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Original Research

Assessment of Cu(In, Ga)Se₂ Solar Cells Degradation due to Water Ingress Effect on the CdS Buffer Layer

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Abstract

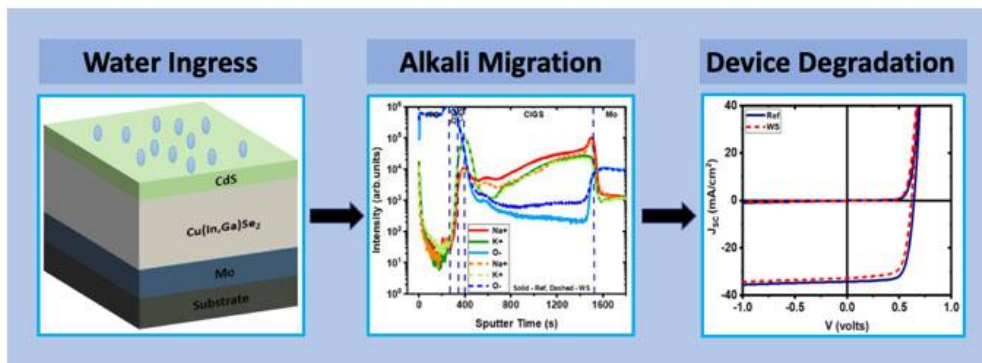
The effect of water ingress on the surface of the buffer layer of a Cu(In, Ga)Se₂ (CIGS) solar cell was studied. Such degradation can occur either during the fabrication process, if it involves a chemical bath as is often the case for CdS, or while the modules are in the field and encapsulants degrade. To simulate the impact of this moisture ingress, devices with a structure sodalime glass/Mo/CIGS/CdS were immersed in deionized water. The thin films were then analyzed both pre and post water soaking. Dynamic secondary ion mass spectroscopy (SIMS) was performed on completed devices to analyze impurity diffusion (predominantly sodium and potassium) and to assess potential degradation mechanisms. The results were compared to device measurements, which indicate a degradation of all device parameters due to an increase in the total and peak trap densities, as shown by simulation. This is potentially due to a modification of the sodium profile in the bulk CIGS, with a decrease



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content after water soaking or because the oxygen profile increased in the bulk CIGS after water soaking.

Graphical abstract



Keywords

Solar cell; corrosion; CdS; CIGS; alkali

1. Introduction

Of all of the degradation mechanisms that can affect a photovoltaic module, water remains one of the most potent ones [1-3]. Degradation can occur all the way from the connection to the electrical system to the degradation of individual layers within the module via corrosion-like processes [4, 5]. Most of the studies performed on CIGS solar cells, with regard to the effect of water, have been performed on the solar cell as a whole not on the individual layers [6, 7]. We have previously reported on the impact of water on Molybdenum, CIGS and TCO (i-ZnO/ITO) components of the CIGS devices [8-10]. We will be focusing on the buffer layer, specifically CdS, here. Among the various choices for buffer layers for CIGS solar cells, cadmium sulfide (CdS) is still the main choice due to its wide bandgap and suitable band alignment with CIGS and TCO [11, 12]. Previous studies into the degradation mechanism due to the CdS layer have mostly focused on the effect on the CIGS layer due to damp heat treatments. Several studies compared the CdS buffer layers to other buffer layers under damp heat treatments and concluded that the CdS layer was often the most stable one. These studies indicate that when degradation occurred, it was often due to a decrease in open circuit voltage, and sometimes due to a decrease in fill factor [13].

In this paper, we focus our study on the effect of water ingress after the CdS deposition on device performance. We assess the potential degradation of the devices using various device characterization and simulation methods.

2. Materials and Methods

CIGS solar cells were fabricated using a three-stage co-evaporation process on soda-lime glass (SLG) substrates with the following structure: SLG/Mo/CIGS/CdS/i-ZnO/ITO. The molybdenum layer was deposited by DC magnetron sputtering using a two-step process, with the first step at high

argon pressure (5 mTorr) and the second at low pressure (1 mTorr) resulting in a tensile/compressive stress dipole. The CIGS films were deposited using a three-stage co-evaporation process [14]. The junction was formed by chemical bath deposition (CBD) of cadmium sulfide (CdS). The initial solution includes a mixture of H₂O, Cd(CH₃COO)₂ and NH₄OH and is kept in a hot bath at 70 °C for 1 min. Then, thiourea (H₂NCSNH₂), is added to the solution. Finally, the samples are placed for 16 min in the heated bath, resulting in an approximate CdS thickness of ~120 nm. This slightly greater thickness compared to standard device structures was intentional to ensure that potential effects due to moisture damage to CdS could be more easily identified. After the CdS deposition, half of the samples were soaked in deionized water (18.2 MΩ) at 50 °C for 24 hours (referred to as water-soaked (WS) samples), while the other half was stored in a dry box until window layer deposition (referred to as reference). Therefore, 24 hours after CdS deposition, all the samples (reference and water soaked) were put together in the sputtering system for window layer deposition. The window layer, consisting of 50 nm of i-ZnO and 150 nm of ITO was deposited at 5 mTorr of argon by RF sputtering. Finally, a metallic grid of Ni/Al/Ni was used as the front contact and was deposited by e-beam evaporation through a shadow mask. Solar cells were then defined by mechanical scribing with an active area of 0.5 cm².

Energy dispersive x-ray spectroscopy (EDS) and x-ray diffraction (XRD) measurements were performed on the reference films and on water soaked films to measure any overall change in composition or crystalline properties. The elemental depth composition was measured by time of flight secondary ion mass spectrometry (ToF SIMS). The solar cell characteristics were measured by current density-voltage (J-V) measurements and by external quantum efficiency measurements under simulated AM1.5G with a light intensity of 100 mW/cm² at 25°C.

3. Results and Discussion

After CdS deposition and water soaking of one set of samples, the overall composition and crystalline properties of both types of structures was assessed via XRD and EDS measurements. Each experiment was repeated a minimum of 10 times. The experiments lead to reproductive results, consistent with each other. As expected, no change was observed by either of these measurements before and after water soaking. Also, no obvious microstructural changes were observed by STEM [9].

Box plots of the device parameters for reference and water soaked samples are shown in Figure 1, while representative J-V and QE curves are shown in Figure 2 for the same type of devices. Note that a total of 75 cells have been tested for Figure 1. The devices after water soaking are systematically less efficient, with a decrease in all three major parameters: open circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF) (Figure 1), which is consistent with previous reports [15, 16]. One can see from Figure 2 that there does not seem to be much shunt in the device even after water soaking, while there is an increase in voltage dependent current collection. No dark-to-light crossover can be observed in either case. The QE curves indicate that the loss in current density is due to an overall decrease in current collection from 500 nm to 1200 nm. To extract diode parameters, a single diode model was used (Table 1). There is an increase in the reverse saturation current density (J₀) and diode ideality factor (A) after water soaking, indicating a deterioration of the diode quality. At the same time, the series (R_s) and the shunt resistance (R_{SH}) do not change significantly.

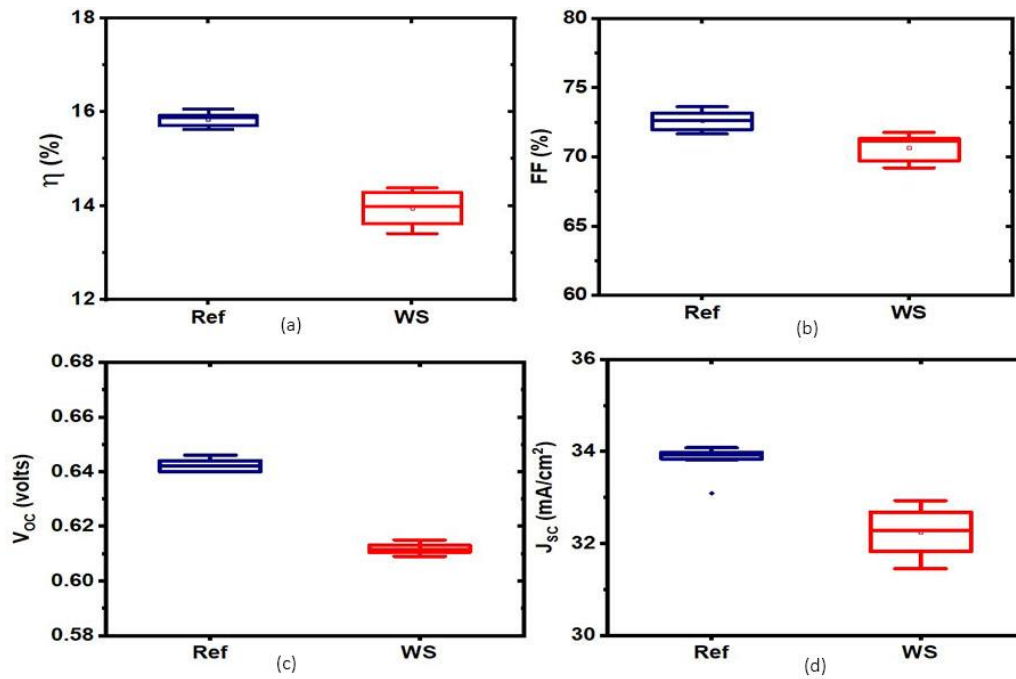


Figure 1 Box plots of device parameters comparing the device characteristics of reference devices (blue) and 24 hour water-soaked devices (red): (a) efficiency; (b): fill factor; (c): open circuit voltage; and (d): short circuit current density.

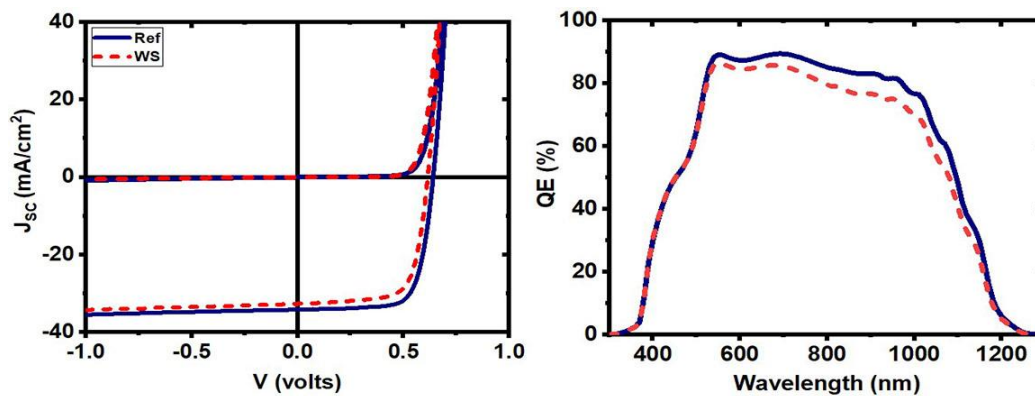


Figure 2 Representative current density-voltage (J-V) and quantum efficiency (QE) curves for reference (solid blue) and water soaked (dashed red) devices.

Table 1 Photovoltaic characteristics and diode parameters (dark j-v) of the representative cells shown in figure 1 and figure 2.

Sample	Voc (V)	Jsc (mA/cm ²)	FF (%)	η (%)	J ₀ (mA/cm ²)	A	R _S (Ω.cm ²)	R _{SH} (kΩ.cm ²)
Reference	0.64	34.0	73.2	15.9	1.0E -9	1.6	0.7	1.4
Water Soaked	0.61	32.7	71.3	14.3	8.0E -9	1.8	0.6	1.8

In order to better understand what could possibly be the underlying mechanism that causes degradation of the devices, simulations of the devices were performed using SCAPS. The main parameters used for the simulations are similar to the ones we used previously [9, 17]. The CIGS baseline parameters, such as electron affinity, dielectric permittivity, density of states, thermal velocity, mobilities, acceptor/donor density, were not changed. Parameters like thickness, transmission of the front contact and trap density were slightly modified to replicate the experimental curves.

One change was in the CdS thickness layer, which was set to 120 nm. The other main changes were in the transmission coefficient, which was changed from 89% for the reference sample to 86% after water soaking, and in the trap density properties. The change in transmission is likely due to a modification of the sample surface after water soaking, leading to an increase reflection.

Both the total trap density and the trap density peak were changed in the SCAPS simulation to fit the experimental data, from $1.2E +15 \text{ cm}^{-3}$ and $6.7E +15 \text{ cm}^{-3}$ for the reference sample to $3.0E +15 \text{ cm}^{-3}$ and $1.6E +16 \text{ cm}^{-3}$ for the water soaked sample. Figure 3 shows the comparison of the J-V and QE simulated data versus the measured data for both types of devices, indicating a good fit between the two.

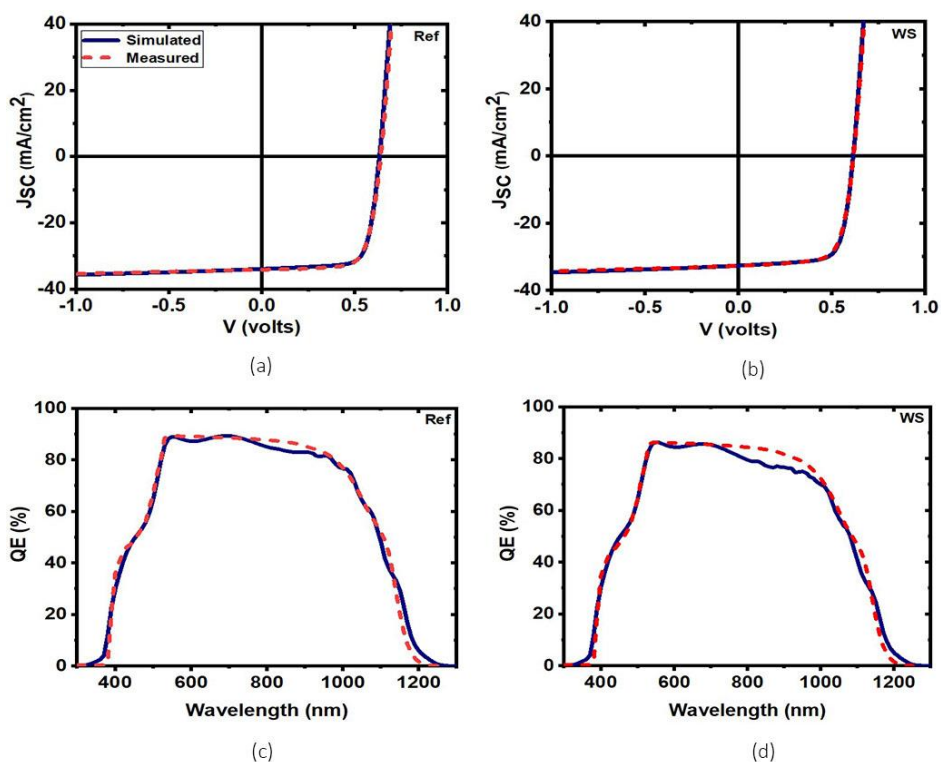


Figure 3 Simulated (dashed red) and measured (solid blue) current density-voltage and external quantum efficiency curves for the reference and water soaked device.

To try to further elucidate where this change in device efficiency could come from, SIMS depth profiles were measured on the samples with and without water soaking. Because we did not have an accurate standard to compare our sample to, no quantitative assessment can be done through the SIMS, but a comparative study of the elemental depth profiles is still possible. Figure 4 indicates clearly that no change in the main elements involved in the CIGS solar cells (Cu, In, Ga and Se) is occurring due to the water soaking, as one would expect, matching the results obtained by EDS and

XRD. The gallium profile is also the one expected via the 3-stage deposition process. The next key elements in a CIGS solar cell are the alkali elements, both Na and K (since we did not use any post-deposition treatment by RbF or CsF here), as can be seen in Figure 5. One can see that no change can be observed for K, while the Na signal decreases in the water soaked sample in comparison to the reference sample. It is known that the alkali metals diffuse from the SLG, through the molybdenum and into the CIGS. Afterwards, notably because the processes are done at much lower temperature, there is less diffusion of the alkali into the other layers. This can be seen for both Na and K from their profiles in the reference sample. Interestingly though, the Na profile is lower in the bulk of the CIGS after water soaking, indicating an out-diffusion of the Na through the CdS into the water during water soaking. The effect of alkali migration has been observed before and was correlated with losses in V_{OC} , FF and consequently in efficiency [18]. Interestingly, one can see that the oxygen content in the water-soaked sample is higher than for the reference sample, in the same location where the sodium is lower. One could therefore assume that both ions diffuse under a similar process at grain boundaries, while leaving K unaffected. The difference of behavior between Na and K might be partially explained by the smaller ionic radius of Na compared to K, or a difference in chemical affinity [19].

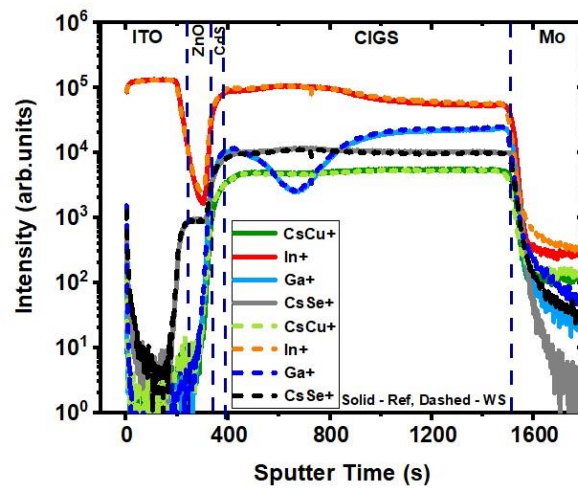


Figure 4 Secondary ion mass spectroscopy (SIMS) depth profiles for the main element of reference (solid lines) and water soaked (dashed lines) device.

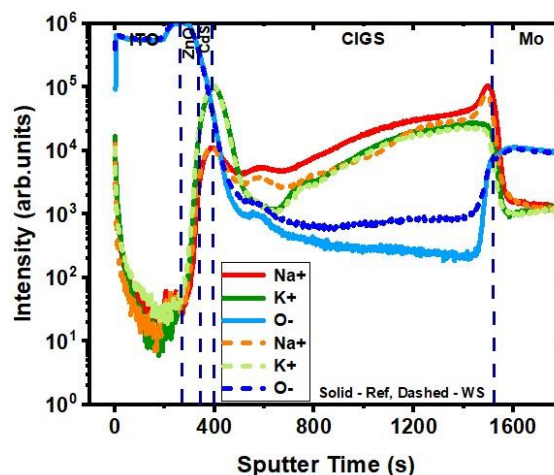


Figure 5 SIMS depth profiles of Na⁺, K⁺ and O⁻ in the reference (solid) and water soaked (dashed) device.

4. Conclusions

Because of the nature of the deposition process, often used for CdS buffer layers in CIGS solar cells, which is an aqueous chemical bath method, one would not assume that the resulting layer would be sensitive to water. However, given enough time, water soaking of a SLG/Mo/CIGS/CdS structure can also degrade the future device performance of completed devices. All device parameters are affected by this degradation, which involves primarily a change in the diode quality factor and reverse saturation current density, leading to an overall efficiency dropping from ~16% down to ~14%. Simulation of the devices via SCAPS indicate that a slight modification of the transmission (decreasing by 3%) and a slight increase in trap density properties (by a factor of 2) can yield such a change. The chemical origin of these changes seem to be in part due to the out migration of Na from the bulk of the CIGS and in-migration of O.

Author Contributions

Conceptualization, Sylvain Marsillac and Angus Rockett; validation, Deewakar Poudel, Shankar Karki, Benjamin Belfore, Grace Rajanand, Sina Soltanmohammad; formal analysis, Sylvain Marsillac, Angus Rockett, Deewakar Poudel, Shankar Karki, Benjamin Belfore, Grace Rajanand and Sina Soltanmohammad; writing—original draft preparation, Sylvain Marsillac, Angus Rockett, Deewakar Poudel, Shankar Karki, Benjamin Belfore, Grace Rajanand and Sina Soltanmohammad; writing—review and editing, Sylvain Marsillac, Angus Rockett, Deewakar Poudel, Shankar Karki, Benjamin Belfore, Grace Rajanand and Sina Soltanmohammad; supervision, Sylvain Marsillac, Angus Rockett.

Competing Interests

The authors have declared that no competing interests exist.

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