

Structural and Optical Characterizations of CIGST Solar Cell Materials

Abhay Kumar Singh

Abstract—Structural and UV/Visible optical properties can be useful to describe a material for the CIGS solar cell active layer, therefore, this work demonstrates the properties like surface morphology, X-ray Photoelectron Spectroscopy (XPS) bonding energy (EB) core level spectra, UV/Visible absorption spectra, refractive index (n), optical energy band (E_g), reflection spectra for the $\text{Cu}_{25}(\text{In}_{16}\text{Ga}_9)\text{Se}_{40}\text{Te}_{10}$ (CIGST-1) and $\text{Cu}_{20}(\text{In}_{14}\text{Ga}_9)\text{Se}_{45}\text{Te}_{12}$ (CIGST-2) chalcogenide compositions. Materials have been exhibited homogenous surface morphologies, broadening /-or diffusion of bonding energy peaks relative elemental values and a high UV/Visible absorption tendency in the wave length range 400 nm-850 nm range with the optical energy band gaps 1.37 and 1.42 respectively. Subsequently, UV/Visible reflectivity property in the wave length range 250 nm to 320 nm for these materials has also been discussed.

Keywords—Chalcogen, Optical energy band gap, UV/Visible spectra, XPS spectra.

I. INTRODUCTION

CONVENTIONALLY photovoltaic (PV) materials are inorganic semiconductors, which can form a suitable junction with other materials having property to exhibit PV effect when incident on light. Several semiconducting materials have been shown the PV effect, but only a few have been getting sufficient commercial interest, cause, satisfying essential constraints to minimizing the thickness and their enough availability. Ideally, absorber material must have an efficient high absorption coefficient ($10^5/\text{cm}$) of the terrestrial light and direct energy bandgap semiconductor with a bandgap of ~ 1.5 eV, high quantum efficiency of excited carriers, long diffusion length and low recombination velocity. The high optical absorption governs the optimum thickness of an absorber in a solar cell cause order of a film thickness inverse of the optical absorption coefficient [1]-[4].

But it is mirror fact there is no suitable semiconductor material available with direct bandgap close to 1.5 eV. Most frequently used silicon has an indirect bandgap with a gap 1.1 eV. Therefore, to resolve this problem investigators have been investigated the metastable alloy a-Si:H, somewhat serendipitously with large tailorable bandgap, easy dopability and high optical absorption coefficient. Beside this metastable a-Si:H alloy has the other two-component (binary) GaAs, CdTe, Cu_2S , Cu_2O , InP, Zn_3P_2 etc attracted much attention to use as a solar cell materials.

In further investigation it has been predicted GaAs, InP and their counterpart alloys ideal for the photovoltaic applications, but their too expensive PV module fabrication cost limits the large-scale commercial production. Due to increasing number of components, the number of possible geometrical proportion

increases in the materials. Such as I-III-VI ternaries/quaternaries alloys or compounds can form a suitable photovoltaic material [4], [5] which emphasize on low cost.

It is well known chalcogenide PV can be substantially contribute in future energy supply upto terawatts capacity [6]. At present, chalcogenide PV module production is in the gigawatts/year range, mainly driven from CdTe module producer [6]. Chalcogenide PV technologies CdTe and $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ have nearly equal low cost perspective for the large scale production. The alloying elements indium and tellurium can be considered most critical, cause, limited amounts of their availability on the earth.

The goal of this work, to present a structural and optical property study on the developed $\text{Cu}_{25}(\text{In}_{16}\text{Ga}_9)\text{Se}_{40}\text{Te}_{10}$ and $\text{Cu}_{20}(\text{In}_{14}\text{Ga}_9)\text{Se}_{45}\text{Te}_{12}$ compositions alloys. The FSEM surface morphology, XPS bonding energy (BE) core level analysis, UV/Visible absorption spectra, refractive index (n), optical energy band gap (E_g) and reflection spectra for these alloys have been discussed.

II. EXPERIMENTAL DETAILS

Bulk materials CIGST-1 and CIGST-2 were prepared by the melt quenched technique. High purity elements have been taken in appropriate compositional ratio. The properly weighed materials kept into clean quartz ampoules were evacuated and sealed under at the vacuum of 10^{-5} torr. The materials sealed ampoules were put into electric furnace and heated up to 1200°C with a slow heating rate and hold this temperature for 36 hours. To ensure the homogeneity of molten materials ampoules were continuously rotated with the help of an electric motor in last 12h heating process, afterward quenched in NaOH containing ice water. Prepared ingots of the materials were collected by breaking the ampoules. To ensure the homogenous surface morphologies of the materials ULTRA 55, Field Emission Scanning Electron Microscope (Karl Zeiss) measurement performed. The XPS core level and valence band spectra were obtained with Al K α -rays (1486.6 eV) under a vacuum of 3×10^{-7} Pa in Multilab 2000 Thermo ScientificUK instrument. The XPS data consisted of survey scans over the entire binding energy core level peaks of interest. For the survey spectra and core level spectra an energy increment 1 eV and 0.05 eV was used for the spectra recording. The core level peaks were recorded by sweeping the retarding field and using the constant pass energy of 30 eV. To ensure experimental data each measurement was averaged over five scans, under the beam current 10 mA and power 150 W. The reproducibility of the measurements was checked on different regions of the investigated surfaces [7]. The adventitious carbon was used as a reference and the BE of the reference C1s line was set as 285.0 eV. For each sample, a calibration factor was calculated from the difference between

Abhay Kumar Singh is with Department of Physics, Indian Institute of Physics, Bangalore-560012, India (e-mail:abhaysngh@rediffmail.com).

the measured C1s BE and the reference value 285.0 eV [8]. The original BE data were corrected according to the calibration factor.

The UV/Visible absorption and reflectivity spectroscopic measurements were performed from the Spectro S-600 equipment, for this fine bulk powder was kept in a sample holder carefully and spectra recorded in UV/Visible absorption spectra and reflectance modes, in the wave length range 300 nm to 1000 nm.

III. RESULTS AND DISCUSSION

A. Structural Property

The FSEM surface morphology (see-Fig. 1) of the as prepared bulk materials provides the information regarding the homogeneous diffusion of the alloying elements. Therefore, these as prepared bulk materials has an overall amorphous nature.

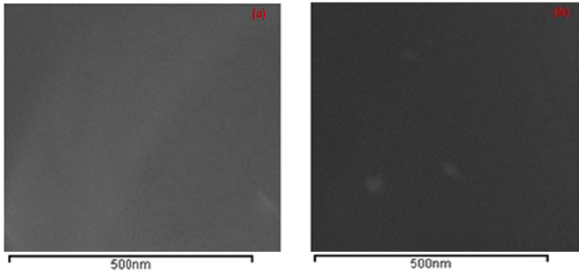


Fig. 1 (a, b). FSEM surface morphologies of the as prepared CIGST-1 and CIGST-2 alloys

In subsequent, to confirm the stoichiometries chemical concentrations in these materials X-ray Photoelectron Spectroscopy (XPS) analysis was also performed. Bonding energy core level spectra of the alloying elements Se, Cu and Te were analyzed correspondence to C1 line 285eV (± 1 eV), obtained carbon C1 line core level XPS spectra for these materials is exhibited in Fig. 2 (a). This outcome reveals count intensity of C1 line is higher for the CIGST-1 composition than CIGST-2. Further Fig. 2 (b) represents Se 3d_{5/2} core level spectra for these materials. Outcome demonstrates the CIGST-2 composition has a sharp Se 3d_{5/2} XPS peak while this peak nearly disappears in the CIGST-1 composition.

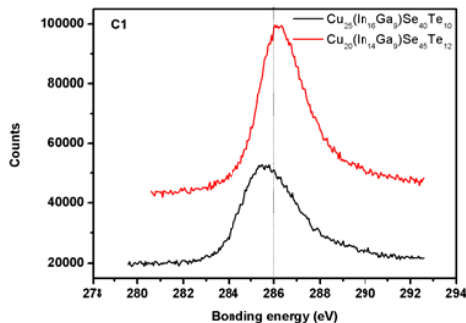


Fig. 2 (a). C1 XPS core levels spectra for the CIGST-1 and CIGST-2 compositions

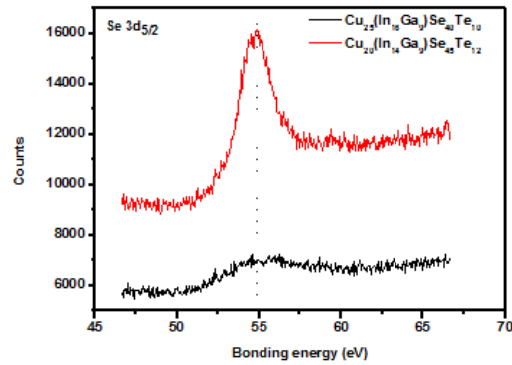


Fig. 2 (b). Se 3d_{5/2} XPS core levels spectra for the CIGST-1 and CIGST-2 compositions

In this subsequent Cu 2p_{3/2} and Te 3d_{5/2} peaks are given in Figs. 2 (c) & 2 (d). Result reveal Cu 2p_{3/2} CIGST-1 has a lower count value broad diffused peak in between 931 to 937 eV accompanied with other nearly spread peaks, while the CIGST-2 material has been exhibited comparatively high count value sharp peaks at 931 and 952 eV. However the Te 3d_{5/2} peak is also appearing in the same manor in these materials with following the same trend, by showing the high order counts peaks at 573, 576, 583 and 587 eV for CIGST-2. Subsequently alloying elements Ga3d_{5/2} high energy XPS peak 285 eV diffused with C1 peak while In3d_{5/2} high energy XPS appears at 446 eV in CIGST-2 and nearly spread form in CIGST-1 composition. The broadening and high diffusion of Se 3d_{5/2}, Cu 2p_{3/2}, Te 3d_{5/2}, Ga 3d_{5/2} and In 3d_{5/2} core energy levels XPS peaks in CIGST-1 material demonstrates it has more random and homogenous structure than CIGST-2 composition.

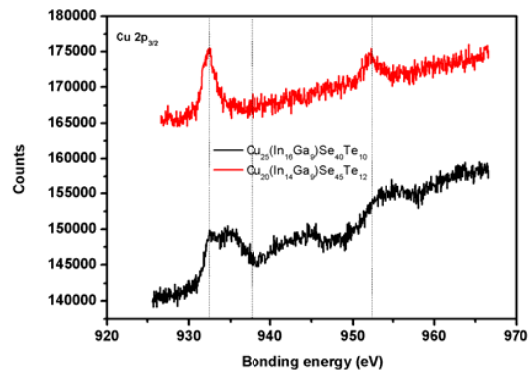


Fig.2 (c). Cu 2p_{3/2} XPS core levels spectra for the CIGST-1 and CIGST-2 compositions

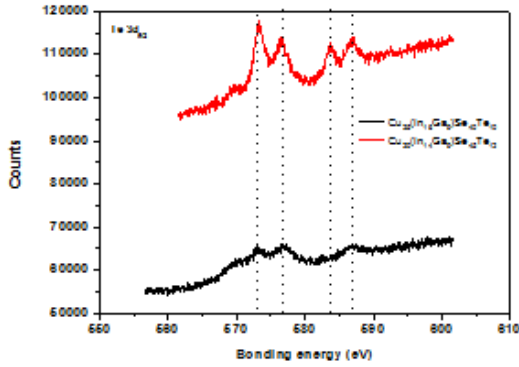


Fig. 2 (d). Te $3d_{5/2}$ XPS core levels spectra for the CIGST-1 and CIGST-2 compositions

B. UV/Visible Optical Property

The obtained UV/Visible spectrums in a common wave length range 300 nm to 1000 nm are exhibited in Fig. 3 (a, b).

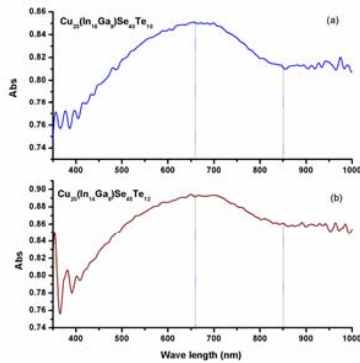


Fig. 3 (a, b). UV/Visible absorption spectrums for the CIGST-1 and CIGST-2 alloys.

Materials CIGST-1 and CIGST-2 have been exhibited a broad absorption peak in the spectral range ~ 450 nm to 850 nm. To analyze the materials different optical properties spectrums a common band tail wave length range 660 nm to 850 nm have been taken.

In multicomponent chalcogenide systems it is well established the refractive index extensively depends on the localized density of states and it influenced from the addition of foreign elements in alloys. Refractive index of the under test materials can be obtained by employing the Kramers-Kronig relation [9]-[11]. Obtained variation of refractive index for the CIGST-1 and CIGST-2 materials is exhibited in Fig. 4. From this outcome it is evident these materials have refractive index order 3 to 4, this result also demonstrates, material CIGST-1 has a refractive index slightly higher than CIGST-2.

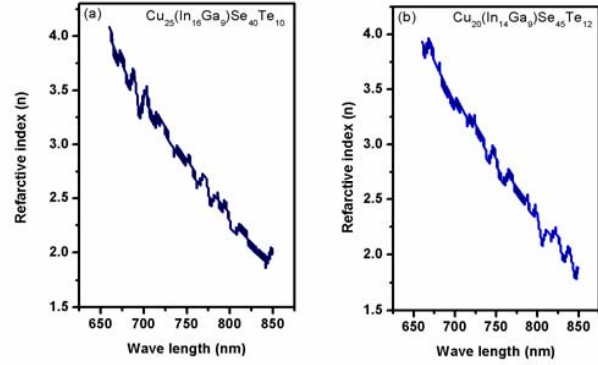


Fig. 4 (a, b). Variation of refractive index for the CIGST-1 and CIGST-2 alloys

Optical energy band of a solar cell or PV material is the crucial parameter because it defines the terrestrial light absorption ability in a specific wave length region. As per requirement, a good solar cell material should have optical energy band gap in the range 1.4 to 1.5 eV. Optical energy band gap essentially describes the minimum energy required for the optical excitation of a material. The optical energy band gaps of the CIGST-1 and CIGST-2 can be described by using the well known Tauc relation [12], [13]. Plot $(\alpha h\nu)^{1/2}$ vs E_g for the CIGST-1 and CIGST-2 is exhibited in Fig. 5 (a, b),

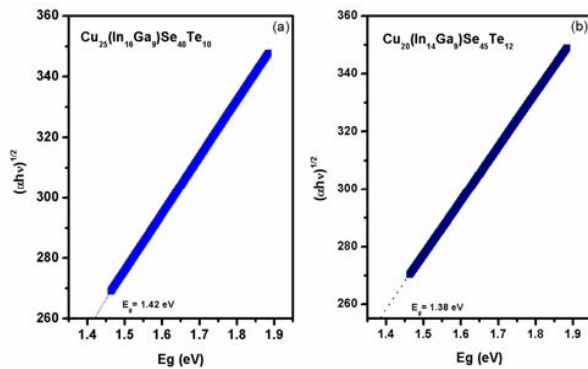


Fig. 5 (a, b). Optical energy band gap (E_g) for the CIGST-1 and CIGST-2 alloys

the E_g values of the materials can be evaluated by extrapolating the plots lines. Outcome demonstrates materials have E_g values 1.42 and 1.38 eV respectively.

Optical reflectivity can also provide useful information regarding the solar cell materials because it reflects the inverse behaviour of the optical absorption. As per essential requirement; material should have a low optical reflectivity. Here optical reflectivity for the CIGST-1 and CIGST-2 materials has been noticed (see Fig.6 (a, b)) in the wave length range 250 to 320 nm and no optical reflectivity peak appears in the higher range.

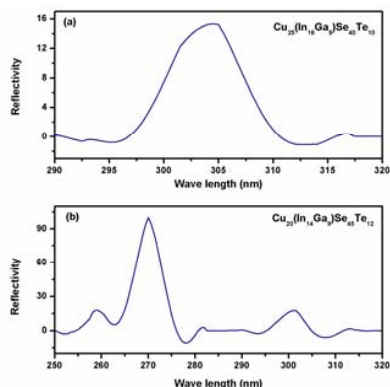


Fig. 6 (a, b). UV/Visible reflection spectra for the CIGST-1 and CIGST-2 alloys

Optical reflectivity of the CIGST-2 material has been exhibited a reflection peak in the wave length range 265 to 278 nm followed with other weak peak, having a maximum order of reflectivity ~ 100 . While CIGST-1 material has been exhibited a broad reflection in the range 297 to 312 nm, with a lower order of the reflectivity. These two materials reflectivity characterizations are indicating that CIGST-1 has a favourable property than CIGST-1 composition.

Structural and optical properties variations in bulk of CIGST-1 and CIGST-2 could be interpreted in term of variation in indusial element atomic size, density and alloying concentrations, they can play an important role. The alloying element Cu can contribute in UV/Visible light absorption as well as improve the thermal and mechanical stability of the material. Element In can restrict the recombination in the complex matrices owing to atomic mismatch ratio in configuration [14]. Ga has ability to tailor the band gap of the materials, while Se can be act as a base element for the PV material, this can be form long chain as well ring within the complex structure, as a consequence, a large number of defect states developed in the complex configuration [15]-[16]. Incorporation of the additional chalcogen element Te can also substantially increase the intrinsic structural steric hindrance and produce more defect states and decrease the Se rings within the complex structures of the under test alloys. Hence the high and low alloying amounts of the metallic element Cu and the chalcogene elements Se, Te, in CIGST-1 composition creates a large number of unsaturated frustrated bonds within the complex structure than the CIGST-2, this could be the reason for the homogenous surface morphology, higher order diffusion XPS core level peaks and an enhanced optical properties in CIGST-1 composition.

IV. CONCLUSION

In-conclusive remarks, the author has presented the structural and optical characterizations of the CIGST-1 and CIGST-2 solar cell materials. Results revealed materials have overall amorphous structures and elemental XPS core energy level peaks are found to higher for CIGST-1 than CIGST-2 composition along with materials also exhibited a strong

UV/Visible light absorption ability in the visible region. CIGST-1 composition material has exhibited higher refractive index, optical energy band gap than the CIGST-2. However, CIGST-2 has a high order optical reflectivity below the wavelength 3000 Å. Thus, this study reveals the CIGST-1 composition material is suitable than the CIGST-2 for the photovoltaic application.

ACKNOWLEDGMENT

AKS thankful to UGC-New Delhi for providing financial support under the Dr. D.S. Kothari program. Also grateful to Prof. K..S. Sangunni and Prof. P.S. Anil Kumar for the valuable suggestions.

REFERENCES

- [1] Z.Q. Ma and B.X.Liu, Boron-doped diamond-like amorphous carbon as photovoltaic films in solar cell, *Solar energy materials and solar cells*, vol.69,no.4 pp.339- 444, Nov.2001.
- [2] K.L. Narayanan and M. Yamaguchi, Photovoltaic effects of a:C/C60/Si (p-i-n) solar cell structures, *Solar energy materials and solar cells*, vol.75, Issue 3-4, pp.345-350, Feb.2003.
- [3] E.A. Katz, D. Faiman and V. Lyubin, "Proceedings of the 29th IEEE Photovoltaic Specialists Conference, pp. 1298-1301, 2002.
- [4] K. L. Chopra, P. D. Paulson and V. Dutta, Thin-film solar cells: an overview, *Prog. Photo.: Res. Appl.* vol. 12, Issue.2-3, pp.69-92, May 2004.
- [5] R.W. Birkmire, Compound polycrystalline solar cells:: Recent progress and Y2 K perspective *Solar Energy Materials and Solar Cells*, vol.65, Issue 1-4, pp.17-28, Jan. 2001.
- [6] K. Zweibel, "The Terawatt Challenge for Thin Film PV, in *Thin Film Solar Cells* (ed. J. Poortmans)," Chichester, John Wiley & Sons, Ltd, pp 427-462, 2007.
- [7] J.F. Moulder, W.F. Sticker, P.E. Sobol, K.D. Bomben, *Hand Book of X-ray Photoelectron Spectroscopy*, Perkin Elmer, 1992.
- [8] F. Tong, X.S. Miao, Y. Wu, Z.P. Chen, H. Tong, X.M. Cheng, Effective method to identify the vacancies in crystalline GeTe, *Appl. Phys. Lett.* vol.97, Issue.26, pp.261904, Dec.2010.
- [9] A. Anedda, C.M. Carbonaro, A. Serpi, N. Chiodini, A. Paleari, R. Scott, G. Brambilla and V. Pruneri, Vacuum ultraviolet absorption spectrum of photorefractive Sn-doped silica fiber preforms, *J. Non-Cryst. Solids*, vol.280, Issue.1-3, pp. 287 - 291, Feb. 2001.
- [10] A. K. Singh, N. Mehta and K. Singh, Optical and FTIR properties of Se93-XZn2Te5InX chalcogenide glasses, *Physica B*, vol. 404, Issue.20, pp. 3470-3474, Nov. 2009.
- [11] A. K. Singh and K. Singh, Composition dependence of UV-visible and MID-FTIR properties of Se98-x Zn2In x (x = 0, 2, 4, 6 and 10) chalcogenide glasses, *J. Modern Optics*, vol. 56, Issue.4, pp.471-476, Mar. 2009.
- [12] J.Tauc, "Amorphous and Liquid Semic- onductors", Plenum Press, New York, pp. 159, 1979.
- [13] F. Urbach, The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids, *Phys. Rev.* Vol.92, Issue.5, pp.1324-1324, Dec. 1953.
- [14] V. A. Akhavan, M. G. Panthani, B. W. Goodfellow, D. K. Reid and B. A. Korgel, Thickness-limited performance of CuInSe2 nanocrystal photovoltaic devices, *Optics Express*, vol.18, Issue. S3, pp. A411-A420, Sep. 2010.
- [15] F. D. Dhlamini, "Growth of pentenary chalcopyrite thin films and characterization of photovoltaic devices from these films", Ph.D. Thesis, Faculty of Science, University of Johannesburg, 2009.
- [16] Q. Cao, O. Gunawan, M. Copel, K. B. Reuter, S. J. Chey, V. R. Deline and D.B. Mitzi, Defects in Cu(In,Ga)Se2 chalcopyrite semiconductors: a comparative study of material properties, defect states, and photovoltaic performance, *Adv. Energy Mater.* vol.1, Issue.5, pp. 845-853, Oct. 2011.



Abhay Kumar Singh has born 1976 in India, he received the B.Sc. and M.Sc. degrees from Chhatrapati Shahu Ji Maharaj University, in 1998, 2000 and Ph.D. degree in physics from Banaras Hindu University, Varanasi, India, in 2009, respectively. He is presently working as a Dr. D. S. Kothari Post-Doctoral Fellow (funded by university grand commission New Delhi) in the Department of Physics, Indian Institute of Science Bangalore, India. His

current research interest including, chalcogenide photovoltaic solar cell, chalcogen-nano composites, chalcogenide metallic/non-metallic multicomponent alloys preparations and their bulk as well as thin films structural, thermal, optical and electrical characterizations. He was successfully introduced the Se-Zn-In and Se-Zn-Te-In two new series of chalcogenide glasses in 2009, 2010, and SZS-MWCNT and SZS-GF in 2012. Experimental findings on these two series as well as other compositions glasses he has been demonstrated in more than 25 technical research publications in reputed international journals. From January 2004 to February 2005, he also worked as a research staff in Notational Metallurgical Laboratory, Jamshedpur, (CSIR Lab), in applied chemistry and corrosion division, under the project on hot dip galvanizing and their metallographic analysis. He has extensive experiences with the process of hot dip galvanizing and their thin films structural analysis by using various characterizing tools and material analysis by using metal analyzer.