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Effect of Deposition Time Period on the Structural properties of Kesterite $\text{Cu}_2\text{ZnSnS}_4$ Thin films

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Abstract: $\text{Cu}_2\text{ZnSnS}_4$ thin films have been prepared by chemical phase synthesis at different deposition time period followed by chemical bath deposition method. The X-ray diffraction pattern confirms the formation of CZTS thin films with tetragonal kesterite structure. Current-Voltage characterization studies reveal that CZTS thin films exhibits ohmic contact with high electrical conductivity. These results show that the as prepared CZTS thin film is well opted for solar cell applications.

Keywords: Deposition time period, XRD, kesterite, I-V characteristic, Ohmic contact

I. INTRODUCTION

$\text{Cu}_2\text{ZnSnS}_4$ is tetragonal kesterite quaternary semiconductor compound. Its structural and electrical properties are optimum as an absorber layer for photovoltaic and thin film solar cell application. Now, CZTS is a good absorber material, low cost, earth abundant and non-toxic alternative to CuInGaSe_2 and CdTe is a scarcity, inexpensive and toxic element. CZTS thin films have been prepared by two types such as physical and chemical methods. Several film deposition processes are vacuum based methods such as Radio Frequency magnetron sputtering [1] Reactive sputtering [2] and Co-evaporation [3]. The solution based routes are Spray pyrolysis [4] Chemical bath deposition [5] Sol Gel spin and dip coating [6,7] and Electro deposition [8]. In this current work, $\text{Cu}_2\text{ZnSnS}_4$ thin film is prepared by chemical bath deposition technique. The CZTS thin films were scrutinized by XRD and I-V characteristics studies.

II. EXPERIMENTAL DETAILS

$\text{Cu}_2\text{ZnSnS}_4$ thin films have been prepared for different deposition time periods by chemical bath deposition method. Precursor solutions were prepared by 0.2 M Copper chloride, 0.1 M Zinc chloride, 0.1 M Tin chloride and 0.4 M Thiourea dissolved in 15 ml of de-ionized water separately and a small amount of stabilizing agent Triethanolamine is added to each of these solutions sustaining the pH at 12. The final precursor solution is stirred for 15 minutes using a magnetic stirrer which in turn changes the color of the solution from sky blue to golden yellow. The cleaned Si substrates were immersed in the solution for different deposition time periods maintaining the bath temperature at 65°C , further the deposited thin films were annealed at 100°C for 1 hr.

III. STRUCTURAL ANALYSIS

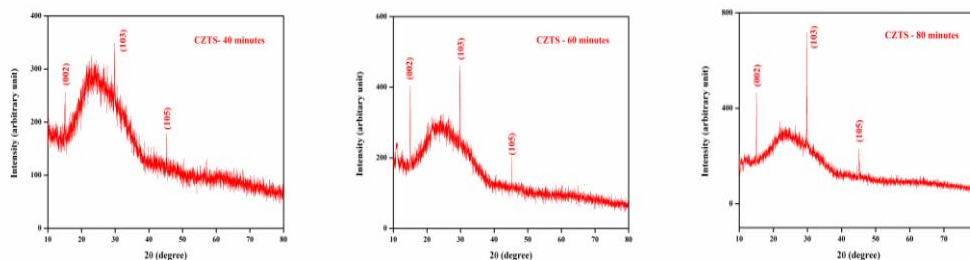


Figure 1 XRD pattern of CZTS thin film deposited at different time period

Figure 1 XRD pattern reveals that all the three CZTS thin films exhibiting polycrystalline nature for different deposition time periods and deposited films demonstrating $2\theta = 15^\circ, 29.8^\circ$ and 45° can be attributed to the (002), (103) and (105) planes respectively. The crystalline nature of all three CZTS thin films is almost the same. This XRD pattern matches well with the standard XRD pattern of CZTS (JCPDS NO: 26-0575). The XRD study confirms the formation of CZTS thin films of tetragonal kesterite structure [16-18].

It is noticed that increasing the deposition time period, the intensity of plane (103) get increased. when increasing deposition time period at 40, 60 and 80 minutes, the crystalline (grain) sizes are increasing in the range 44 nm, 86 nm and 134 nm and also film thickness are increasing in the range is 2808 Å, 3310 Å and 5012 Å respectively (Table 1).The crystalline size and micro strain can be calculated from the XRD pattern for different CZTS thin films. The average crystalline size (D) of CZTS thin film was calculated from the full width half maximum (FWHM) at (002), (103) and (105) planes using Scherrer formula $D = \frac{0.91}{\beta \cos \theta}$. Where, θ is the Braggs angle (diffraction angle) of the related peak, λ is the wavelength of the X-ray source, β is the full width half maximum (FWHM) [16-18]. The average grain size calculated for different deposition time period of CZTS thin films using at (002), (103) and (105) planes are tabulated.

The microstrain (ϵ) can be estimated by the following relation

$$\epsilon = \frac{\beta \cos \theta}{4}$$

The dislocation density (δ) can be estimated by the following relation

$$\delta = \frac{1}{D^2}$$

Table 1 shows the grain size (D), microstrain (ϵ), dislocation density (δ) values of CZTS thin films.

Table 1 Comparison Of Structural Parameters of CZTS Thin Films

Deposited time period (minutes)	Annealed temperature (°C)	hkl plane	Lattice Constant C (Å)	Dislocation density (Lines/m ²) 10 ¹⁰	Micro Strain (ε) (Lines ⁻² m ⁴) 10 ⁻⁴	Grain Size D (nm)	Average Grain Size (nm)
40	100	002	11.7810	0.000023	11.31	62.53	44.36
		103	9.4717	0.000031	8.39	42.76	
		105	10.0772	0.000046	8.64	27.79	
60	100	002	11.8600	0.000006	5.91	119.69	86.91
		103	9.4730	0.000008	4.20	85.50	
		105	10.1073	0.000012	4.33	55.55	
80	100	002	11.7688	0.000006	5.90	119.70	133.91
		103	9.4730	0.000002	2.10	171.00	
		105	10.0986	0.000003	2.19	111.04	

IV. ELECTRICAL CHARACTERIZATION

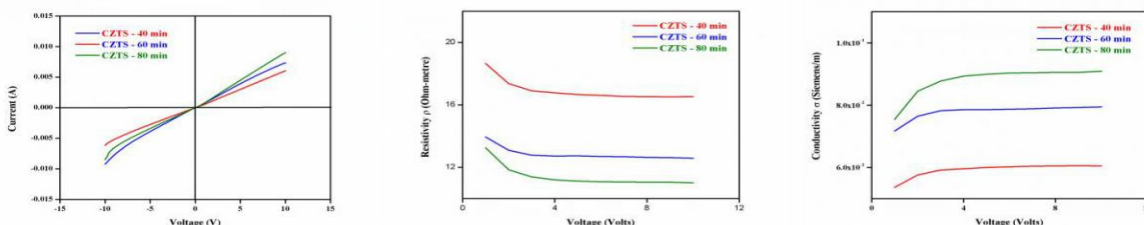


Figure 2(a) Current-Voltage (b) Resistivity – Voltage (c) Conductivity – Voltage plot of CZTS thin film deposited at different time period

Figure 2(a) shows the current – voltage (I-V) characteristic of CZTS thin films examined with I-V Interface set up measured in the dark region. The I-V measurement shows that current is directly proportional to the applied voltage and all the three CZTS thin films exhibits ohmic (Mott-Gurney) contact for dark region [17, 22]. Electrical parameters of CZTS film can be estimated by following relation (Table 2) $\rho = \frac{RA}{L}$ and $\sigma = \frac{L}{RA}$ Where, ρ is the resistivity of a material (Ohm-metre), R is the resistance of a material (Ohms), A is the cross-sectional area of the deposited material (m^2), L is the length of the film, σ is the electrical conductivity of a material. Figure 2(b) and 2(b) the resistivity decreases with increasing the electrical conductivity of CZTS thin films. The decrease in the resistivity range is due to the improvement in the crystallinity of film and an increase in the film thickness when there is an increase in the film deposition time period [23, 24].

Table 2 Electrical Parameters Of Czts Thin Films For Different Deposition Time Periods

Deposition Time Period (minutes)	Film Thickness (nm)	Applied voltage (V)	Current I (A)	Resistance R (Ohms)	Resistivity ρ (Ohmmeter)	Conductivity σ (Siemens/meter)
40	281	1.00E+00	5.36E-04	1.87E+03	1.33E+03	5.36E-02
		2.00E+00	1.15E-03	1.74E+03	1.18E+03	5.76E-02
		3.00E+00	1.78E-03	1.69E+03	1.14E+03	5.92E-02
		4.00E+00	2.38E-03	1.68E+03	1.12E+03	5.96E-02
		5.00E+00	3.61E-03	1.67E+03	1.11E+03	6.00E-02
		6.00E+00	3.61E-03	1.66E+03	1.11E+03	6.02E-02
		7.00E+00	4.23E-03	1.66E+03	1.11E+03	6.04E-02
		8.00E+00	4.84E-03	1.65E+03	1.10E+03	6.05E-02
		9.00E+00	5.45E-03	1.65E+03	1.10E+03	6.05E-02
		1.00E+01	6.05E-03	1.65E+03	1.10E+03	6.05E-02
60	331	1.00E+00	7.18E-04	1.39E+03	1.39E+01	7.17E-02
		2.00E+00	1.53E-03	1.31E+03	1.31E+01	7.65E-02
		3.00E+00	2.35E-03	1.28E+03	1.28E+01	7.82E-02
		4.00E+00	3.14E-03	1.27E+03	1.27E+01	7.86E-02
		5.00E+00	4.69E-03	1.27E+03	1.27E+01	7.86E-02
		6.00E+00	4.69E-03	1.27E+03	1.27E+01	7.87E-02
		7.00E+00	5.41E-03	1.27E+03	1.27E+01	7.89E-02
		8.00E+00	6.10E-03	1.26E+03	1.26E+01	7.91E-02
		9.00E+00	6.75E-03	1.26E+03	1.26E+01	7.92E-02
		1.00E+01	7.35E-03	1.26E+03	1.26E+01	7.94E-02

80	501	1.00E+00	7.55E-04	1.33E+03	1.33E+01	7.17E-02
		2.00E+00	1.69E-03	1.18E+03	1.18E+01	7.65E-02
		3.00E+00	2.64E-03	1.14E+03	1.14E+01	7.82E-02
		4.00E+00	3.58E-03	1.12E+03	1.12E+01	7.86E-02
		5.00E+00	5.42E-03	1.11E+03	1.11E+01	7.86E-02
		6.00E+00	5.42E-03	1.11E+03	1.11E+01	7.87E-02
		7.00E+00	6.33E-03	1.11E+03	1.11E+01	7.89E-02
		8.00E+00	7.25E-03	1.10E+03	1.10E+01	7.91E-02
		9.00E+00	8.15E-03	1.10E+03	1.10E+01	7.92E-02
		1.00E+01	9.02E-03	1.10E+03	1.10E+01	7.94E-02

V. CONCLUSION

Cu₂ZnSnS₄ thin films have been prepared by chemical phase synthesis at different deposition time period. The XRD analysis the result shows that all the films are polycrystalline nature and confirms the formation of CZTS thin films are tetragonal kesterite structure. When increases the film deposition time period, the crystalline size and film thickness are also increases. Current-Voltage characterization studies revealed CZTS thin films exhibits ohmic contact and high electrical conductivity. This CZTS thin film is well suitable for solar cell application.

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