Characterization of Cadmium Doped Zinc in Copper-Zinc-Tin-Sulphide Cu2ZnSnS4 (CZTS) Absorber Material for Solar Energy Application

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Abstract:
Characterization of cadmium doped Zinc in copper-zinc-tin-sulphide (CZTS) absorber material for solar energy application was experimented in this research. Cadmium doped at various percentages was successfully deposited on sodalime glasses by spin coating technique. The samples were obtained by preparing Solution A containing copper acetate monohydrate Cu(CH3COO)2·H2O, Tn (ii) chloride SnCl2 and Thiourea CH3N2S all dissolved in 5ml methoxyethanol and solution B contained cadmium acetate Cd(CH3COO)2, Zinc acetate ZnC2H3O2 in 5ml methoxyethanol C6H5O2 both are then mixed, this was repeated at various concentrations of Zinc acetate and cadmium acetate to get different ratio composition. The electrical measurement showed a p-type conductivity, resistivity ranges between (0.054-0.193)Ωcm, carrier or bulk concentration range between (1.775×1019-1.864×1019)/cm3 and mobility with the range of (2.473-551) cm2/vs at room temperature. The CZTS films prepared showed optical absorption coefficient between (2.87–299.932) m−1 and an optical band gap between (1.35-1.76) eV, peak absorbance of 0.907 at visible region and peak optical conductivity of 0.895E+10 were obtained. The Copper-Zinc-Cadmium-Tin-Sulphide CZTS films created has thickness range between (1-87) nm, and a calculated power conversion efficiency of (0.48-8.48) % and showed best properties for low and moderate cadmium composition and was considered excellent for solar energy application.

Keywords: CZTS, absorbance, Efficiency, thin films, cadmium, band gap

1. Introduction
Optical property of thin films found a large number of disparate applications in science and technology coatings (Valkonen E, Ribbing C.G and Sundgren J.E, 1986). Cu/ZnSnS4 (CZTS) film has gained much interest in recent years, due to the fact that its optical property is optimum (1.4 -1.5) eV for photovoltaic application (Subramaniyan E.P, Rajesh G, Thambidurai M, 2014). CZTS is a p-type semiconductor which has an optimum band gap, and large absorption coefficient (>104cm−1) these make it an alternate potential candidate for thin film solar cells (Kumar A.V, Park N.K and Kim E.T, 2014). In the present century researchers have developed cost effective and non-toxic film based solar panels using inorganic chemicals with improved efficiency, due to lack of power sources, photovoltaic cells are much needed for the mankind which can be used in their daily life” (Shanenoor, S. K, Rao, M.C, Page1, 2018). In modern science and technology, effective and non-toxic development of thin film solar cells with high efficiency has emerged as a promising area of research in the field of solar cell technology (Kalowekamo, J., Baker, E., 2009). CZTS thin films are one of the promising absorber materials in solar cell industry because of their excellent material properties for obtaining high efficiency. The employment of these films in solar cells can improve the conversion efficiency by reducing recombination rate of photo-generated charge carriers due to larger grain size (M.Jiang, X.Yan, 2013). Hence CZTS thin films are attributed to have significantly increased in production due to the demand for renewable energy resources (Losanthan, k., Tyler, J., 2016).

Initially researchers have developed silicon based solar cell. Due to its high efficiency it is transformed into a promising candidate material in photovoltaic cell technology (Ericson,T., Kubart,J.J., Scragg,C., and Platzer, B, 2012). However there are certain disadvantages with the silicon based solar cells, chiefly their high fabrication cost. Hence these photovoltaic cells, are not used in household purposes. To avoid this problem there is a need for design or fabrication of modern technology solar cell incorporating high efficiency, low cost and non-silicon based photovoltaic cell.

In the past there have been different solar cells such as CdTe, Si, CIGS (Cu(InGa)Se2) and CTS (CuSnS3). However CZTS is used as an ideal material in solar energy application and showed excellent properties like low cost, non-toxic, band gap of 1.4 – 1.5eV and good electrical properties with P-type nature (Sun Z., Sun, K., Han, Z., Liu, F., and Lai, J., 2012). In view of cost effective device fabrication for solar energy applications, some of the direct band gap semiconductor materials have been introduced such as copper indium gallium sulphides (CIGS) and cadmium telluride (CdTe). Some problems are associated with these materials are: Cadmium is toxic and tellurium is rare, Selenium is a toxic material but indium and gallium are rare (NREL, 2016).
The world of thin film research is now strongly on CZTS thin films since they show properties that is attractive for fabrication of large scale solar cells. A CZTS thin film has absorption coefficient (> 10^4 cm^-1) direct band gap (of 1.5eV) and low thermal conductivity (Katagire et al, 2008). There are different methods of deposition of thin films such as beam sputtering, hybrid sputtering, RF magnetron sputtering, thermal evaporation, pulsed laser deposition, sulfurization of electron-beam evaporated precursors, single step electrodeposition method, spray pyrolysis, sol-gel sulfurizing method, ion-beam sputtering, hydrothermal and so on. This research work made use of sol-gel spin coating techniques and annealing in open atmosphere of about 250°C. Also the zinc is doped with cadmium at varying percentage.

CZTS thin films have a lot of advantages in the solar industry. Because CZTS is a quaternary compounds of stannite structure and the band gap is about 1.5eV which is very close to the best band gap required by semiconductors solar cells (1.35eV). Compared with the currently commercialized crystalline silicon, CdTe, CIGS, non-toxic and environmentally friendly CZTS thin film solar absorbing layer, It is expected to become the ideal absorption layer material of next generation thin films solar cells(Xiangbo Song, Xu Ji, Ming Li, Weidong Lin, Xi Luo, and Hua Zhang, 2014).

Motivated by the interest for climate change and in view of the limited resources for energy, electricity generation by photovoltaic (PV) is increasing in capacity worldwide. The merits of PV are obvious: it is silent, renewable and solar energy is the most abundant sources of energy on earth, more than 35Gw of photovoltaic power (Wp) has been installed and for its generation to become competitive with the conventional sources of electricity (Marika, E., 2012). Evidently, the ideal photovoltaic system would employ solar panels with very low production costs, high efficiency and a good design/ enabling easy and low-cost installation (Marika, E., 2012). To a greater extent we cannot solve the problem of energy demands of the modern world without using solar energy resources and there is the need for more research on CZTS which might be the material for the ideal solar cell.

2. Materials and Methods

The experiment started by treating the slide or glass using piranha solution (H_2SO_4 + H_2S) which is a 1:3 or 1:4 mixture of H_2SO_4 or H_2S. However, for this research a 1:3 piranha solution is used to treat the slide/glass, the process is exothermic and a large vessel is used for the reaction to prevent it from being explosive. The whole process is to remove the organic residue present in the slides or glass substrates. The glasses are left in the piranha solution for 30minutes after which they are further clean with distilled water.

Two sets of solutions were prepared. Solution A contained copper acetate monohydrate Cu(CH_3COO)_2.H_2O gotten from kernel chemicals; Tin (II) Chloride obtained from (BDH) Polabo chemicals and thiourea obtained from lab tech chemicals. The copper acetate was made to a concentration of 0.40 M and Thiourea to a concentration of 3 M and they were all dissolve in 5ml of methoxy ethanol this becomes solution A.

Solution B contained 5ml of (0.25 M) Zinc acetate and 5ml of (0.25 M) cadmium acetate both obtained from BDH (LAB CHEM) both dissolved in 5mL of methoxy ethanol. The complex formed from solution A was yellowish and on reacting with solution B form a gel-like nature CZTS with cadmium. Nine (9) different substrate/slides where prepared with different concentration of zinc and cadmium acetate.

The Sol-gel approach was adopted and Cu_2ZnSnS_4 thin films were deposited by spin coating techniques. Before depositing the thin film on the substrate/glass the glass is dried for 20s by spinning on a 3000-rpm electronic centrifuge. The CZTS is deposited by spin coating on the glass spinning on the centrifuge, after every 6 to 7 drops the glass is removed from the centrifuge and heated at 200°C in an open atmosphere; it is allowed to cool down and the spin coating repeated again, the heating and cooling continues. Until three layers deposition has been done. This process is repeated for each sample. The films created where then subjected to a temperature of 250°C for annealing in an open atmosphere. The films were investigated by studying their optical and electrical properties. Spectral absorbance of the films was recorded in the wave length of 200–1500nm by using Perkin Elmer Lambda 1050 UV-NIS-NIR spectrophotometer. Electrical resistivity of the films was done at room temperature and was determined using an Ecopia HMS-5000 Vander Pauw Hall Effect measurement to find mobility, carrier concentration, hall coefficient and so on. The film thickness was determined using a Profilometer and also Four Point Probe Analysis was done to determine the resistivity. Profilometer measurement was done on sample 1, spectrophotometer measurement was done on all samples to find the absorbance, Hall Effect on samples (2, 6 and 10) and four probe analysis on (9, 8, 7, 5, 4, 1)

3. Result and Discussion

Analysis of data started with data reduction process. Followed by computational analysis and plotting of graph.
From figure 1 above the cut off wavelength is 702.6nm
Band gap ($E_g$)=$\frac{1240}{702.6}$ = 1.76ev
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Power conversion Efficiency (PCE%) = ($P_{max}$ x 100%)/(1000000x cell active area)
1 SUN = 1000000mW/m²
$P_{max}$= $I$(mA)x $V$(mV)
$Imax$= 0.1mA
Substrate size= 2.5cmx 2.5cm Area of substrate = 6.25cm² = 6.25x 10⁻⁴m²
### Table 1: Table Summarizing Result for Efficiency and Band Gap

| Samples        | Maximum Voltage(mV) | Maximum Current(mA) | (P.C.E) % | Band gap in Ev |
|----------------|---------------------|---------------------|-----------|----------------|
| 20% Zn, 80% Cd | 100                 | 0.1                 | 1.60      | 1.76           |
| 30% Zn, 70% Cd | 390                 | 0.1                 | 6.24      | 1.80           |
| 40% Zn, 60% Cd | 350                 | 0.1                 | 5.60      | 1.35           |
| 50% Zn, 50% Cd | 30                  | 0.1                 | 0.48      | 1.76           |
| 60% Zn, 40% Cd | 110                 | 0.1                 | 1.76      | 1.75           |
| 70% Zn, 30% Cd | 130                 | 0.1                 | 2.08      | 1.75           |
| 80% Zn, 20% Cd | 200                 | 0.1                 | 3.20      | 1.74           |
| 90% Zn, 10% Cd | 530                 | 0.1                 | 8.48      | 1.76           |
| 100% Zn, 0% Cd | 240                 | 0.1                 | 3.84      | 1.76           |

The efficiency values where within the range of (0.48-8.48) %. The highest efficiency value was noticed among low cadmium ratio composition. This is very close to the values obtained by team of researchers at Australia University of New South Wales headed by Xianojing Hao in August 2018 who obtained an efficiency of 10% using 1.11cm² substrate size. Also David Mitzi an American Scientist has also recorded an efficiency of 12.6% in 2013 at IBM.

Figure 2 shows that for most of the samples there is an increase in absorbance from 300nm to about 320nm and it steadily fall for the samples from 320nm to 800nm. The high absorbance value in the visible region for the CZTS value indicate its usefulness for solar cell application. In the visible region the highest absorbance was for 80% Zn, 20% Cd a value of about 0.927 which is effective for solar cell use. The range of absorbance for the sample is 0.022-0.927. Generally there is decrease in absorbance with increase in wavelength in the visible region. The peak absorbance of most of the samples occurs at wavelength of slightly greater than 300nm. The sample without cadmium composition that is 100% Zn, 0% Cd has the lowest peak absorbance of 0.721. This shows that cadmium improves the CZTS. Table 1 showed that the highest transmittance value is about 0.9661 and is for 40% Zn, 60% Cd and the lowest transmittance value is for 80% Zn, 20% Cd and is value of 0.1132(11.32% transmittance) which is suitable for solar cell application. This indicate that CZTS has good optical property. However, we are interested in the transmittance value in the visible region of the spectrum (400-700nm) where there can sufficient excitation of electrons and holes. There is increase of transmittance with wavelength in this region. This range is similar to that gotten by Hurtado.M, Mike& Gerardo.G, (2012) which carry out co-evaporation synthesis of CZTS used as absorbent layer and got transmittance as high as 70%. Figure 4 shows optical conductivity of CZTS at varying concentration the peak value of optical conductivity occurred for 80% Zn, 20% Cd and it is a value of $8.985 \times 10^{10}$ for the visible region of the spectrum. General the optical conductivity increases with increase in photoenergy. The range of optical conductivity in these regions is $(0.0017-0.8985) \times 10^{-10}$, which is suitable for solar cell technology. For 20% Zn the range is $(0.0092-1.0162) \times 10^{-10}$. For 30% Zn the range is from $(0.0115-1.0514) \times 10^{-10}$. For 40% Zn the range is $(0.0038-0.8536) \times 10^{-10}$. For 50% the range is from $(0.00112-1.0366) \times 10^{-10}$.

![Figure 3: A Graph of Transmittance versus Wavelength](image-url)
The graph in figure 5 shows a decrease in absorption coefficient with wavelength in the visible region of the spectrum. The peak absorption coefficient was $299.932\text{m}^{-1}$ or $2.99932 \times 10^4 \text{cm}^{-1}$ and was observed for 70%Zn, 30% Cd. The range of absorption coefficient for the substrates in the visible region is $(2.87-299.932) \text{m}^{-1}$. These values are suitable for solar energy application. This is similar to research by XianZhong et.al (2011), Sanjay Kumar et.al (2012), kannan.A.G et.al,(2016), Shanenoor.S.K. et.al (2018), Krishnaiah.M, et.al (2007) who all reported absorption coefficient $> 10^4 \text{cm}^{-1}$.
at seems to have high spectrum. The optical conductivity increases with increase in photo energy the peak being occurs for 40% Zn, 60% Cd. The increase in wavelength but decreases with decrease in photo energy and the peak value of absorbance is 0.907 and it (1.864)(10)/cm for CZTS in the sample. This discovering is in line with earlier report by (Kannan.A, G, Manjulavalli.T, E, & et al.2014) that working devices are obtained with ‘copper poor’ and ‘zinc rich’ composition. However, for similar samples whose resistivity was determined by Hall Effect the resistivity was low as compared to the ones that seems to have high resistivity for the four-point probe analysis.

### 4. Conclusion

Cadmium improves the optical and electrical properties of CZTS. The average value of transmittance is moderate and that of reflectance is low in the visible region of the spectrum. The average absorption coefficient is greater than 10E+2m⁻¹ or 10E+4 cm⁻¹. CZTS is a p-type semiconductor material with bulk concentration in the range of (0.01795 - 1.8640)E+19/cm³ and mobility in the range of (0.0247 - 5.550)E+2 cm²/Vs. The absorbance of the samples decreases with increase in wavelength but decreases with decrease in photo energy and the peak value of absorbance is 0.907 and it occurs for 40% Zn, 60% Cd. The I–V characteristics showed that the current and voltage has a linear relationship or are directly proportional to each other. The optical conductivity increases with increase in photo energy the peak being 0.8955E+10 in the visible region of the spectrum and this occur with sample having composition of 80%Zn, 20% Cd. Thickness of film is within the range of (1-87) nm. The best optical and electrical properties occur for moderate and low ratio composition of Cadmium. Deviation from known resistivity by some samples might be due to the formation of secondary phases of CZTS. The band gap is within the range of (1.35-1.80) eV. The Efficiency is within the range of (0.48-8.48)%.

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