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EFFECT OF COMPLEXING AGENT (Na_2EDTA) ON THE DEPOSITION OF COPPER TIN SULPHIDE THIN FILMS

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Abstract

Copper tin Sulphide (CTS) thin films were prepared by chemically bath deposited in aqueous solutions containing sources of copper, tin and sulphur. The effect of different molar concentration of complexing agent on the growth of thin films was reported. The structure, optical and surface topography characteristics of thin films of copper tin sulphide grown on glass substrates were investigated by X-ray diffraction, UV-Vis spectrophotometry and atomic force microscopy techniques. The X-ray diffraction showed that the most prominent peak at $2\theta = 50.60°$ which belong to (223) plane of Cu_4SnS_4. The atomic force microscopy indicated that the film deposited at the concentration of 0.1 M complexing agent exhibited narrow optical band-gap which is the requisite for light absorber layer in solar cell application. The band gap energy was found to be 1.5 eV with direct transition.

Keywords –copper tin sulphide, complexing agent, chemical bath deposition

Introduction

Solar cell energy applications took a great importance in the last few decades. This is because of the energy crisis and population caused by the traditional energy sources lie fossil fuels. So it’s important to develop low cost light absorber materials for thin film solar cell energy applications. Recently, relatively high efficient materials were discovered and investigated for example copper indium gallium diselenide (CIGS) and CdTe. Such materials have the problems of being expensive and lower availability, especially indium tellurium and gallium. Also the toxicity of elements lie cadmium makes these materials lower applicable.

Copper containing chalcogenides, especially compounds of group I-IV-VI have been reported to have wide applications in photovoltaic devices, light emitting diodes, nonlinear optical materials. Copper and tin could form several ternary sulphides[1]. Wu et al. reported five stable phases of ternary copper tin sulphides in the Cu–Sn–S system in the temperature range of 400–650°C: Cu_4SnS_4, Cu_2SnS_3, $Cu_2Sn_3S_7$, $Cu_5Sn_2S_7$, and $Cu_{10}Sn_2S_{13}$. Phase relations in a 500°C isothermal section show the first three of these phases lying on the Cu_2S-SnS_2 line. A monoclinic cell with $a = 12.68$ Å, $b = 7.351$ Å, $c = 12.76$ Å, and $\beta = 109.60°$ for $Cu_2Sn_3S_7$ and an orthorhombic (OR) cell with $a = 13.5$ Å, $b = 7.66$ Å, and $c = 6.395$ Å for Cu_4SnS_4 are the crystal structures reported[2]. The compound Cu_2SnS_3 is reported as dimorphic or polymorphic with a phase transition occurring at 780 °C. The high temperature form of this material is isomorphic with cubic ZnS (sphalerite), and the low temperature phase could be tetragonal, monoclinic, or triclinic.[2-4] The unit cell of triclinic Cu_2SnS_3 is reported to be identical to that of the mineral mohite (triclinic),[2] with $a = 6.64$ Å, $b = 11.51$ Å, $c = 19.93$ Å, a = 90°, $\beta = 109.75°$, and $\gamma = 90°$. On the basis of ellipsometric studies, Fiechter *et al.* reported for the material a fundamental band gap of 0.93 eV and a high absorption coefficient of 105 cm^{-1} in the visible region.

In this work, Cu_4SnS_4 thin films were prepare by chemical bath deposition method using Na_2EDTA as a complexing agent. The effect of Na_2EDTA on the properties of thin films was studied. X-ray diffraction was used to study the structural properties of films. Meanwhile, the morphological and optical properties of *CTS* films were investigated by using atomic force microscope and UV –Vis spectrometer, respectively.

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Experimental Details

The *CTS* thin films were prepared by the chemical bath deposition (CBD) method on the glass substrates. All the chemicals used for the deposition were prepared in distilled water. The *CTS* thin films were prepared from an acid bath using copper sulphate ($CuSO_4.5H_2O$), tin chloride ($SnCl_2.2H_2O$) and sodium thiosulphate ($Na_2S_2O_3.5H_2O$) acted as a source of copper, tin and sulphide ion, respectively. The disodium ethylenediamineteraacetic acid (Na_2EDTA) was used as a complexing agent during deposition process. It is used to chelate with Cu^{2+} and Sn^{2+} to obtain Cu-EDTA and Sn-EDTA complex solution which can improve the lifetime of the deposition bath as well as the adhesion of deposited films on the glass substrate. In order to investigate the effect of complexing agent, we prepare precursor solution with complexing agent by varying molar concentration (0.05M - 0.15M) and without complexing agent.

The glass substrates were thoroughly cleaned before dipping into the reaction bath. To do this, the substrates were degreased by washing with detergent solution. Thereafter they were degreased with ultrasonic cleaner using distilled water, acetone and isopropyl alcohol (*IPA*) for each 15 minutes. The degreased, cleaned surface has the advantage of providing nucleation centre for the growth of the films, hence, yielding highly adhesive and uniformly deposited films.

In the preparation of reference solution, 0.05 M $SnCl_2$ and 0.05 M $CuSO_4$ were added in 100 ml beaker. Then this solution was stirred about 10 minutes and 0.05M $Na_2S_2O_3$ solution was then added into a beaker slowly under stirred condition. The resultant solution was stirred for 20 min. The pH values of the chemical bath were adjusted to pH 1.5 by adding hydrochloric acid.

For deposition of *CTS* films on the glass substrate, they were immersed vertically into acid bath. The deposition process was carried out for 2 hours at 50 °C. After deposition the glass substrates with *CTS* films were washed by distilled water to remove the contamination in the surface. The flow chart for growth process of *CTS* thin films is shown in Figure 1.

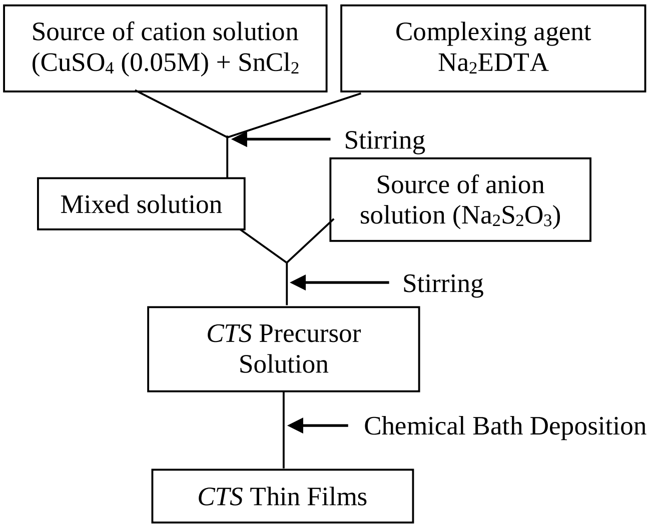


Figure 1 The flow chart for growth process of *CTS* thin films

Results and Discussion

In this section, the effect of complexing agent Na_2EDTA concentration on the optical and surface topography of *CTS* films were discussed.

Figure 2 shows the XRD patterns of *CTS* thin films chemically deposited with different molar concentrations of complexing agent (0.05 - 0.15M). The *CTS* thin films were found to be polycrystalline in nature. All the samples show four diffraction peaks at 26.69°, 30.80°, 47.22°, and 50.60° which are indexed to the (311), (112), (620), and (223) reflections of orthorhombic Cu_4SnS_4 structure. The intensity of observed major diffraction peaks increased with increasing molar concentration of complexing agent indicating the better crystallinity of *CTS* films with EDTA. The observed *d*-spacing values were compared with standard *d*-spacing values and are in good agreement with standard *d*-spacing values.

The peak positions (2θ) of the (311), (112), (620) and (223) reflections were used to calculate the lattice parameters using the following Equation

$$d = \frac{1}{[(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2})]^{1/2}}$$

where, d is the interplanar spacing that is determined from Bragg's Law ($2d\sin\theta = \lambda$, λ is the wavelength of X-ray and θ is the Bragg's angle). The lattice parameter values for the dominant orthorhombic structure are a = 13.6840 Å, b = 7.5001 Å, c = 6.4647 Å for *CTS* (Non EDTA), a = 13.6025 Å, b = 7.6484 Å, c = 6.4411 Å for *CTS* (0.05M EDTA), a = 13.6329 Å, b = 7.7164 Å, c = 6.4291 Å for *CTS* (0.1M EDTA), and a = 13.6440 Å, b = 7.7422 Å, c = 6.3244 Å for *CTS* (0.15M EDTA). It is found that the lattice constants of *CTS* structure are not significantly altered upon introducing EDTA.

A peak of *CTS* corresponding to the plane (223) was selected to determine the crystallite size of *CTS* thin filmusing Scherer's equation:

$$t = \frac{0.9\lambda}{\beta\cos\theta}$$

where, t is the crystallite size, λ is the X-ray wavelength, β is the Full-width half-maximum (*FWHM*) of the peak and θ is the Bragg's angle. The crystallite size of *CTS* thin film is estimated to be 109 nm, 102 nm, 73 nm, and 82 nm for *CTS* thin film without EDTA, with 0.05 M, 0.10 M and 0.15 M EDTA respectively.

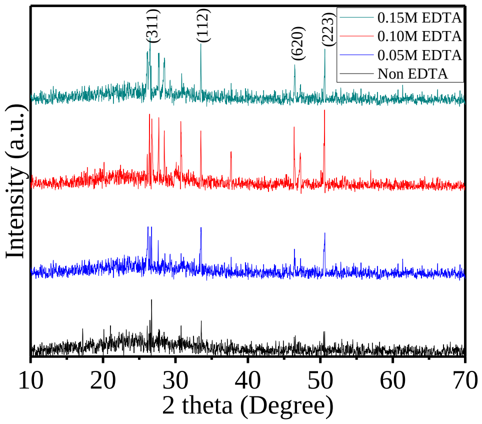
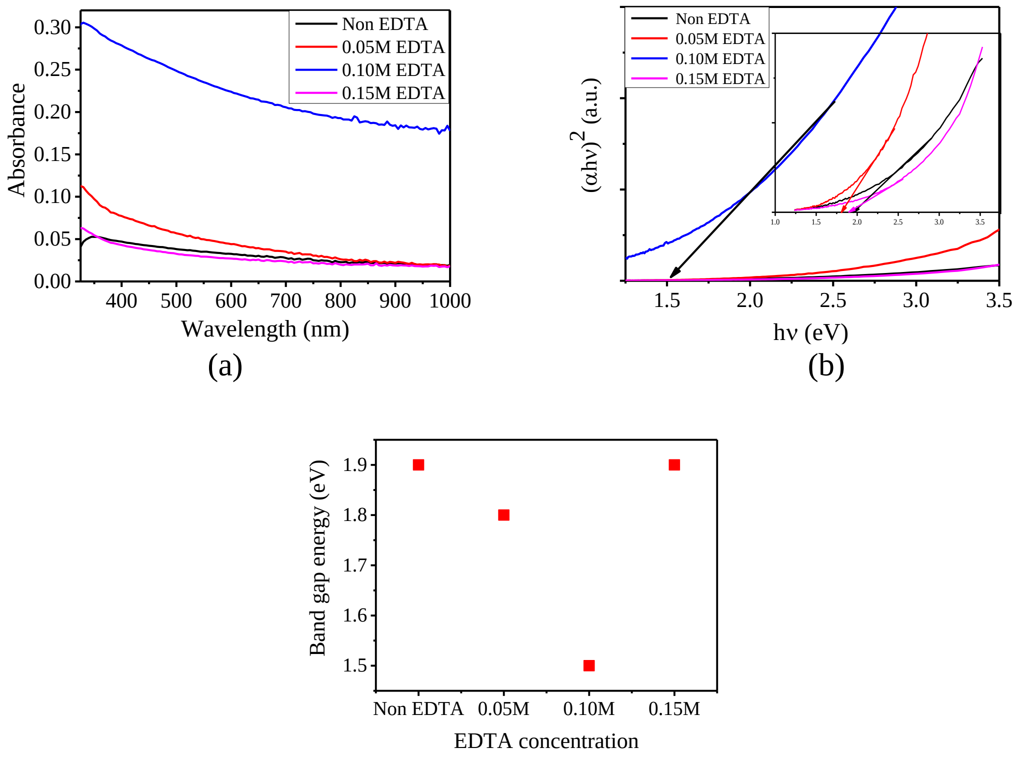


Figure 2 XRD diffraction patterns of *CTS* thin films with different molar concentration of complexing agent



(a) (b)

(c)

Figure 2 (a) Absorption spectra, (b) Plot of $(\alpha h\upsilon)^2$ Vs. hυ for *CTS* films with varying Na_2EDTA concentrations and (c) plot of E_gVs EDTA concentration

The optical properties of *CTS* films deposited in the solution with different Na_2EDTA concentrations were observed by using UV-vis Spectrophotometry. Figure 3 (a) shows the absorption spectra of *CTS* films with varying Na_2EDTA concentration. As seen in Figure 3, the absorption of *CTS* film with 0.1M Na_2EDTA is higher than those without Na_2EDTA and with 0.05 M Na_2EDTA. This higher absorption indicates the formation of more Cu_4SnS_4 with better adhesion to the substrate under this condition. Upon further increasing EDTA concentration to 0.15 M, the absorption of *CTS* films decreased again which is probably due to the fact that complexing reaction would complete at EDTA concentration of 0.10 M and exceeding concentration of complexing agent (0.15M) hindered the deposition of *CTS* films.

Band-gap energy is a key criterion to determine if the material of interest can be used as light absorber material in solar cells. The optical band-gap energies of *CTS* films were calculated on the basis of the optical absorption spectra using Equation (3).

$$\alpha = \frac{A(h\upsilon - Eg)^n}{h\upsilon} \qquad (3)$$

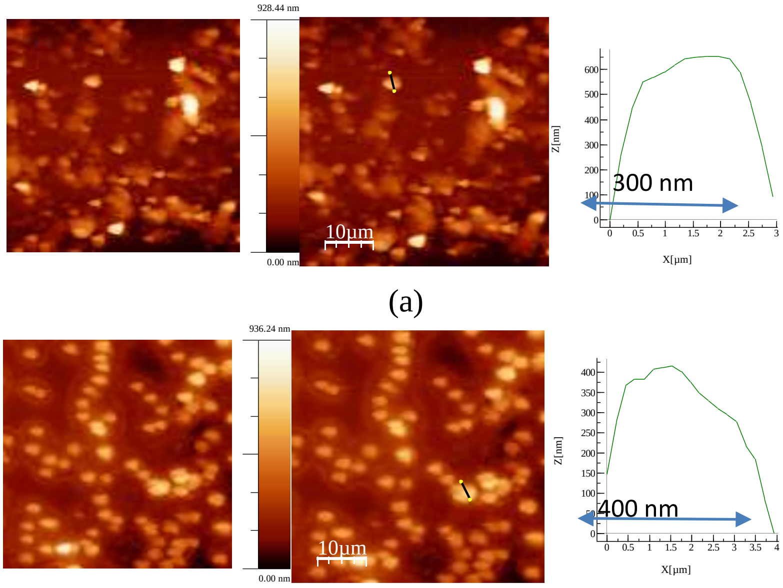
where, α is absorption coefficient, hν is the incident photon energy, A is the proportionality constant, E_g is the band-gap energy and n is either 2 for indirect band gap semiconductor or 1/2 for direct band-gap semiconductor. Since *CTS* is a direct band-gap semiconductor, the optical band-gap of *CTS* was attained by plotting $(\alpha h\upsilon)^2$ versus incident photon energy (hν). Figure 3 (b) shows the plot of $(\alpha h\upsilon)^2$ vs. hυ for the *CTS* films with different Na_2EDTA concentrations where the optical band gap was deduced from the extrapolation of the linear part of the plot. The obtained band gap energies are plotted against the EDTA concentration and the plot is shown in Figure 3 (c). It is observed that the band-gap energy of *CTS* film (Non EDTA) is about 1.9 eV. The band gap energy of the *CTS* films decreased to 1.8 eV at 0.05M and 0.15 M EDTA concentration. The lowest band gap energy of 1.5 eV was realized for EDTA concentration of 0.1 M. The direct band gap energy of 1.5 eV is good enough for light harvesting in solar cell.

The atomic force microscopy measurements were performed to study the differences in the surface topography for the samples deposited under different concentrations of Na_2EDTA. Figure 4 shows three dimensional AFM images for an area of 50µm x 50µm of CTS films. The morphological features are readily recognized by visual inspection of Figure 4. Comparing the AFM images, it is clearly seen that the surface of the film deposited at 0.10M Na_2EDTA was found to cover the surface of the substrate completely (Figure 4 (c)).

A detail analysis on size and shape of the grains seen on the surface of the films were performed by generating the line profiles shown on the right side of the AFM images. From the line profiles, the average grain size is 300 nm, 400 nm, 800 nm and 300 nm for CTS film with Non EDTA, 0.05M EDTA, 0.10M EDTA and 0.15M EDTA respectively. There are several big grains in the film obtained by 0.10M EDTA solution, which is due to the agglomeration of the smaller crystallites. However, the images show the film is more uniform and compacter than that prepared in the other concentrations of Na_2EDTA. The thin film obtained with Non EDTA and 0.05M EDTA are very thin, not compact and incomplete coverage over the substrate surface (Figure 4 (a) and (b)).

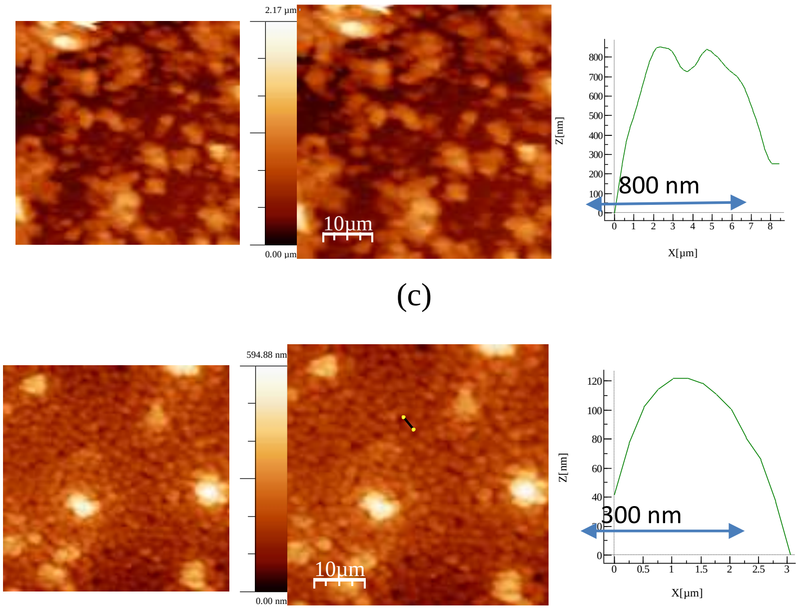
The thickness of the films was studied using AFM images. At the right side of the images, an intensity strip is shown, which indicates the depth and height along the z-axis. The thickness of the film was increased from 930 nm to 2200 nm as the concentration of Na_2EDTA increased from 0.05M to 0.1M. However, the thickness was reduced (595 nm) as the concentration of EDTA was further increased to 0.15M. It is probably due to the complexing reaction was complete with high concentration (0.1M) of complexing agent. Therefore, hinders the deposition of the films. The thicknesses of the films were listed in Table 1.

The roughness parameter is the most used parameter for observation of changes in surface topography. The surface roughnesses of the films were obtained using the analysis software (WSxM 5.0). The roughness values are calculated over the surface area of 50µm x50µm of *CTS* films and listed in Table 1. It is noted that the RMS (root mean square) roughness increase with increasing the concentration of the solution up to 0.10M EDTA. This may be due to the larger grain size of films. But the molar concentration (0.15M EDTA), the RMS (root mean square) roughness decrease again which is due to the thickness of the film was reduced.



(a)

(b)



(c)

(d)

Figure 4 Atomic force microscopy images of *CTS* thin films chemically deposited in the solution of different concentration of (a) Non EDTA (b) 0.05M EDTA (c) 0.10M EDTA (d) 0.15M EDTA. The line profiles correspond to the markings in the AFM images.

Table 1 The film thickness and RMS (root mean square) roughness for *CTS* films

EDTA concentration	Film thickness (nm)	RMS roughness (nm)
Non	~930	103.29
0.05M	~935	108.40
0.10M	~2200	254.10
0.15M	~595	59.39

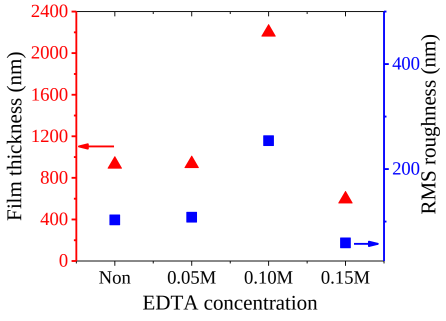


Figure 5 Plot of film thickness and RMS surface roughness of *CTS* films against EDTA concentration

Summary and Conclusion

Copper tin sulphide (*CTS*) films were deposited on glass substrates using chemical bath deposition method. The effect of complexing agent (Na_2EDTA) concentration on the structural, optical properties and surface topography were investigated. The XRD showed that *CTS* films exhibit orthorhombic structure with preferential orientation along the (223) plane. The *CTS* films deposited with 0.1M Na_2EDTA concentration have narrow optical band-gap which is the requisite for light absorber layer in solar cell application.The band gap was found to be 1.5 with direct transition.

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References

A. Kassim *et al.*, J. Chem. Chem. Eng., **29 (1)** (2010) 97.

A. Kassim *et al.*, Bull. Chem. Soc. Ethiop., **24 (2)** (2010) 259.

A. Kassim *et al.*, Mater. Sci.(Medziagotyra), **14** (2008) 101.

C. Gautier *et al.*, Thin Solid Films, **315**(1998) 118.

M. Atif *et al.*, Appl. Surf. Sci., **253 (**2006) 1198.

M. Ristov *et al.*, Sol. Energ. Mater. Sol. Cells, **69**(2001) 17.

N. Kamoun *et al.,* Thin Solid Films **515** (2007) 5952.

S. Seghaier *et al.*, Mater. Chem. Phys., **97**(2006)71.

W. Li *et al.*, J. Solid State Electrochem., **10** (2006) 48.

Z. Zainal *et al.*, Mater. Sci. Eng., **107** (2004) 181.