Contract Report

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

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TABLE OF CONTENTS

1. INTRODUCTION 3

2. Si_xN_y/Mo DEPOSITION 4

3. CIGS2 THIN FILM SOLAR CELLS 8

4. SUMMARY 20

5. ACKNOWLEDGEMENTS 21

6. REFERENCES 22

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Year 3, Quarter 3 Report, FSEC-CR-1748-08, March 07, 2008.

1. INTRODUCTION

High Throughput, Low Toxic Processing of Very Thin, High Efficiency CIGSS Solar Cells has been undertaken through the project funded by NREL. This is the Year 3, Quarter 3 Report, **FSEC-CR-1748-08** for the period of November 2007-February 2008.

2. Si_xN_y/Mo DEPOSITION

Sodalime glass substrates were cut to the size 1" x 4" and thoroughly washed with ultrasonic cleaning using cold soap solution, warm soap solution, isopropanol, and distilled, deionized water and dried. The clean glass substrates were then mounted in sputtering chambers for sputter deposition of Si_xN_y and molybdenum. Partial pressures of sputtering gases during the Si_xN_y deposition were as follows: nitrogen 8 x 10^{-4} Torr and argon 8 x 10^{-4} Torr, the total pressure being 1.6 x 10^{-3} Torr. During earlier Si_xN_y depositions, the sputtering power used was 225 Watt. Since relatively lower sputtering power was used it was essential to carry out the sputter deposition over long time. The deposition was carried out using RF power of 425 Watt instead of RF power of 225 Watt used for earlier experiments so as to reduce the Si_xN_y deposition time. Moreover, the substrate movement duration of 300 seconds per inch was used, instead of 600 seconds per inch used in earlier experiments. Si_xN_y films were transparent. Thickness and sheet resistance of Si_xN_y films were measured using surface profilometer and multimeter respectively. These measurements showed that the thickness was approximately 1000 Å and the Si_xN_y films were insulating.

Molybdenum was sputter-deposited on Si_xN_y layers. Mo being a refractory material develops stresses. It is essential to deposit stress-free and relatively inert Mo films in order to achieve well adherent and highly efficient CIGSeS absorber thin film solar cells [1]. There is a correlation between the residual stress developed in the molybdenum films deposited using dc magnetron sputtering and the sputtering gas (argon) pressure and power. Molybdenum films deposited at sputtering power of 300 W and argon pressure of 3 x10^{-4} Torr develop compressive stress; while the films deposited at sputtering power of 200 W and argon pressure of 5x10^{-3} Torr pressure develop tensile stress. It has been suggested that such stress reversals are dependent on energetic bombardment by reflected neutrals and/or sputtered atoms. The working gas pressure is expected to moderate the flux and energy of these particles. At relatively low pressures and high power, the arriving atoms have high kinetic energy and the resulting film has dense microstructure and develops compressive stress. This compressive stress is explained by atomic peening caused by the impact of energetic particles. At relatively high pressures and low power, less energy is provided to the film because of scattering and the resulting film exhibits an open porous microstructure and develops tensile stress. Attempts were made to reduce the overall stress. A composite molybdenum film was sputter-deposited consisting of a total 5 Mo layers in which two Mo layers with tensile stress were sandwiched between three Mo layers having compressive stress. Three (initial, middle and final) Mo layers with compressive stress were sputtered using high sputtering power and low sputtering gas pressure. The remaining two Mo layers having tensile stress were sputtered using low sputtering power and high sputtering gas pressure. The intended sputtering parameters for high power/low pressure cycle were 300 Watt while the argon sputtering pressure was 3 x 10^{-4} Torr. Since the current corresponding to this pressure was tended to exceed 1 Ampere i.e. the maximum allowable current of the power supply, the sputtering pressure was reduced to obtain the current in the range of ~0.85 to 0.9 Ampere; the exact pressure could not be measured as it was lower than the range of Convectron gauge. A baratron gauge is being mounted on to the sputtering chamber so as to measure the pressure in future experiments. The substrate movement duration of 32 seconds per inch was used for each cycle. And the sputtering parameters for low power/high pressure cycle were 200 Watt and 5 x 10^{-3} Torr and the substrate movement duration of 37.5 seconds per inch was used

for each cycle. The average sheet resistance measured at various locations of the sputtered molybdenum films was ~ 0.6 Ω/□.

Figures 1 to 4 show the sequence in which molybdenum films were deposited. The total molybdenum thickness deposited is kept constant at 0.7 μm.

Mo Compressive ~ 1500 Å
Mo Tensile ~ 1250 Å
Mo Compressive ~ 1500 Å
Mo Tensile ~ 1250 Å
Mo Compressive ~ 1500 Å
Si_xN_y ~ 1000 Å
Glass

Figure 1: 5 layers Mo, top layer compressive, Si_xN_y, 80 Å NaF

Mo Tensile ~ 1250 Å
Mo Compressive ~ 2250 Å
Mo Tensile ~ 1250 Å
Mo Compressive ~ 2250 Å
Si_xN_y ~ 1000 Å
Glass

Figure 2: 4 layers Mo, top layer tensile, Si_xN_y, 80 Å NaF

Mo Compressive ~ 1500 Å
Mo Tensile ~ 1250 Å
Mo Compressive ~ 1500 Å
Mo Tensile ~ 1250 Å
Mo Compressive ~ 1500 Å
Glass

Figure 3: 5 layers Mo, top layer compressive, and no NaF

Mo Tensile ~ 1250 Å
Mo Compressive ~ 2250 Å
Mo Tensile ~ 1250 Å
Mo Compressive ~ 2250 Å
Glass

Figure 4: 4 layers Mo, top layer tensile, and no NaF

In addition to the above sets, single layer molybdenum films were also deposited on sodalime glass substrates with no Si_xN_y. These single layer molybdenum films had a thickness of 0.7 µm. The single layer molybdenum films were deposited in tensile, compressive and intermediate modes. The details are described in the following.

In each case, the substrate movement duration was adjusted to obtain the desired thickness of 0.7 µm. Compressive mode sputtering parameters were, sputtering power of 300 Watt; and the sputtering pressure was reduced from the value of 3×10^{-4} Torr to obtain current in the range of ~0.85 to 0.9 Ampere. The substrate movement duration of 300 seconds per inch was used for each cycle. Tensile mode sputtering parameters were sputtering power of 200 Watt; and the sputtering pressure was 5×10^{-3} Torr. The substrate movement duration of 420 seconds per inch was used for each cycle. Intermediate mode sputtering parameters were sputtering power of 250 Watt; and the sputtering pressure was 2.6×10^{-3} Torr. The substrate movement duration of 360 seconds per inch was used for each cycle.

A comparison of complete of CIGSeS thin film solar cells prepared on commercially available molybdenum coated glass substrates as well as on the in-house sputtered molybdenum films with and without the Si_xN_y diffusion barrier layer is planned. This will allow comparison of CIGSeS cells completed under identical conditions.

CuGa and In layers were deposited on the substrates mentioned in figures 1-4. However, after selenization and sulfurization of the precursors using RTP the films peeled off. Hence the cells could not be completed. Figure 5 shows one of the CIGSeS films that peeled off during RTP.

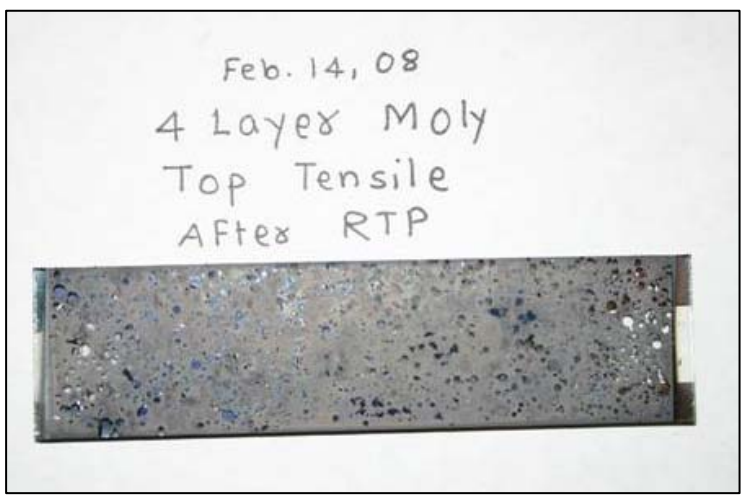


Figure 5: CIGSeS film on 4 layers Mo, top layer tensile, and no NaF after RTP

All the films were deposited with starting layer of molybdenum in compressive stress mode that are known to be less adherent to glass substrate as compared to films grown in tensile mode [2]. This could be the reason for peeling off the absorber films. Therefore, experiments are being continued with starting layer of molybdenum in tensile stress mode.

Figure 6 shows the sequence of molybdenum layer deposition for this experiment.

Mo Tensile ~ 2000 Å
Mo Compressive ~ 7000 Å
Mo Tensile ~ 2000 Å
Si_xN_y ~ 1000 Å
Glass

Figure 6: 3 layers Mo, top layer tensile, Si_xN_y, 80 Å NaF

The sputtering parameters for this experiment were similar to the earlier experiments except that the sputtering pressure during the tensile mode is 7 x 10^{-3} Torr instead of 5 x 10^{-3} Torr used during earlier experiments.

3. **CIGS2 THIN FILM SOLAR CELLS**

Chalcopyrites are important contenders among thin film solar cells due to direct band gap and higher absorption coefficient. Copper-Indium-Gallium Sulfide (CIGS2) is a chalcopyrite material with a near-optimum band gap of 1.5 eV. At FSEC PV Materials Laboratory, record efficiency of 11.99 % has been achieved on a 2.7 µm CIGS2 film prepared by sulfurization [1]. Copper indium sulfide modules are being manufactured by Sulfurcell in Germany. The availability and cost of Indium can be a limiting factor for large scale production of CIGS2 thin film solar cells (70 GW_p per year) [2]. The required amounts of metals can be lowered by using a thinner absorber. Efforts are being made to reduce the thickness while maintaining a comparable performance. Initially small size grains are formed during the film growth [3]. With continuing growth to large thicknesses, more favorably oriented grains grow faster and coalesce to form compactly packed large-grain morphology. It is clear that when the thickness of the film decreases, there is possibility of the growing film remaining only in the small grain region because the coalescence of grains does not have an opportunity to enhance the grain size to the maximum. Solar cell performance in smaller grain chalcopyrite absorber could deteriorate due to larger fraction of grain boundaries [4]. In a series of experiments, CIGS2 solar cell parameters were optimized for an absorber thickness of 1.2 – 1.5 µm.

CIGS2 thin films were prepared in two stages. Stage one consists of the deposition of CuGa-In metallic precursors with Cu/(In+Ga) ratio of 1.4 on molybdenum coated glass substrates. Stage two consists of the sulfurization of these metallic precursors in dilute H_2S (4-8% H_2S) ambient. The copper rich layer ($Cu_{2-x}S$) that segregated on the surface of near stoichiometric, copper-poor CIGS2 thin film was etched away in a 10% KCN solution. Scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and transmission electron microscopy (TEM) were performed at the materials characterization facility at UCF. X-ray diffraction (XRD), current-voltage, I-V and quantum efficiency, QE measurements were performed at NREL.

Scanning Electron Microscopy

SEM micrographs of CIGS2 samples are as shown in Figures 7 and 8. The grain size as measured by the line intercept method was 1.36 µm. Figure 7 shows well-faceted, compact grains for the 1.5 µm absorber sample. As shown in the Figure 8, for the 1.2 µm absorber sample the grain size decreases to 0.90 µm.

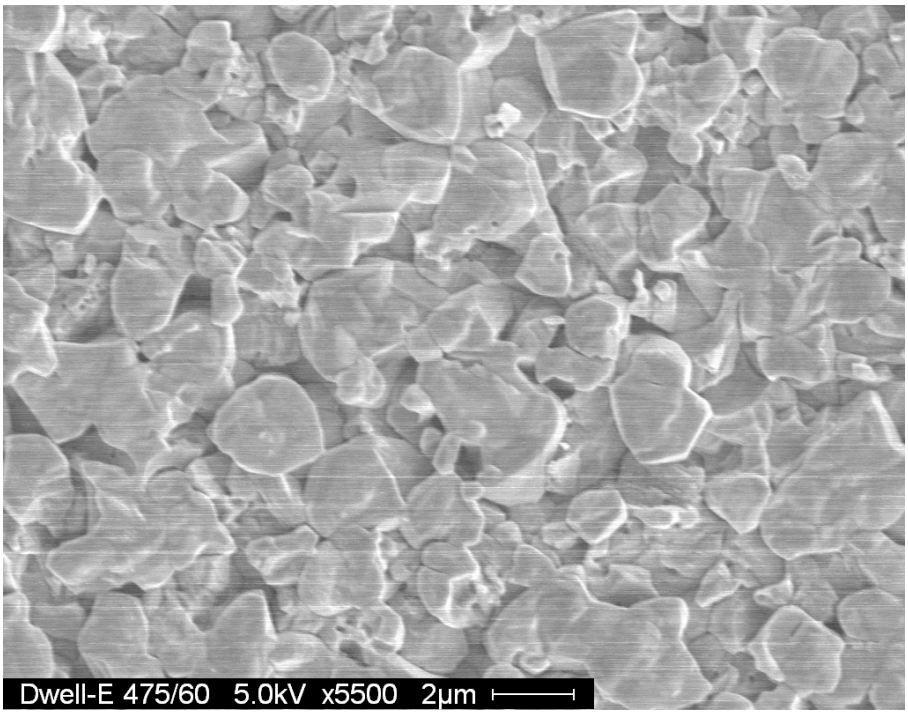


Figure 7: SEM for a 1.5 µm absorber

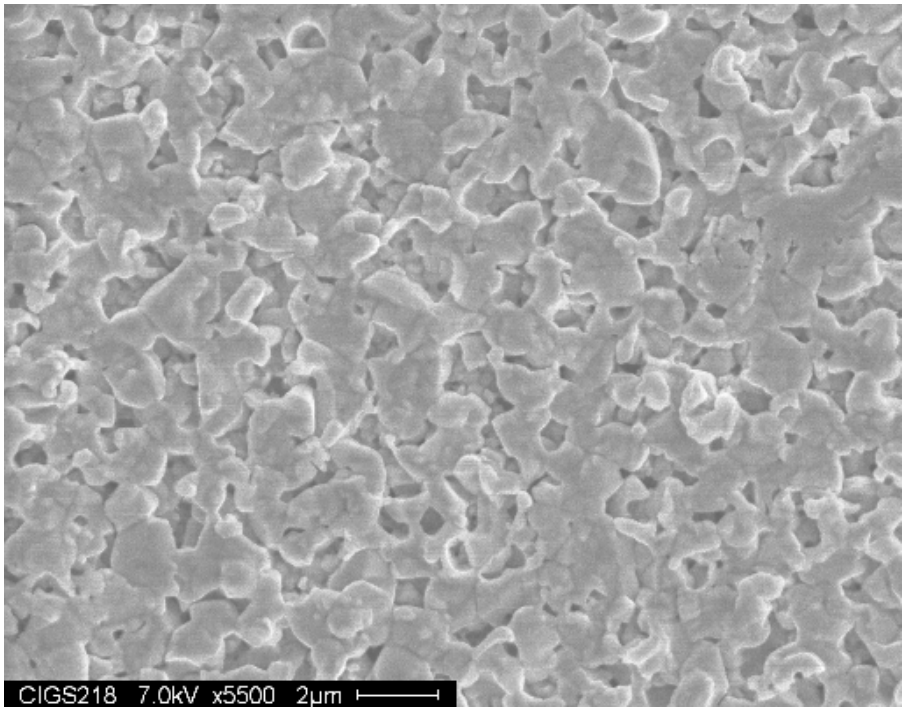


Figure 8: SEM for a 1.2 µm absorber

X-Ray Diffraction

XRD pattern of etched CIGS2 thin film shows (101), (112), (103), (200), (220), (312) and (316) reflections of highly crystalline chalcopyrite CIGS2 and also reflections from molybdenum (Figure 9). The strongest reflection was from (112) plane at 2θ = 28.04°. The calculated lattice parameters were a = 5.49 Å and c = 11.12 Å. Molybdenum reflection was observed at 2θ = 40.66°. XRD peaks exhibit reduction in peak intensity with reduction in absorber thickness while as expected Mo peak becomes stronger for a 1.2 µm absorber.

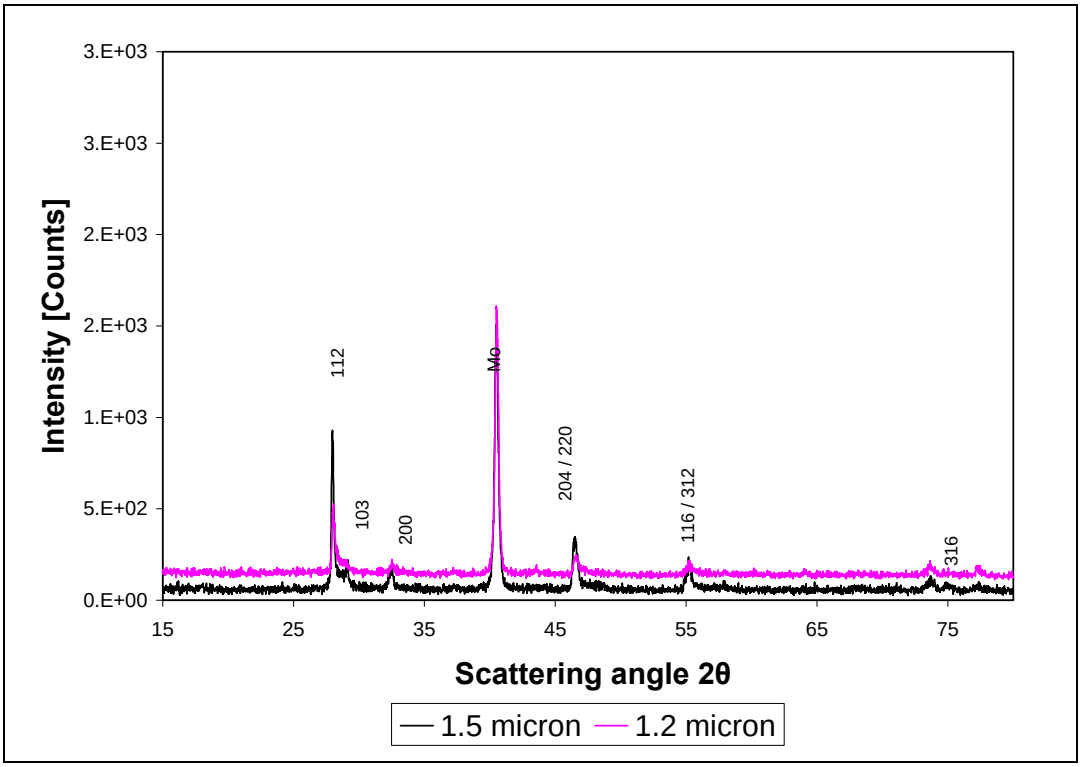


Figure 9: XRD for a 1.5 µm and 1.2 µm CIGS2 absorber layer

Auger Electron Spectroscopy (AES)

Figure 10 shows AES depth profile for a CIGS2 sample with 1.2 µm absorber thickness. Copper and sulfur signals are constant in the CIGS2 thickness. As has been observed earlier, gallium is increasing towards back contact while indium is decreasing. This happens as the reaction of gallium with sulfur is slower than that of indium with sulfur. Hence, gallium is not incorporated in the top layer and accumulates at the bottom of the solar cell near the back contact forming a gallium rich chalcopyrite layer. This is also due to the tendency of smaller atoms viz. Ga to migrate towards the region of stress.

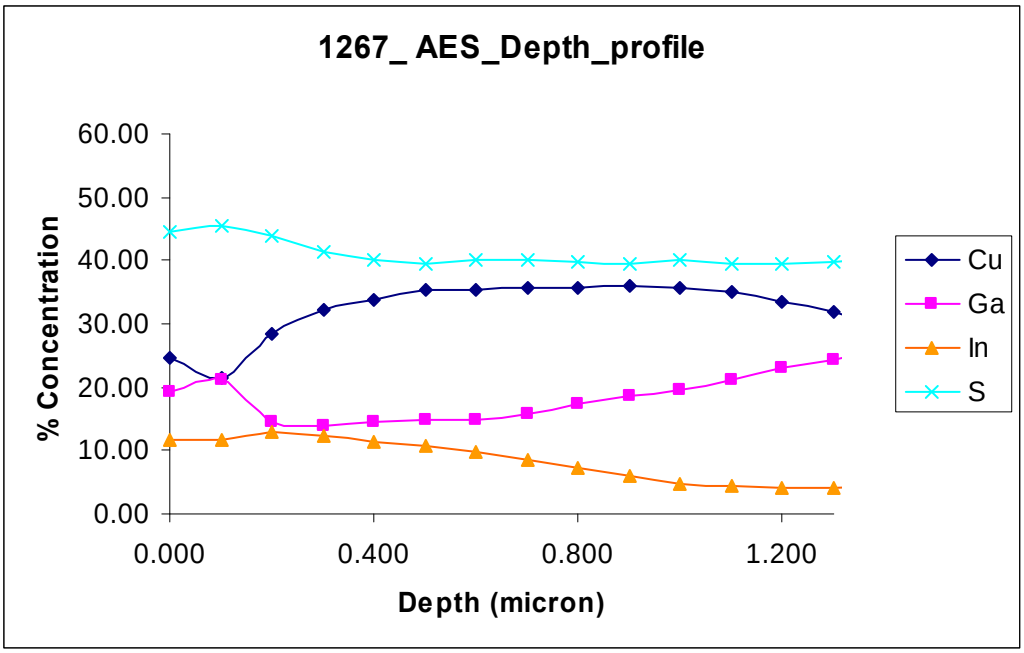


Figure 10: Auger depth profile for a CIGS2 sample with 1.2 µm absorber thickness

Transmission Electron Microscopy

Figures 11, 12 and 13 show TEM images for a CIGS2 solar cell with 1.2 µm absorber thickness. TEM images show no porosity at the CIGS2/Mo interface and there is some porosity in the bulk. This porosity may be already present in absorber or may also have been introduced during the TEM sample preparation.

Figure 14 shows a line scan profile of peak height of elements versus depth. The oxygen peak (red) seen beneath the back contact is due to the sodalime substrate. At the depth of ~2 µm on the X-axis, two very intense molybdenum peaks (orange and purple) are seen from the Mo back contact. Between X-axis depth positions of 0.7 µm to 2 µm, elemental peaks from CIGS2 absorber layer are seen. Sulfur peak (orange) shows the maximum intensity followed by copper peak (yellow). Copper and sulfur signals are constant in the absorber bulk. This is followed by indium (orange) peak decreasing towards back contact and gallium (azure) peak increasing towards back contact. The cadmium (red) peak in the absorber region may be due to the inward diffusion of Cadmium in CIGS2. Zinc (green) and Oxygen (red) peaks are seen from the surface to a depth of 0.7 µm from the transparent and conducting ZnO/ZnO:Al bilayer. Gallium signal is also seen in the ZnO region. This is due to the trace amount of gallium introduced during the focused ion beam (FIB) sample preparation.

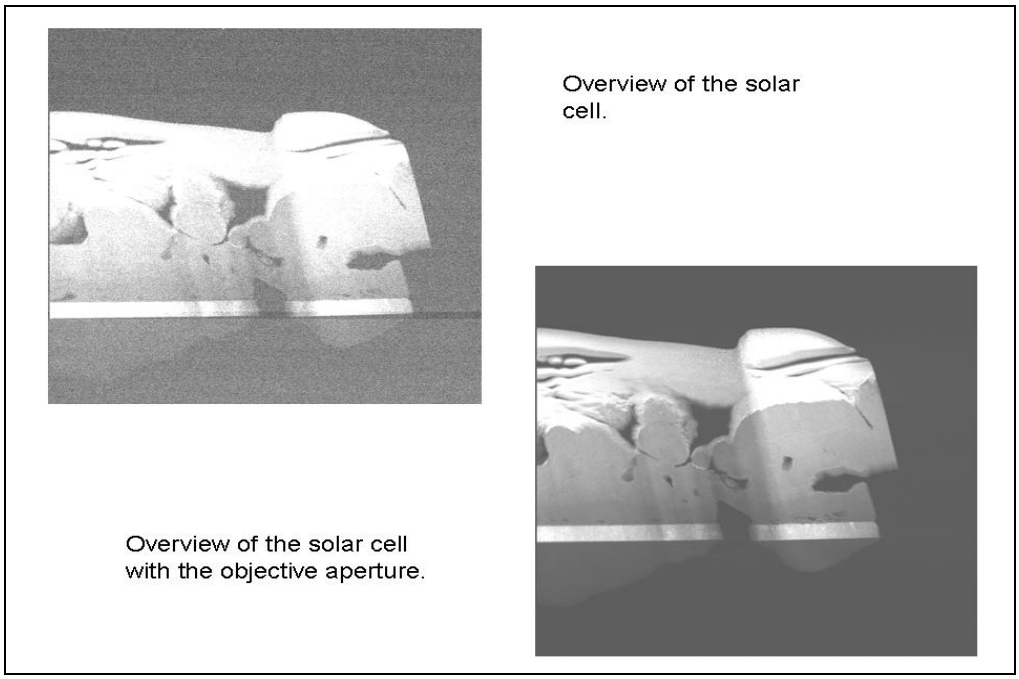


Figure 11: TEM overview of the 1.2 µm absorber sample solar cell

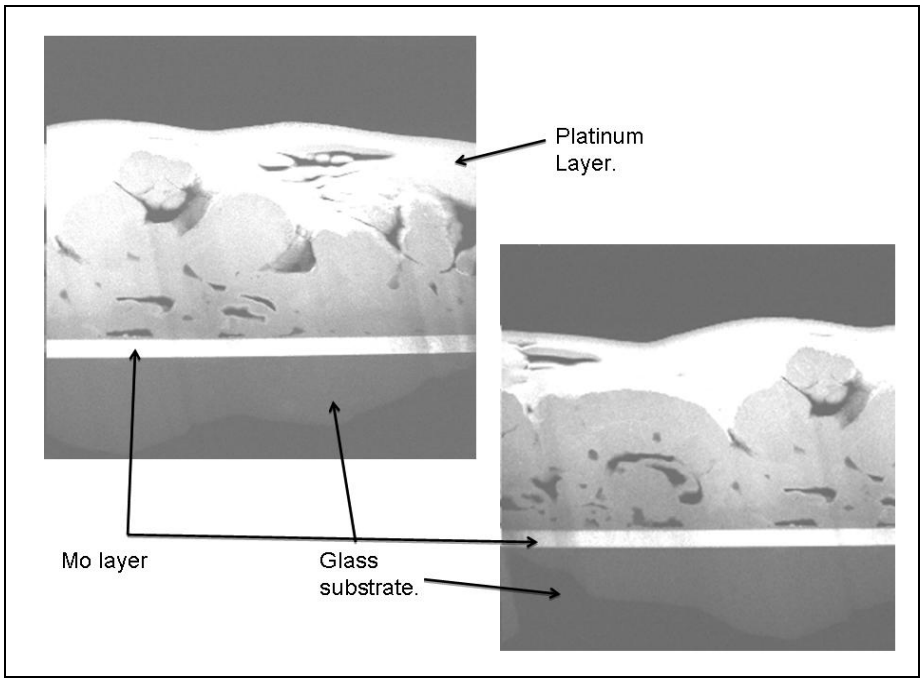


Figure 12: TEM cross-section of the sample

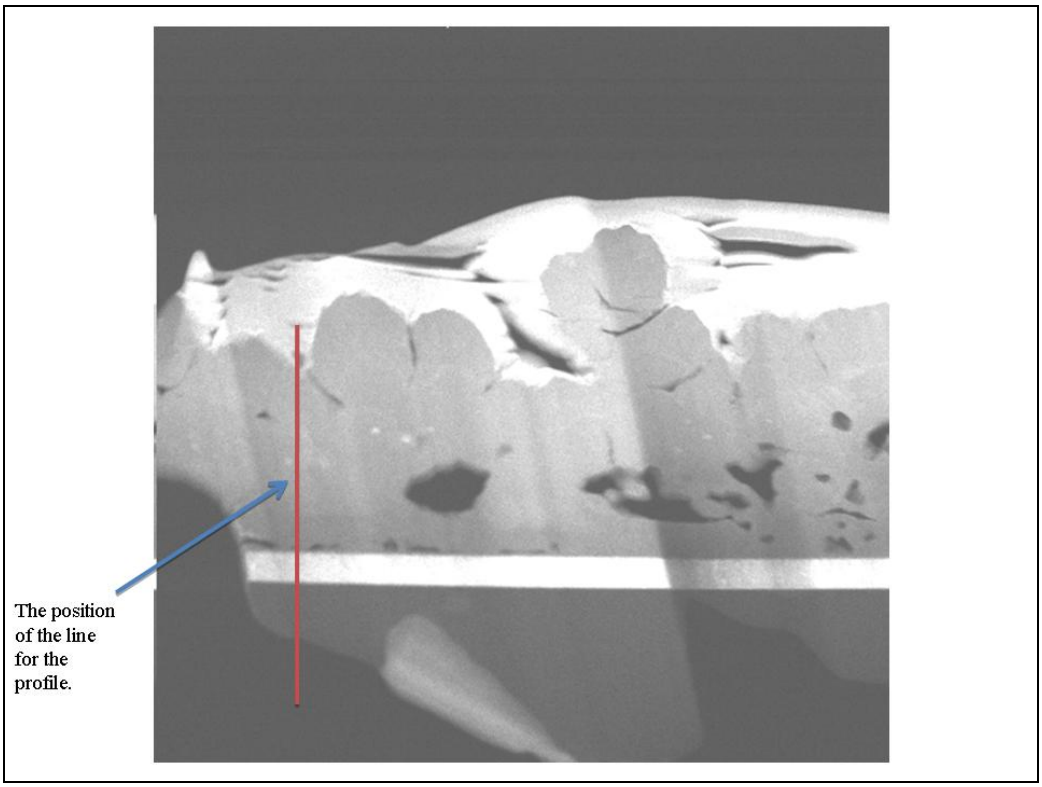


Figure 13: TEM image showing position of the line scan in the cross-section

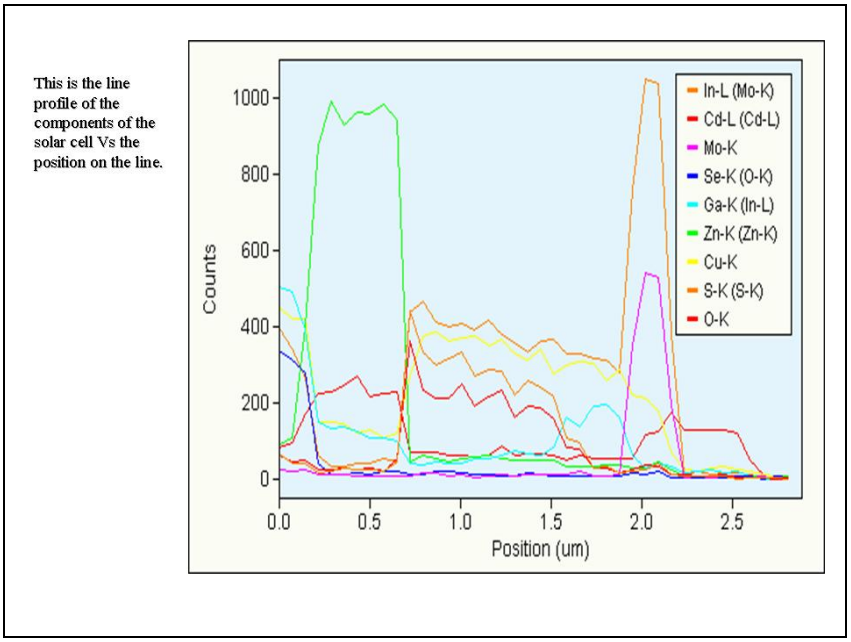


Figure 14: Line profile of the components of the solar cell against the position on the line in Figure 12

Photovoltaic Characteristics and Quantum Efficiency Measurements

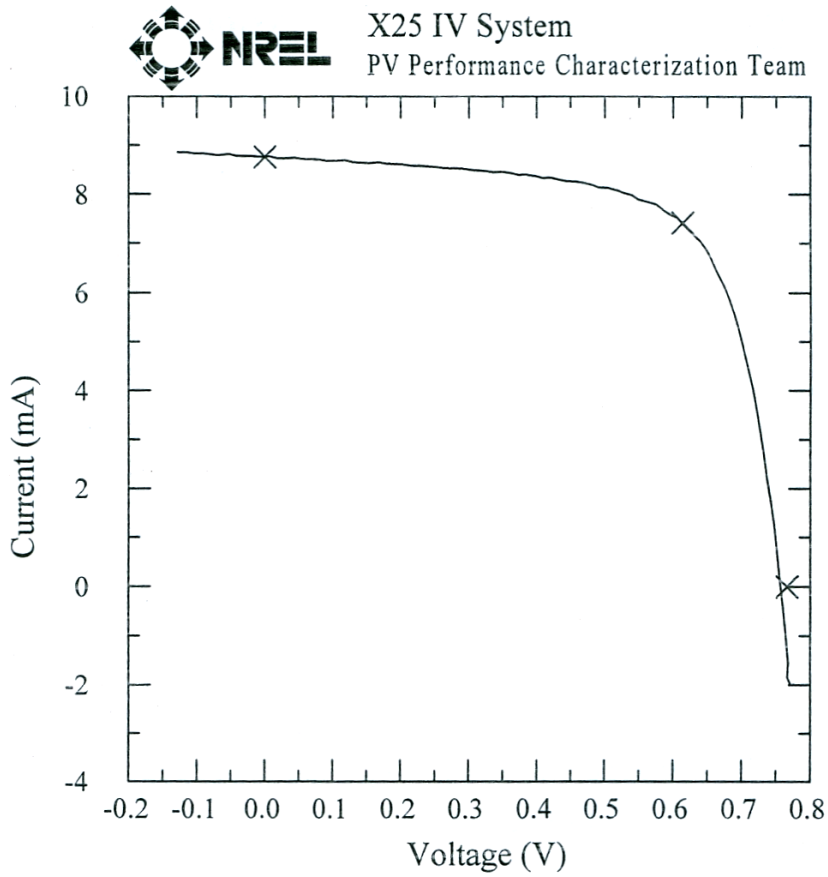
Photovoltaic performance of CIGS2 thin film solar cells were studied using current-voltage (I-V) characteristics. Figure 15 shows the I-V characteristics of CIGS2 solar cell of 1.5 μm absorber measured at the National Renewable Energy Center (NREL) under AM1.5 conditions. Photovoltaic characteristics of the CIGS2 thin film solar cells were as follows: short circuit current density, J_{sc} of 19.46 mA/cm^2, open circuit voltage, V_{oc} of 765.9 mV, fill factor, FF of 67.85% and photovoltaic conversion efficiency, η of 10.12%. Figure 16 shows QE characteristics. Figure 17 and figure 18 exhibit I-V and 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%.

Florida Solar Energy Center

CdS/Cu(In,Ga)Se_2 Cell

Device ID: 2387A-5
Nov 15, 2007 11:38
Spectrum: AM1.5-G (IEC 60904)

Device Temperature: 25.0 ± 1.0 °C
Device Area: 0.450 cm^2
Irradiance: 1000.0 W/m^2



V_{oc} = 0.7659 V
I_{sc} = 8.7590 mA
J_{sc} = 19.464 mA/cm^2
Fill Factor = 67.85 %

I_{max} = 7.4130 mA
V_{max} = 0.6140 V
P_{max} = 4.5510 mW
Efficiency = 10.12 %

After 10 minute soak at P_{max}, 5 minute cool.

Figure 15: I-V characteristics for a 1.5 µm absorber

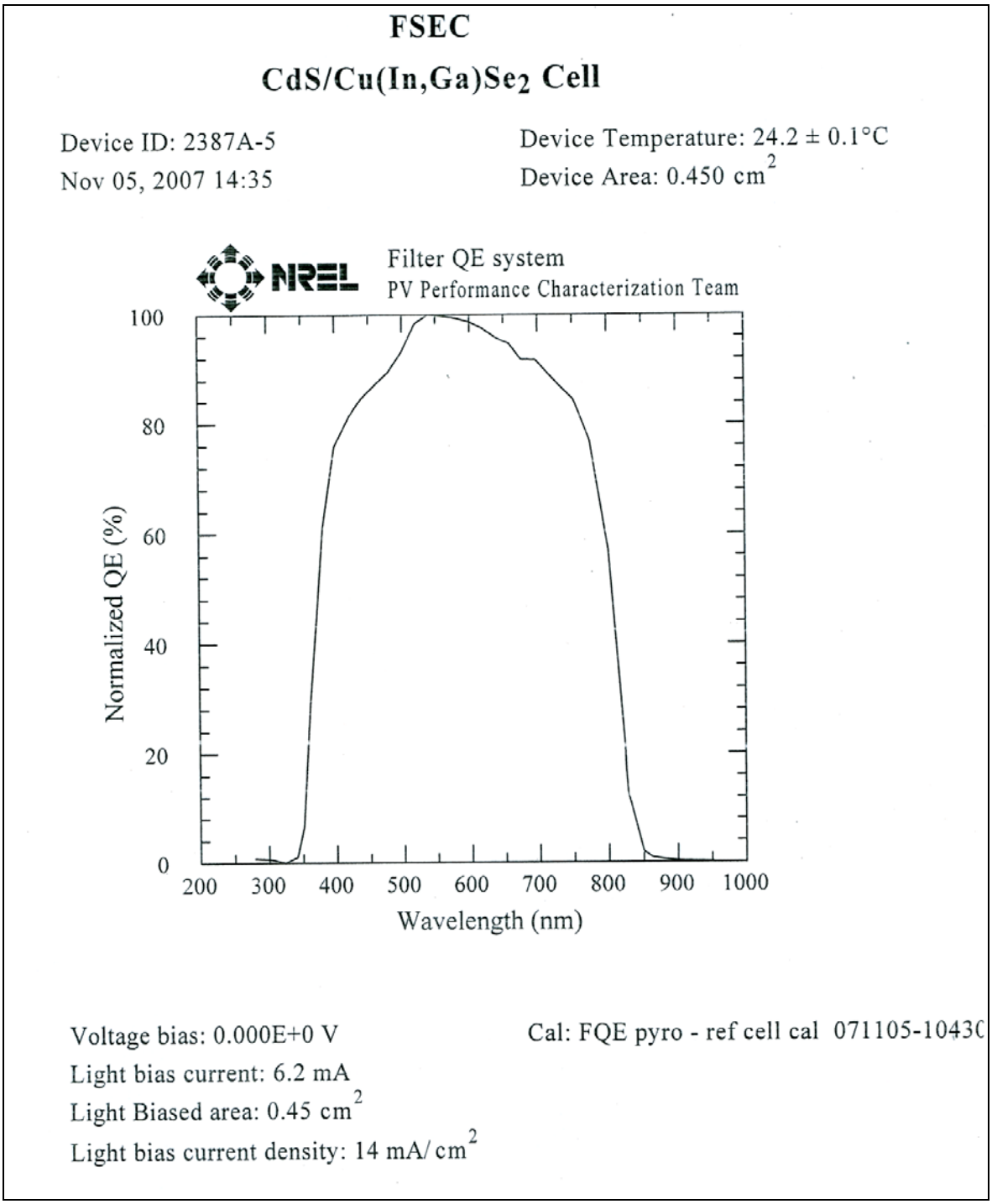


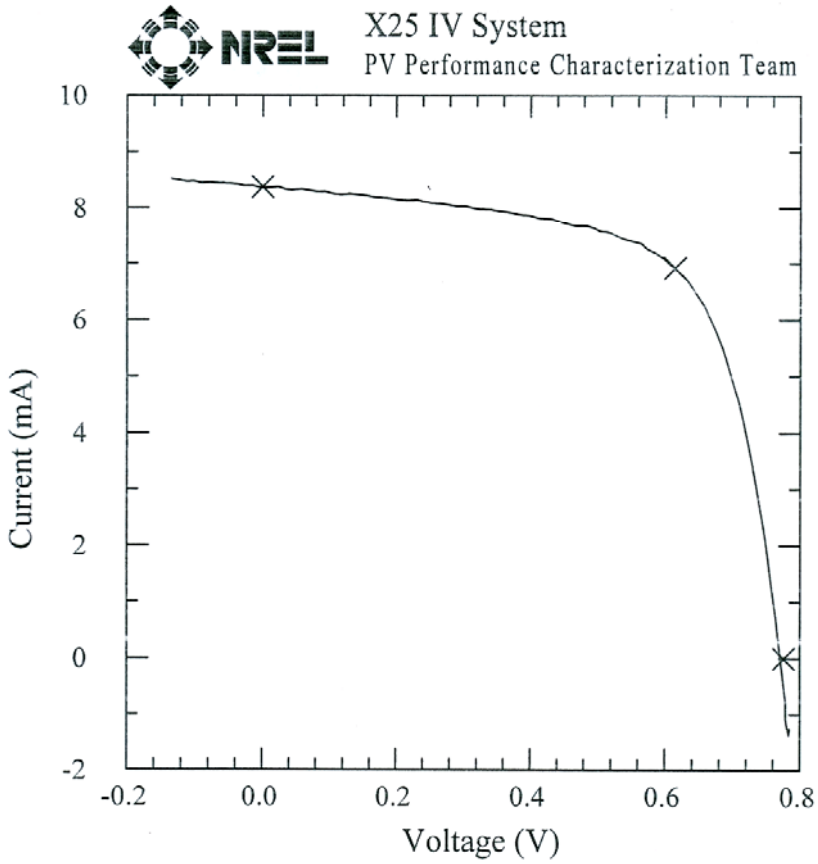
Figure 16: QE characteristics for a 1.5 µm absorber

Florida Solar Energy Center

CdS/Cu(In,Ga)Se_2 Cell

Device ID: 1267D-6
Nov 14, 2007 10:21
Spectrum: AM1.5-G (IEC 60904)

Device Temperature: 25.0 ± 1.0 °C
Device Area: 0.442 cm^2
Irradiance: 1000.0 W/m^2



V_{oc} = 0.7759 V
I_{sc} = 8.3749 mA
J_{sc} = 18.948 mA/cm^2
Fill Factor = 65.40 %

I_{max} = 6.9148 mA
V_{max} = 0.6146 V
P_{max} = 4.2499 mW
Efficiency = 9.62 %

After 10 minute soak at P_{max}, 5 minute cool.

Figure 17: I-V characteristics for a 1.2 µm absorber

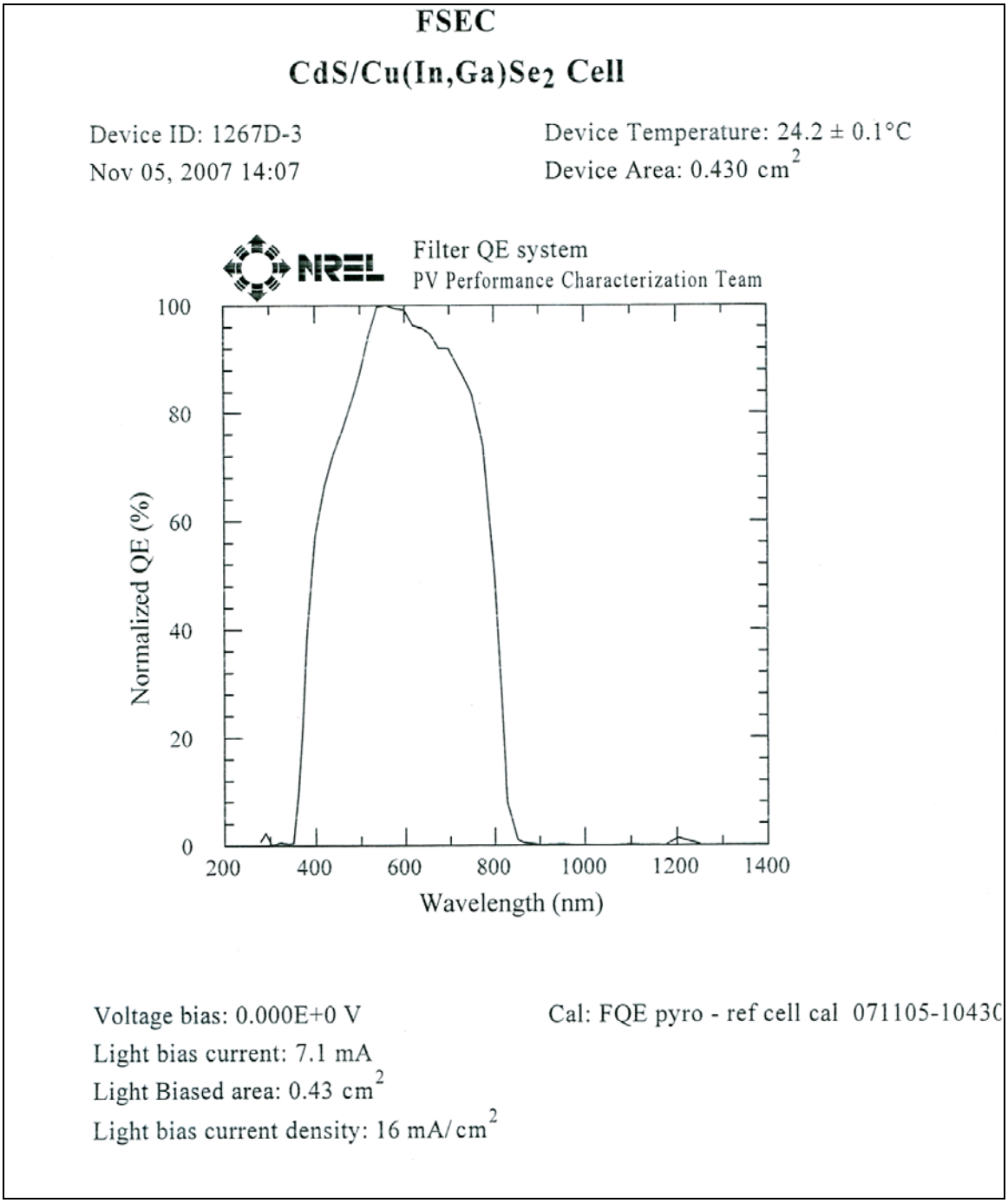


Figure 18: QE characteristics for a 1.2 µm absorber

The band-gap value of CIGS2 absorber as calculated from the QE analysis is 1.495 eV. From the QE analysis it can be seen that the CdS heterojunction partner layer is well optimized as losses in <520 nm (corresponding to CdS bandgap of 2.42 eV) wavelength are comparatively

low. Also it can be seen from the QE analysis that absorber quality can be improved near the molybdenum back-contact to improve the collection efficiency in the long wavelength region. The curves are steep in the long wavelength region, showing the uniformity of composition.

4. SUMMARY

Experiments were initiated for the comparison of CIGSeS absorber layers prepared under identical conditions on commercial Mo coated substrates and in-house prepared Mo coated back contact layers with or without SixNy diffusion barrier layers. In the preliminary experiments described in this report. CIGSeS absorber layers prepared on sodalime glass substrates with in-house prepared molybdenum back contact peeled off during selenization/sulfurization by RTP. All the films were deposited with starting layer of molybdenum in compressive stress mode that is known to be less adherent to glass substrate as compared to film grown in tensile mode. This could be the reason for peeling off the absorber films. Therefore, experiments are being continued with starting layer of molybdenum in tensile stress mode.

CIGS2 solar cells were optimized for lower thickness values of absorber. Photovoltaic conversion efficiency of 10.12% was obtained for an absorber of thickness 1.5 μm and an efficiency of 9.62% was obtained for an absorber of thickness 1.2 μm.

5. ACKNOWLEDGEMENTS

The help of Dr. Helio Moutinho and Bobby To, NREL for XRD and EPMA analysis as well as of Tom Moriarty and Keith Emery, NREL for current-voltage and quantum efficiency measurements of CIGS2 thin film solar cells and of Kirk Scammon, AMPAC, Materials Characterization Facility, UCF for AES analysis of CIGS2 thin film solar cells is gratefully acknowledged.

6. REFERENCES

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