Chalcogenide Letters Vol. 15, No. 2, February 2018, p. 83 - 89

STRUCTURAL AND ELECTRICAL PROPERTIES OF Cu_2SnS_3 AND Cu_3SnS_4 THIN FILMS PREPARED BY CBD TECHNIQUE

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Thin CTS (Cu_2SnS_3 and Cu_3SnS_4) films prepared by chemical bath deposition (CBD) technique on glass substrates at 80 min deposition time. The influence of deposition parameters such as a substrate temperature (T_s=313, 323, 333 and 343 K) and pH value of chemical bath (1, 1.5 and 2) on the structural and electrical properties of the prepared Cu_2SnS_3 and Cu_3SnS_4 thin films were investigated using X-ray diffraction(XRD), Raman spectroscopy and Hall effect measurements, respectively. The results showed that the peak at 475 cm^{-1} that correspond to $Cu_{2-x}S$ hexagonal phase was appeared in all prepared films with high intensity, whereas the weaker peaks at 268-273 cm^{-1} were also founded by fitting the Raman spectra which correspond to cubic Cu_2SnS_3 phase. The optimum substrate temperature is 343 K for Cu_2SnS_3 thin films deposited at different pH values. The weaker peaks for Cu_3SnS_4 films found also at same wave number, those correspond to cubic Cu_2SnS_3 phase. These peaks were appeared in all T_s at pH equal 1.5 except for films deposited at 333 K substrate temperatures, where the peak was weak. The values of electrical resistivity, mobility, and carrier's concentration for thin Cu_2SnS_3 films according to T_s and pH value were varied within the range (1.316×10^{-3} - 1.117×10^{5} Ω. cm), (0.340 - 46.59 $cm^2/V.S$) and (2.937×10^{11} - 4.394×10^{21} cm^{-3}), respectively, while for thin Cu_3SnS_4 films according to T_s only were varied (8.349×10^{-3} - 5.470×10^{4} Ω. cm), (0.551 - 106.5 $cm^2/V.S$) and (1.072×10^{12} - 1.232×10^{21} cm^{-3}), respectively.

(Received October 29, 2017; Accepted February 5, 2018)

Keywords: Thin Cu_2SnS_3 and Cu_3SnS_4 films, substrate temperature, pH value,
Chemical bath deposition, Raman spectroscopy and electrical properties

1. Introduction

Performance of any solar cell is intimately related to the material properties which they are made, even though materials that exhibit properties suitable for photovoltaic applications are many, environmental friendly material or devices capable of converting solar power to electrical energy with moderate efficiency at low cost and possessing high stability [1].

Recently, researchers found that the polycrystalline semiconductors of I_2-IV-VI_3 group compounds have a potential usage in cost reduction of devices for photovoltaic applications. Furthermore, utilization of silicon wafer based solar cell can also be reduced [2].The main advantage of thin CTS film solar cells compared to silicon solar cells is lower cost, less energy is consumed for processing, and large-scale production is feasible. Therefore, photovoltaic conversion of solar energy from low cost solar cells will be a very important solution to supply the increasing energy demands when conventional source of energy is depleted in the future [2].

Raman spectroscopy offers an alternative to detect the phases that have similar structure because of the differences in the phonon spectra from these compounds [3]. Raman spectroscopy used by several research groups to find the Raman peak shift, which detect the secondary phases, structure type and measuring crystallinity for prepared thin films. The extent of crystalline or noncrystalline

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detected by the X-ray diffraction technique which reflected in the Raman spectra of the thin films as well as, the bands are broad in the amorphous materials and sharp in the crystalline materials [4].

Raman peak shifts for different structures of thin Cu_2SnS_3 films reported at 298 and 338 [5], 336-337 and 355 [6], 296, 335 and 351 [7], 297, 337 and 352 [8]. The tetragonal phase appeared at 290 and, 352 [3], 352 [9], 290 and 314 [6], whereas for monoclinic, 318 [8, 10] and for orthorhombic at 303and 355 [6], 303 [11], 267, 303 and 356 cm^{-1} [8,10], while for cubic phase, whereas secondary phases of hexagonal $Cu_{2-x}S$ was reported at 475 cm^{-1} [6,8,10].

This study is focused on the effect of substrate temperatures (313, 323, 333 and 343 K) and pH values (1, 1.5 and 2) on the structural and electrical properties for thin Cu_2SnS_3 and Cu_3SnS_4 films prepared by chemical bath deposition onto glass substrates at 80 min time deposition.

2. Experimental Procedure

Thin Cu_2SnS_3 films were deposited on 76mm × 26mm × 1mm clean glass slide by chemical bath deposition (CBD) technique. All the solutions were prepared using deionized water; the chemical compounds that used were copper sulfate ($CuSO_4.5H_2O$), tin chloride ($SnCl_2.2H_2O$), sodium thiosulfate ($Na_2S_2O_3.5H_2O$), disodiumethylenediaminetetraacetic ($Na_2EDTA.2H_2O$).The copper sulfate, tin chloride and sodium thiosulfate were acted as a source of copper, tin and sulfide ion, respectively. Na_2EDTA was as a complex agent with Cu^{2+} and Sn^{2+} to obtain Cu-EDTA and Sn-EDTA complex solutions. The presence of a complex agent EDTA in solution help to improve the lifetime of the deposition bath and adhesion of deposited films on glass substrate. The ratio of atomic weights is (2:1:3) and (3:1:4) for Cu: Sn: S in all deposition parameters, for more details see [12].

Set hot plate heater or water bath temperature at (313, 323, 333 and 343 K), pH value by pH-meter to (1, 1.5 or 2) where maintained by HCl solution and deposition time at 80 minute according to deposition parameters in this work. Cleaning process for substrate was performed to remove any contamination for substrates by using detergent at 373 K for ten minutes, distilled water at 373 K for ten minutes, followed by distilled water in ultrasonic bath for ten minutes, finally substrates immersing into ethanol and acetone solution for five minutes in ultrasonic bath then dry at room temperature. Place the substrate after cleaning process into beaker vertically. Two slides face to face used, then masked tightly together by paint or Teflon tape from one edge of their ends. After the deposition processes, the prepared films removed and washed by distilled water carefully. The substrates placed in air at room temperature until it has dried. After the deposition processes, the adhesion of prepared samples can be test by place it through path of vapor of distilled water.

Twelve samples of thin Cu_2SnS_3 films were fabricated by changing the deposition parameters depending on the symbol of sample where L, M, N and R refer to temperature substrate (Ts = 313, 323, 333 and 343 K), whereas A, without symbol, B refer to pH value 1, 1.5 and 2 respectively, and with constant deposition time (80 min). Four samples of thin Cu_3SnS_4 films were fabricated by changing the substrate temperature depending on the symbol of sample where (S, T, V and W) refer to substrate temperature (313, 323, 333 and 343 K), respectively, with constant deposition time (80 min.) and pH value (1.5).

The structural properties of prepared films were examined by using an X-ray diffraction (XRD) with Cu K_α radiation (λ= 1.5406 A°). Raman spectrometer model (RENISHAW invia) with an excitation wavelength of 532 nm which used with the ultra-low frequency (ULF) filter to measure Raman shifts as low as 15 cm^{-1}, with a spectral resolution of ~ 1cm^{-1}. The electrical properties measured using a Hall measurement system (HMS-3000 VER 3.5, Ecopia).

3. Results and discussion

The thin Cu_2SnS_3 and Cu_3SnS_4 films deposited by CBD technique on glass substrates at fixed deposition time(80min.) characterized by X-ray diffraction (XRD) and Raman spectroscopy with the excitation wavelength from an argon ion laser was 514.5nm at 20 mW. Raman spectra were taken for all prepared thin films within wave number from 150 cm^{-1} to 500 cm^{-1}. Fig (1) showed the X-ray diffraction pattern of as deposited (RT) thin Cu_2SnS_3 and Cu_3SnS_4 films onto the amorphous glass substrate. The amorphous structure of the prepared thin films were observed. This may be due to the substrate amorphous and to low thickness of prepared films, which causes losses in intensity. The prepared films by CBD technique tend to deposit films in low thickness and consisted nano particles, which have small grain size, therefore nano materials have small particles size, and this causes the lines in their diffractions peak to broaden. The broadening of the peak is due to a small number of crystal planes. This broadening cause a loss of intensity in the signal of their diffraction patterns, on the contrary of bulk have sharp, narrow and high intensity peaks [13, 14].

There is some improvement in structure of prepared thin films when T_s increase, and this clear for sample 6RB at T_s = 343 K for thin Cu_2SnS_3 film, while improvement not obtained for thin Cu_3SnS_4 films.

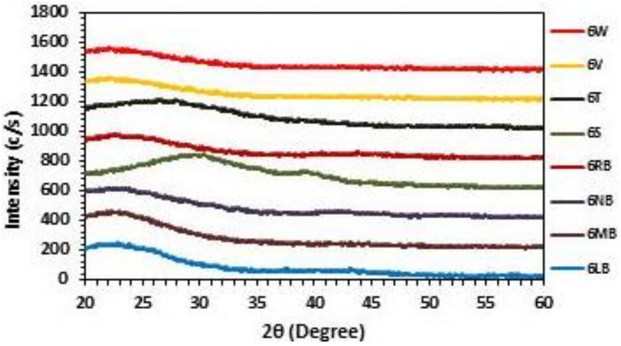

Fig. 1. XRD patterns for thin Cu_2SnS_3 and Cu_3SnS_4 films at 80 min deposition time and different T_s

The Raman spectroscopy pattern results showed in Figs. 2 - 5 for Cu_2SnS_3 thin films at different T_s (313, 323, 333, and 343 K) and pH values (1, 1.5 and 2). The peak at 475 cm^{-1}, which correspond to $Cu_{2-x}S$ hexagonal phase, appeared in all prepared films with large intensity. This may be due to increase the composition of copper in prepared films. This peak reported earlier in case of CTS films prepared by different technique and different researchers [4, 6, 10, 15].

The weaker peaks were found also at 268-273 cm^{-1} by fitting the Raman spectra, which correspond to cubic Cu_2SnS_3 phase [8, 10]. These peaks were appeared in different pH value when T_s increased, while the peak appear for sample 6LB at T_s= 313 K only, at T_s=323 K for the samples 6M and 6MB, at T_s= 333 K for the samples 6N and 6NB, whereas the peaks were appeared at T_s= 343 K for 6R, 6RA and 6RB samples. This indicates the 343 K substrate temperature represented the better for deposited thin films in different pH values.

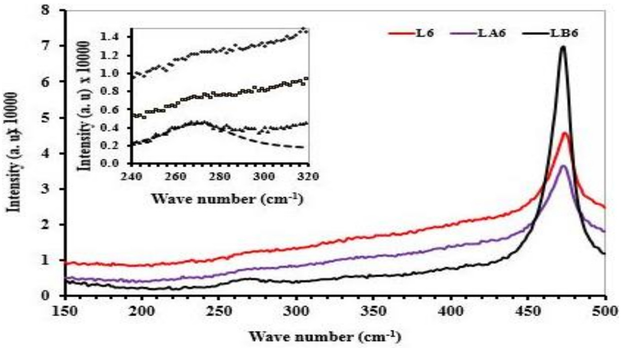

Fig. 2. Raman spectra of thin Cu_2SnS_3 films for different pH values (1, 1.5 and 2) at T_s= 313 K and deposition time= 80 min

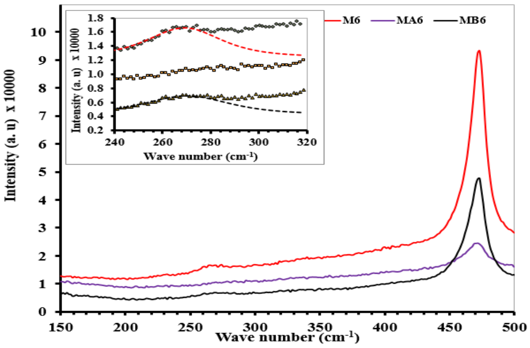

Fig. 3. Raman spectra of thin Cu_2SnS_3 films for different pH values (1, 1.5 and 2) at T_s= 323 K and deposition time= 80 min.

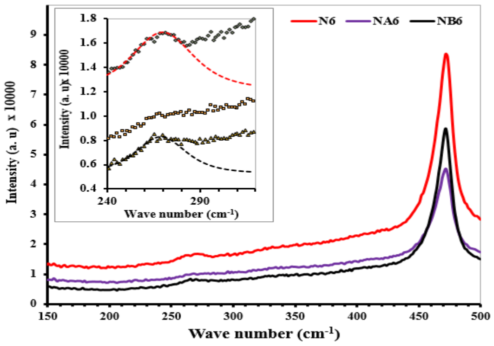

Fig. 4. Raman spectra of thin Cu_2SnS_3 films for different pH values (1, 1.5 and 2) at T_s= 333 K and deposition time= 80 min.

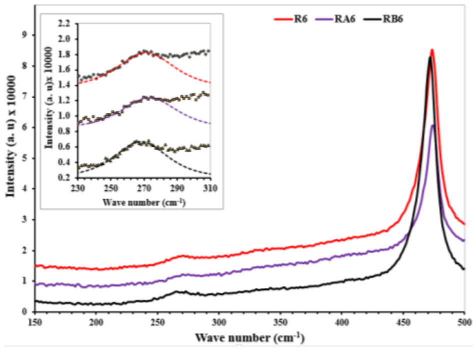

Fig. 5. Raman spectra of thin Cu_2SnS_3 films for different pH values (1, 1.5 and 2) at T_s= 343 K and deposition time= 80 min.

Fig. 6 represented the structure for Cu_3SnS_4 thin films at various T_s (313, 323, 333, and 343 K) and pH value 1.5. The weaker peaks were found also at 268-273 cm^{-1} which corresponds to cubic Cu_2SnS_3 phase, the peak appeared in all T_s at pH equal 1.5 for 6S, 6T and 6W samples except for sample 6V where the peak was very weak.

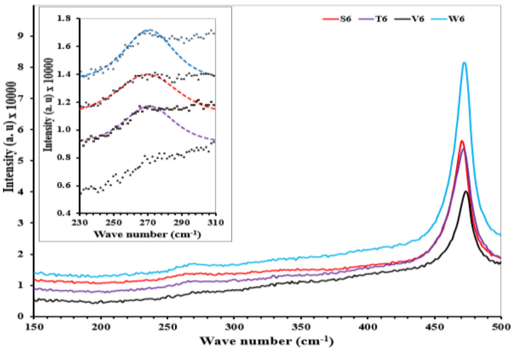

Fig. 6. Raman spectra of thin Cu_3SnS_4 films for different T_s= (313,323,333 and 343 K) at pH value 1.5 and deposition time= 80 min

The electrical properties of Cu_2SnS_3 and Cu_3SnS_4 thin films measured by Hall measurement at room temperature. Table (1) shows the electrical properties of thin Cu_2SnS_3 films prepared at deposition time= 80 min. for different T_s (313, 323,333 and 343 K) and pH values (1, 1.5 and 2).

It is obvious that the electrical resistivity (ρ) for thin Cu_2SnS_3 films in general decreased with increasing pH value and substrate temperature. Conductivity (σ) the manner inversely compare with that obtained for resistivity. The mobility (μ) in general decreased when pH increased, and start with high value at substrate temperature equal to 313 K after that it was decreased when substrate temperature equal to 323 and 333K, and finally increased at 343 K.

In general, the carrier concentrations (n) increased when T_s and pH value increase. From this, one can find that the best values obtained at high substrate temperature and pH values.

Table (2) illustrated the electrical properties for thin Cu_3SnS_4 films prepared at 80 min deposition time, 1.5 pH and different T_s (313, 323,333 and 343 K). The electrical resistivity decreased when T_s increased from 313 to 343 K. The behavior of conductivity inversely compare with that obtained for resistivity, i.e., it increased when T_s increased from 313 to 343 K. The mobility increased when T_s increased from 313 to 343 K. The concentration of carriers has large value at low T_s (313 and 323 K), and has low value at high substrate temperature (333 and 343 K).

Table 1. Electrical properties values (μ, n, ρ, σ and conductivity type) for thin Cu_2SnS_3 films at deposition time= 80 min., different pH and T_s

Name of sample	Type of conductivity	ρ (Ω.cm)	σ $(Ω.cm)^{-1}$	μ $(cm^2/V.S)$	n $(cm)^{-3}$
6LA	n-type	4.714×10^{4}	2.121×10^{-5}	46.59	2.842×10^{12}
6L	n-type	1.117×10^{5}	8.949×10^{-6}	190.2	2.937×10^{11}
6LB	n-type	7.500×10^{-3}	1.333×10^{2}	1.690	4.926×10^{20}
6MA	n-type	9.247×10^{-3}	1.081×10^{2}	0.418	1.615×10^{21}
6M	n-type	5.709×10^{-3}	1.752×10^{2}	0.467	2.337×10^{21}
6MB	n-type	1.119×10^{-2}	8.933×10^{1}	0.512	1.088×10^{21}
6NA	n-type	8.925×10^{-3}	1.120×10^{2}	0.401	1.743×10^{21}
6N	p-type	5.104×10^{-3}	1.959×10^{2}	5.693	2.148×10^{20}
6NB	p-type	4.175×10^{-3}	2.395×10^{2}	0.340	4.394×10^{21}
6RA	p-type	2.861×10^{-2}	3.496×10^{1}	3.905	5.588×10^{19}
6R	p-type	3.645×10^{-2}	2.743×10^{1}	2.323	7.373×10^{19}
6RB	p-type	1.316×10^{-3}	7.600×10^{2}	1.662	4.084×10^{21}

Table 2. Electrical properties values (μ, n, ρ, σ and conductivity type) for thin Cu_3SnS_4 films at deposition time= 80 min., pH= 1.5 and different T_s

Name of sample	Type of conductivity	ρ (Ω.cm)	σ $(\Omega.cm)^{-1}$	μ $(cm^2/V.S)$	n $(cm)^{-3}$
6S	p-type	1.112×10^{-2}	8.991×10^{1}	0.551	1.017×10^{21}
6T	p-type	8.349×10^{-3}	1.198×10^{2}	0.607	1.232×10^{21}
6V	p-type	5.470×10^{4}	1.824×10^{-5}	106.5	1.072×10^{12}
6W	p-type	8.703×10^{-3}	1.149×10^{2}	8.767	8.181×10^{19}

4. Conclusions

The CTS thin films (Cu_3SnS_4 and Cu_2SnS_3) have been prepared by chemical bath deposition under different substrate temperature and pH at 80 min deposition time. The outcome foundation of above data is the following:

The prepared films showed the amorphous structure. The increment in substrate temperature make some improvement in structure of prepared thin films, and this clear for thin Cu_2SnS_3 film at T_s = 343 K, while for thin Cu_3SnS_4 film the improvement obtain at low T_s (313 K).

The strong peak of Raman spectra was found at 475 cm^{-1} which correspond to $Cu_{2-x}S$ hexagonal phase in all prepared films due to have cu-rich.

The weaker peaks found at 268-273 cm^{-1} that corresponds to cubic Cu_2SnS_3 phase. These peaks appeared in all pH values at T_s 343 K, which represented that it is optimum temperature for deposited thin films. For Cu_3SnS_4 films, the weaker peaks found also at 268-273 cm^{-1} that corresponds to cubic Cu_2SnS_3 phase, and these peaks appeared in all T_s at pH equal 1.5 for samples 6S, 6T and 6W except the sample 6V where the peak was weak. The electrical resistivity for thin Cu_2SnS_3 and Cu_3SnS_4 films decrease when T_s and pH value increase. Mobility of CTS varied. In general, the concentration of carriers increases when T_s and pH value increase.

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