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Characterization of Cadmium Doped Zinc in Copper-Zinc-Tin-Sulphide $\text{Cu}_2\text{ZnSnS}_4$ (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 $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, Tin (ii) chloride SnCl_2 and Thiourea $\text{CH}_4\text{N}_2\text{S}$ all dissolved in 5ml methoxyethanol and solution B contained cadmium acetate $\text{Cd}(\text{CH}_3\text{COO})_2$, Zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2$ in 5ml methoxyethanol $\text{C}_3\text{H}_8\text{O}_2$ 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 $(0.054-0.193)\Omega\text{cm}$, carrier or bulk concentration range between $(1.775 \times 10^{17} - 1.864 \times 10^{19})/\text{cm}^3$ and mobility with the range of $(2.473-551)\text{cm}^2/\text{Vs}$ at room temperature. The CZTS films prepared showed optical absorption coefficient between $(2.87-299.932)\text{m}^{-1}$ and an optical band gap between $(1.35-1.76)\text{eV}$, peak absorbance of 0.907 at visible region and peak optical conductivity of 0.895×10 were obtained. The Copper-Zinc-Cadmium-Tin-Sulphide CZTS films created has thickness range between $(1-87)\text{nm}$, 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). $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) film has gained much interest in recent years, due to the fact that its optical property is optimum $(1.4 - 1.5)\text{eV}$ for photovoltaic application (Subramaniam E.P, Rajesh G, Thambidurai M, 2014). CZTS is a p-type semiconductor which has an optimum band gap, and large absorption coefficient $(>10^4\text{cm}^{-1})$ 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 ($\text{Cu}(\text{InGa})\text{Se}_2$) and CTS (Cu_2SnS_3). However CZTS is used as an ideal material in solar energy application and showed excellent properties like low cost, non-toxic, band gap of $1.4 - 1.5\text{eV}$ 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 ($> 10^4 \text{ cm}^{-1}$) 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, sulphurization 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 1.50eV 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 ($\text{H}_2\text{SO}_4 + \text{H}_2\text{S}$) 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 30 minutes after which they are further clean with distilled water.

Two sets of solutions were prepared. Solution A contained copper acetate monohydrate $\text{Cu}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ 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 were prepared with different concentration of zinc and cadmium acetate.

The Sol-gel approach was adopted and $\text{Cu}_2\text{ZnSnS}_4$ 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 were 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.

Figure 1: A graph Absorbance vs. Wavelength for 20% Zn, 80% Cd

Figure 2: A Graph of Absorbance vs. Wavelength

From figure 1 above the cut off wavelength is 702.6nm

Band gap (E_g) = $1240/702.6 = 1.76\text{eV}$

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Power conversion Efficiency (PCE%) = $(P_{\text{max}} \times 100\%) / (1000000 \times \text{cell active area})$

1 SUN = 1000000mW/m^2

$P_{\text{max}} = I(\text{mA}) \times V(\text{mV})$

$I_{\text{max}} = 0.1\text{mA}$

Substrate size = $2.5\text{cm} \times 2.5\text{cm}$ Area of substrate = $6.25\text{cm}^2 = 6.25 \times 10^{-4}\text{m}^2$

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

Table 1: Table Summarizing Result for Efficiency and Band Gap

The efficiency values were 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 indicates 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 be 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 0.8985×10^{10} for the visible region of the spectrum. Generally the optical conductivity increases with increase in photoenergy. The range of optical conductivity in these regions is (0.0017-0.8985) E+10, which is suitable for solar cell technology. For 20% Zn the range is (0.0092-1.0162) E+10. For 30% Zn the range is from (0.0115-1.0514) E+10. For 40% Zn the range is (0.0038-0.8536) E+10. For 50% the range is from (0.00112-1.0366) E+10. For 60% Zn the range is from (0.0115-0.9996) E+10. For 70% Zn the range is from (0.0096-1.2821) E+10. For 80% Zn the range is from (0.0165-1.0148) E+10. For 90%Zn the range is from (0.0165-1.0148) E+10. For 100% Zn the range is from (0.0137-1.0536) E+10.

Figure 3: A Graph of Transmittance versus Wavelength

Figure 4: Optical Conductivity versus Photoenergy

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 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 $(2.87\text{-}299.932)\text{ m}^{-1}$. 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 $> 10^4\text{ cm}^{-1}$.

Figure 5: Showing Absorption Coefficient Vs Wavelength at Varying Concentration of Cadmium

Parameters	30%Zn, 70% Cd	40%Zn, 60%Cd	80%Zn, 20%Cd
Bulk Concentration(/Cm ³)	1.755e+17	-1.864e+19	1.479e+18
Mobility (Cm ² /Vs)	5.551e+2	2.473e+0	2.218e+1
Sheet Resistance (Ω)	6.408e+3	1.354e+4	1.903e+4
Resistivity (Ω cm)	5.408e-2	1.354e-1	1.903e-1
A-C Cross Hall Effect (Cm ³ /C)	6.925e+1	-1.951e+1	3.442e+1
Magneto-Resistance (Ω)	2.996e+3	1.905e+2	4.973e+2
Sheet Concentration/Cm ²	1.755e+12	-1.864e+14	1.479e+13
Conductivity(Ω cm) ⁻¹	1.561e+1	7.386e+0	5.254e+0
Average Hall Coefficient (Cm ³ /C)	3.557e+1	-3.348e-1	4.221e+0
B-D Cross Hall Coefficient (Cm ³ /C)	1.890e+0	1.884e+1	-2.598e+1
Ratio Of Vertical/ Horizontal	8.359e-1	8.737e-1	-1.356e-1

Table 2: Hall Effect Measurement

Table 2 showing the various parameters for Hall Effect measurement

Samples	Resistivity
20%Zn,80%Cd	0.69378
40%Zn,60%Cd	3.39680
50%Zn,50%Cd	0.04042
70%Zn,30%Cd	3.21452
80%Zn,20%Cd	7.98230
90%Zn,10%Cd	0.02118

Table 3: Four Point Probe Measurement

Table3 showing resistivity values gotten for CZTS samples at various concentration of Cadmium using four-point probe

The four point probe shows low resistivity for Cd rich and poor Zn ratio, equal zinc to cadmium ratio and Zn rich and cadmium poor ratio. The high resistivity of the other samples might be due to the formation of secondary phases of CZTS in the sample. This discovering is in line with earlier report by (Kannan.A. G, Manjulavalli.T. E, & et.al2014) 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 $(0.01795-1.8640)E+19/cm^3$ and mobility in the range of $(0.0247-5.550)E+2 cm^2/Vs$. 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)%.

5. References

- Araki.H., Kubo.Y. and Mikaduki.A. (2009). Preparation of Cu_2ZnSnS_4 thin films by sulfurizing electroplated precursors. Solar Energy materials and Solarcells, vol.93.no.6-7, pp. 996-999.
- Dalapati.G.K., Batabyal.S.K., Masudy-Panah.Z. S., Kushwaha.T. I., Wong.H.F., Bhat.T., Iskander.A., Lim.Y., Wong.L.H., Tripathy.S.(2010). Sputter Grown Sub-micrometer thick Cu_2ZnSnS_4 for photovoltaicdevice application. Materials Letters, 160(20 10): 45-50.
- Digraskar.R., Dhanayat.S., Gattu.K., Mahajan.S., Upadhyi.D., Ghuleland.A. and Sharma.R.(2013). ALP confproc. 15 12,236-237.
- Edoff M. (2012). Thin film solar cells: research in an industrial perspective. Ambio, 41(Suppl 2), 112–118. doi:10.1007/s13280-012-0265-6
- Ericson.T., Kubart.T., Scragg.J.J.(2012). Reactive Sputtering of Precursors for Cu_2ZnSnS_4 thin films solarcells. Thin Solid Films, 520(20 12): 7093-7099
- Frahofer ISE. (2014). Photovoltaics Report, July 28, 2014: 18-19
- "First Solar CdTe photovoltaic Technology": Environmental, Health and Safety Assessment." National Renewable Energy Centre. October 2013. P.3 2.

- ix. Lasantha Korala, Tyler, J., (2016) McGoffinACS Appl. Mater. Interfaces 2016874911-4917 <https://doi.org/10.1021/acsami.5b11037>
- x. Friedmeier, T.M., Wiesner, N.N., Walter, T., Dittrich, H. and Schock, H.D. (1997). Heterojunctions based on $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ thin films. In proceeding of the 14th European Photovoltaic Solar Energy Conference, pp.1242-1245.
- xi. Fthenakis, V. and Kim, H.C. (2010). Life cycle uses of water in U.S. electricity generation. Renewable and Sustainable Energy Reviews. 14(7):2039-2048.
- xii. Guo, Q., Ford, G.M. and Yang, W.C. (2010). Fabrication of 7.2% efficient CZTSSe solar cells using CZTS nanocrystals. Journal of The American Chemical Society, Vol.132, no.49, PP.17384-17386.
- xiii. Guo, Q., Hillhouse, H.W. and Agrawal, R. (2009). Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ nanocrystal ink and its use for solar cells. The Journal of the American Chemical Society, vol.131, no.33, pp.11672-11673.
- xiv. Henry, J., Mohanraj, K. and Sivakumar, G. (2016). Electrical and optical properties of CZTS thin films prepared by SILAR method. Journal of Asian Ceramic Societies. 4(2016):81-84.
- xv. Hurtado, M., Mike, Romero, E., And Gerardo, G. (2012). Novel Co-evaporation synthesis of $\text{Cu}_2\text{ZnSnS}_4$ semiconductors used as absorbent layer.
- xvi. http://www.Greenpeace.org/international/global/international_publications/climate/2011/final%20SolarGeneration%20V1%20full%20report%20%r.pdf.
- xvii. https://www.wikilecture.eu/w/Lambert-Beer's_law
- xviii. Jimbo, K., Kimura, R., Kaminura, T. (2007). $\text{Cu}_2\text{ZnSnS}_4$ type solar cells using abundant materials. Thin Solid Films. Vol.515, no.15, PP.5997-5999.
- xix. Kannan, A.G., Manjulavalli, T.E. and Chandrasekaran, J. (2016). Influence Of Solvent On The Properties of CZTS nanoparticles. Procedia Engineering, 141(2016):15-22.
- xx. Katagiri, H., Jimbo, K., Maw, W.S., Oishi, K., Yamazaki, M., Araki, H., Takeuchi, A., (2016) Development of CZTS-based thin films prepared by SILAR method. Journal of Asian Ceramic Societies. 4(2016):81-84.
- xxi. Katagiri, H., Jimbo, K. and Yamada, S. (2008). Enhanced conversion efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ based thin film solar cells by using preferential etching technique. Applied Physics Express, Vol.1, no. 4, Article ID 041201.
- xxii. Kalowekamo, J., and Baker, E. (2009). Estimating the manufacturing cost of purely Organic solar cells. Solar Energy, 83(2009): 1224-1231.
- xxiii. Kumar, A.V., Park, N.K., Kim, E.T. (2014). Physical Status Solidi C. 6, 1233-1236. Krishnaiah, M., Sudhanshu, M., and Parag, B. (2007). Low temperature synthesis and characterization of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanoparticle by solution based solid state reaction method. Energy Procedia, 57(2014): 73-78.
- xxiv. Lineot, D. (2005). Electroposition of semiconductors. Thin solid Films, vol.487, no.1-2, pp.40-48.
- xxv. Max, M., and Armin, R. (2012). Future recycling flow of tellurium from Cadmium Telluride photovoltaic waste. Resources, Conservation and Recycling. 69(4): 35-49.
- xxvi. M Jiang, X Yan, (2013). Solar Cells-Research and Application. Interchopen. comanced. Conductivity in
- xxvii. CZTS? Cu_{2-x}Se Nanocrystal Thin Films: Growth of a Conductive shell.
- xxviii. Moholkar, A.V., Shinde, S.S. and Babar, A.R. (2011). Development of CZTS thin films solar cells by pulsed laser deposition: Influence of pulse repetition rate. Solar Energy, Vol.85, no.7, PP.1354-1363.
- xxix. Muhunthan, N., Pal Singh, O.M., Thakur, M.K., Karthikyan, P., Dinesh, M., Saravan, M. and Singh, V.N. (2014). Interfacial properties of CZTS thin film solar cell. Journal of Solar Energy, Vol(2014), Article ID 476123, 8 pages.
- xxx. Muhunthan, N., Singh, S. and Singh, V.N. (2013). Growth of CZTS thin Films by Co-Sputtering of metals targets and sulphurization in H_2S . International Journal Of Photoenergy, Vol.2013, Article ID 752012, 7 pages.
- xxxi. Moriya, K., Tanaka, K. and Uchiki, H. (2008). $\text{Cu}_2\text{ZnSnS}_4$ thin films solar cell prepared by pulsed laser deposition. Japanese Journal of Applied Physics, Vol. 46, no.9A, PP.5780-5781.
- xxxii. Nateprov, A., Krastov, V., Gurieva, G. and Schorr, S. (2013). Single crystal X-ray structure investigation of $\text{Cu}_2\text{ZnSnSe}_4$. Surface Engineering and Applied electrochemistry, Vol.49, no5, pp.423-426.
- xxxiii. Olekseyuk, I.D., Dudchak, I.V., and Piskach, L.V. (2004). Phase Equilibria in the Cu_2S - ZnS - SnS_2 system. Journal of Alloys and Compounds, vol.368, no.1-2, pp.135-143.
- xxxiv. Olekseyuk, I.D., Gulay, I.D., Dydchak, I.V., Piskach, L.V., Parasyuk, O.V. and Marchuk, O.V. (2002). Single crystal preparation and crystal structure of the $\text{Cu}_2\text{ZnSnS}_4$, Hg/SnSe_4 compound. Journal of Alloys and Compounds, vol.340, no. 1-2, pp.141-145.
- xxxv. Paier, J., Asali, R., Nagoya, A., Kresse, G. (2009). Rev. B.79 (2009): 115-126. "publications, Presentations, and News Database: Cadmium Telluride": National Renewable Energy Laboratory
- xxxvi. Parasyuk, O.V., Piskach, L.V., Roman, Y. E., Olekseyuk, I.D., Zarembo, V.I. and Pekhnyo, V.I. (2005) Phase relations in the quasi-binary Cu_2GeS_3 - ZnS and quasi-ternary Cu_2S - Zn(Cd)S-GeS_2 system and crystal structure of $\text{Cu}_2\text{ZnGeS}_4$. Journal of Alloys and compounds, vol.397, no.1-2, pp.8S-94.
- xxxvii. Pamplin, B.R. (1960). Super-cell Structure of Semiconductors. Nature, vol.188, no.4745, pp.136-137.
- xxxviii. Persson, C. (2010), electronic and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnS}_4$. Journal of Applied physics, vol.107, no.5, Article ID 053710.
- xxxix. Reaction (SILAR) method. J Matter. Chem. 22(32)PP: 16346-16352.
- xxxix. Raugei, M., and Fthenakis, V. (2010). "Cadmium flows and emissions from CdTe PV: Future expectations. Energy Policy. 38(9): 5223-5228.

- xl. Shah (2016). Optimization of Buffer Layer For Copper —Zinc-Tin-Sulphide-based solar cells. Department of physics Tallin University of Technology. MSC thesis.
- xli. Sanjay.K., Anuj.K., Viresh.D. (2012). Deposition of Kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) Thin films by Spin Coating Technique For Solar cell Application. *Energy Procedia*, 33(2013):198-202.
- xlvi. Shanenor.S.K., and Rao.M.C.(2018). Effect of annealing temperature on structural and morphological studies of electrodeposited CZTS thin films. *International Journals of Ceramics*. 44(2018). PP. 648-656.
- xlvi. Subramanian.E.P., Rajesh.G., Muthukumarasamy. N., Thambidurai.M., Asokan.V.,Velauthapilla.D. (2010). Study of CZTS materials. *Indian Journal of Pure and Applied Physics*, 52,620-624.
- xlvi. Su.Z.,Sun.K., Han.Z., Liu.F., Lai.Y., Li.J., Liu.Y.(2012). Fabrication of ternary Cu-Sn-S sulphides by a modified successive ionic layer adsorption and Reaction(SILAR) method. *J. Mater. Chem.*22(32)PP:16346-16352.
- xlvi. Schafer. W. and Nitsche.R. (1974). Tetrahedral quaternary Chalcogen of the type $\text{Cu}_2\text{ZnSnS}_4(\text{Se}_4)$. *Materials Research Bulletin*, Vol.9, no5, pp.645-654.
- xlvi. Schorr.S., Hoebler.H.J. and Tovar.M.(2007). A neutron diffraction study of the stannite —Kesterite solid solution series. *European Journal of mineralogy*, vol.19,no.1, pp.65-7.
- xlvi. Schurr.R., Holzing.A. and Jost.S. (2009). The crystallization of $\text{Cu}_2\text{ZnSnS}_4$ thin film Solar absorber for Co-electroplated Cu-Zn-Sn precursors. *Thin Solid Films*, Vol.517, no7,pp.2465-2468.
- xlvi. Shinde.N.M., Dubal.D.P., Dhawale.D.S., Lokhande.C.D., Kim.J.H. and Moon.J.H.(2012). Room temperature novel chemical synthesis of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) absorbing layer for photovoltaic application. *Material Research Bulletin*, Vol.47,no.2, PP.302-307.
- xlvi. Schubert.B.A., Marsen.S. and Cinque.S., (2011). $\text{Cu}_2\text{ZnSnS}_4$ thin films solar cells by fast co-evaporation. *Progress In Photovoltaics Research and Applications*, Vol.19, no.1, pp.93-96.
- xlvi. Tanaka.K., Oonuki.M., Moritake.N. And Uchiki.H.(2009). $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells prepared by Non-vacuum processing. *Solar Energy Materials and Solarcells*, Vol.93, no.5. PP.583-587.
- xlvi. Tanaka.K., Fukui.Y., Moritake.N. and Uchiki.H.(2009). Chemical composition dependence of Morphological and Optical Properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films deposited by Sol-gel sulphurization and $\text{Cu}_2\text{ZnSnS}_4$ thin film Solarcells efficiencies. *Solar Energy Materials and Solarcells*, Vol.95, no.3, PP.838-842.
- xlvi. Tauc. J., Grigorovici.R., Vancu.A. (1966). Optical properties and electronic structure of Amorphous Germanium. *Physical status solidi B*. 15.
- xlvi. "Tellurium"(PDF). Mineral commodities summaries. United states Geological Survey. January 2008.
- xlvi. Tanka.T., Yoshida.A. and Saika.D.(2010). Influence of composition ratio on properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films fabricated by Co-evaporation. *Thin Solid Films*, vol.518, no.21,PP.S29-S33. Valkonen.E., Ribbing.C.G., Sundgren.J.E.,(1986).proc. SPIE, 652,235-242
- xlvi. Washio.T., Shinji.T. and Tajima.S. (2012). 6% Efficiency $\text{Cu}_2\text{ZnSnS}_4$ based thin film Solar cells using Oxide precursors by open atmosphere CVD. *Journal Of Materials Chemist*,vol.22, no.9, pp.4021 -4024.
- xlvi. Weber.A., Krauth.h. and Perlt.S.(2009). Multistage Evaporation of $\text{Cu}_2\text{ZnSnS}_4$ thin films. *Thin solid films*, vol.517, no.7, pp.2524-2526
- xlvi. Wang.W.,winkler.M.T.Gunawan.O.,Gokmen.T.,Todorov.T.K.,Zhu.Y.,Mitzi.D.B.(2013). Device characterization of CZTS thin film solar cells with 12.6% efficiency. *Advanced Energy Materials*, 4(7): 130-146.
- xlvi. XianZhang. L., Ahmed.E., Martha.C.L.(2011). Thin-film Solar cell Absorber $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) by annealing of Monodisperse Kesterite nanoparticlesprecursors. *Proceeding of 26th European Photovoltaic Solar Energy Conference and Exhibition*:2896-2899.
- xlvi. Xiangbo.S., Xu.J., Ming.L., Weidong.L., Xi.L. and Hua.Z.(2014). A Review on Development Prospect of CZTS Based Thin Film Solar cells. *International Journal of Photoenergy*. Vol, 2014:1-11.
- xlvi. Zhang.X., Guo.G., Ji.C., Hang. K., Zha.C., Wang.Y., Shen.L., Gupta.A., Bao.N.(2014). Efficient thermolysis route to monodisperse $\text{Cu}_2\text{ZnSnS}_4$ nanocrystal with controlled shape and structure, *Sd. Rep.* 28:1-8.
- xlvi. Zhang.S. (2010). CZTS thin film and its research progress of solar cell. *Engineering and Technology*,no.8, PP.67-69.