

Low Toxic Processing of Thin and Ultra-thin CIGSeS Absorber Solar Cells

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ABSTRACT

CuIn_{1-x}Ga_xSe_{2-y}S_y (CIGSeS)/CdS thin-film solar cells were prepared on molybdenum coated glass substrates. A low toxic selenium precursor, diethylselenium (DESe) was used for selenization of metallic precursors. 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 and diluted H₂S. 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. Experiments were performed to reduce absorber thickness to reduce indium consumption using both conventional as well as the RTP approach.

1. Objectives

The objective of the project is to develop a high throughput, very thin, and highly efficient CIGSeS solar cell using low toxicity reactants. The work is oriented to fulfill the DOE goal of developing technology capable of reducing the cost to make it competitive.

2. Technical Approach

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 have been carried out with various NaF thicknesses. The CuGa-In 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 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). 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

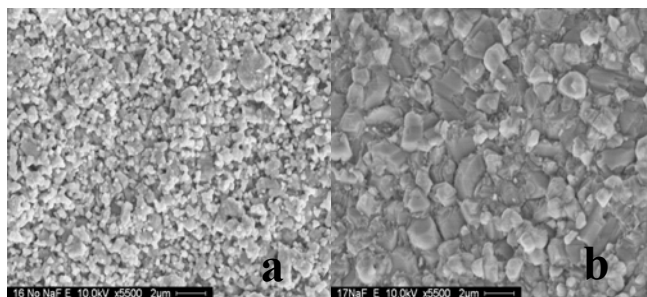


Fig. 1: SEM micrographs (a) No NaF (b) 120 Å NaF.

contact fingers by thermal evaporation for both approaches.

3. Results and Accomplishments

3.1 Selenization/Sulfurization – Conventional Furnace

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 films¹. Moreover, the grains were well faceted and compactly packed (Fig. 1). Initially CuIn_{1-x}Ga_xSe₂ (CIGS) absorbers were prepared by selenization of the precursors. Thin film solar cells prepared by using CIGS layers having Cu/(In+Ga) ratio of 0.83 had an efficiency of 12.33%. At this stage, the Cu/(In+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). To the best of our knowledge this is the highest officially measured efficiency for a small-area CIGSeS thin film solar cell prepared by a two-stage technique.

3.2 Rapid Thermal Processing

CIGSeS thin-films were also being prepared by rapid thermal processing (RTP). Glass substrates were coated with Mo back contact and CuGa-In 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 as described in technical approach. 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 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. Experiments are being carried out to improve photovoltaic properties of these cells.

3.3 Very thin (~1 μm) CIGS

Very thin CIGS film was prepared in the conventional furnace by selenization of these metallic precursors in diluted DESe ambient at 515°C for 30 minutes. Very thin CIGSeS films were prepared using the RTP approach. In both cases the cells were completed. Figure 4 shows the I-V and QE curve measured at NREL for a CIGSeS ultra thin (0.9 μm) solar cell prepared using RTP. An efficiency of 8.65% was achieved with very thin CIGSeS solar cells prepared by RTP.

3.4 CIGS2

It is customary in the preparation of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) or $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ (CIGS2) solar cells, to use an intrinsic ZnO layer (i-ZnO) on the CdS layer prior to the deposition of Al doped ZnO layer (ZnO:Al). Experiments were carried out to optimize this i-ZnO thickness were prepared and a photovoltaic conversion efficiency of 11.99% with open circuit voltage, V_{oc} of 830.5 mV under AM 1.5 conditions were obtained. To our knowledge this is the best, officially measure, small area efficiency CIGS2/CdS cell prepared by this technique and also the highest V_{oc} value of 830.5 mV (Fig. 5).

4. Conclusion

The work presents the use of DESe as a low toxic alternative source for preparation of a high quality absorber. The addition of small amount 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 a world record efficiency of 13.73 % was prepared by sputtering and selenization/sulfurization in a conventional furnace. 12.78 % efficiency with 2.0 μm absorber thickness and 8.65 % efficiency 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. Two approaches for reducing the cost of photovoltaics have been demonstrated. First, indium can be reduced by preparing ultra-thin CIGSeS layer while maintaining device quality and second, high throughput can be obtained by RTP. Future work will focus on improving the absorber quality and solar cell efficiency by materials characterization as well as fine tuning of the process steps.

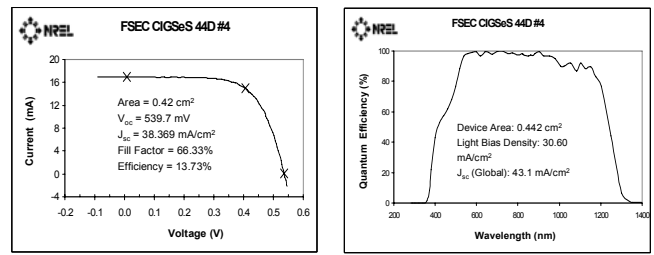


Figure 2: I-V and QE curve: Conventional furnace CIGSeS cell

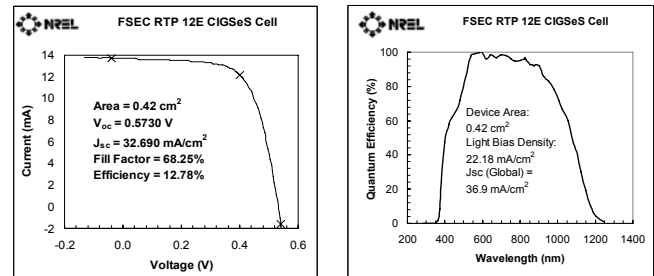


Figure 3: I-V and QE curve: RTP CIGSeS cell

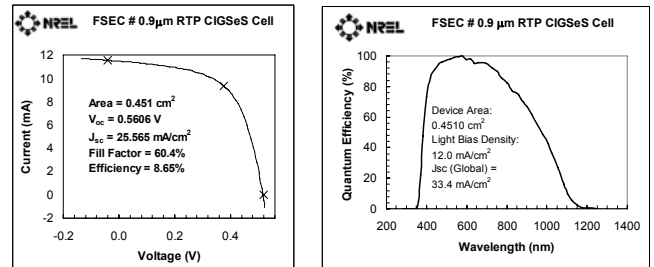


Figure 4: I-V and QE curve: 0.9 μm RTP CIGSeS cell

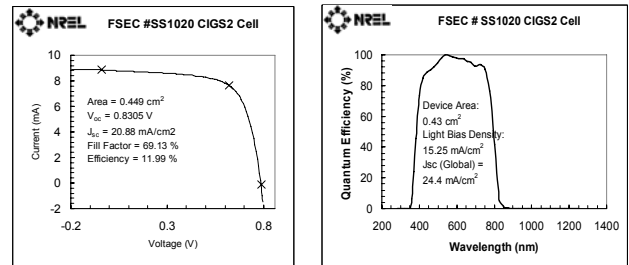


Figure 5: I-V and QE curve: CIGS2 cell

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REFERENCES

1. N.G. Dhere, and R.G. Dhere, JVST A, Vol.23, No.4, 1208-1214 (2005)

MAJOR FY 2006/2007 PUBLICATIONS

1. S. S. Kulkarni, J.S. Shirolkar, N.G. Dhere, ISEC 2006 proceedings.