

EXCELLENT OUTDOOR STABILITY AND RADIATION HARDNESS: CUINGASE2 BASED THIN FILM SOLAR CELL DEVICES

Dr. Sushil Sharma and Dr. Ekta Sharma, Yatendra Sharma

¹Editor, E-Cronicon Chemistry UK

²Assistant Professor (Sr. Scale), Textiles and Apparel Designing, Ethelind School of Home Science, Sam Higginbottom Institute of Agriculture, Technology and Sciences, (Formerly Allahabad Agriculture Institute) (Deemed –to-be-University), Allahabad, Uttar Pradesh, INDIA

³M.P.Ed Student, Amity School of Physical Education & Sports Sciences, Amity University, Noida, INDIA

ABSTRACT: *Energy crisis in the present circumstances require sustained activities on the renewable sources of energy. India has a lot of potentials to harness and harvest solar energy through photovoltaic devices. In this connection, several industries and institutions are concentrating on the development of solar cell devices in India. The proposed research will be complimentary and very well add many patents or results to the existing literature for the betterment of devices from thin film solar cell materials. Earnest attempts on the development of solar cells mainly, high efficient solar cells are very much needed for the development of photovoltaic industries in India. CuInGaSe₂ thin film solar cells have a potential for highest efficiencies on the laboratory scale as well as on the level of large area modules. Thin film modules from CuInGaSe₂ show excellent outdoor stability and radiation hardness. Though good efficiencies and other favorable conditions were achieved with these materials, the knowledge of this material is still extremely low compared to what is known for other thin film materials like amorphous Si, crystalline Si or CdTe. The role of intrinsic defects in CuInGaSe₂ and their implication on device performance will also be studied in detail. Microstructural characterisation of the cross-sectional device, as well as the depth analysis of the defect distribution, will be carried out to analyze the factors influencing the properties of CuInGaSe₂. Efforts will be made to design the material properties of CuInGaSe₂ for tailoring the device performance. In addition, it is proposed to develop HYBRID (inorganic-organic) bulk junction solar cell structures with different approaches. The developed bilayer and hybrid bulk junction solar cell structures will be evaluated. The performance of the developed structures will be optimized from the feedback of the characterization results.*

KEYWORDS: Outdoor Stability, Radiation Hardness, Cuingase2, Based Thin, Cell Devices

INTRODUCTION

Objectives

CuInGaSe₂ thin film solar cells have a potential for highest efficiencies on the laboratory scale as well as on the level of large area modules. Thin film modules from CuInGaSe₂ show excellent outdoor stability and radiation hardness. Though good efficiencies and other favorable conditions were achieved with these materials, the knowledge of this material is

still extremely low compared to what is known for other thin film materials like amorphous Si, crystalline Si or CdTe.

(a) Objectives of High Efficient CuInGaSe₂ based Thin Film Solar Cell Devices

This proposed project is focused on the understanding of growth processes of CuInGaSe₂. This is important, as for every tandem device the top single junction has to be optimized first. CuInGaSe₂ absorber materials will be prepared by physical vapour deposition (Multi-source sputtering /evaporation) methods on molybdenum coated glass substrates. Suitable window layers for this absorber material are CdS, ZnO or ZnSe for efficient solar cells. Experiments will be carried out to prepare CdS buffer and undoped as well as doped ZnO layers as window layers. The complete fabrication processes from bottom contact to absorbers, buffer, window and top contacts will be integrated in a in-line system. The solar cells structure of Mo/CuInGaSe₂/CdS-ZnS/ZnO:Ga/ZnO/Ni will be fabricated from the system. The performance of the solar cell device will be evaluated. In addition, efforts will be made to develop Cd-free, solar cells with ZnS or ZnSe as buffer. The performance and steps for improvement of the device quality as well as for high efficiency will be studied in detail. After this research it's easy to (a) Development of in-line multi-source sputtering / evaporation system for the growth of chalcopyrite based thin film Absorber materials (b) Optimisation of the conditions for the growth of CuInGaSe₂ absorbers on glass as well as metal-coated glass substrates (c) Structural, morphological, optical and electrical characterization of the CuInGaSe₂ Absorbers. (d) Development of suitable buffer and window materials for these absorbers. (e) Integration of Multi-source sputtering, evaporation and solution process in-line in a single system (f) Development of Solar cells from the CuInGaSe₂ absorbers with suitable Heterostructures (g) Microstructural and Electrical Characterization of the solar cells for high efficiency and optimize the conditions for the same. (h) Fabrication of the test modules from the optimized solar cells utilising these thin film absorbers.

(b) Objectives of Hybrid Solar Cell Devices with CdTe composites

Development of CdTe-based nanostructures by wet chemical and by electron-beam evaporation process. Fabrication of hybrid (inorganic-organic) solar cell structure with PEDOT: PSS substrate and CdTe and P3HT based active layers. Characterization of the materials and the solar cell structure. Comparison of efficiency and material properties for terrestrial application. After that we also able to define (a) Development of inorganic (CdTe) and organic (P3HT) composites (b) Development of CdTe nanoparticles – P3HT blends (c) Fabrication of Hybrid Solar Cell structure with ITO/PEDOT:PSS/ inorganic-organic blends/BBL/Ni-Al multi-layers (d) Fabrication of Hybrid Bulk Junction with (CdTe nanomaterials) inorganic active layer complexed with (P3HT) organic polymer and sandwiched between polymers (PEDOT:PSS and BBL) and design of the solar cell structure with ITO/PEDOT:PSS/Active layer/BBL/Ni-Al multi-layers (e) Evaluation of the Solar Cell structures and optimization of the Hybrid Bulk Junction Solar Cell Devices

METHODOLOGY

(a). High Efficient CuInGaSe₂ based Thin Film Solar Cell Devices

It is proposed to develop a physical vapour deposition (multi-source sputtering) system for the preparation of CuInGaSe₂ thin film absorbers on glass as well as on metal sputtered glass substrates. Complete solar cell structure will be carried out in an integrated in-line process with evaporation, sputtering, CBD and metallization. Structural, optical and electronic properties of the deposited films will be analyzed. Solar cell structures will be completed with chemical bath deposited buffer layers and evaporated window layers. Efforts will be made to develop good quality and high efficiency cells. The possible solar cell heterostructure arrangement will be Mo\CuInGaSe₂\CdS-ZnS\ZnO:Ga\ZnO\Ni. Understanding of the transport properties for these heterostructure devices and their dependence on different processing steps during device preparation will be elaborately studied. The role of intrinsic defects in CuInGaSe₂ and their implication on device performance will also be studied in detail. Microstructural characterisation of the cross-sectional device as well as the depth analysis of the defect distribution will be carried out to analyze the factors influencing the properties of CuInGaSe₂. Efforts will be made to design the material properties of CuInGaSe₂ for tailoring the device performance. Estimated deposition rates for Ga, Cu, and In from the six deposition Zones in the inline CIGS deposition system is as shown in fig.1.

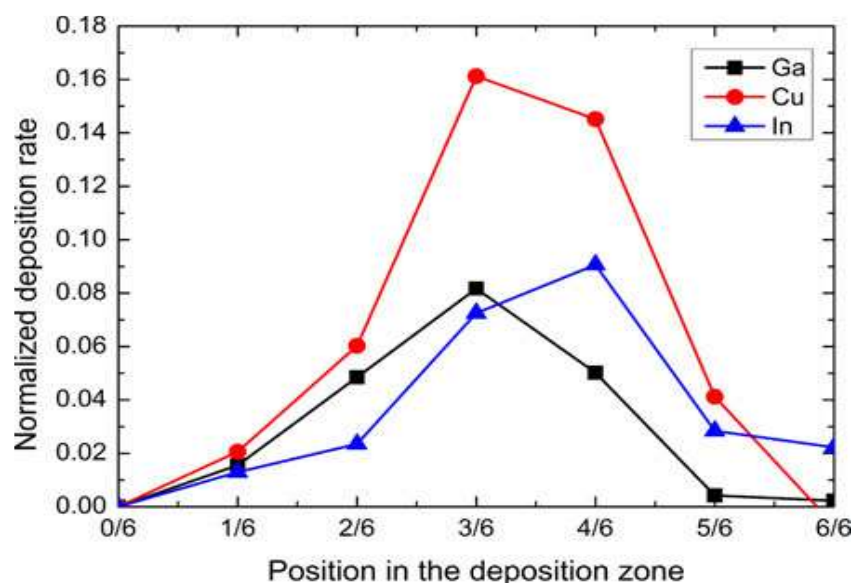


Fig.1. Estimated deposition rates for Ga, Cu, and In from the six deposition Zones in the inline CIGS deposition system.

CuInSe₂ (CIS) solar cells are promising candidates for thin film photovoltaic applications; one key limitation in their performance is surface recombination in these thin films. We demonstrate that passivating CIS films with Trioctylphosphine Sulfide (TOP: S) solution increases photoluminescence (PL) intensity by a factor of ~30, which suggests that this passivation significantly reduces surface recombination. X-ray photoelectron spectroscopy (XPS) reveals that TOP:S forms both eS and eP bonds on the CIS film surface, which leads to a ~4-fold increase in the surface Na peak intensity. This value is significantly higher than

what would be expected from high temperature annealing alone, which has been linked to improvements in surface morphology and device efficiency in CIS solar cells. We use Energy- Dispersive X-ray Spectroscopy (EDS) to measure the solid-state transport of Na within CIS films with and without passivation. EDS spectra on CIS film cross-sections reveals a saddle-shaped Na profile in the as fabricated films and a concentration gradient towards the film surface in the passivated films, with 20% higher surface Na content compared with the un-passivated films. We employ Hybrid (B3PW91) Density Functional Theory (DFT) to gain insight into energetics of Na defects, which demonstrate a driving force for Na diffusion from bulk towards the surface. DFT Calculations with TOP: S-like molecules on the same surfaces reveal a ~ 1 eV lower formation energy for the NaCu defect. The experiments and computations in this work suggest that TOP: S passivation promotes Na diffusion towards CIS film surfaces and stabilizes surface Na defects, which leads to the observed substantial decrease in surface recombination.

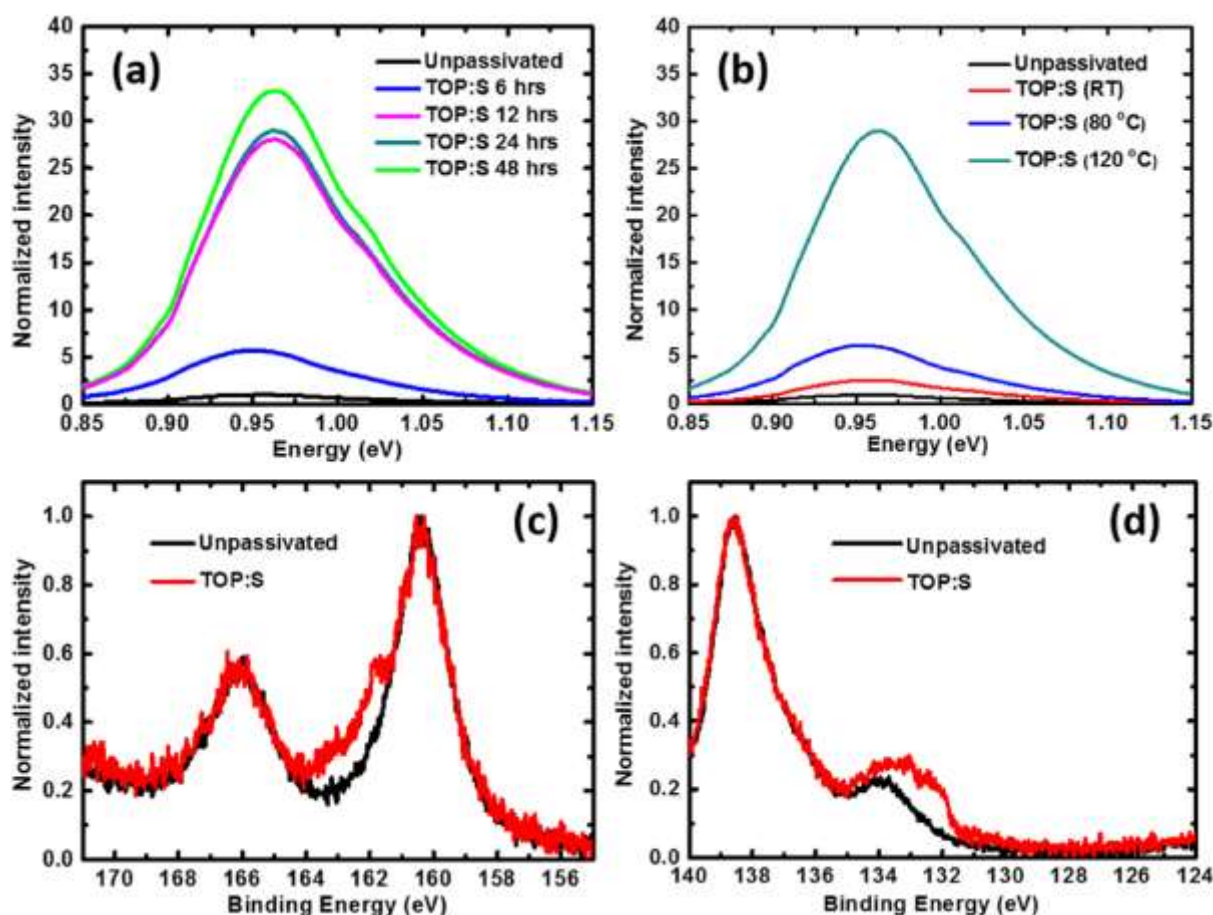


Fig.2 (a) Normalized PL intensity for un-passivated (baseline) CIS films, and films with passivation times up to 48 h. (b) Normalized PL intensity for un-passivated (baseline) CIS films, and films for passivation temperature up to 120 °C. (c, d) Surface XPS spectra of (c) S 2s and (d) P 2p peaks for CIS thin films with (red) and without (black) TOP:S treatment (120 °C, 24 h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(b). Hybrid Solar Cell Devices with CdTe composites

In addition, it is proposed to develop HYBRID (inorganic-organic) bulk junction solar cell structures with different approaches.

In the first approach, Cadmium telluride (CdTe) absorber materials will be synthesized by electrochemical deposition and/or by an electron-beam evaporation process. These inorganic materials will be used to make hybrid composites with organic polymer P3HT (poly (3-hexylthiophene)). Conducting polymer PEDOT: PSS will be spin coated on the ITO coated glass plates. These hybrid composites and polymer coated substrates will be used to prepare bulk junction solar cell structures like ITO/PEDOT: PSS/Hybrid Composites/Ni-Al.

In the second approach, cadmium telluride nanoparticles will be prepared by the wet-chemical process with thiocarboxylic acid as the capping agent. These nanoparticles will be blended with organic polymer P3HT and will be the active layer in the hybrid bulk junction. The polymer PEDOT: PSS and the active layer will be spin coated. The developed solar cell structure will be ITO/PEDOT: PSS/ CdTe (Nanomaterial)-P3HT composite/Ni-Al. Alternatively, the active layer will also be stacked in a P3HT template to complete the solar cell structure.

The developed bilayer and hybrid bulk junction solar cell structures will be evaluated. The performance of the developed structures will be optimized from the feedback of the characterization results.

Advantages**(a). Advantages of Bulk Junction Solar cell Design:**

Bilayer hybrid solar cell structure with single active layer inorganic materials or organic semiconducting polymers led to the poor charge separation for photogenerated excitons. This approach was modified with the insertion of an additional buffer layer of electronic conductor polymer in the proposed solar cell structure and the blended active layer with proper interconnected networks. This additional layer of the active inorganic medium improves the photocurrent response, which is not limited by the absorption depth of the films. In addition the holes generated in the inorganic medium move along the PEDOT: PSS network towards the high work function electrode ITO and the electrons, in turn can move through the electron conductor BBL (the additional polymer layer on the top of the inorganic active layer) layer, where the holes are blocked by the high ionization energy of the BBL layer. However, the current generation can be significantly improved by adding BBL, which is a strong electron acceptor. BBL is an ideal polymer with thermal stability up to 500° C in air and also photochemically stable due to its ladder structure. BBL has also complementary absorption to that of CdTe, in the sense that, CdTe has a higher absorption coefficient at wavelengths below 500 nm and above 700 nm, BBL has a higher absorption coefficients between these wavelengths. Hence, BBL can be an active participant in photocurrent generation in addition to the buffer layer activity.

(b). Advantages of Nanoparticle-polymer blend in Hybrid Junction cells:

The use of inorganic nanoparticles embedded into organic semiconducting polymer blends is promising because, the nanoparticles can have high absorption coefficients, higher photoconductivity, the suitable common solvent can be visualized with the organic polymer,

suitable geometry and band gap for high efficiency. The interaction between the inorganic particles and polymer should be good enough to disperse high nanoparticle concentrations in the polymer solution and to prepare high-quality films to form this solution. The nanoparticles are not easily dispersed in polymer matrices. Because of the small size of the clusters, they have a high surface energy, which leads to aggregation or oxidation. Hence, the synthesis of nanoparticles shielded with various organic ligands is important in determining the morphology of the polymer/nanoparticles composites. Thiol-capped CdTe layers does not interfere in the photovoltaic suppression due to the ligands and a photovoltaic response was detected even without removing the organic ligand. Also, thiol-capped CdTe particles easily form dispersions with P3HT in toluene and it is easier to promote charge separation and transfer.

Definition of the problem

(a). High Efficient CuInGaSe₂ based Thin Film Solar Cell Devices

A key issue for the optimization of CuInGaSe₂ based solar cells is to obtain a correlation between device characteristics and the material properties important for photovoltaic applications such as defects and impurities. The optical and electrical properties of CIGS films are strongly affected by intrinsic defects. In order to investigate the correlation of stoichiometry deviation and semiconducting properties, it is proposed to characterize the material with structural characterisation, morphological studies, photoluminescence, and temperature dependent I-V Characteristics and admittance spectroscopy.

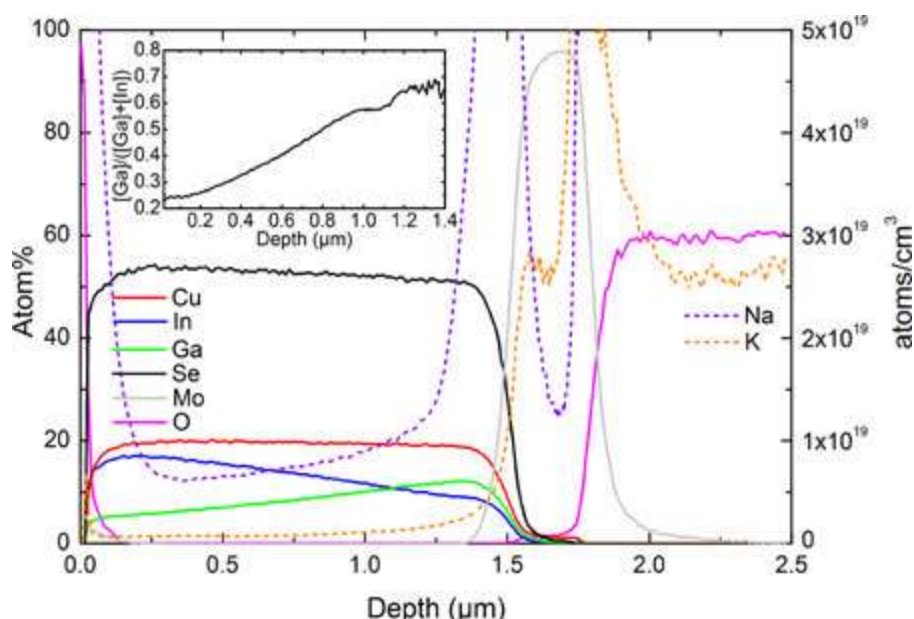


Fig.3. SIMS depth profile over a baseline device from the CIGS layer down to the glass substrate. Na and K are measured in atoms/cm³ on the right axis, whereas Cu, In, Ga, Se, Mo, and O are measured in atom percentage on the left axis. The inset shows the $[Ga]/([Ga]+[In])$ ratio as a function of depth.

(b). Microstructural Characterisation:

The microstructure of the CIGS absorber layer such as grain size, the presence of twins and the stacking faults density plays an important role in CIGS solar cells. The optimized condition for the deposition of high-quality CIGS film had larger grains than a single layer with comparable composition and the larger grains lead to better performance. Cross-sectional micrographs can be used to clearly observe the interface properties between the absorber and the substrate as well as the absorber and the window structures. Proper interface and uniformly distributed layers free from voids, twins and inclusions will be needed for the better performance of the cells.

(c). Admittance Measurements:

The present knowledge on the electronic transport properties of these materials and on the physical impact of variations of the preparation parameters is not available. The interdependence of the impurity content and the effective doping concentration of the solar cell structure can be evaluated by means of temperature and frequency dependent measurements of the complex admittance

$$Y = G + i2p n C$$

With conductance G and capacitance C . The admittance of the ZnO/CdS/CuGaSe₂ heterostructure is a superposition of the free carrier capacitance across the width of the space charge region (SCR) and the contribution from the charging and discharging of deeper impurity levels within the SCR of the junction. It is convenient to consider the frequency dependent part of the conductance or capacitance spectra i.e. to measure the derivative of the conductance G with respect to the frequency at particular n . The differentiated conductance dG/dn measured at a particular n can be plotted as a function of temperature for these solar cell structures. From the spectra it is possible to identify the role of different impurities in the structure and also to speculate the nature and quantity of free carrier concentration.

The admittance measurements will yield valuable information on the band diagram to investigate more precisely the cross-over effect. From the admittance measurements it is possible to find the thickness of the CdS and the existence/non-existence of the undoped ZnO influence on the dependence of the capacitance C on the probe frequency at low temperature. The result is that the electron Fermi level at the CGS/CdS interface is pinned by donor-like interface states and lies close to the conduction band edge at this interface. Within the specific temperature range the capacitance spectra $C(\omega)$ are determined by the capacitance resulting from charging and discharging of these interface states and the capacitance of the space charge region (SCR) of the heterostructure. Thus the admittance spectroscopy allows the position of the Fermi level at the surface of the absorber layer to be determined. A detailed analysis of the frequency dependence of the $C(\omega)$ curves indirectly allows an estimate of the maximum conduction band offsets between CdS and the absorber material, as well as between CdS and ZnO. Admittance measurements will be carried out for the proposed solar cell structure and the role of different window layer composition and their thickness on the band diagram and free carrier concentration will be evaluated.

Recently, the influence of incorporation of Na into the absorber layer of CIS solar cells has become the focus of interest. Controlled incorporation of Na displayed higher efficiencies compared to similar devices without Na. Admittance measurements on Cu(InGa)Se₂ have

been used to identify the Na-induced, shallow, acceptor like defect at about 75 meV from the valence band. Then the beneficial effect of this acceptor impurity on the device performance at room temperature has been attributed to the increase of free carrier concentration by this acceptor state. It has to be investigated, whether these findings hold also true for CIGS cells and if so, sustained efforts will be made to prepare Na-doped absorber layers and the influence of doping on the performance of the solar cell structures will be studied in detail.

Measurements

For CIS type solar cells, the conversion efficiencies were improved by light irradiation and applied voltage. From the standpoint of power output, CIGS solar cells are stable or the performance are improved under irradiation. But, being new devices CIGS solar cells must prove their long-term reliability for their actual usage, because it is not certain that the military compounds in the cells are in stoichiometric balance. Different defects in the material both in the form of donors like states or acceptor-like states invariably modify the solar cell performance and can be directly observed with the I-V characteristics. Hence, from the I-V characteristics and evaluating, typical changes of V_{oc} , J_{sc} , FF and efficiency direct correlation of the defect states can be made. The diode factor n and series resistance R_s will also be evaluated under irradiation and dark conditions. The change in defect density on illumination can be identified with the diode factor variations with irradiation and under dark condition. Dark and illuminated current -voltage characteristics of the CIGS solar cells reveal cross-over between dark and illumination region. This crossover has been explained by an illumination-dependent series resistance of the buffer layer. Then there is type inversion of the CIGS surface at the CIGS/CdS/ZnO heterojunction. Interface states play a dominant role at the CIGS surface on this type inversion. This has been revealed by the admittance and DLTS studies.

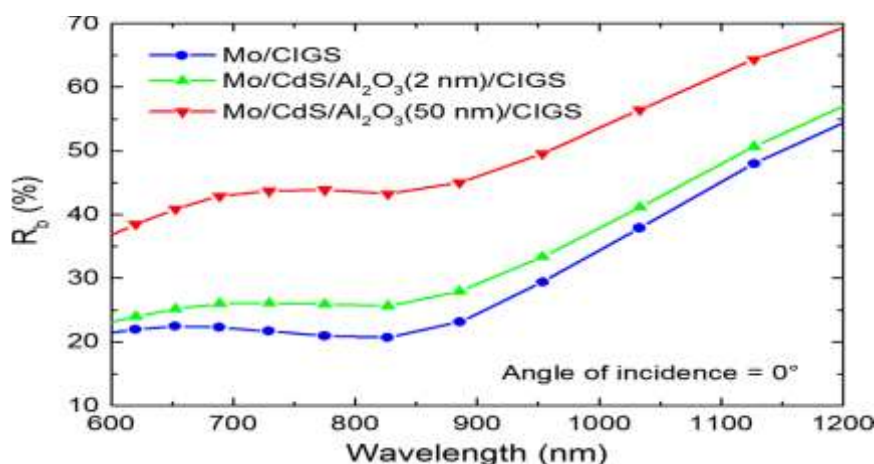


Fig.4. Calculated rear internal reflection as a function of wavelength for a Mo/CdS/Al₂O₃(2 or 50 nm)/CIGS device or an unpassivated reference

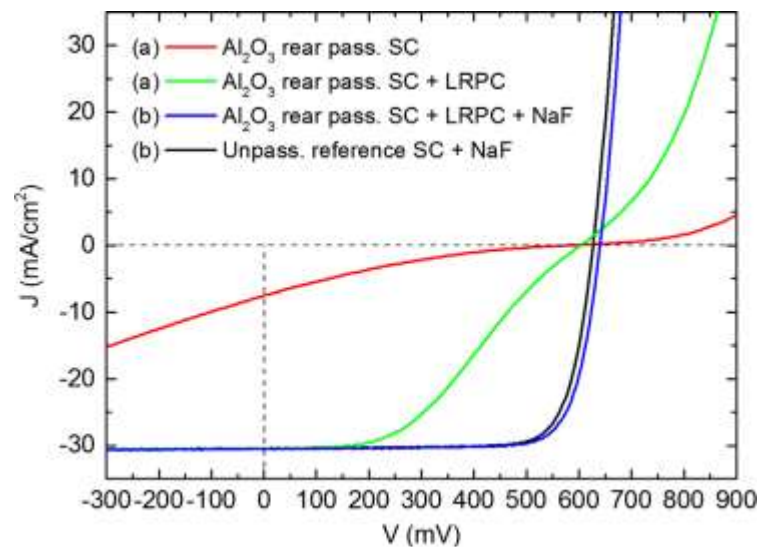


Fig.5. Representative J–V curves for (a) Al₂O₃ (2 nm) rear surface passivated CIGS solar cells (SC) with and without nano-sized local rear point contacts (LRPC) and (b) Al₂O₃ rear passivated cells having nano-sized local rear point contacts and unpassivated reference cells with 15 nm of NaF evaporated on top of the Al₂O₃ or Mo layer, respectively.

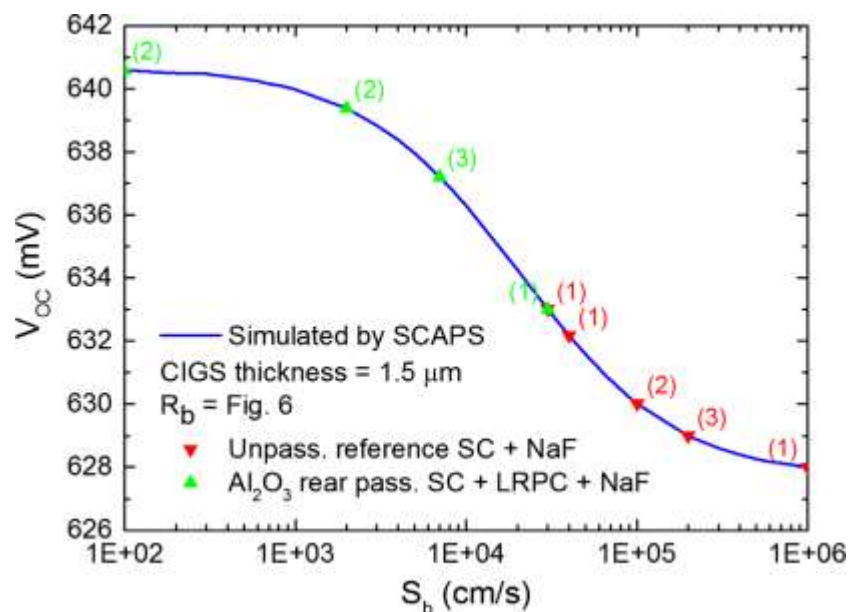


Fig.6. SCAPS simulated open circuit voltage as a function of surface recombination velocity for a CIGS thickness of 1.5 μm and arearinternal reflection asdefined

In Fig.6. Also the solar cell devices of Table 1 with $V_{OC} \geq 628$ mV are shown, and the quantity of devices having this specific V_{OC} is displayed between brackets.

(a) Photoluminescence Studies:

Photoluminescence results can be used to evaluate the decay mechanisms, localized defects (traps) in the inter-band, the temperature dependence of the band gap and composition

variation with depth. Typical PL Spectra of CIGS at 77 K consist of two or more emission bands. The origin of the PL peaks are not clear but, by considering the formation energies of the defects the peaks were related to the Cu-vacancies, Se vacancies and or substitutional Ga or In on Cu-sites. In addition, Majority carrier trap level with activation energy and an average trap density as well as Minority carrier trap level with activation energy and average trap density can be evaluated by combining PL with DLTS measurements.

CONCLUSION AND SCOPE OF WORK

After several research on the deposition of thin films of CuInSe₂, CuInS₂, CdTe, CdSe and CdSeTe by electrodeposition from an aqueous solution by potentiostat and periodic pulse techniques by optimized procedure. It was confirmed that thin films deposited by potentiostat technique have large porosity, non-uniform thickness, have spurious deposits on the edges of the substrate and high concentration of spherulites on the surface. With suitable modifications in the growth procedure (with variations in parameters) like Concentration of the source materials, substrates, temperature, deposition potential, pH of the solution and time of deposition, good quality deposits were obtained. The reason for this good quality deposits has been attributed to favourable growth sequence in this process. As like potentiostat method, in this process also there will be spurious deposits on the edges initially, but further application of pause time with negative sweep of potential and growth pulses, the deposits are more uniform with no spurious deposits on the edges. The crystalline states as well as the composition of the deposits are better in this technique.

Chalcopyrite compounds were deposited on substrates like titanium, graphite, nickel and molybdenum. The deposits were analyzed with x-ray powder diffraction, SEM, UV-Vis spectroscopy and voltammetry techniques. The properties were evaluated from the characterization results. Influence of substrate on the crystalline state and annealing properties were addressed explicitly. The expertise and experience on the large area thin film development will be highly useful for the proposed template assisted processes.

REFERENCES

- [1]. Green MA, Emery K, Hishikawa Y, Warta W, Dunlop ED. Solar cell efficiency tables (version 43). *Progress in Photovoltaics: Research and Applications* 2014; 22: 1–9.
- [2]. Chirilă A, Reinhard P, Pianezzi F, Bloesch P, Uhl AR, Fella C, Kranz L, Keller D, Gretener C, Hagendorfer H, Jaeger D, Erni R, Nishiwaki S, Buecheler S, Tiwari AN. Potassium-induced surface modification of Cu(In,Ga)Se₂ thin films for high-efficiency solar cells. *Nature Materials* 2013; 12: 1107–1111.
- [3]. Wätjen JT, Scragg JJ, Ericson T, Edoff M, Platzer-Björkman C. Secondary compound formation revealed by transmission electron microscopy at the Cu₂ZnSnS₄/Mo interface. *Thin Solid Films* 2013; 535: 31–34.
- [4]. Bart Vermang, Employing Si solar cell technology to increase efficiency of ultra-thin Cu (In, Ga)Se₂ solar cells, *Progress In Photovoltaics: Research And Applications Prog. Photovolt: Res. Appl.* 2014; 22:1023–1029, published online 2 July 2014 in Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/pip.2527.
- [5]. Bart Vermang n, Viktor Fjällström, Jonas Pettersson, Pedro Salomé, Marika Edoff “Development of rear surface passivated Cu(In,Ga)Se₂ thin film solar cells with nano-

- sized local rear point contacts” <http://dx.doi.org/10.1016/j.solmat.2013.07.025> , Available online 15 August 2013
- [6]. P.K.Nayak, J.Bisquert, D.Cahen, Assessing possibilities and limits for solar cells, *Advanced Materials* 23(2011) 2870–2876.
- [7]. Shi Luo a, *, Carissa Eisler b, Tsun-Hsin Wong” Suppression of surface recombination in CuInSe₂ (CIS) thin films via Trioctylphosphine Sulfide (TOP:S) surface passivation” <http://dx.doi.org/10.1016/j.actamat.2016.01.021> , Available online 21 January 2016.
- [8]. Johan Lindahl, Uwe Zimmermann, Piotr Szaniawski, Tobias Törndahl, Adam Hultqvist, Pedro Salomé, Charlotte Platzer-Björkman, and Marika Edoff “Inline Cu(In,Ga)Se₂ Co-evaporation for High-Efficiency Solar Cells and Modules” *IEEE Journal Of Photovoltaics*, Vol. 3, NO. 3, July 2013, Digital Object Identifier 10.1109/JPHOTOV.2013.2256232.
- [9]. A.Niemegeers, M.Burgelman, R.Herberholz, U.Rau, D.Hariskos and H.W.Schock, *Progress in Photovoltaics: Research and Applications*, 6 (1998) 407-421
- [10]. T.Kojima, T.Koyanagi, K.Nakamura, T.Yanagisawa, K.Takahisa, M.Nishitani and T.Wada, *Solar Energy Materials and Solar Cells*, 50 (1998) 87-95
- [11]. W.W.Lam, L.S.Yip, J.E.Greenspan, I.Shih, *Solar Energy Materials and Solar Cells*, 50 (1998) 57-62