

Surface Treatment of CuInGaSe₂ Thin Films and Its Effect on the Photovoltaic Properties of Solar Cells

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K. Ramanathan, F.S. Hasoon, S. Smith, D.L. Young,
and M.A. Contreras
*National Renewable Energy Laboratory
Golden, Colorado*

P.K. Johnson, A.O. Pudov and J.R. Sites
*Colorado State University
Fort Collins, Colorado*

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K. Ramanathan, F. S. Hasoon, S. Smith, D.L. Young, and M.A. Contreras
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden CO 80401
and

P. K. Johnson, A. O. Pudov, and J. R. Sites
Physics Department, Colorado State University, Fort Collins CO 80523

Abstract

Solar cells have been fabricated with partial electrolyte treatments of CuInGaSe₂ (CIGS) thin film absorbers in lieu of a CdS layer. Treatment of the absorbers in a Cd or Zn containing solution is shown to produce conditions under which efficient solar cells can be fabricated. A similar effect is also observed in CuInGaSSe₂ (CIGSS) graded band gap absorbers. These observations can be explained by the ability of Cd and Zn to produce n-type doping or inversion in the surface region. We also provide a brief review of similar work done elsewhere and identify directions for future investigations.

1. Introduction

Thin film solar cells based on CuInSe₂ (CIS) have been developed as a competitive option for low cost power generation. Photovoltaic cells and modules made using alloys of CIS with Ga and or S have demonstrated the highest efficiencies and good stability in outdoor tests [1]. In research laboratories, CIGS thin films are generally fabricated by co-evaporation from elemental sources [2]. The processes used for large area module manufacture, however, involve deposition of metallic precursor stacks and the subsequent formation of the compound in a selenium and sulfur ambient [3]. The two examples represent a sharp contrast in preparation methods, and the commonality is

that one attempts to fabricate a single-phase, chalcopyrite CIS alloy thin film with a specific Ga or S content and a Cu/(In+Ga) ratio. The photovoltaic junction is generally completed by the deposition of a thin CdS layer by chemical bath deposition. Though the most efficient CIGS solar cells are fabricated in this manner, there are a few problems associated with the CdS technology. First, the band gap of the CdS layer is still low enough to limit the short wavelength part of the solar spectrum that can reach the absorber, and this leads to a reduction in the current that can be collected. This reduction becomes proportionally more severe for higher band gap CIGS cells. From a practical standpoint, the generation of large quantities of hazardous waste and its disposal present challenges to the manufacturer.

Finding an equally attractive alternative to the CBD CdS technology has been a recurring theme in many studies. Among the alternative layers that have been investigated are ZnS, ZnO, Zn(S,O), ZnSe, In₂S₃, In(OH)_xS_y, and perhaps others [4]. When these alternative “buffer layers” have been inserted in place of CdS, the deposition processes have often still involved wet chemistry, and not uncommonly, the devices fabricated in this manner require post deposition anneals or light soaking to become fully active. It has also been found useful in many cases to chemically modify the surface of the absorber before deposition of the alternative n-type layer [5]. In this paper, we

report the results of surface treatments of CIGS thin films in an aqueous solution containing Cd or Zn ions followed by the completion of the solar cells with a ZnO layer.

2. Experimental Techniques

CIGS thin films were grown at NREL by the three-stage process on Mo/soda lime glass substrates. The resulting absorber material was 2.5 μm thick, and it was p-type with a hole density of $1\text{-}3 \times 10^{16} \text{ cm}^{-3}$. The nominal composition was $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$. The Cu concentration in the near-surface region was carefully controlled so that the overall Cu/(In+Ga) ratio is less than unity. Samples provided by Shell Solar Industries, formerly Siemens Solar Industries, (SSI) were graded band-gap CIGSS absorbers. Reference cells were made with CdS thin films deposited from an aqueous solution containing 0.0015M CdSO_4 , 1.5M NH_4OH , and 0.0075M thiourea. The temperature of the bath was gradually raised from room temperature to 60°C, and the samples were held in the bath for 15 min, during which a 40 to 60 nm CdS film was deposited. For the non-CdS cells, partial electrolyte treatments of the absorber surface, designated as Cd PE and Zn PE, were performed by immersing the samples in a bath similar to the CdS deposition, but excluding thiourea. The maximum temperature during the Cd PE treatment was 80°C, and the total immersion time was 22 min. Solar cell fabrication was completed by depositing a two-layer ZnO film. The first layer of 80 to 100 nm was deposited from a pure ZnO target, and the second layer of 120 nm was deposited from an Al_2O_3 doped target. Ni/Al contacts were evaporated on the ZnO. Current-voltage characteristics of the solar cells were measured in dark and under light simulated to correspond to AM1.5 Global spectrum. Photoluminescence (PL) spectra of CIGS thin films were measured at 4K. To minimize the

effects of sample inhomogeneity, the micro-Photoluminescence (micro-PL) technique was used to excite and collect the PL within a 1 micron diameter spot size (excitation wavelength 632.8 nm, excitation power 120 nW) and subsequently dispersed onto an InGaAs diode array. Linear scans were taken with up to 50 spectra, separated by 1 μm steps.

3. Results and Discussion

Fig. 1 shows the current-voltage (J-V) characteristics of three types of solar cells fabricated from NREL-deposited CIGS absorbers. For the case of ZnO deposited with neither CdS nor the Cd PE treatment,

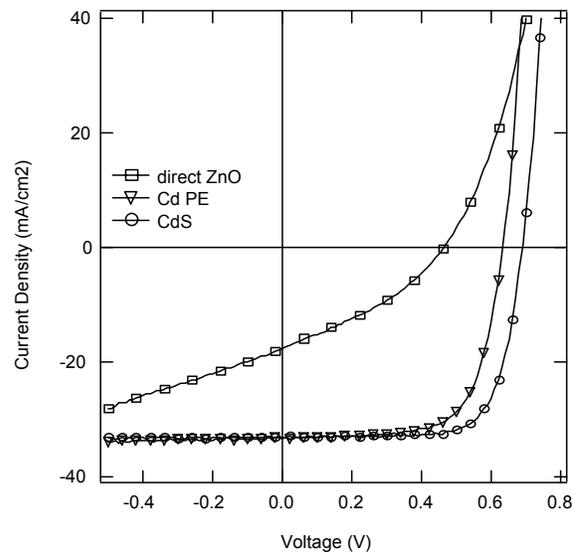


Fig. 1. Current-voltage characteristics of CIGS solar cells with no treatment, Cd PE treatment, and CdS layer. All have ZnO window layers.

inferior photovoltaic activity is observed. The open circuit voltage and the fill factor are low. A detailed analysis of the J-V curves reveals that the reverse saturation current density and the diode factor are higher compared to the CdS case. The shape of the J-V curve under illumination indicates that the light generated current may be controlled by voltage-dependent recombination. The

treatment of the absorbers in a Cd PE solution prior to the deposition of ZnO helps remove these limitations. A comparison of the J-V curves of this diode and the one with the CdS window layer shows that the Cd treatment alone is sufficient to produce an efficient photovoltaic cell. We had shown previously that similar results are obtained with CIS thin films [6].

In Fig. 2, the spectral dependence of the internal quantum efficiency of the two types of devices are compared. The CdS-containing cell exhibits a lower collection in the short wavelength part of the spectral range, which is attributed to the absorptive and collection losses in the CdS layer. The absence of these losses in the Cd PE device is evident, and an increase of the short circuit current density of 1-2 mA/cm² is obtained

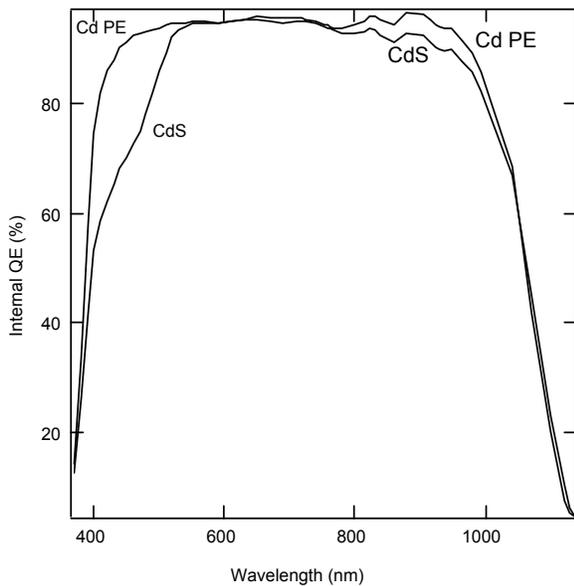


Fig. 2. Quantum efficiency vs. wavelength of CIGS solar cells with Cd PE treatment and CdS layer.

when the CdS layer is eliminated or a comparable wide-gap window layer is substituted. This is the obvious attraction to removing the CdS window layer. However, one finds that the devices without CdS layers

exhibit slightly lower open circuit voltages and fill factors. These can be attributed to the nature of the interface created by the dissimilar materials and the defect states introduced during the processing steps. The lattice constants of CdS and CIGS are closely matched, and the interface created between the two will have minimal lattice mismatch and lower defect density compared to other window layers. It has also been shown that there is some inter-diffusion across the CdS/CIGS interface [7], and the resulting compositional mixing will further reduce the deleterious effects of interface recombination. The best cell fabricated using the Cd PE treatment had a conversion efficiency of 15.7%. The use of Zn PE treatments, in which the Cd compound is replaced by a Zn compound, lead to J-V and QE curves similar to those shown in Figs. 1 and 2. We also find that similar Cd PE results are observed with CIGSS alloy thin films fabricated by a manufacturing process. An example is shown in Fig. 3 where the cells were completed on absorbers provided by SSI.

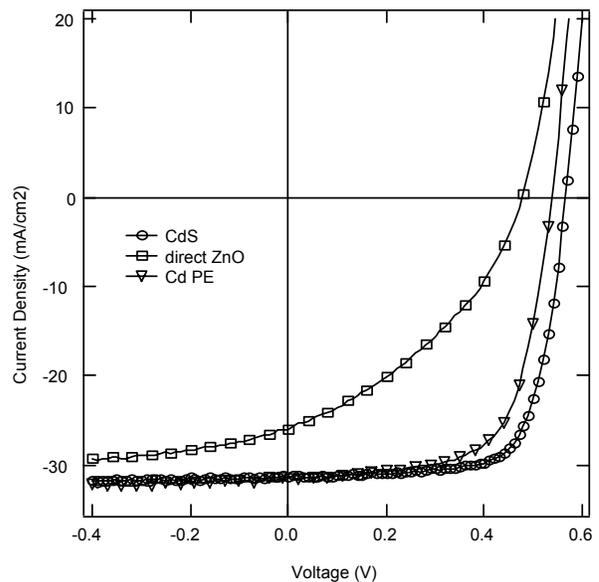


Fig. 3. Current-voltage characteristics of CIGSS solar cells with no treatment, Cd PE treatment, and CdS layer. All have ZnO window layers.

Fig. 4. shows the PL spectra of a CIGS thin film treated in ammonium hydroxide only and one in Cd PE. The two pieces were cut from the same sample along the direction of uniform Ga distribution. The PL intensities exhibited minor variation along the length probed, but the spectral features remained constant. The spectral dependence shows two broad peaks centered around 1.05 eV and 1.12 for the ammonium hydroxide case. It is well known that the two transitions are donor-to-acceptor pair transitions between shallow donor and acceptor energy levels close to the band edge [8]. In the Cd PE sample, the higher energy emission is quenched by the action of Cd. This involves a transition between a donor level and the shallowest acceptor, and its disappearance indicates that the acceptor level is neutralized by Cd. This can cause a change in the compensation ratio, and can result in a change of conductivity type in the surface region.

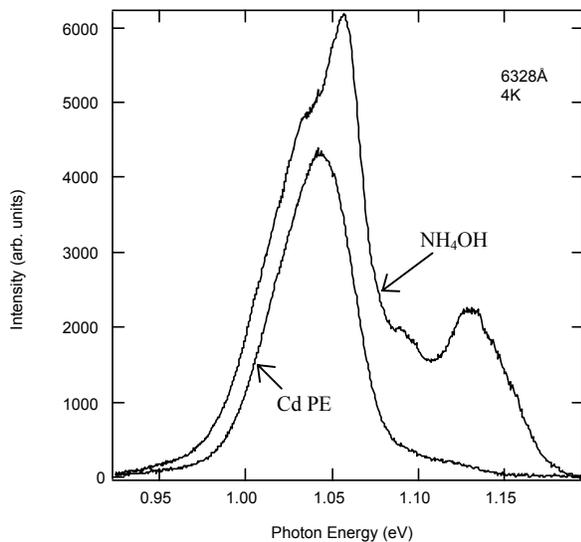


Fig. 4. Photoluminescence spectra of CIGS thin film treated in ammonium hydroxide and Cd PE. Excitation wavelength is 6328 Å, sample temperature 4 K.

The above observations lead us to a discussion of the effect of the surface treatments on the electrical properties of the

surface region. It is well known that the electrical properties of the I-III-VI₂ compounds are determined by a critical balance of electrically active native defects and complexes arising from deviations from stoichiometry [9]. The effect of extrinsic impurities tends to be marginal because of limitations to dopant solubility and the readiness with which compensating defects of the opposite kind form to neutralize the donor or acceptor impurities introduced externally [10]. However, the lower band gap Cu-In-VI₂ compounds, CuInSe₂ and CuInS₂, can be made n- and p-type conducting by annealing the crystals in minimum or maximum chalcogen pressure [9]. Efficient n-type conductivity is also obtained in CuInSe₂ by the use of extrinsic doping with Cd and Zn. The donor level introduced by Cd doping was found to have an ionization energy of 5 meV, and a rapid diffusion of Cd was observed at low temperatures [11]. In a separate study of thermally evaporated CdS on CIS single crystals, it was found that homojunctions were formed by the deposition of CdS, and the photovoltaic effect was still present after the CdS layer was removed [12]. Hence, we find ample evidence in the foregoing studies for the ability of II_B impurities (Cd, Zn) to produce n-type doping.

Our experiments with the Cd and Zn PE solutions and the resulting solar cell properties indicate that a similar effect could be created in a CBD environment involving Cd or Zn compounds and ammonium hydroxide. The polycrystalline films are deliberately grown Cu-poor (III rich), which creates an abundance of Cu vacancies. The ionic radii of Cu and Cd are very close, and the substitution of Cd in Cu vacancy sites is most likely. One can envisage out-diffusion of Se and the formation of sulfo-selenide compounds or solid solutions at the interface. Compositional profiles of Cd PE treated samples indicate that there is an appreciable concentration of Cd in the near surface

region. We further assume that the Cd impurities are readily ionized, leading to an increase in the electron density in the surface region and resulting in band bending or inversion. Controlled incorporation of Zn impurities in CIGS thin films grown by the three-stage process has clearly demonstrated that high efficiency solar cells can be fabricated by Zn doping of the surface region of polycrystalline films [13]. Nakada et al [14] find that the ZnS window layers deposited by CBD do not directly yield the best solar cells, but that a post deposition annealing step is needed to optimize the Zn diffusion profile. It is quite possible that the ionization of Zn donors is also taking place during the anneal step. A similar combination of effects can occur in any junction formation step in which Zn or Cd compounds are deposited on a heated substrate, and where the precursors are reactive.

Although the notion of n-type doping is not new to the ternary chalcopyrites, it is to the thin film solar cell field and is still a contentious issue. The experimentalist is challenged to develop measurement techniques that can probe the electrical activity and conduction type in a very thin, surface layer of polycrystalline film. This is a difficult task, but it is central to the development of alternative device structures in II-VI and I-III-VI₂ thin films.

5. Conclusions

We have compared the properties of solar cells fabricated in CIGS thin films by Cd PE treatment with those containing standard CdS window layers, and we show that the presence of Cd alone is sufficient to produce efficient solar cells. Similar results are obtained by using Zn PE baths. These results suggest that the column II_B impurities help change the electrical properties of the surface region. Hence, a model for the operation of

the CdS/CIGS solar cell must consider the role of the absorber and window layer properties and the electrical and compositional changes to the intermediate region influenced by the processing conditions.

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