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Optical Study of Copper Zinc Tin Sulfide Thin Films by Chemical Bath Deposition Technique

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Abstract: ***Solar cell absorber Copper Zinc Tin sulfide (CZTS) thin films have been prepared by chemical bath deposition (CBD) method using Triethanolamine as stabilizing agent in 60 ml precursor solution at different time interval on a pre-cleaned glass substrate. CZTS is a good absorber material for low cost and non-toxic. The prepared CZTS thin films were scrutinized by UV-Visible spectroscopy revealed that optical energy gaps decreases with increase in deposition time intervals and it contain the direct energy band gap is ~ 1.6 eV.***

Keywords: ***Thin Films, Chemical bath deposition, UV-Visible spectroscopy, Time interval, Direct band gap, Solar cells***

I. INTRODUCTION

Cu_2ZnSnS_4 (CZTS) belongs to I_2-II-IV-VI_4 quaternary semiconducting compound and famous in recent years as their optical and electrical properties are optimum for photovoltaic and solar cell application. Three types of crystal structure are observed in CZTS such as kesterite, stannite and wurtzite [1,2]. Besides, it is renowned that CZTS have a quaternary semiconductor has tetragonal kesterite structure such as more stable than other crystal structure like stannite because it has ~ 100 meV higher energy gap than others [2-4]. CZTS is good absorber material for photovoltaic cell because of its direct energy band gap ~ 1.6 eV and high absorption coefficient which create it highly appealing for single junction solar devices.

Now, CZTS is good absorber material, low cost, earth abundant and non-toxic alternative to $CuInGaSe_2$ (CIGS) and CdTe is an scarcity, inexpensive and toxic element such as indium and cadmium its toxicity exhibits to produce larger scale manufacture of solar cells. CZTS thin films have been obtained by various researches using numerous methods. Vacuum based methods such as Co-evaporation [5]

Radio Frequency magnetron sputtering [6] Reactive sputtering [7] and Pulsed laser deposition technique [8] are widely used for fabrication of CZTS thin films. Nowadays, the solution based routes are much attractive such as Chemical bath deposition (CBD) method [9] Sol Gel [10]

Successive ionic layer adsorption and reaction (SILAR) method [11] and Spray pyrolysis [12]. In this current work, Cu_2ZnSnS_4 (CZTS) thin film is prepared by chemical bath deposition technique (CBD) because of their advantages such as controlling of concentration of precursor and deposition parameters (pH, bath temperatur, deposition area), simple and low cost method. The CZTS thin films were scrutinized by UV-Visible spectroscopy, Photoluminescence studies.

II. EXPERIMENTAL DETAILS

The Cu_2ZnSnS_4 (CZTS) thin films have been prepared by chemical bath deposition method. Precursor solution were prepared by (2:1:1:4) ratio of 0.2M Copper chloride ($CuCl_2$), 0.1M Zinc chloride ($ZnCl_2$), 0.1M Tin chloride ($SnCl_2$), and 0.4M Thiourea (CH_4N_2S) dissolved in 15 ml of distilled water separately. To each of this solution a small amount of Triethanolamine (TEA) is added it acts as stabilizing agent. The pH of the solution is maintained about 12. The pH of the solution is measured using pH meter. The final precursor solution is stirred for 15 minutes using magnetic stirrer. Before stirring, the color of precursor solution is sky blue. After completing the stirring process the color of precursor solution was turned from sky blue to golden yellow. The final volume of bath solution is 60 ml. The pre-cleaned glass substrate is immersed on precursor solution for different deposition time intervals and simultaneously maintained constant bath temperature about 65°C. The deposited thin film substrates were annealed in a furnace at 100°C for 1 hr.

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III. RESULT AND DISCUSSION

A. *Optical Analysis*

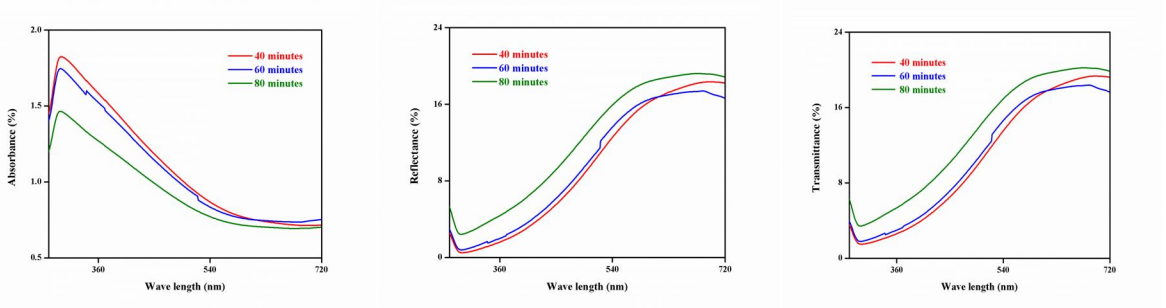

Figure 1: UV-Vis (a) Absorbance, (b) Transmittance and (c) Reflectance spectra of CZTS thin film deposited different time intervals

Figure 1: show (a) absorbance, (b) transmittance and (c) reflectance spectra of CZTS thin film examined with a UV-Visible spectrometer. The absorbance spectra of CZTS thin film of all the three samples, the absorbance is gradually decreasing from a peak value with increasing the wavelength in the visible region and the transmittance, reflectance of CZTS thin films is gradually increases with increasing film deposition time intervals [13-17]

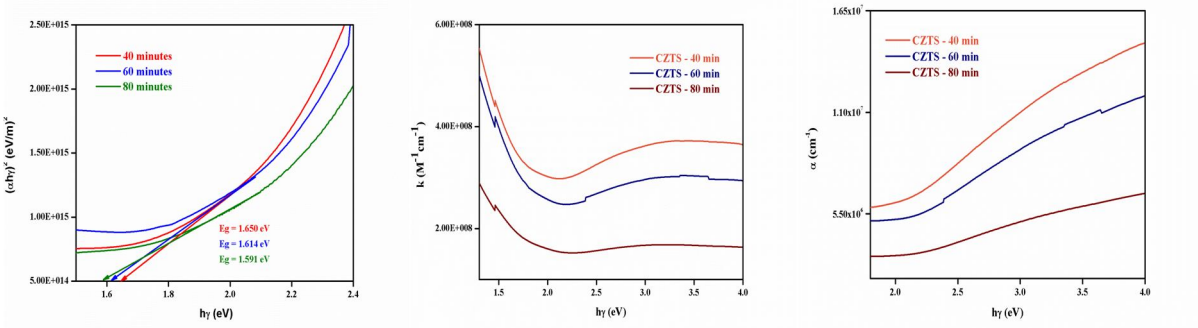

Figure 2: (a) Band gap energy (b) Absorption Coefficient Vs Photon energy (c) Extinction Coefficient Vs Photon energy of CZTS thin film deposited at different time intervals

Figure 2 shows a plot of (a) band gap energy (b) absorption coefficient (c) extinction coefficient of CZTS thin film estimated for different deposition time intervals. From Figre 2(a) ,the optical band gap can be calculated from the following relation $\alpha h\nu = B(h\nu - E_g)^{1/2}$ by plotting the line of the $(\alpha h\nu)^2$ Vs (hν) plot to meet the hν axis. The energy gaps of CZTS thin film achieved is E_g = 1.650 eV, 1.614 eV and1.591 eV for the film deposited at 40, 60 and 80 minutes respectively. It is in good agreement with previously reported works [18,19].

The band gap plot shows the band gap energy of CZTS thin film is decreases with increasing the deposition time intervals. When the deposition time interval of CZTS thin film increases, the crystalline size and thickness of the film also increases which in term allow less transparent and decrease in the optical band gap. The best band gap of CZTS thin film is 1.591eV obtained for the film deposited at 80 minutes [18-21].

Figure 2 (b) shows the absorption coefficient (α) can be estimated to either absorbance (A) data or transmittance data (T). In the present work, the absorption coefficient (α) of CZTS thin film is estimated for the absorbance data (A) using the following relation [3] $\alpha = \frac{2.303 \times A}{t}$, where A is the absorbance of the film, t is the thickness of the film [18,22]. Figure: 2 (c) The extinction coefficient (k) can be estimated from the absorption coefficient (α) using the following relation $k = \frac{\alpha\lambda}{4\pi}$ Where α is the absorption coefficient, λ is the wavelength of UV light.

The result shows that there is a decrease in extinction coefficient (K) with increases in photon energy [15]. The optical properties of CZTS thin films show that could be applicable for thin film solar cells.

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B. Photoluminescence Analysis

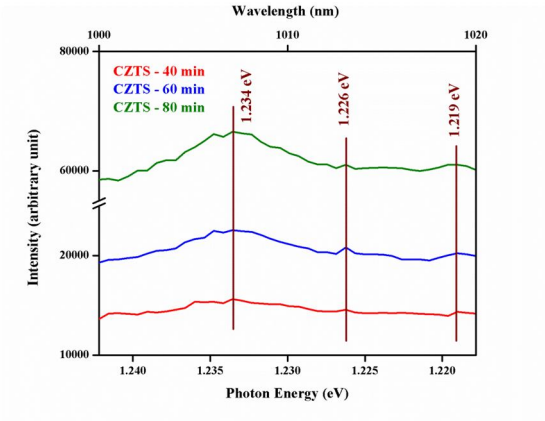

Figure 3: Photoluminescence plot of CZTS thin film deposited at different time intervals

Figure 3 shows the photoluminescence plot of CZTS thin films deposited at different time intervals recorded in the infrared region excited at wavelength 900 nm. PL spectra have an asymmetrically broad band with a maximum of intensity at 1.234 eV that is a typical band for semiconductor [23-26]. When the deposition time intervals of CZTS thin film increases, there is an increase in intensity, emission wave length and decrease in the photon energy. The main peak appears at 1007, 1013 and 1019 nm which is corresponding to the optical band gaps of 1.234, 1.226 and 1.219 eV respectively. The band gap range confirmed the presence of Cu_2S secondary phases in CZTS material. The secondary phases Cu_2S is p-type semiconductor with highly conductive nature and high defect concentration that is atomic vacancies, substitutions, intersticials etc [25].

IV. CONCLUSION

Copper Zinc Tin Sulfide (CZTS) thin films were prepared by chemical bath deposition (CBD) technique using TEA (Triethanolamine) for the purpose of stabilizing agent in 60 ml precursor solution and deposited at different time interval on a glass substrate. The prepared CZTS thin films were scrutinized by using UV-Visible spectroscopy and Photoluminescence. The optical band gaps are decreases with increasing film deposition time intervals and the direct optical band gap obtained in the range ~1.6 eV. PL spectra have an asymmetrically broad band with a maximum of intensity at 1.234 eV. The band gap range confirmed the presence of secondary phases in CZTS material which is more impact on solar cell performance.

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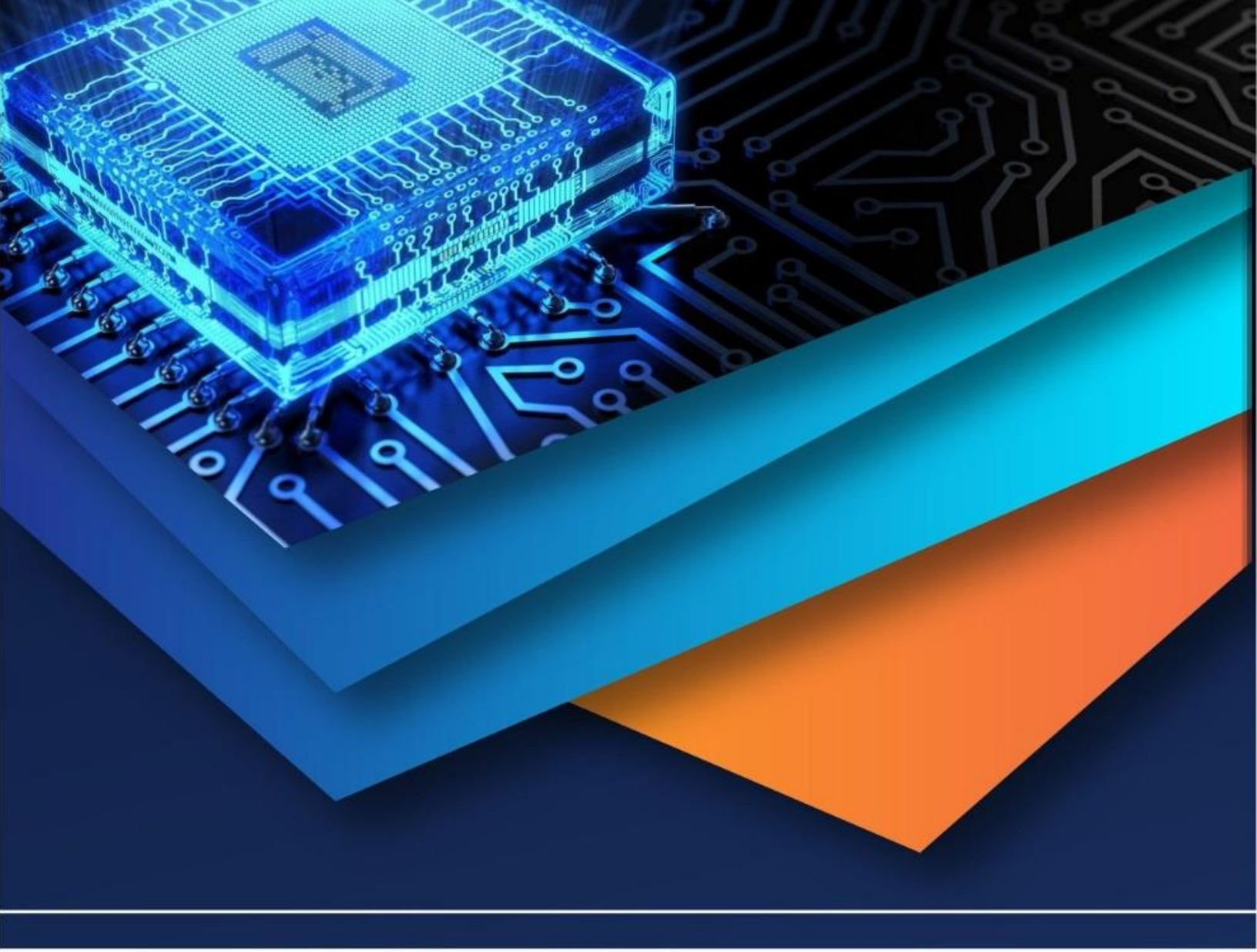

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