar concentration of precursors gives simple enhancement in structure of prepared films, and this is clear in the thin CuAlS₂ film at molar concentration 1.5 and 2 M. The average thickness of deposit films increases with increasing the molar concentration of precursors from 1 to 1.5 M.

The deposited films were a good surface morphology, homogenous and uniform spherical nanoparticles over the substrate surface with very little agglomerated particles. While the topography of deposited films showed nanoparticles with structures like conical shape at concentration 1 M and 1.5 M, while at 2 M the structure likes lobes shape covering all surface of film was observed. Average grain size, root mean square (rms) roughness, and surface roughness of thin films increase with increasing the molar concentration of precursors from 1 to 2 M.

The prepared films showed direct band gaps which were decreased from 3.6 to 3.5 eV with increasing molar concentration from 1 to 1.5 M, and increase to 4 eV at 2 M. The absorption spectrum shows high absorption in the ultraviolet region, and absorption edge decreases with increasing the molar concentration.

At deposition time 30 min., the prepared films exhibit the minimum value for carrier concentration and conductivity, while the maximum value for resistivity and mobility. The type of conductivity of prepared films was n-type at all molar concentrations of precursors.

The obtained results of the prepared CuAlS₂ thin films can be suitable in many optoelectronics applications.

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