Effect of complex agent concentration on the structural and morphological properties of $CuAlS_2$ thin films prepared by chemical bath deposition technique

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$CuAlS_2$ 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, and fixed deposition time 40 minutes. In this study effect of molar concentrations (0.03, 0.05, and 0.06 M) of complex agent Na_2EDTA on structural, morphological, and topological properties of deposit thin films were studied by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) with cross section, and atomic force microscopy (AFM), respectively. The result showed that all prepared films were amorphous structures. The cross section analysis showed a good adhesion between prepared films and glass substrates, average thickness of films was affected by concentration of complex agent, where was low at 0.03 and 0.06 M, while was high at 0.05 M. The prepared films showed homogenous and uniform spherical nanoparticles with average grain size (64 to 79 nm) increased with increasing complex agent concentration. AFM images showed that the prepared films at 0.05 and 0.06 M had the same structures as conical and spherical shapes with the homogenous distribution on the surface of the films compared with that at 0.03 M. Also, the surface roughness, and root mean square (rms) roughness were varied in the range (0.33 to 1.74 nm) and (0.44 to 2.34 nm), respectively, where the less roughness were found at 0.05 M complex agent. The prepared films at 0.05 M complex agent showed the best properties which can be useful for many applications in optoelectronics devices.

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1. Introduction

The ternary chalcopyrite compounds have revealed much interest as semiconductors[1][2], among chalcopyrite semiconductors, $CuAlS_2$ is one of the members of the ternary chalcopyrite family having the direct optical band gap of 3.5 eV, and this is highest among those of all the chalcopyrite compound semiconductors can be suitable for using as transparent p-type back contact in CIGS based solar cells[3], and making it an interesting material for applications in solar cell, photovoltaic, a window layer in solar cell, optical detectors, light emitting diodes, in laser diodes [4], thin film transistors, transparent electronics, and flat screen displays [5].

There are many techniques used to prepare ternary $CuAlS_2$ thin films, such as powder metallurgy technique [6], chemical spray pyrolysis [7], metal organic chemical vapour deposition (MOCVD) [8], Electrophoretic Deposition (EPD) [9], Electron beam evaporation [10], hydrothermal method (HT) [11], vacuum thermal evaporation [12], chemical vapour transport (CVT) technique [13], wet chemical method [14][15], direct polyol methods [16][17], simple colloidal route [18], spark plasma sintering [19], sulfurization of metallic precursors in a vacuum [20]. Chemical bath deposition technique (CBD) has been used to prepare the $CuAlS_2$ thin films because their advantages comparing with other techniques such as low cost, 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

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dissolved in distilled water, nontoxic for using, and simplicity of the films preparation of films on various substrates. [21][22]

The role of a complex agent for prepared thin films by CBD technique was very important to deposit thin films on the substrates. The Triethanolamine (TEA) represents one of the most types of complex agent which have been used to prepare $CuAlS_2$ thin films by many researches. Where, Tariq J. et al., prepared $CuAlS_2$ thin films by CBD technique on glass substrates, from aqueous solutions with Triethanolamine (TEA) as a complex agent, structural properties showed all films were amorphous as deposited and annealing [23]. S.M. Ahmad prepared $CuAlS_2$ thin films by SPS and CBD technique from aqueous solutions with Triethanolamine (TEA) a complex agent, with deposition time 48h at room temperature, structural properties showed a polycrystalline nature of thin films by CPS and amorphous nature by CBD technique [24]. Sunil H. Chaka et al. prepared $CuAlS_2$ thin films by dip coating deposition from aqueous solutions with Triethanolamine (TEA) as a complex agent, and with pH 9.5, and the structural studies showed a tetragonal structure [4].

In the present work the disodium salt dehydrate $Na_2EDTA.2H_2O$ as the complex agent has been used for the first time to deposited $CuAlS_2$ thin films by CBD technique.

In this study $CuAlS_2$ thin films were deposited at T_s 75°C in alkaline medium with pH 10.5, using an aqueous solution of copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$), aluminium sulphate [$Al_2(SO_4)_3.16H_2O$], thiourea [$(NH_2)_2CS$], ammonia solution (NH_3). EDTA disodium salt dehydrate $Na_2EDTA.2H_2O$ was used as a complex agent. Effect of different molar concentrations of complex agent (0.03, 0.05, and 0.06M) on the optical and electrical properties of prepared thin films was studied. The aim of this study to find the best molar concentrations of complex agent for getting the highest quality of deposited thin films to use it in different optoelectronic devices.

2. Experimental details

Solution of $CuAlS_2$ was prepared with molar concentrations of precursors (0.075, 0.0375, 0.15M) from copper (II) sulphate pentahydrate [$CuSO_4.5H_2O$] (Honyewell Fluka, Germany), Aluminium sulphate [$Al_2(SO_4)_3.16H_2O$] (Thomas Baker, India), and Thiourea [$(NH_2)_2CS$] (Merck, Germany), which used as a source of Cu, Al, and S ions, respectively. EDTA disodium salt dihydrate [$Na_2EDTA.2H_2O$] (Glentham, UK) with three different molar concentrations (0.03, 0.05, and 0.06M) 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 wished 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 wished by distilled water and lifted to dry in air. The advantage of cleaned procedure to enhance the nucleation and adherent thin films on glass substrates.

The solution was performed for concentrations of precursors (0.075, 0.0375, 0.15M), by mixing 10ml of copper sulphate $CuSO_4.5H_2O$ (0.05M) added into beaker 100 ml, and stirred on hotplate heater at 40°C by magnetic dipole for five min., and this process was repeated continuously for all prepared solution, added to it 10ml of Na_2EDTA (0.03M), and stirred for 5 min., 5 ml of $Al_2(SO_4)_3.16H_2O$ (0.0375M) 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 $(NH_2)_2$ CS (0.15M) 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 wished by distilled water and lifted to dry in air.

The XRD patterns of deposit $CuAlS_2$ thin films were taken by the Phillips X-pert High Score PANalytical X-ray diffractometer with CuKα ($\lambda = 1.5406\ \dot{A}$) radiation as a source, with the range of 2θ degree from 10.35° to 80.00°, with a step size (2θ) 0.05°, and scan step time 1s.

The Surface morphology and cross section of deposit films were characterized 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 was tested by atomic force microscopy (AFM), model JPK Nanowizard, Germany, where the physical size of surface topography of films is observed approximately from (2000, 2000) to (3500, 3500) nm.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction patterns of deposit $CuAlS_2$ thin films onto the amorphous glass substrate for complex agent concentration (0.03, 0.05, and 0.06 M), are shown in Fig.1. The amorphous structure of all prepared thin films was observed, where no peaks in all films. This behaviour has been mentioned by other researchers [23],[24]. 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 [25].

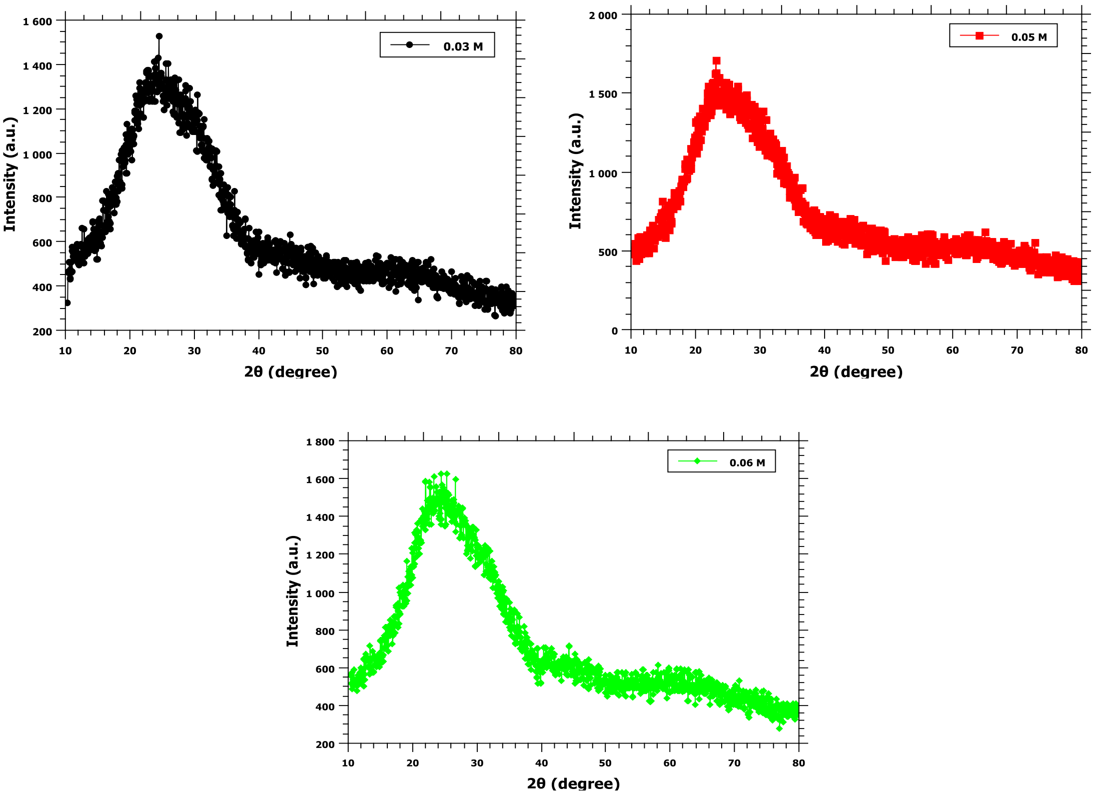


Fig. 1. XRD patterns for $CuAlS_2$ thin films for complex agent a) 0.03, b) 0.05, and c) 0.06 M.

3.2. Cross section and average of thickness

The cross section and average thickness of $CuAlS_2$ thin films were done by cross section analysis of deposit films which are shown in Fig.2.

The cross section shows the interfacial adhesion between $CuAlS_2$ thin films and substrates are good in all complex agent concentrations. The amount of deposit films onto the substrate is affected by concentration of complex agent, where is low at 0.03 and 0.06 M, while being high at

0.05 M, and this means the growth process of deposited films is high and uniform. Therefore the formed films at this molarity 0.05 M of complex agent are smooth and homogenous structure, uniform distribution of particles on the film surface as are seen in fig.2 (b).

The values of thickness average were 17, 780, and 300 nm for molarity of complex agent 0.03, 0.05, and 0.06 M, respectively. The thickness increases with complex agent from 0.03 to 0.05 M, and then decreases at 0.06 M. Therefore, the thicknesses of deposit films were affected by the molarity of complex agent, where the thickness was not exceeded by increasing the molarity of complex agent after 0.05 M, this may be the solution of prepared films arrived to saturation state, and this means the homogenous processes on deposit layer of films were reduced with increasing the molarity of complex agent.

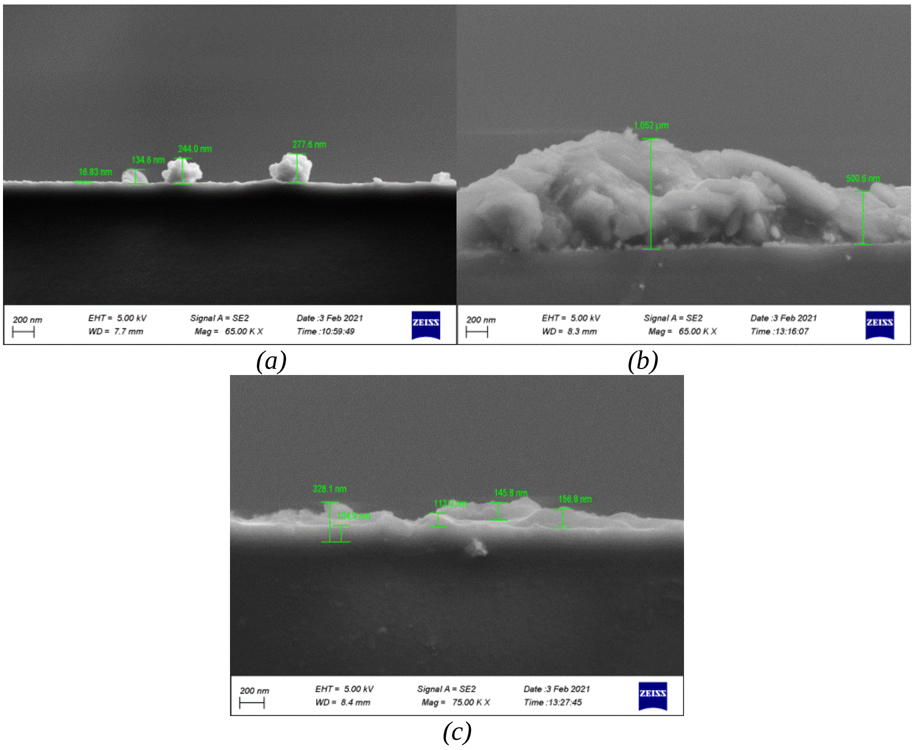


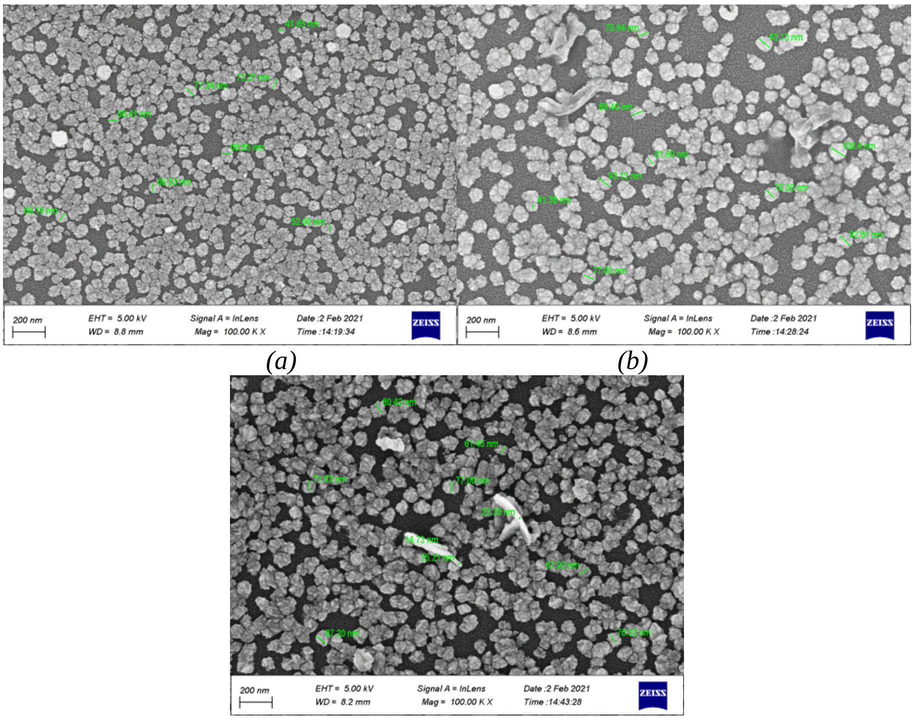
Fig. 2. Cross section images of $CuAlS_2$ thin films for complex agent a) 0.03, b) 0.05, and c) 0.06 M.

3.3. FESEM characterization

Morphological properties of $CuAlS_2$ thin films were done by field emission scanning electron microscopy (FESEM). FESEM images of prepared films for complex agent concentration (0.03, 0.05, and 0.06 M) were shown in Fig.3.The prepared film at 0.03 M shows homogenous and uniform spherical nanoparticles with a good surface morphology over the surface of substrate with the average grain size of about 64 nm, therefore the vacancies between the grains is very little.

At complex agent 0.05 M, the prepared film shows spherical nanoparticles with increasing in the average grain size of about 79 nm. While the prepared film at 0.06 M shows spherical nanoparticles covering large areas of total film with an average grain size about 75 nm, and very few agglomerated particles were found. The morphological properties at 0.05 M showed enhancement in the microstructure of prepared film, and the highest average grain size was observed. The grain sizes of deposited films increase with the increasing the molar concentration of complex agent are shown in Table 1, and this may due to the increasing the growth process in the prepared films.

The values of G.S in this work are smaller than with that found (380 nm and 150 nm) by Ahmad [24], and greater than with that found (19.09 nm) by Moataz et al [6].



(a) *(b)*

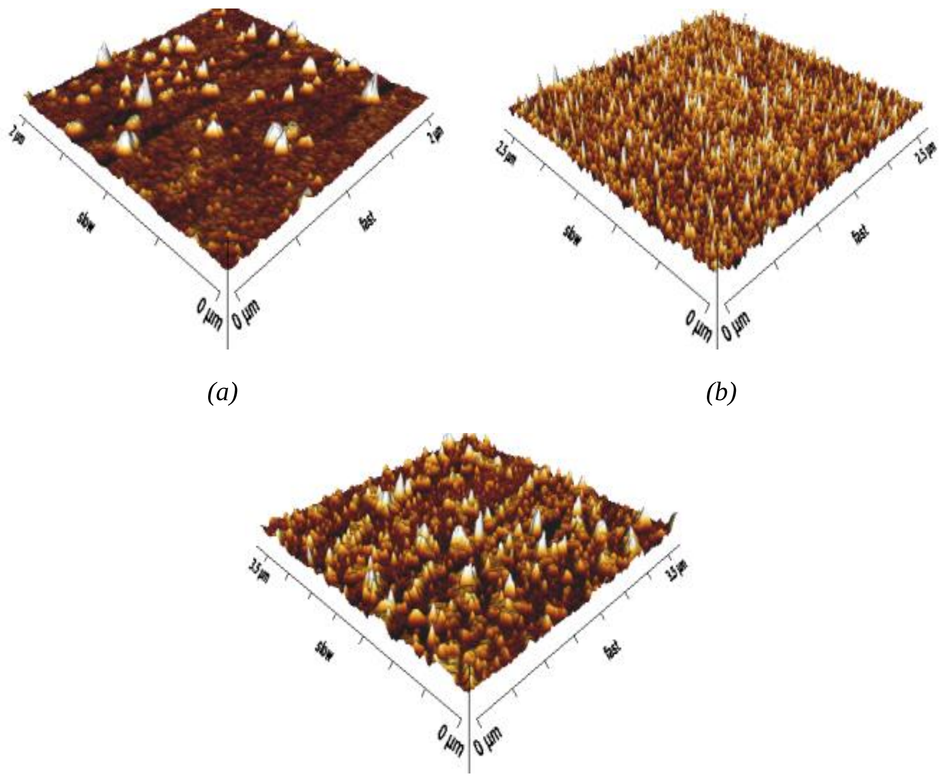
(c)

Fig. 3. FESEM images of prepared $CuAlS_2$ thin films for complex agent a) 0.03, b) 0.05, and c) 0.06 M.

3.4. AFM characterization

Topography properties of prepared $CuAlS_2$ thin films were taken by atomic force microscopy (AFM). AFM images for prepared $CuAlS_2$ thin films on glass substrate for complex agent concentration (0.03, 0.05, and 0.06 M) are shown in Fig.4. Values of average grain size (G.S), surface roughness, and root mean square (rms) roughness for prepared films were tabulated in Table 1.

Prepared film at 0.03 M show some agglomerated particles, therefore the distribution on the film surface is not homogenous, may be as a result the low thickness. While for prepared films at 0.05 and 0.06 M have the same structures as conical and spherical shapes with the homogenous distribution on the surface of the films, where the thickness is high. At complex agent 0.05 M, the deposited film exhibit smooth surface and cover all area of the film with less surface roughness 0.33 nm, and gran size 45 nm compared with that 1.74 and 136 nm, respectively, for deposited film at 0.06 M. The increasing in the complex agent concentration leads to increase the nanoparticles to the large crystals due to the increasing the growth process [26].



(a) (b)

(c)

Fig. 4. AFM images of prepared $CuAlS_2$ thin films for complex agent a) 0.03, b) 0.05, and c) 0.06 M.

Table 1, shows values of the average grain size $(G.S)_{AFM}$ from AFM measurements which are varied in the range (45 to 136 nm), and average $(G.S)_{SEM}$ by FESEM measurements which are varied in the range (64 to 79 nm). Whereas root mean square (rms) roughness vary in the range (0.44 to 2.34 nm). Also, the surface roughness are varied in the range (0.33 to 1.74 nm).

Table 1. Values of (G.S from FESEM and AFM, surface roughness, rms roughness) of deposit $CuAlS_2$ thin film for different complex agent concentrations.

Molar of complex agent (M)	$(G.S)_{SEM}$ (nm)	by AFM measurements		
		$(G.S)_{AFM}$ (nm)	surface roughness (nm)	rms roughness(nm)
0.03	64	108	0.9	1.56
0.05	79	45	0.33	0.44
0.06	75	136	1.74	2.34

The manner of surface roughness is the same as rms roughness for all concentration of complex agent.

The different manner was observed for average grain sizes which were found from FESEM and AFM results which are shown in the Table 3, and the difference values of G.S due to the different characterization between FESEM which analyses morphological properties in two dimensions, and AFM which analyses topography of films in three dimensions. The observed behaviour is same for the surface roughness, and rms roughness with the changing the concentration of complex agent.

4. Conclusions

In this study, $CuAlS_2$ thin films on amorphous glass substrates were prepared by using the CBD technique at a fixed deposition time 40 minutes, substrate temperature 75°C, pH value 10.5, and with different complex agent concentration (0.03, 0.05, and 0.06 M).

The outcome of the results is included:

The amorphous structures were exhibited in all prepared films. Increasing of complex agent concentration gives simple enhancement in structure of prepared films.

The high value of thickness average was 780 nm at molarity of complex agent 0.05 M, while being 17 and 300 nm at 0.03 M and 0.06 M, respectively.

From FESEM characterization, all prepared films reveal homogenous and uniform spherical nanoparticles with a good surface morphology over the surface of substrate. The grain sizes of deposited films increase with the increasing the molar concentration of complex agent. The high average grain size 79 and 75 nm are observed at complex agent 0.05 and 0.06 M, respectively, while lower average grain size is observed at 0.03 M of complex agent.

From AFM characterization, the deposited film exhibit smooth surface and cover all areas of the film at complex agent 0.05 M, with less surface roughness 0.33 nm, and grain size 45 nm. While at 0.03 and 0.06 M of complex agent, the prepared films have high grain size 108 and 136 nm, with surface roughness 0.9 and 1.74 nm, respectively.

The obtained values at different concentration of complex agent of the prepared $CuAlS_2$ thin films can be useful for many applications in optoelectronics devices.

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