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Structural, optical and electrical properties of Cu(InGa)SeTe device with the varying laser pulses

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ABSTRACT

Next generation high performance heterojunction photovoltaic (PV) modules can be fabricated with an appropriate active layer material. Therefore, it is worth to examine physical properties of the recent developed $Cu_{25}(In_{16}Ga_{9})Se_{40}Te_{10}$ (CIGST) material for the potential photovoltaic application. This, report demonstrates the structural, optical and electrical properties of the 8000 and 16000 pulses deposited CIGST films on top of the ITO coated soda lime substrate (CIGST/ITO/substrate); whereas, the substrate temperature was 550^0 C. The 16000 pulses deposited thin film surface roughness (45 nm) and thickness (~1.4 µm) are obtained lower and higher than the 8000 pulses thin film. The cross sectional EDS elemental mapping also gives the fewer interlayer inclusions for the 8000 pulses deposited thin film. With the increasing thin films thicknesses a distinguishable UV/Visible peak shift toward the high wave length side and enhance in optical energy band gap (1.13 and 1.2 eV) are noticed. Device fabricated (CIGST/ITO/substrate) with the 16000 pulses have a sharp current growth upto 2.0×10^{-2} amp with a lower resistance under the applied voltage range 0-20V. The internal (IQE) and external (EQE) quantum efficiencies charge carriers transport for the fabricated devices are also discussed. Copyright © 2015 VBRI Press.

Keywords: CIGST; PLD; thin films; optical property.

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Introduction

Prospect of the photovoltaic devices based on thin-film technologies on cheap, light-weight substrates is highly appealing to cut down costs in industrial production .With the key strategic objective multi GW photovoltaic production in the up-coming years. In the running decade the emergence of thin film technology as a credible alternative of the conventional silicon solar cells has encouraged the development of the copper indium gallium selenide (CIGS) technology **[1]**. Indeed, CIGS thin film technology is only has record efficiencies comparable and higher than polycrystalline silicon more than 21.7% **[2-5]**. The CIGS has recognized one of the most promising alternative for the low-cost photovoltaic devices. Typical device structure of the CIGS solar cell consists heterostructure thin films layer in the sequence ZnO:Al(1 micron)/ ZnO-I(50 nm)/CdS(50 nm)/CIGS(2 microns)/Mo (0.5 micron)/glass. The Mo & ZnO:Al layers act as back electrical and front transparent conducting oxide contacts, while CIGS and CdS are the active and buffer layers. The most frequent used co-evaporation deposition process of CIGS absorber layer demonstrates at high temperature (≥ 500 °C) depending on choice of the substrate.

The soda-lime substrate has been used for the highest efficiency CIGS solar cell at the laboratory scale. Although, to fabricate the low cost modules **[3]** the CIGS technology has also demonstrated on the flexible substrates such plastic or metallic foils. These modules performance can drive from the defects in grain boundaries in polycrystalline materials and existence of the effective recombination centres **[4]**. The thickness, crystal sizes, grain boundaries, defect density and elemental diffusion/ or inclusion properties of the polycrystalline film layer can be described with the help of the microstructure **[2-4]**. Therefore, allying elements interlayer diffusion at the interface is crucial parameter for a solar cell module. Predominantly, active layer elemental diffusion into the back contact layer can influence (1 to 2 %) overall efficiency of the solar module. Here we have fabricated the $Cu_{25}(In_{16}Ga_9)Se_{40}Te_{10}$ (CIGST)/ITO/substrate (soda-lime glass) devices by using the Pulse Laser Deposition (PLD) technique. With the prime goal CIGST/ITO/substrate device fabrication using varying laser pulses and role of additional alloying element Te in CIGS active layer, its impact on the CIGST/ITO inter layer elemental diffusion. The fabricated varying laser pulses (8000 and 16000) CIGST/ITO/substrate devices structural, optical, electrical (like I-V, R-V) and internal (IQE) and external (EQE) quantum efficiencies are discussed. It expected incorporation of the additional element Te can increase the thermal stability, as a consequence enhancement in structural hindrance and creation a large number charge carriers sits **[6]**. Therefore, diffusion of CIGST layer ingredients into the ITO layer (at the interface) could be improved. The improved active layer/back contact layer junction of the CIGST system can enhance overall efficiency the module.

Experimental

Materials

Used high purity (99.999) materials Cu, In, Ga, Se and Te were purchased from the international supplier Sigma Aldrich. Each material was used as received in solid form. To made a PLD target the appropriate compositional amounts of the CIGST (25:16:9:40:10) was taken into the quartz ampoule (8 × 11 mm). Evacuated (10^{-5} Torr) and sealed ampoule was heated upto to 1000^0 C in a horizontal resistance furnace under a slow heating rate (2-3^0 C/min). To get the homogeneous material mixing ampoule was continuously rotated with the help of the electric motor. At the desire (1000^0 C) temperature ampoule was kept for the 12 h; afterward it was quenched into ice cooled NaOH containing water. The final product was extracted by breaking the ampoule. The prepared CIGST material 2 inch circular PLD target pellet was made by employing the 400 N loads at the temperature 200^0C.

Method

Material PLD target and ITO coated 2.5 × 2.5 mm substrate were mounted in a high vacuum chamber for the films deposition under the pressure 4 × 10^{-2} Torr; while the substrate temperature was 550^0C. The excimer pulse laser energy, current and frequency were used 300 mJ, 3A, 5Hz/sec respectively. The PLD deposited thin films crystallographic structure, surface morphology, roughness and depth profile, cross sectional view, energy dispersive X-ray pattern and interlayer cross sectional mapping, UV/Visible absorption spectra, I-V, R-V and internal (IQE) and external (EQE) quantum efficiencies were characterized by employing the relevant techniques.

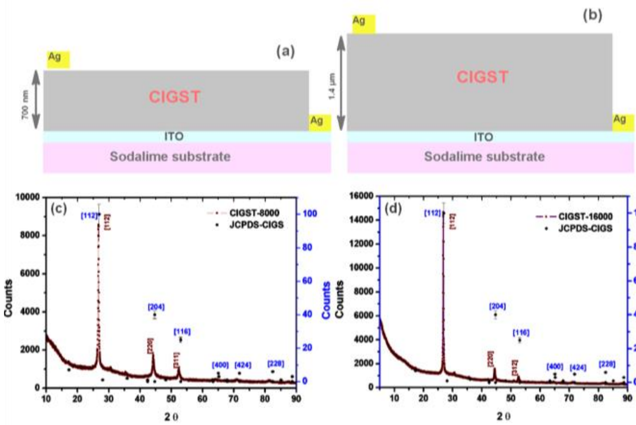

Fig. 1. (a, b). Schematic of the 8000 and 16000 pulses deposited CIGST film devices, (c, d). XRD patterns of the CIGST films matching with the CIGS (data points only) data from the JCPDS.

Results and discussion

XRD phases for the CIGST deposited thin films is given in **Fig. 1(a, b)**. The 8000 pulses film exhibits a strong CIGS composition peak correspond to 2θ value 26^0 (counts 8545) accompanied with other low intensity peaks at 44, 52 and 70^0 and planes 220, 311, 332. However, the 16000 pulses film is also exhibited the CIGS composition strong peak at 2θ value 26^0 with a higher counts (14668) value. While the low intensity counts value 220 and 311 plane (2θ values 44 and 52^0) peaks in a decline order with a noticeable difference very low intensity peak (2θ value 70^0) is disappeared. Therefore, XRD analysis gives these PLD deposited thin films have CIGST homogenous compositional plane peaks. This reflects the polycrystalline structure of the CIGST films. Moreover, it has also noticed with the increasing laser pulses (or increasing thickness) thin films count values corresponding to 220 and 311 planes is decreased. This can be directly correlated with the significant information; the involvement of element Te affects the intensity (except prime peak) of the RDX peaks, they either reduced or disappear in comparison to CIGS pattern. This could be considered as evidence about higher order phase mixing of the alloying elements in CIGST configuration; it could be due to increase reaction rates in between the metallic and non-metallic elements with the metallic chalcogen Te.

Surface property of the active layer can also play a vital role in PV technology **[7]**. AFM surface morphological view, 3D roughness view and depth profile histogram is demonstrated in **Fig. 2(a-f)**.It is evident the 16000 pulses deposited film has a larger and homogenous grains along with a higher roughness parameter value 87 nm. While, 8000 pulses deposited film has an uneven surface morphological grains with a low roughness parameter value 45 nm. The inferior value of the depth profile histogram (see **Fig. 2(c, f)**) for the 16000 pulses film is revealed throughout surface area (25μ × 25μ) developed grains in a consistent manner than 8000 pulses film.

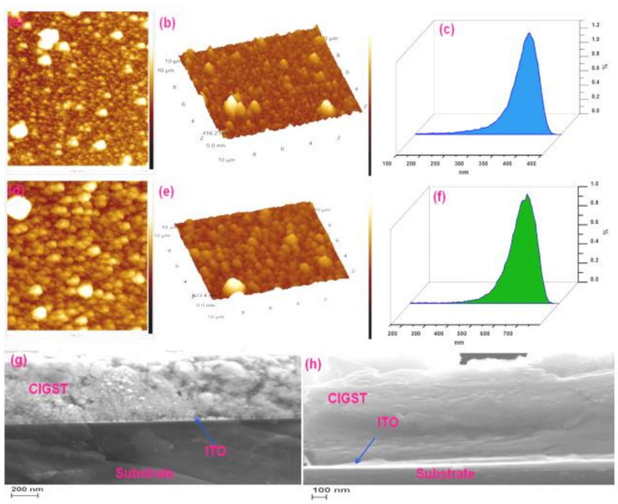

Fig. 2. (a, b, c; d, e, f). AFM surface morphology, 3D roughness view, depth profile and (g, h) FESEM cross sectional surface view, for the 8000 and 16000 pulses deposited films.

The less deviated grains growths surface morphology is would desire for the high performance module. Cause, it offers higher order consistent interlayer phase mixing with the buffer layer ingredients. Nonetheless, this study is limited to the active layer not beyond that. Moreover, compactness, thickness and adherence of the developed CIGST films is important for the even charge carrier generation and limit to overall module size with the typical required charge carrier diffusion length **[8-10]**. Along these the appropriate interfacial mixing with the back contact layer (ITO) **[4]** is also a crucial parameter for the performance. Here cross sectional surface morphological view reveals (See **Fig. 2(g, h)**) the developed films thickness ~ 700 nm and ~ 1.4 μm with a higher order compactness and adherence appearance for the thicker film.

The stoichiometric elemental presence for the deposited films has been verified from the EDS patterns (see **Fig. 3(a, g)**). The smooth individual element diffusion/ inclusion at the junction are an important parameter for the multi layers photovoltaics. Because uneven elemental diffusion of the active layer at the junction (or interface) of the ITO layer can affect the electronic charge transport; resulting inferior in working performance **[11]**. The developed CIGST films individual elemental diffusion into the ITO layer can be verified from the cross sectional EDS mapping (see **Fig. 3(b-f, h-l)**). It is evident with the increasing (thickness) number of laser pulses Cu, In and Se alloying element diffusion increases at the ITO layer interface (see **Fig. 3(b ,d ,e and h, j, k)**).

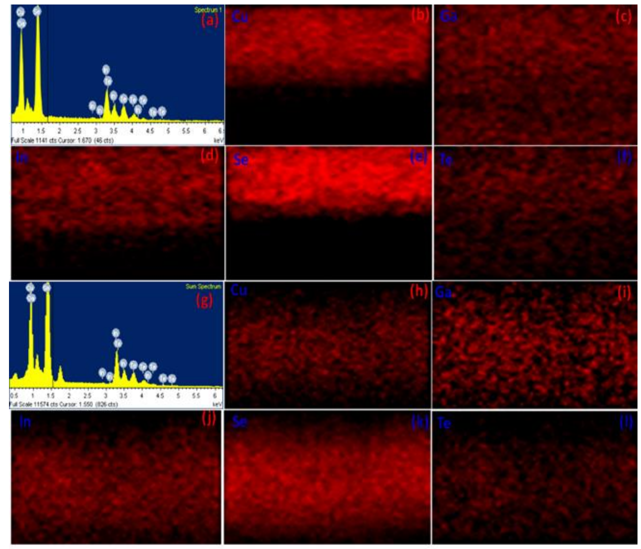

Fig. 3. (a, b, c, d, e, f). EDS pattern and cross sectional elemental EDS mapping for the 8000 pulses deposited film, (g, h, i, j, k, l) EDS pattern and cross sectional elemental EDS mapping for the 16000 pulses deposited film.

While the homogeneously distributed Ga and Te (see **Fig. 3 (c, f and i, l)**) seems unaffected. Therefore, interlayer CIGST/ITO junction in 8000 pulses film is suffering from the lack of the alloying elements homogeneity; on the other hand, 16000 pulses film has exhibited rather homogeneous distribution at the interface. This can make an impact in easy charge carrier transportation for the 16000 pulses deposited device.

It is well established for the high performance multilayer module PV, the UV/Visible optical property can consider a key physical parameter **[12]**. Active layer material should have good UV/Visible light absorbance (α ~ 10^5 cm-1) ability in the wave length range 300 to 800 nm. The CIGST films recorded UV/visible spectrum (see **Fig. 4**) in the reflection mode demonstrates the existence of a broad absorbance peak in the wave length range 300 nm to 1100 nm. The absorbance peak shift toward the high wave length side is appeared with the increasing thickness. The corresponding optical energy band gap (E_g) of the CIGST films has been evaluated with help of the Tauc plot (see inset **Fig. 4(a, b)**).

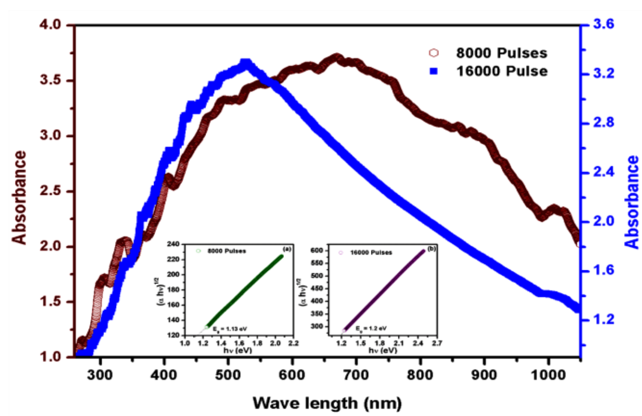

Fig. 4. UV-Visible absorption spectra and tauc plot (inside profile) for the 8000 and 16000 pulses deposited films.

The obtained optical energy band gaps (1.13 and 1.2 eV) slightly differ for the subjected CIGST films. I-V and R-V characteristics of the developed (CIGST/ITO/substrate) devices are given in the **Fig. 5(a, b)**. Under the applied voltage range 0- 100 V, 8000 pulses deposited device is exhibited the fewer charge carrier transport with the lower and higher values of I and R in comparison to 16000 pulses deposited device. With the noticeable feature I and R values in a fluctuating manner for the fewer pulses device. Moreover in the initial applied voltage range ~ 4 to ~ 25 V a continuous decline in I (1.55 × 10^{-6} amp to 8.0 × 10^{-7} amp) value is appeared for the 8000 pulses device.

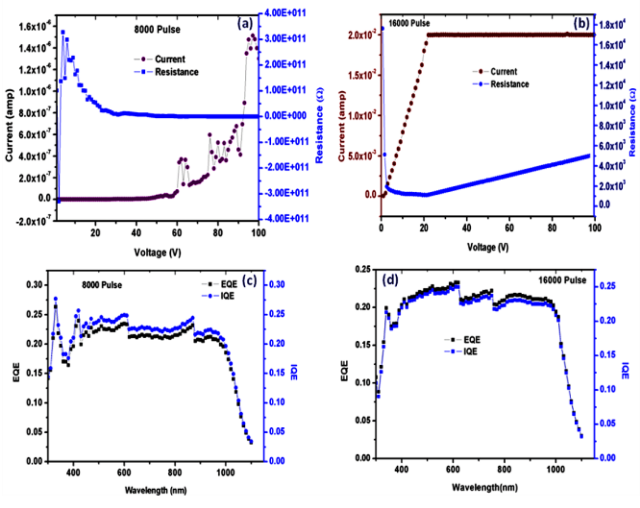

Fig. 5 (a, b). I-V and R-V in the applied voltage range upto 100V, (c, d) EQE and IQE in the wave length range 300 to 1100 nm, for the 8000 and 16000 pulses deposited films.

While, the 16000 pulses deposited device has exhibited a continuous sharp current growth 5.6 × 10^{-5} amp to 2.0 × 10^{-2} amp and it reaches upto maximum instrumental limit (2m amp) under the applied voltage range ~ 0- 22 V, afterward it reflects the flat data points. Below the 5 × 10^{3} Ω nearly constant resistance is recorded for this device. The sharp positive current growth in 16000 pulses device could be connected to the high order atomic miss-match, resulting a large number of defects in the CIGST active layer. This can create a huge amount of the localized trap (electrons and holes pairs) within the configuration. The enhanced polycrystalline surface morphology of the CIGST/ITO interface mixing can also contribute substantially to provide easy path for free flow of the charge carries.

The internal (IQE) and external (EQE) quantum efficiencies is the useful physical parameter for a photovoltaic modules/materials. This can directly provide the relationship in between the number of incident photons over the unit cross sectional surface area and corresponding photon absorption/ (charge carrier creation) within the active layer. The IQE and EQE are meaningful for a complete solar cell module; nonetheless, to access the active layer high level performance could be useful. Predominantly EQE is the significant to access charge carrier creation ability of the active layer material. The IQE and EQE of the described CIGST/ITO/substrate devices are given in the **Fig. 5 (a, b)**. The 8000 pulses deposited device has exhibited lower value of the EQE than the IQE in the wave length range 400 nm to 1000 nm. Means, it has high photon absorption ability but charge carrier conversion rate is low. It could be correlated to less thickness of the active layer of the device; because, in defect drive system incident photon absorbed correlated electron is produced charge carrier pairs **[13, 14]** with the interaction of the deep localised lone pair (or electron- hole pair). Therefore, it might be due to insufficient thickness of the active layer the energetic electron could not interacts a suitable lone pair before reaching on the surface. Thus energy is dissipated without the charge creation; as a consequence IQE appears higher than the EQE. While the 16000 pulses deposited device has optimum (or sufficient) active layer thickness (~ 1.4 μm), therefore, it has comparatively a large amounts of the electron holes pairs, as a consequence EQE is slightly higher for this device (see **Fig. 5 b**).

Conclusion

Thus this work has demonstrated the CIGST/ITO/substrate combination devices different physical properties. The structural analysis has revealed a few low intensity peaks of the CIGS is absent in CIGST active layer XRD patterns. The surface morphological growth and thickness of the 16000 pulses can be considered appropriate for the photovoltaic use. The stoichiometric elemental existence in the active layer and the interlayer (CIGST/ITO) diffusion in respect varying pulses and thickness have verified from the EDS patterns and cross sectional EDS elemental mapping. High order elemental diffusion/ or inclusion at the interface has noticed for the higher number of pulses deposited device. Moreover, the optical properties of the active layer films have also verified for the photovoltaic purpose. The devices active layers have exhibited good optical absorption ability in the desire UV/Visible wave length range with the thickness dependent peak shift toward the lower value side. The described laser pulses varying devices lower and higher values of I-V characteristics can correlate to even polycrystalline surface morphological growth, homogenous elemental interlayer diffusion and creation of a large number of lone pairs in the configuration. Moreover, with the help of active layer thickness dependence charge carrier creation the variation in IQE and EQE of the devices has also interpreted. Thus, this study has introduced the recent developed CIGST material based device physical properties for the prospective photovoltaic application with the aim overall solar cell module efficiency may enhance. An intensive research requires, to explore photovoltaic cell fabrication with this materials by varying the deposition technique as well conditions.

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Reference

1. Fleutot, B.; Lincot, D.; Jubault, M.; Kao, Z. J. L.; Guillemoles, N. N. J. F.; Donsanti, F.; *Adv. Mater. Interfaces* **2014**, *1*, 1400044. **DOI:** 10.1002/admi.201400044
2. Bhattacharya, R. N.; Contreras, M. A.; Egaas, B.; Noufi, R. N.; Kanevce, A.; Sites, J. R.; *Appl. Phys. Lett.* **2006**, *89*, 253503.

DOI: 10.1063/1.2410230

3. Blösch, P.; Pianezzi, F.; Chiril, A.; Rossbach, P.; Nishiwaki, S.; Buecheler, S.; Tiwari A. N.; *J. Appl. Phys.* **2013**, *113*, 054506. **DOI:** 10.1063/1.4789616
4. Jiang, C. S.; Noufi, R.; Ramanathan, K.; Shama, J. A.; Moutinho, H. R.; Al-Jassim, M. M.; *Appl. Phys. Lett.* **2004**, *85*, 2625. **DOI:** 10.1063/1.1793346
5. Jackson, P.; Hariskos, D.; Wuerz, R.; Kiowski, O.; Bauer, A.; Friedlmeier, T. M.; Powalla, M.; *Phys. Status Solidi RRL* **2014**, *9*, 1. **DOI:** 10.1002/pssr.201409520
6. Singh, A. K.; *J. Photo. and Opto.* **2013**, *3*, 43. **DOI:** paperInfo.aspx?ID=5256
7. Andreani, L. C.; Kowalczewski, P. A.; Mura, C. I.; Patrini, M.; Acciarri, M.; Binetti, S.; Sassella, A.; Marchionna, S.; 27th European Photovoltaic Solar Energy Conference and Exhibition **2012**, 2334. **DOI:**http://fisica.unipv.it/nanophotonics/Pubs/CIGS_27EUPVSEC_3CV.1.41.pdf
8. Reshak, A. H.; Shahimin, M. M.; Fauzi, I. F.; *Int. J. Electrochem. Sci.* **2014**, *9*, 700. **DOI:**http://www.electrochemsci.org/papers/vol9/90200700.pdf
9. Kuciauskas, D.; Li, J. V.; Contreras, M. A.; Pankow, J.; Dippo, P.; Young, M.; Mansfield, L. M.; Noufi, R.; Levi, D.; *J. Appl. Phys.* **2013**, *114*, 154505. **DOI:** 10.1063/1.4825211
10. Park, J. K.; Kang, J. C.; Kim, S. Y.; Son, B. H.; Park, J. Y.; Lee, S.; Ahn, Y. H.; *J. Phys. Chem. Lett.* **2012**, *3*, 3632. **DOI:** 10.1021/jz301751j
11. Yamada, N.; Tatejima, T.; Ishizaki, H.; Nakada, T.; 15th International Photovoltaic Science & Engineering Conference (PVSEC-15) Shanghai China. **2005**, 507. **DOI:**http://www.chubu.ac.jp/english/faculty/profile/198b210ddd6c932c7d62c412249fd28a05acbd4d.html
12. Chopra, K. L.; Paulson, P. D.; Dutta, V.; *Prog. Photovolt: Res. Appl.* **2004**, *12*, 69. **DOI:** 10.1002/pip.541
13. Juma, A. O.; Physics Department, Freie Universität Berlin, PhD thesis. **2013**. **DOI:**http://www.diss.fuberlin.de/diss/servlets/MCRFileNodeServlet/FUDISS_derivate_000000014557/Dissertation_Juma.pdf
14. Song, T.; PhD Thesis "Department of Physics, Colorado State University Fort Collins, Colorado Fall. **2013**. **DOI:**http://www2.physics.colostate.edu/groups/photovoltaic/Tao%20Thesis.pdf