

# **Recent Progress in CIGS Thin Film Solar Cell Research at NREL**

**Preprint**

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# RECENT PROGRESS IN CIGS THIN FILM SOLAR CELL RESEARCH AT NREL

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**Abstract:** This paper summarizes our work toward improving reproducibility in fabricating high efficiency absorbers and devices. This resulted in the fabrication of a CIGS cell with an efficiency of 21% under concentrated light. We compare devices fabricated with CdS and with Cd solution treatment alone. A high conversion efficiency of 15.7% is obtained with the latter, and we attribute this to the n-type doping afforded by Cd. The work is extended to absorbers provided by Siemens Solar Industries (SSI).

**Introduction:** Thin film solar cells based on  $\text{CuInSe}_2$  and its alloys with Ga and S have demonstrated excellent efficiencies. In our laboratory, a champion device was fabricated with a  $\text{CuInGaSe}_2$  (CIGS) absorber that demonstrated a conversion efficiency of 18.8%. Siemens Solar Industries has demonstrated large area modules with a conversion efficiency of >12% using  $\text{CuInGa}(\text{SSe})_2$  absorbers. Results such as these speak well for the viability of Cu-chalcopyrite thin film PV products. Further advancement and potential simplification of process steps are hindered by a limited understanding of material properties, the role of impurities and native defects, and the effect of stoichiometry. Reports of material properties tend to be very specific to thin films prepared by multi source co-evaporation or three stage process, and the applicability to materials made by dissimilar processes such as selenization is unclear. This gap can be narrowed by identifying the common thread in these apparently dissimilar material/device structures, and by quantifying the dominant effects.

**Experimental:** Polycrystalline  $\text{CuInGaSe}_2$  thin films were grown on Mo/ soda lime glass substrates by the three stage process. We employed real-time composition monitoring to detect the change of film composition and this was useful in improving reproducibility. Absorbers provided by SSI were used as received. CdS layers were grown from an aqueous solution containing 0.0015M  $\text{CdSO}_4$ , 1.5M  $\text{NH}_4\text{OH}$ , and 0.0075M thiourea at a maximum temperature of 60°C for 15 min. ZnO films were deposited in two stages: the first layer from an undoped ZnO target, and the second layer from an  $\text{Al}_2\text{O}_3$  doped target to produce a total thickness of 0.3  $\mu\text{m}$ . For the Cd solution treatments, the procedure was similar to the CdS deposition, but the thiourea was omitted. This step is described as a "Cd partial electrolyte (Cd PE)" treatment. In the following, we compare the characteristics of the two types of devices, i.e., ZnO/CdS/CIGS and ZnO/CIGS with Cd PE treatment.

**Results and Discussion:** We conducted a study of the effect of Mo sputter conditions and optimized them for our CIGS process. As a result of this and the compositional control during the CIGS deposition, we were able to fabricate absorbers with repeatable compositional profiles. The CdS process parameters

were varied, and the effect of thickness was carefully studied. The ZnO film thickness, particularly of the undoped, i-layer, was also varied. This resulted in a family of curves from which some trends could be identified. For example, when the CdS layer was sufficiently thick, the device properties showed little sensitivity to the i- ZnO layer thickness. With the use of thinner CdS layers, there was a precipitous drop in the voltages and fill factors. These results are summarized in another publication (1). This work resulted in several important outcomes.

Table 1 shows a summary of device results obtained on absorbers grown in one evaporator during a three month period at different intervals (XT-25 data). The suffixes indicate adjacent devices on a substrate. We find that the overall process control is adequate to demonstrate device efficiencies above 18%, and high voltages and fill factors are obtained routinely. These data are not statistically significant, but point to an important consideration, i.e., high efficiency devices can be fabricated readily.

There is an increasing appreciation of the suitability of thin film photovoltaic cells for concentrator applications. To demonstrate this, we used the present cell structure up to the ZnO, but defined the collector grid by photolithography as is commonly used for crystalline devices. The cells were tested under global and AM0 spectra for concentrations of up to 15 suns. Device efficiencies of 21% were measured. These results are described fully in a companion paper presented at this meeting (2).

| CIGS sample # | Cell# | $V_{oc}$ (V) | $J_{sc}$ (mA/cm <sup>2</sup> ) | FF    | Efficiency |
|---------------|-------|--------------|--------------------------------|-------|------------|
| S1518-12      | 3     | 0.675        | 35.10                          | 76.39 | 18.1       |
| S1518-23      | 3     | 0.6798       | 34.93                          | 77.34 | 18.4       |
|               | 2     | 0.6824       | 34.90                          | 77.38 | 18.4       |
|               | 4     | 0.6789       | 34.96                          | 77.63 | 18.4       |
|               | 5     | 0.6799       | 35.00                          | 77.75 | 18.5       |
|               | 6     | 0.6793       | 35.07                          | 77.68 | 18.5       |
| S1523-23      | 6     | 0.6834       | 34.38                          | 77.23 | 18.1       |
|               | 7     | 0.6872       | 34.39                          | 76.77 | 18.1       |
| S1546-23      | 7     | 0.6830       | 34.3                           | 77.39 | 18.1       |
| S1583-23      | 1     | 0.6923       | 34.18                          | 78.00 | 18.5       |
|               | 2     | 0.6897       | 34.3                           | 77.78 | 18.4       |
|               | 3     | 0.6864       | 34.3                           | 77.75 | 18.3       |
|               | 4     | 0.6844       | 34.61                          | 76.84 | 18.2       |

Table 1. Device data for ZnO/CdS/CIGS devices made during 3 months at various intervals.

**Role of Cd in CdS/CIGS junctions:** Our strategy to solve this seemingly intractable problem has been to view the CdS/CIGS device as an interactive system, and try to separate out the most important effects. Our prior work with CuInSe<sub>2</sub> (no Ga) had shown that a treatment in a partial bath containing only Cd (no sulfur) is sufficient to change the electrical properties of the absorber and the quality of the junctions made subsequently. Zn baths were also shown to produce a similar effect (3). This led us to the conclusion that the ability of Cd and Zn (group II<sub>B</sub>) to afford n-type doping in CuInSe<sub>2</sub> must be a key factor in the formation of junctions. Here, we show the results on CIGS absorbers fabricated at NREL and on CIGSS absorbers provided by SSI. Fig. 1 shows three illuminated J-V curves for devices fabricated on NREL absorbers. Our starting point is a ZnO/CIGS cell where the ZnO was deposited directly on a CIGS absorber without any treatment. The second case is for the same structure, but after the CIGS has been treated in a Cd PE bath. We compare the above with the CdS case. The effect of Cd PE treatment is striking when we compare the characteristics of the direct ZnO and Cd PE cases. We have tested the effect of ammonium hydroxide treatment alone, and

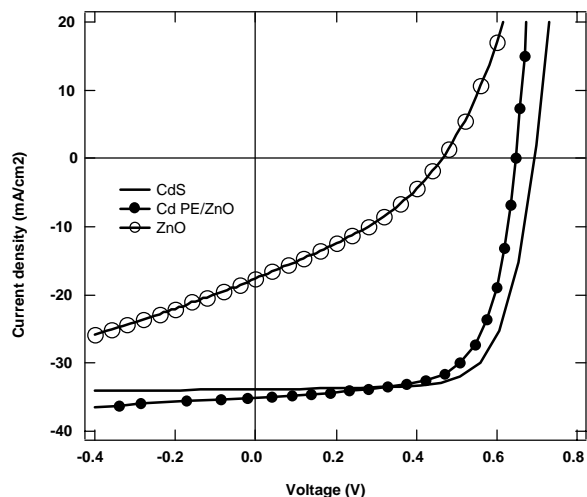


Fig. 1. Light J-V curves for solar cells fabricated on NREL CIGS absorbers with various treatments.

we do not see a similar improvement as we do with the (Cd+ ammonia) combined. Hence, we conclude that the Cd is instrumental in enhancing the n-type doping at the surface region, and forming a strong n-p junction in the absorber. We expect the n- region to be quite thin, and we have not identified a technique to measure the doping. The photovoltaic parameters of many Cd PE treated devices were measured by the Cell Performance Characterization Team at NREL. We have observed high open circuit voltages (650 mV) and fill factors of 72%. The highest efficiency was 15.7%. A comparative analysis of the CdS and Cd PE cells performed at Colorado State University indicates that the efficiency of the latter is reduced by loss of open circuit voltage and an increase in reverse saturation current density.

Fig. 2 shows a similar family of curves for the SSI absorber. The trend is similar to the NREL material described before and shows that the effect of Cd in junction formation is a common thread among the variety of CIG(SeS)<sub>2</sub> materials.

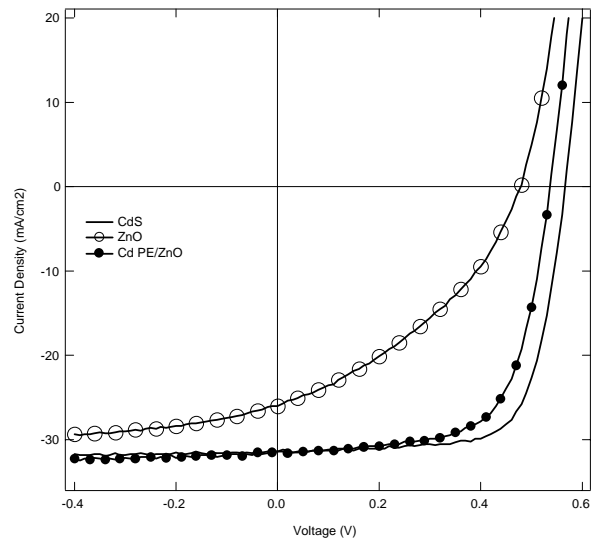


Fig. 2. Light J-V curves for a solar cells fabricated on SSI CIGSS absorbers with various treatments.

**Conclusions:** We have optimized the various process steps involved in fabricating CIGS solar cells and show that high efficiency devices can be fabricated repeatedly. By comparing the properties of Cd treated cells with the CdS cells on two types of absorbers processed very differently, we show that the n-type doping by Cd is a dominant factor in the operation of CdS/CIGS solar cells.

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