



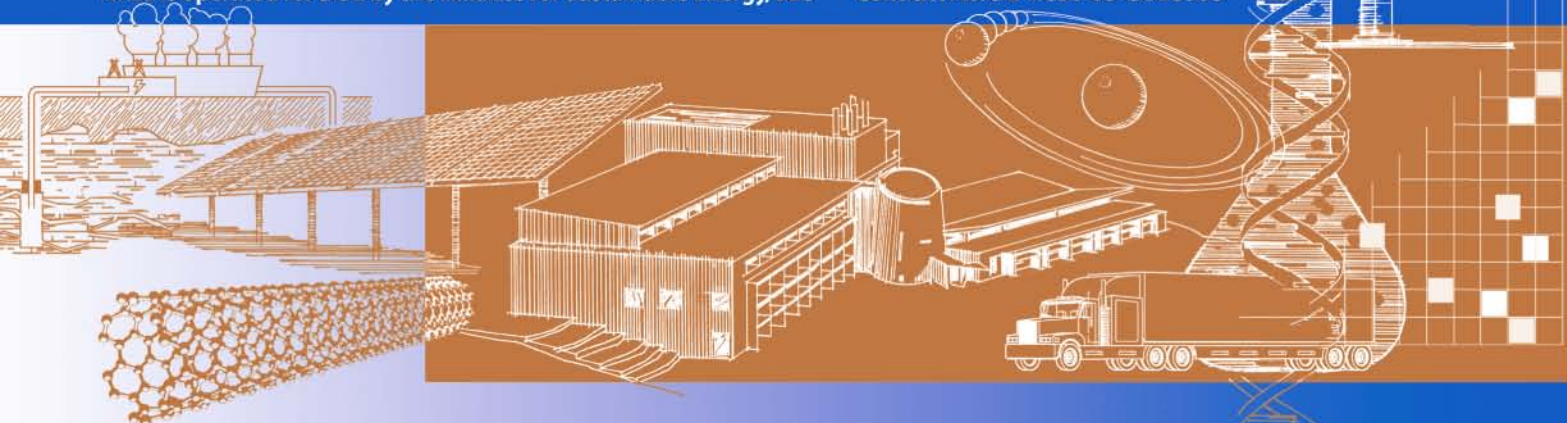
High Throughput, Low Toxic Processing of Very Thin, High Efficiency CIGSS Solar Cells

Final Report
December 2008

N.G. Dhere
*Florida Solar Energy Center
Cocoa, Florida*

Subcontract Report
NREL/SR-520-45544
April 2009

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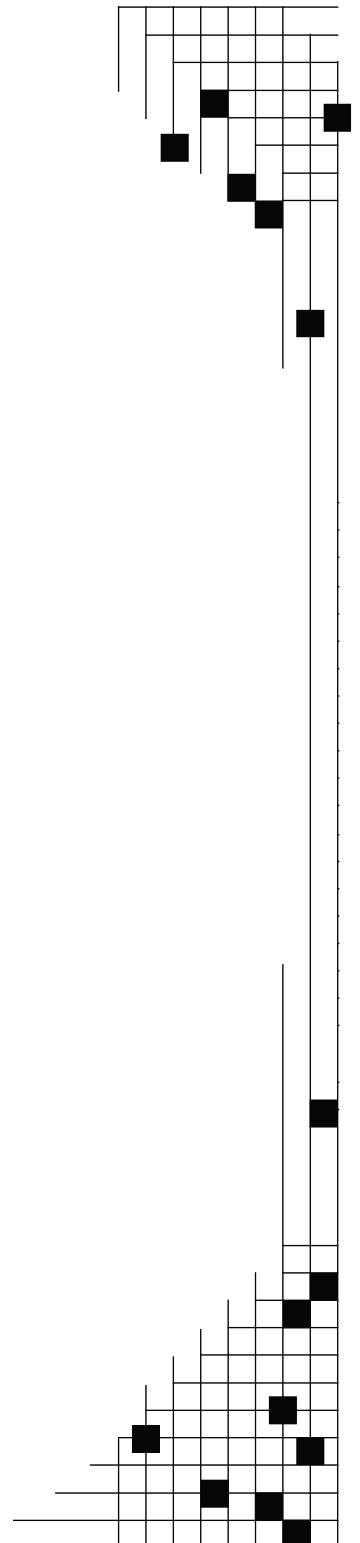
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NREL Technical Monitor: Bolko von Roedern
Prepared under Subcontract No. XXL-5-444205-08

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1. INTRODUCTION

This is the Final Report for the project “High Throughput, Low Toxic Processing of Very Thin, High Efficiency CIGSS Solar Cells” NREL contract no. XXL-5-44205-08, UCF/FSEC Account no. 2012 8098.

During this project $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2-y}\text{S}_y$ (CIGSeS)/CdS thin-film solar cells were prepared on molybdenum coated sodalime glass (SLG) substrates. Low toxicity selenium precursors, diethylselenium (DESe) or other organometallic precursors were used for selenization of metallic precursors. Rapid Thermal Processing (RTP) technique was developed as an alternative to conventional selenization and sulfurization to reduce the process time and thermal budget thus enhancing throughput. $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ (CIGS2) thin-film solar cells were also developed. Easily scaleable magnetron sputtering technique was used for deposition of back contact, metallic precursors and transparent and conducting oxides. A compact and large-grain, 0.9-2.75 μm thick absorber layers were prepared by selenization/sulfurization of elemental precursors at 475-515°C in diluted DESe or other organometallic precursors and diluted H_2S . Experiments were performed to reduce absorber thickness so as to minimize the indium consumption using both conventional as well as the RTP approach. Experiments were carried out on thinner i.e. 1.2 μm -1.5 μm CIGS2 absorbers. Effect of sodium addition on copper poor CIGS2 absorbers and thin-film solar cells was studied. Alternate heterojunction partner layers were developed for CIGS2 thin-film solar cells.

2. SELENIZATION/SULFURIZATION IN THE CONVENTIONAL FURNACE

Mo-back contact was deposited by DC magnetron sputtering over 15 cm x 10 cm sodalime glass substrates. Presence of small amount of sodium during CIGSeS formation has proven to be beneficial. Sodium containing precursor, NaF was deposited over the back contact prior to the precursor deposition. Experiments were carried out with various NaF thicknesses. The Cu-In-Ga precursors were deposited by DC magnetron sputtering. The thickness of layers was adjusted by varying the linear speed of substrate movement over the target. Selenization and sulfurization were carried out by heating the metallic precursors in diluted DESe or other organometallic precursors and diluted H₂S respectively. Materials characterization was carried out by scanning electron microscopy (SEM), x-ray diffraction (XRD), electron probe microanalysis (EPMA), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS) and transmission electron microscopy (TEM).Electrical/photovoltaic/device characterization was carried out by current-voltage (I-V), external quantum efficiency (EQE), capacitance-voltage (C-V), and light beam induced current (LBIC). Both of these characterizations were mentioned in earlier reports. Cells were completed by deposition of CdS heterojunction partner layer by chemical bath deposition, i:ZnO/ZnO:Al window bilayer by RF magnetron sputtering and Cr/Ag contact fingers by thermal evaporation.

Initially, the thickness of absorber layers was maintained in the range of 2.5 - 2.7 μm . Experiments were carried out to optimize the process parameters of DC magnetron sputtering of metallic precursors and temperature, time, and reactant quantities of selenization/sulfurization for absorber preparation. Addition of minute quantities of sodium was found to improve the morphology of the absorber films [1]. Moreover, the grains were well faceted and compactly packed (Fig. 1).

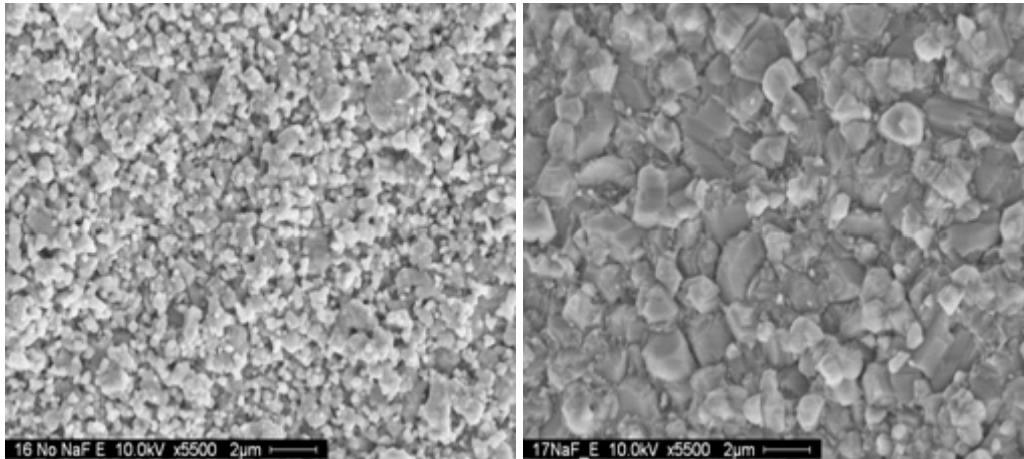


Figure 1: SEM micrographs (a) No NaF (b) 120 Å NaF.

Initially $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) absorbers were prepared by selenization of the precursors. Thin film solar cells prepared by using CIGS layers having $\text{Cu}/(\text{In}+\text{Ga})$ ratio of 0.83 had an efficiency of 12.33%. At this stage, the $\text{Cu}/(\text{In}+\text{Ga})$ ratio was further optimized to 0.86. Side-by-side, selenization/sulfurization process was optimized to prepare CIGSeS layers in the conventional furnace. An efficiency of 13.73%, as measured at NREL under AM1.5 irradiance, was achieved with cells prepared using these CIGSeS layers (Fig 2). At the time, this was the highest officially measured efficiency for a small-area CIGSeS thin film solar cell prepared by a two-stage technique.

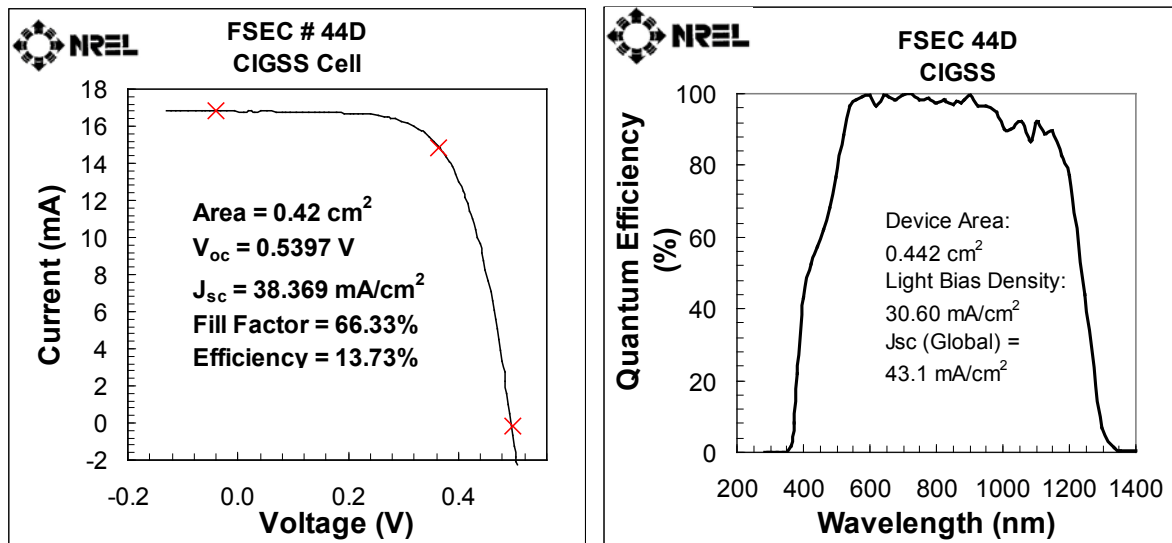


Figure 2: a) Current –voltage characteristics (I-V), b) Quantum efficiency (QE) characteristics of the cell having 8 nm layer of NaF and selenized/sulfurized

3. RAPID THERMAL PROCESSING

CIGSeS thin-films were also prepared by rapid thermal processing (RTP). Glass substrates were coated with Mo back contact and Cu-In-Ga precursor layers by DC magnetron sputtering. Selenium and NaF were deposited by thermal evaporation. RTP was carried out in a mixture of H₂S and nitrogen at a temperature of 550°C to prepare CIGSeS absorber films. CIGSeS thin film solar cells were completed similar to cells for CIGSeS absorber films prepared by selenization/sulfurization in a conventional furnace described earlier. Small-area cells with an efficiency of 12.78% were prepared by a two stage process using RTP for selenization/sulfurization (Fig 3). This is the highest, officially measured efficiency till date achieved by any University or National Lab, for small-area CIGSeS thin film solar prepared by two-stage technique using RTP.

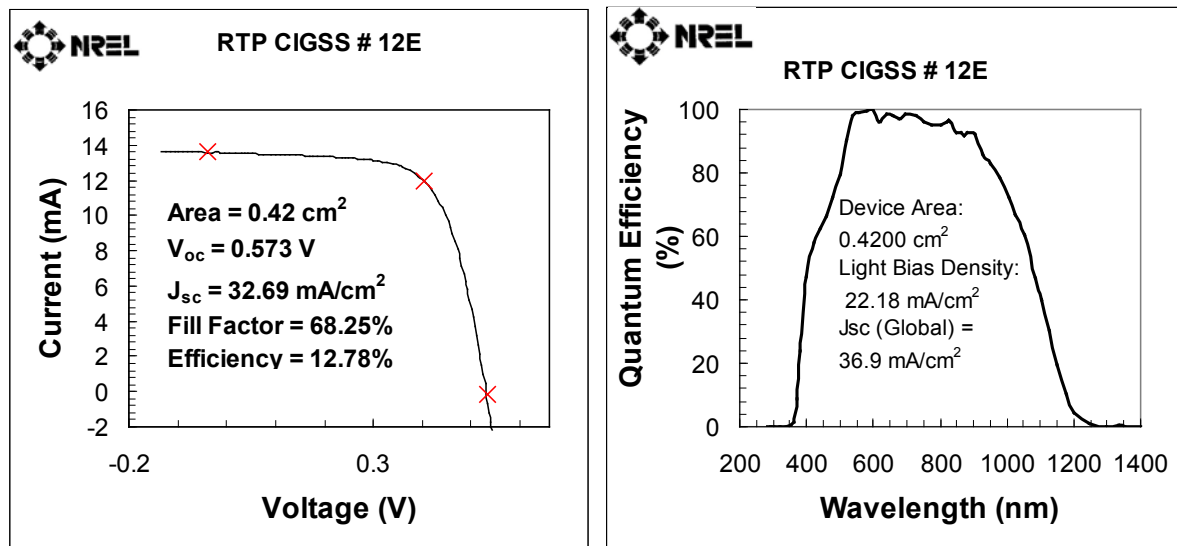


Figure 3: a) Current-Voltage (I-V) and b) Quantum efficiency (QE) Characteristics of cell 12E

4. CIGS2 THIN FILM SOLAR CELLS

CIGS2 thin-films were prepared on Mo-coated sodalime glass substrates. Cu-In-Ga precursor layers were deposited on Mo back contact layers by DC magnetron sputtering. Sulfurization of these precursor layers was carried out in a mixture of H₂S and nitrogen. Cells were completed by etching of the CIGs2 film in 10% KCN solution, deposition of CdS heterojunction partner layer by chemical bath deposition, i:ZnO/ZnO:Al window bilayer deposition by RF magnetron sputtering and Cr/Ag contact fingers by thermal evaporation. World record V_{oc} of 830 mV was obtained on CuIn_{1-x}Ga_xS₂ (Fig 4). The efficiency (11.99 %) is the highest ever demonstrated using sputtering technique.

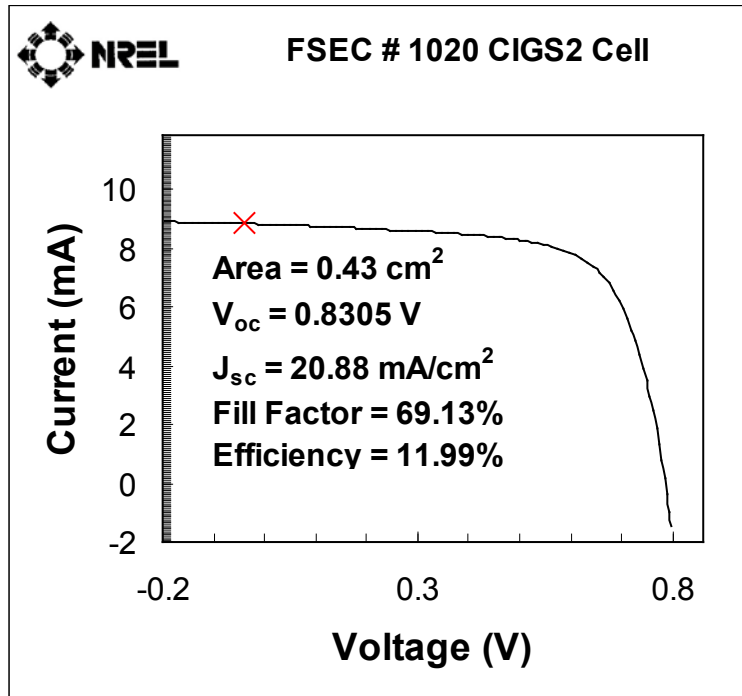


Figure 4: Current-voltage (I-V) characteristics of CIGS2 solar cell

The CIGS2 thin-film solar cells development work was continued for thinner absorber layers. Figure 5 shows the current-voltage (I-V) characteristics measured at the National Renewable Energy Center (NREL) under AM1.5 conditions of CIGS2 solar cell prepared using a 1.5 μm thick CIGS2 absorber layer. Photovoltaic characteristics of the CIGS2 thin film solar cells were as follows: short circuit current density, J_{sc}, of 19.46 mA/cm², open circuit voltage,

V_{oc} , of 765.9 mV, fill factor, FF, of 67.85% and photovoltaic conversion efficiency, η , of 10.12%. Figure 6 shows quantum efficiency (QE) characteristics. Figure 7 and Figure 8 exhibit current-voltage (I-V) and quantum efficiency (QE) characteristics for a 1.2 μm absorber respectively. Photovoltaic characteristics of the CIGS2 thin film solar cells were as follows: short circuit current density, J_{sc} , of 18.94 mA/cm^2 , open circuit voltage, V_{oc} , of 775.9 mV, fill factor, FF, of 65.40% and photovoltaic conversion efficiency, η , of 9.62%.

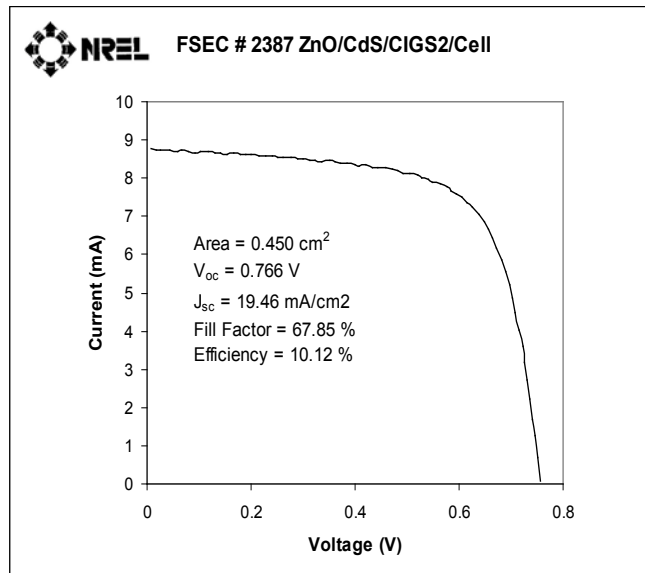


Figure 5: Current-voltage (I-V) characteristics for a 1.5 μm CIGS2 absorber

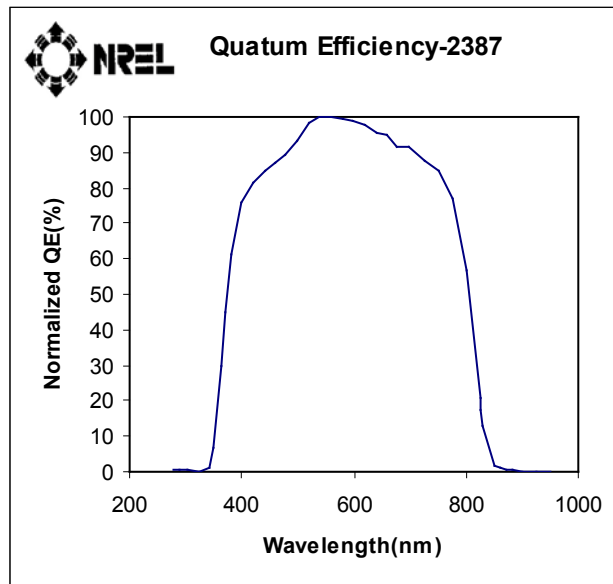


Figure 6: Quantum efficiency (QE) characteristics for a 1.5 μm CIGS2 absorber

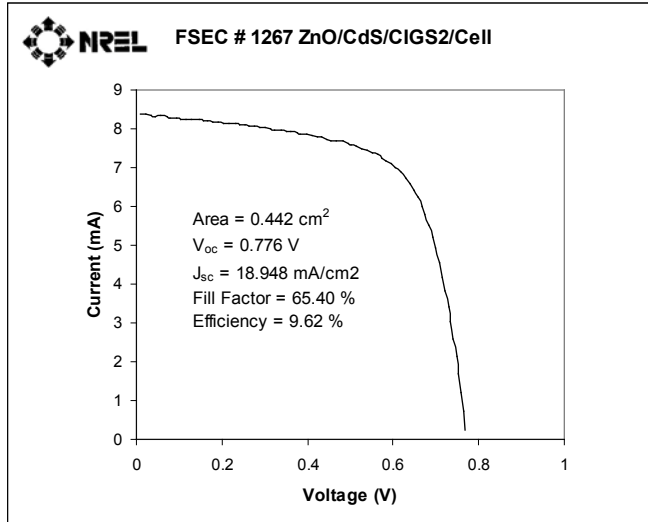


Figure 7: Current-voltage (I-V) characteristics for a 1.2 μm CIGS2 absorber

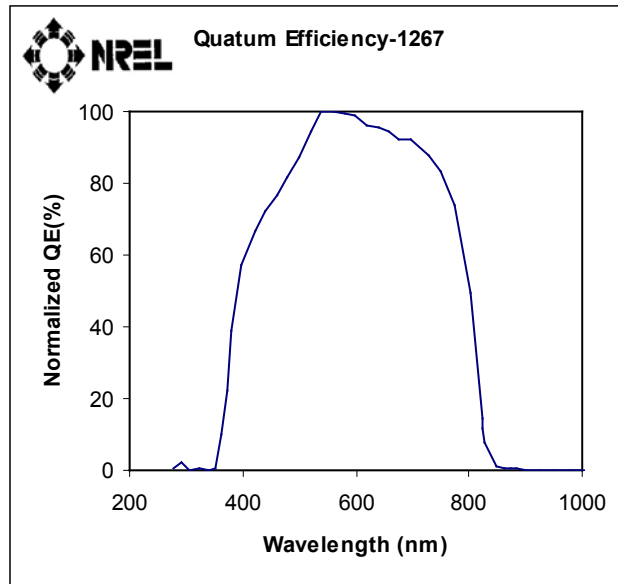


Figure 8: Quantum efficiency (QE) characteristics for a 1.2 μm CIGS2 absorber

5. $Zn_xCd_{1-x}S$ AS ALTERNATIVE BUFFER LAYER FOR CIGS2 SOLAR CELLS

The aim of this work is to develop an alternative heterojunction partner for CIGS2 solar cells. $Zn_xCd_{1-x}S$ has been shown to be a strong contender as an alternative heterojunction partner [2-7]. Effect of various chemical bath deposition parameters on device performance was studied and attempts were made to optimize the deposition parameters in order to improve the device performance. Device properties were studied using current–voltage characteristics. The device performance of CIGS2/ $Zn_xCd_{1-x}S$ solar cells was comparable to CIGS2/CdS solar cells. This indicates that with further optimization of the deposition parameters of the heterojunction partner and improvement in the absorber layer might lead to better device performance of CIGS2/ $Zn_xCd_{1-x}S$ solar cells as compared to CIGS2/CdS solar cells. Moreover, it should be noted that here the optimization of the deposition parameters were carried out on a $\sim 2 \mu\text{m}$ thick CIGS2 absorber layer.

The current-voltage(I-V) characteristics (Figure 9) shows the highest efficiency cell fabricated with CdS and $Zn_xCd_{1-x}S$ as heterojunction partners for $2 \mu\text{m}$ CIGS2 absorber. CIGS2/ $Zn_xCd_{1-x}S$ cell had an efficiency of 5.45%, whereas CIGS2/CdS cell had efficiency of 6.21%. The CIGS2/CdS cell has series resistance value of 18.1Ω , and shunt resistance value of 2500Ω . The CIGS2/ $Zn_xCd_{1-x}S$ cell has series resistance value of 25.9Ω , and shunt resistance value of 1100Ω . CIGS2/ $Zn_xCd_{1-x}S$ has higher V_{OC} of 0.73 volts as compared to 0.71 V of CIGS2/CdS cell. Short circuit current density for CIGS2/ $Zn_xCd_{1-x}S$ cell was 12.57 mA/cm^2 . This value is lower than that of the CIGS2/CdS cell of 12.8 mA/cm^2 . It is expected that CIGS2 solar cell with $Zn_xCd_{1-x}S$ as the heterojunction partner should provide higher current density due to lower blue photon losses as compared to one with CdS as the heterojunction partner. However, an increase in the current density is not observed probably due to the highly resistive ZnS film as compared to CdS. Due to the higher resistance the fill factor of CIGS2/ $Zn_xCd_{1-x}S$ cell is 29.45%, lower than the fill factor value of 68.35% for CIGS2/CdS cell.

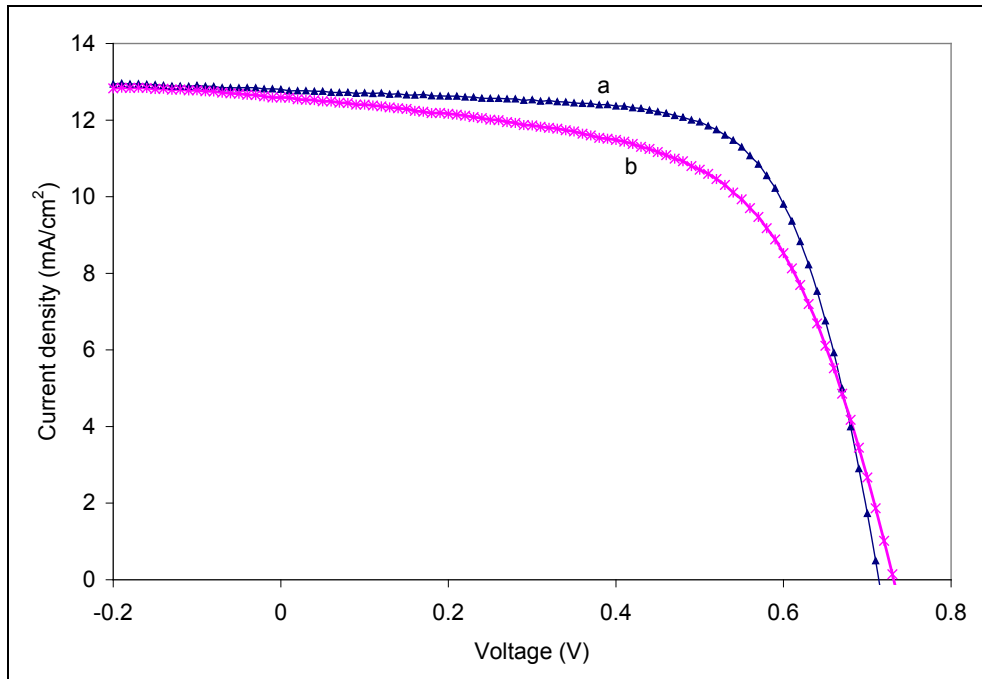


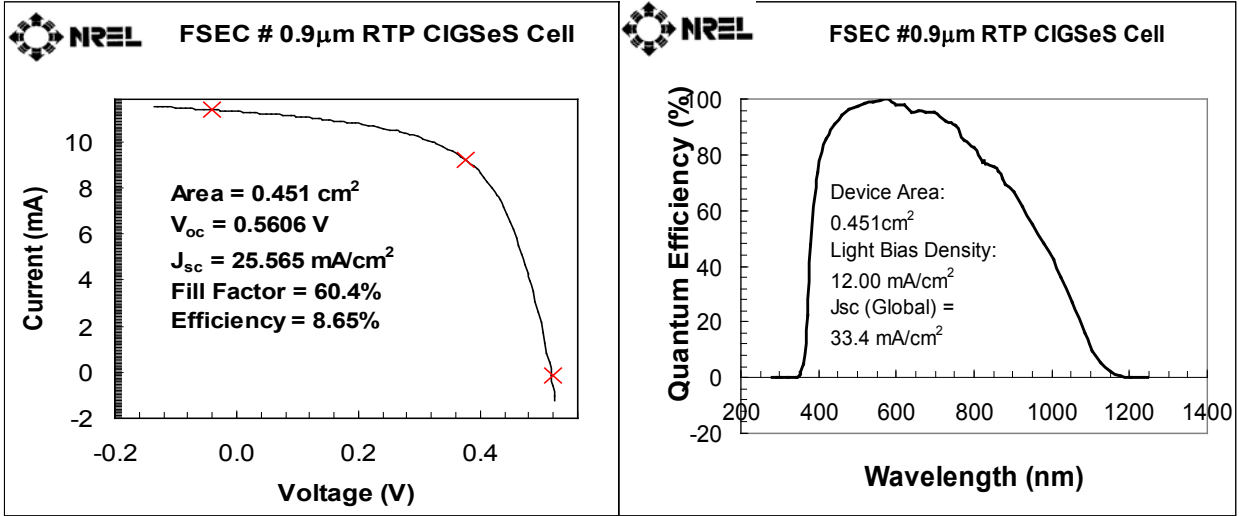
Figure 9: The J-V characteristics for (a) SLG/Mo/CIGS2/CdS/i-ZnO/ZnO:Al and (b) SLG/Mo/CIGS2/ $Zn_xCd_{1-x}S$ / i-ZnO/ZnO:Al devices

6. ULTRA THIN CIGS/CIGSS ABSORBER LAYER

Experiments were carried out for reducing the thickness of the absorber layer from the present $\sim 2.5 \mu\text{m}$ to $\sim 9000 \text{ \AA}$. The metallic precursors Cu-In-Ga were deposited using DC magnetron sputtering technique. The thickness of the metallic precursors was reduced proportionately. Selenization and sequential selenization/sulfurization of these metallic precursors were carried out using the conventional and rapid thermal processing approaches respectively. Cells were completed by deposition of CdS heterojunction partner layer by chemical bath deposition, i:ZnO/ZnO:Al window bilayer by RF magnetron sputtering and Cr/Ag contact fingers by thermal evaporation.

The cells prepared by rapid thermal processing were sent to NREL for current-voltage (I-V) and quantum efficiency (QE) measurements which are shown in Figure 10. An efficiency of 8.65% was achieved on CIGSeS thin-film solar cells using $0.9 \mu\text{m}$ thick CIGSeS absorber layer. The open circuit voltage was measured to be 560 mV which suggests that there was sulfur incorporation into the bulk of the material also the bandgap calculated from the quantum efficiency curve is about 1.13 eV which again suggests the bandgap shift due to sulfur incorporation. The short circuit current density measured using the current-voltage characteristics is 25.57 mA/cm^2 . This lower value of short circuit current density could be due to the diffusion of sulfur into the bulk of the absorber rather than just the surface. This could also be because of poor absorber quality as can be seen from the quantum efficiency curve. The red response shows that the recombination losses are very high which results in the low current density. This suggests poor absorber film material.

The sulfur diffusion can be controlled by further optimization of the sulfur and sodium content which could lead to better currents.



7. HUMAN RESOURCE DEVELOPMENT

During this project, Anant H. Jahagirdar and Ankur A. Kadam have completed their Ph.D. Anil U.Pai, Vinay V. Hadagali, Upendra S. Avachat, Jyoti S. Shirolkar, and Bhaskar Kumar have completed their master's degrees. Two students, Sachin S. Kulkarni and Parag S. Vasekar are completing their Ph.D. dissertation this semester. Vinay V. Hadagali will also be completing his Ph.D. dissertation. Shirish Pethe has already completed his candidacy exam. Ashwani Kaul will be completing his candidacy exam during the spring 2009 semester. A new student, Eigo Takahashi has joined for M.S. (Materials Science and Engineering).

8. SUMMARY AND CONCLUSION

The work carried out during this project presents the use of DESe or other organometallic precursors as a low toxicity alternative selenium sources for preparation of a high quality absorber. The addition of small quantity of sodium in the form of NaF layer was beneficial in improving the morphology of the film which showed large, well faceted and compactly packed CIGSeS grains. A small area cell with an efficiency of 13.73 % was prepared by sputtering and selenization/sulfurization in a conventional furnace. At the time, this was the highest officially measured efficiency for a small-area CIGSeS thin film solar cell prepared by a two-stage technique. 12.78 % efficiency with 2.0 μm absorber thickness has been achieved on CIGSeS films prepared by RTP. This is the highest, officially measured efficiency till date achieved by any University or National Lab, for small-area CIGSeS thin film solar prepared by two-stage technique using RTP. An efficiency of 8.65% with 0.9 μm absorber thickness has been prepared by RTP. 11.99% efficiency CIGS2 solar cells have been prepared with a world record V_{oc} value of 830.5 mV. An efficiency of 10.2% was obtained on CIGS2 solar cell having 1.5 μm thick absorber and 9.62% on CIGS2 solar cell having a 1.2 μm thick absorber. $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ has been demonstrated as an alternate heterojunction partner layer for CIGS2 cell.

Two approaches for reducing the cost of photovoltaics have been demonstrated. First, indium quantity can be reduced by preparing ultra-thin CIGSeS layer while maintaining device quality and second, high throughput can be obtained by RTP.

Recently, the Florida Solar Energy Center has received substantial funding for development of renewable energy technologies. Part of this funding will be used to upgrade the equipment and facilities at the FSEC Photovoltaic Materials Laboratory. It may be noted that most of the equipment and facilities at the FSEC Photovoltaic Materials Laboratory were built several years ago, and hence the frequency of outage has increased recently. Now using the newly available funds the maintenance and, if necessary, replacement of the equipments and facilities will be carried so as to put the PV Materials lab back in good shape for carrying out future research and development.

9. REFERENCES

- [1] N.G. Dhere, and R.G. Dhere, JVST A, Vol.23, No.4, 1208-1214 (2005)
- [2] T.L. Chu, S.S. Chu, J. Britt, C. Ferekides, C.Q. Wu, J. Appl. Phys. 70,2688, (1991)
- [3] Von Hortmann and H treptow, Z. Naturforshg., 16a, 910 (1961)
- [4] D.W.G. Ballentyne and B. Ray, Physica, **27**, 337(1961)
- [5] V. D. Vankar, S.R. Das, P.Nath and K.L. Chopra, Phys. Status.Solidi, **45**, 665 (1978)
- [6] C.M.Mbow, D.LaPlaze and A. Cachard, Thin Solid Films, **88**, 203(1982)
- [7] Y.F. Nicolau, M. Dupuy and M. Brunel, J. Electrochem. Soc. Vol. 137, No. 9 (1990), 2915.

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