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Comparative Study: Phase formation of Cu2ZnSnS4 Thin Films

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Abstract

Cu_2ZnSnS_4 is an alternative to the traditional p-type semiconductors such as CIS and CIGS. The traditionally obtained structure in literature till now is either Kesterite or Stannite which shows, tetragonal crystal symmetry. Here we have approached a novel method to get an orthorhombic CZTS, Synthesized by solution growth dip coating technique. The traditional Kesterite CZTS was also obtained synthesis at room temperature but there was a phase formation observed at annealing temperature at 300^{o}C for 1hour in hot air furnace without any presence of an inert gas. The structure was confirmed by XRD, SEM. The optical analysis reveals the bandgap(1.5-1.51) eV , Refractive Index (n) (2.09-2.13), Absorption coefficient **(α)** more than $10^4 cm^{-1}$, Optical conductivity (σ_{opt}) $10^{13}(sec)^{-1}$,and electrical conductivity (σ_{elct}) $10^{-6}(Ohm\ Cm)^{-1}$of both the films have potential application in photovoltaic devices.

Keywords: Thin Film, Bandgap, CZTS Orthorhombic, Photovoltaic, Dip coating solution growth technique, etc.

Introduction

Recent research on photovoltaic has been developing the decrease in the fabrication cost as well as price of the energy obtained. In this regard, suitable material should be easily available, inexpensive and must have stable behavior for a cost effective solar cell technology. There is a need to explore the new materials like Cu_2ZnSnS_4 and like that other ternary or quaternary chalcopyrite semiconductors.

In this context, the Cu_2ZnSnS_4 is a promising alternative to semiconductor based on Ga and In as a solar absorber material[1].CZTS thin film is one of the most promising photovoltaic materials as an absorber of thin film solar cells because it has a high absorption coefficient above 10^4 cm^{-1} and a direct bandgap 1.48-1.82eV [2]. Cu_2ZnSnS_4, which has a similar structure to CIGS, suitable optical bandgap energy and is naturally abundant in the environment, is anticipated to be a substitute for CIGS [3]. This semiconductor film can be regarded as an alternative to CIS and CIGS materials in which extremely expensive and resource limited Indium is replaced by cheap and abundant Zinc (Zn) and Tin (Sn) [4].

Each component of CZTS is abundant in the earth's crust (Cu; 50ppm, Zn; 75ppm, Sn; 2.2ppm, S; 260ppm) and posses extremely low toxicity. Till now, there are several methods by which CZTS thin films have been prepared such as, RF magnetron sputtering deposition[5], Electron beam evaporation[6], Thermal evaporation[7], etc. are the physical method to deposit the films which are relatively expensive and complicated methods[1].Thus, non vacuum methods comes into play such as, Sol-gel deposition[8], Electro deposition[9], Spray pyrolysis deposition[10], Photo-chemical deposition[11], Screen printing[12]and nanoparticle based method[13].

In this research, we investigate an alternative synthesis way for the prepation of Cu_2ZnSnS_4 by multiple dipping of glass substrate into solution containing metal salt and thiourea as a sulfur source via solution growth dip coating technique. The samples were annealed at 300^{o}C for 1 hour in hot air furnace without presence of any inert gas.

Materials and Methodology

In this work, glass is used as substrate. The glass substrates were cut into a size of 10cm*10cm and soaked in the concentrated HNO_3 for 48 hrs, then cleaned with acetone and made dry in the hot air oven if any residue / dust particles left on the substrates. CZTS precursors were prepared by using the metal salts of $CuCl_2.2H_2O$, $ZnCl_2$, $SnCl_4.5\ H_2O$ and thiourea as a source of sulfur, all from Merck and used without any further purification, dissolved in water and ethanol as the solvent. The metal ion ratio of the base solution was not exactly to the stochiometric.

All the sources of metal salt and sulfur were in mixture of water and ethanol, stirred at room temperature for hundreds of seconds. Ethylene glycol

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was used as a stabilizing agent. The PH≈ 6 remains maintained for the films. Kept the solution for 48 hrs self electrochemical reaction occurred. Now, substrates were dipped 17 times into the chemical solution to get the desired film and made them dry at room temperature for 12hrs, so as to remove the solvent from the deposited films. Further, the samples were kept in hot air furnace for 1hr.

Result and Discussion

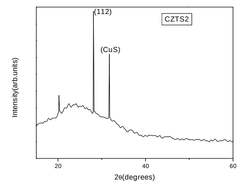
Structural Analysis

XRD pattern of Kesterite CZTS was synthesized solution growth dip coating method at room temperature. Earlier to annealing it shows a Kesterite structure of the film at 2θ=28.3 which was confirmed by JCPDS Card no. 26-0575 with a phase formation of Cu_2S at 2θ=31.7 But after annealing, there was a phase formation from Kesterite CZTS to Orthorhombic CZTS at 2θ=27.3 observed[3]. So there was a phase formation of metastable orthorhombic structure, which is only due to disorder of Cu and Zn elements in the CZTS structure and moreover, the atomic number and similar ionic radii such as Cu^{2+} (0.73 Å) and Zn (0.74 Å) is very close to each other as shown in Fig.1(a-b). The average crystallite size (D) of the films was determined by using Debye-Scherer's relation as,

$$D = K\lambda/\beta\cos\theta$$

Where λ is the X ray wavelength, β is the line width of the half maximum intensity, K is a constant whose value is close to1and θ is the Bragg's angle corresponding to the main diffraction peak. So the crystallite of both the samples was calculated as 7.55 nm and 3.07 nm respectively. The crystallite size decreases as the annealing temperature increases, this is only due to the change in the volume fraction by the relation given by[14] , Volume fraction = 1- (1 - /D) ^{2}

Where D is the average crystallite size.



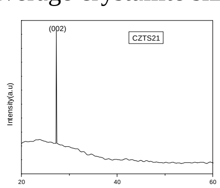


Fig.1 (a) XRD of CZTS2 (b) CZTS21

Optical Analysis

UV-Visible absorption spectroscopy was analyzed at room temperature, used to estimate the optical properties of the CZTS thin films. As shown in Fig.2(a-b) the bandgap of the as deposited as well as annealed films can be estimated by hν (h is the Planck's constant, ν is frequency) represents the photon energy. The estimated bandgap value is 1.5eV and 1.51eV for as deposited and annealed CZTS thin films respectively, by extrapolating the linear portion to the x-axis at hν. Both the bandgap values is close to the optimum value for solar cell applications.

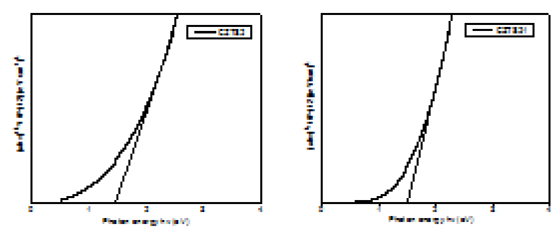


Fig.2 (a) Bandgap of CZTS2 (b) CZTS21

To further analyzed the optical properties of CZTS thin films such as, refractive index, extinction coefficient, absorption coefficient and optical and electrical conductivity vs Photon energy (hν) as follows,

The refractive index (n) of the as deposited and annealed films as shown in fig.3(a-b) has a value at 1.5eV is 2.09 and 2.13 respectively. AS the photon energy increases the values of refractive indices also increases.

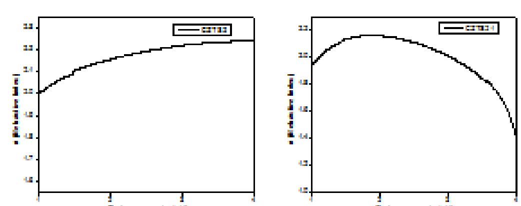


Fig.3 (a) Refractive index of CZTS2 (b) CZTS21

The absorption coefficient (α) for both the films is larger than $10^4 cm^{-1}$. So it reveals that films have very large no. of photons to participate in the solar cell operation as shown in fig.4 (a-b).

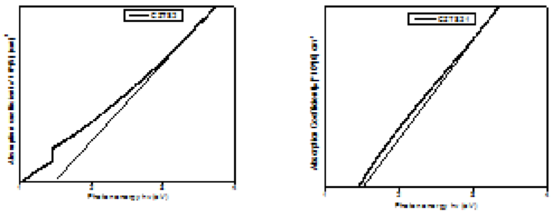


Fig.4 (a) Absorption coefficient(α) CZTS2 (b) CZTS21

The extinction coefficient for both the films was observed to be greater than 0.1, which shows the semi-insulating behavior of Cu_2ZnSnS_4 material as shown in Fig.5 (a-b)

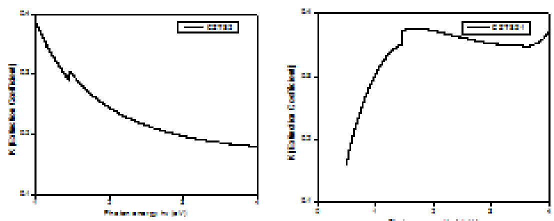


Fig.5 (a) Extinction coeffecient of CZTS2 (b) CZTS21

The **optical conductivity** is a measure of frequency response of the material when white falls on it, which is determined by the following relation[15],

$\sigma_{opt} = \alpha nc/4\pi$

Where c is the velocity of light, n= refractive index of the material.

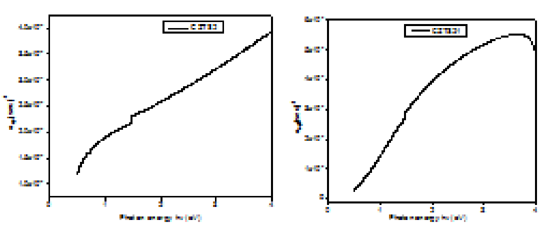


Fig.6 (a) Optical conductivity of CZTS2 (b) CZTS21

We can estimate the electrical conductivity by using the relation given below as,

$\sigma_{elct} = 2\lambda\ \sigma_{opt} / \alpha$

The higher order magnitude of optical conductivity $(10^{13}\ sec)^{-1}$ for both the films shows that there is very high photo response of the films. As the photon energy increases there is an increase in the optical conductivity of the films, this may be only due to the high absorbance of CZTS thin films and moreover, due to the electron excited by photon energy as shown in Fig.6 (a-b).

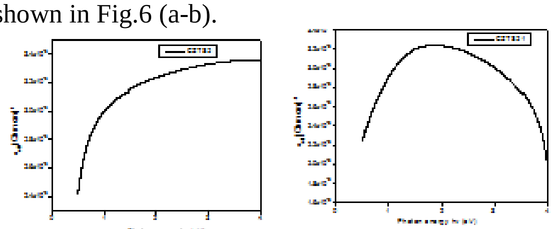


Fig.7 (a) Electrical conductivity of CZTS2 (b) CZTS21

The **electrical conductivity** have an inverse image of the optical conductivity , by increasing photon energy the electrical conductivity also increases for the as deposited film but for annealed film it starts decreasing i.e. as temperature increases it shows that there exist a positive temperature coefficient resistance which tells that the CZTS is p-type material as shown in Fig. 7(a-b).The magnitude of the electrical conductivity of the films is of the order of 10^{-6}, which is within the electrical conductivity range 10^{12} to 10^{2} $(\text{Ohm-cm})^{-1}$ for the semiconductor published elsewhere[16].

Morphological Analysis

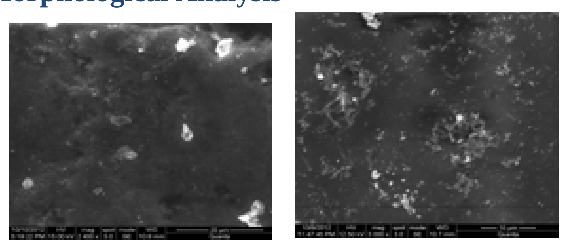


Fig.8 (a) SEM Photograph of CZTS2 (b) CZTS21

Fig.8(a-b) shows the SEM images of as deposited as well as annealed CZTS thin films. The SEM images reveals that as deposited CZTS film displays a crystal like morphology while annealed CZTS thin film displays a non uniform with few spherical and just formation of rod and agglomeration like morphology.

Conclusion

CZTS thin films were synthesized at room temperature by solution growth dip coating technique, having a molar concentration ratio of 2:1:1:3 .we found that XRD pattern predicts that there is a phase formation from KesteriteCZTS at preferred orientation (112) with a phase formation to Orthorhombic CZTS(002) after annealing. Both the samples have an absorption coefficient of more than $10^4 cm^{-1}$ and having a bandgap of 1.5 to 1.51eV respectively. Not only Optical and electrical conductivity shows that both the films are suitable for thin film solar cell but also refractive index and extinction coefficient has optimum values for photovoltaic applications. SEM photograph reveals that there is a crystal like structure with some spherical as well as agglomeration along with few rod like particle formation.

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References

[1] *Tauan Troung Mau and Kyoo Ho Kim,:J. Ceramic Processing Research,13,301(2012).*
[2] *Feng Jiang, Honglie Shen, Wei Wang and Lei Zhang,:J.Applied Physics Express,4,074101(2011).*
[3] *Hechun Jiang, Pengcheng Dai, Zhenyu Feng, Weilliu Fan and Jinhua Zhan,;J. Material Chemistry,22,7502(2012).*
[4] *Sawanta S.Mali, Bharmana M.Patil, Chitriyath A. Betty, Popatrao N.Bhosale,Young Woo Oh ,Sandesh R. J adkar, Rupesh S.Devan, Yuan-RonMa, Pramod S.Patil,: J.Electrochimica Acta,66,216(2012).*
[5] *J. Seol,S. Lee, J.Lee, H.Nam, K.Kim.,:J.Solar Energy Materials & solar cells,75,155(2003).*
[6] *H.Katagiri, K.Saitoh and T.Washio,:J. Solar Energy Materials & solar cells,65,141(2001).*
[7] *H.Yoo and J.Kim,: J. Solar Energy Materials & solar cells,95,239(2011).*
[8] *B.Schubert, B.Massen, S.Cinque, T.Unold, R.Klenk, S.Schorr, and H.W.Schock,: J. Progress in Photovoltaics,19,93(2010).*
[9] *J.J.Scragg, D.M.Berg, and P.J.Dale,: J.Electroanal Chemistry,52,646(2010).*
[10] *Y.B.Kumar, P.U. Bhaskar, G.S.Babu, and V.S.Raja,: J.Physics Status Solidi A, 2.7, 149 (2010).*
[11] *K.Moriya, K.Tanaka, and H.Uchiki,: J.Japaness journal of Applied Physics,44,715(2005).*
[12] *Z.Zhou, Y.Wang, D.Xu, and Y.Zhang,: J. Solar Energy Materials & solar cells,94,2042(2010).*
[13] *C.Chory, F.Zutu, F.Witt, H.Borchert and J.Parisi,:J.Physics Status Soldi C,7,1486(2010).*
[14] *S.Chellammal, S.Sankar, S.Selvakumar, E.Viswanathan, R. Murugaraj,K.Sivaji,: J. Materail Science,45,1242(2009).*
[15] *A.M.Bakry,: J Egypt Journal of Solids, 31, 11 (2008).*
[16] *P.A.Ilenikhena, J.African Physical Review, 2, 0007 (2008).*