Characterization of Cu(In,Ga)Se_2 Electrodeposited and Co-Evaporated Devices by Means of Concentrated Illumination

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***Abstract*—We present a new Cu(In,Ga)Se_2 characterization tool: Cu(In,Ga)Se_2 microcells. By creating pixels on a Cu(In, Ga)Se_2 substrate, we are able to test electrically different locations. Moreover, because of the reduced size of the cells, (5-to 500-μm wide), heat and spreading resistance losses are made negligible, which make high flux characterizations available. We analyze current–voltage curves under high concentration to gain insight in the physical properties of Cu(In,Ga)Se_2 cells. From our analysis, Cu(In,Ga)Se_2 electrodeposited absorbers present resistivity fluctuations that are much more important than co-evaporated ones. These absorbers, as they present more electronic defects, are also more affected by the V_{oc} increase under intense fluxes, and the efficiency gains can be very significant: up to 6% absolute efficiency points at less than 50 suns.**

***Index Terms*—Current–voltage characteristics, photovoltaic cells.**

I. Introduction

THE chalcopyrite compound Cu(In,Ga)Se_2 has proven to be very efficient as a solar cell absorber, with over 20% efficiency reached in 2011 [1]. Various techniques are available to synthesize Cu(In,Ga)Se_2, such as co-evaporation, sputtering, electrodeposition, and printing, to name a few. Each absorber deposition process leads to distinct opto-electronic properties of the corresponding solar cells. It is thus important to have characterization tools that can link final devices characteristic to features of the deposition process. In this paper, we propose to compare Cu(In,Ga)Se_2 solar cells with either co-evaporated or electrodeposited absorbers. In order to gain insight into the differences between these two processes, we use a novel technique. We characterize a pixilated substrate under various illumination conditions (dark, AM1.5 G, or concentrated illumination). Conclusions on material quality, homogeneity, or sensitivity to temperature elevation are given.

II. Fabrication and Characterization Methods

A. Approach

Cu(In,Ga)Se_2 solar cells are studied by creating pixels on a large substrate. Thus, local characterization of opto-electronic properties is possible. The cells studied here are of the type sodalime glass/Mo/Cu(In,Ga)Se_2/CdS/ZnO/ZnO:Al, where Mo and ZnO layers are deposited by sputtering and CdS by chemical bath deposition. Two types of absorbers are used in this study.

B. Absorber Synthesis

Two different Cu(In,Ga)Se_2 absorber synthesis processes are compared in this paper.

The first absorber type is obtained by co-evaporation, in a three-stage process, as described in [2].

The second process is the electrodeposition of Cu(In,Ga)Se_2 precursors and subsequent annealing. The electrodeposition is carried out in a single step, in an aqueous solution of Cu(II), In(III), and Ga (III) nitrates [3]. The precursor layer is then transformed in a metallic layer by annealing in a reducing atmosphere (H_2 containing atmosphere). The Cu(In,Ga)Se_2 layer is formed after selenization by annealing in a selenium saturated atmosphere. This process can give on conventional laboratory cells (0.1 cm^2) around 10% efficiency [3].

C. Microcells Fabrication

The CdS and ZnO layer are subsequently deposited by chemical bath deposition and sputtering. In order to pixelate the substrate, microcells are created by using a patterned insulating layer. A SiO_2 layer is deposited on top of the ZnO layer prior to the deposition of ZnO:Al and patterned by UV-lithography. Thus, microdiodes are only created in the holes patterned in the insulating layer. More details on the patterning process can be found elsewhere [4].

The microcell size varies from 500-μm down to less than 10-μm in diameter. On each sample, 244 microcells are patterned. The pixels are distant from one another by 1 mm.

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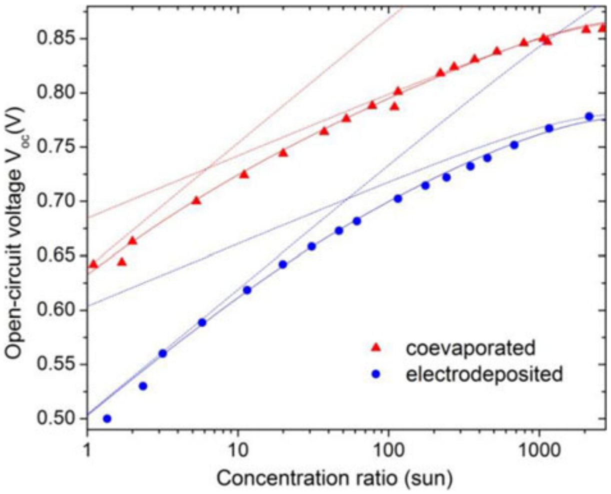

Fig. 1. $V_{\rm oc}$ versus concentration ratio for co-evaporated and electrodeposited Cu(In,Ga)Se$_2$ absorbers. The microcells have a diameter of 15 μm. The lines correspond to the component of open-circuit voltage of ideality factor 1 and 2. The lines deviates from linearity at high concentration because of a temperature increase [4].

D. *Microcell Electrical Characterization*

The microcells are tested individually by current–voltage measurements under dark and AM1.5 G illumination (class AAA Newport solar simulator). Tests under 532-nm laser illumination are also carried out, with varying incident light intensities, using neutral density filters.

The AM1.5 G tests enable us to determine the average short circuit current density. Then, in the range where short-circuit current density is proportional to the incident light power, the concentration ratio is calculated as $C = J_{\rm sc}/J_{\rm sc}\,(AM1.5G)$.

III. RESULTS AND DISCUSSION

A. *Comparison of Electrodeposited or Coevaporated Cu(In,Ga)Se$_2$ in Terms of $V_{\rm oc}$–$J_{\rm sc}$*

Both Cu(In,Ga)Se$_2$ solar cells show logarithmically increasing open-circuit voltage under concentrated illumination (see Fig. 1). This behavior is in accordance with expected behavior, as the concentrated illumination increases the photogenerated carrier densities and, thus, the quasi-Fermi level splitting.

In Fig. 1, the experimental data are fitted with two lines, corresponding respectively to an ideality factor of 1 and 2, according to the equation

$$V_{\rm oc} = \frac{2kT}{q}\ln\left(\frac{-J_{02} + \sqrt{J_{02}^2 + 4J_{01}C \times J_{\rm sc}\,(AM1.5)}}{2J_{01}}\right) \tag{1}$$

where J_{01} and J_{02} are the saturation currents of ideality 1 and 2, respectively, and C is the concentration ratio, as defined earlier by $C = J_{\rm sc}/J_{\rm sc}(AM\,1.5\,{\rm G})$.

It is clear that the slope of the $V_{\rm oc}$ curve corresponding to the electrodeposited sample is steeper. This is because of the fact that on an electrodeposited sample, the saturation current corresponding to an ideality factor of 2, J_{02}, is more important than for the co-evaporated samples. Indeed, from dark measurements, we obtain J_{02} between 10^{-3}–10^{-2}mA/cm^2, compared with 10^{-4}–10^{-3}mA/cm^2 for co-evaporated samples, whereas J_{01} stays of the order of 10^{-10}mA/cm^2 for both samples. Thus, the points where the $V_{\rm oc}$–$J_{\rm sc}$ curve change from a n = 2 slope to a n = 1 slope is pushed to higher concentration ratios on electrodeposited samples, which results in a higher $V_{\rm oc}$ gain under concentration. This behavior is in line with previously published results, which shows that defective solar cells are more sensitive to gains under concentration [5], [6].

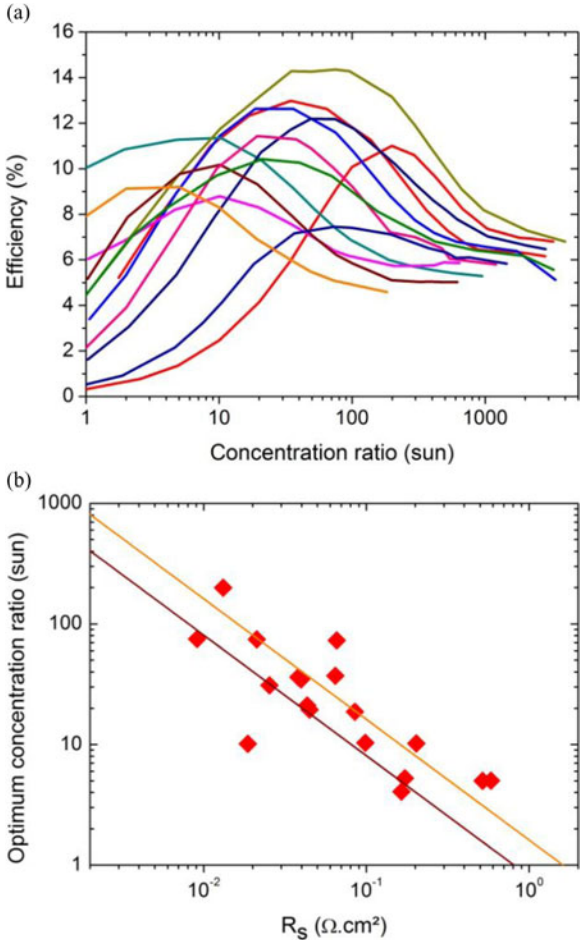

Fig. 2. (a) Efficiency versus concentration for the electrodeposited sample for different microcells of various sizes and (b) optimum concentration ratio as a function of the series resistance under AM1.5 G illumination. The orange line corresponds to the theoretical relation (2) with n = 2 and the brown one with n = 1.

B. *Resistivity Analysis*

To gain more insight in the differences between co-evaporated and electrodeposited samples, we analyze the efficiency as a function of the concentration level.

The efficiency increases with concentration at low concentration because of $V_{\rm oc}$ gains [see Fig. 2(a)]. Then, the efficiency decreases because of excessive resistive losses, according to the expected relationship [7]

$$R_s \times C \times J_{\rm sc}\,(AM\,1.5) = nkT/q \tag{2}$$

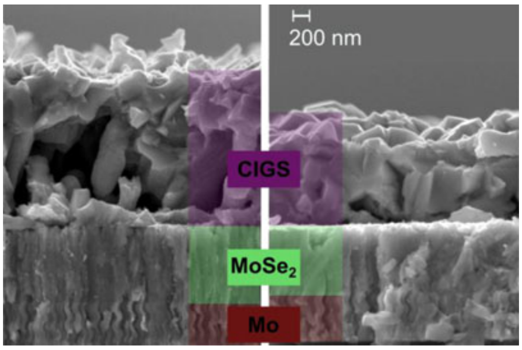

Fig. 3. SEM images of the cross section of the same electrodeposited Cu(In,Ga)Se_2 layer at two different locations. The colors highlight the Mo, $MoSe_2$, and Cu(In,Ga)Se_2 layers with various thicknesses.

where R_s is the series resistance, C is the concentration ratio, and $J_{\text{sc}}(AM\,1.5)$ is the short-circuit current at AM1.5 G illumination.

Contrary to what is usually seen on co-evaporated samples [4], the concentration ratio at which the efficiency is maximum, which is called optimum concentration ratio, is not constant over the sample. It varies from pixel to pixel, independently of the microcell size. Fig. 2(a) contains the characteristics of microcells of different sizes, but no correlation is found between the size and the form of the efficiency versus concentration curve. This indicates that the resistivity of the electrodeposited sample varies on the substrate at the mm scale, whereas that of the co-evaporated samples is highly homogeneous. We can directly correlate the optimum concentration ratio to the pixel series resistance under AM1.5 G illumination [see Fig. 2(b)].

A possible explanation for these local variations of resistivity is the inhomogeneity of Cu(In,Ga)Se_2 and $MoSe_2$ layer thickness on electrodeposited samples. A scanning electron microscopy analysis of an electrodeposited sample shows that the absorber thickness can vary up to a factor three on the sample. Moreover, during selenization, $MoSe_2$ is formed from the Mo layer, and its thickness varies on the sample from 750 to 1100 nm (see Fig. 3). On the contrary, on co-evaporated samples, the $MoSe_2$ layer is usually less than 20-nm thick. Another possible explanation for resistivity variations is the fact that the Cu(In,Ga)Se_2 electrodeposited layer can be denser or more porous, especially at the $MoSe_2$/Cu(In,Ga)Se_2 interface depending on the location. Thus, vertical current flow in the solar cell can encounter higher or lower resistance.

For the record microcell obtained on an electrodeposited substrate, we note a 15% efficiency at 33 suns equivalents, compared with 9% efficiency under AM1.5 G illumination.

It is interesting to note that the series resistance varies with the concentration level (see Fig. 4). This is primarily because of the photodoping of the Cu(In,Ga)Se_2 absorber. This behavior was observed on co-evaporated samples [8]. From the decay of series resistance, one can extract an effective diffusion length, as the series resistance can be expressed as [8]

$$R_{s_{\text{microcell}}} = R_c + \frac{R_{s0}}{\left(1 + \left(1 + \frac{\mu_p}{\mu_n}\right) \times \left(\frac{L_n}{t}\right)^2 \times \frac{q^2 \times EQE \times R_{s0} \times P_{\text{light}}}{kT \times h\nu}\right)} \quad (3)$$

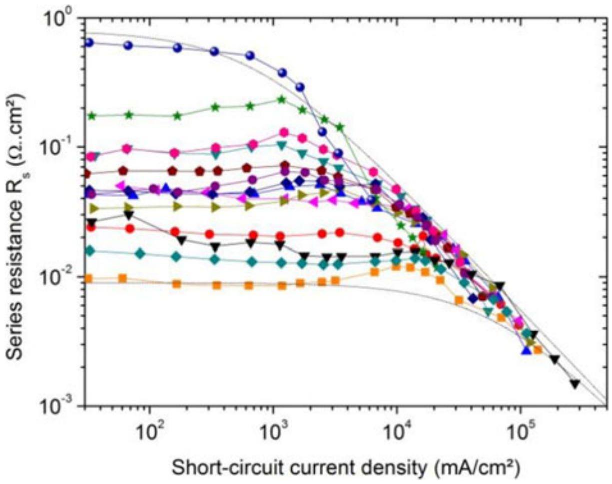

Fig. 4. Evolution of series resistance with concentration ratio of various electrodeposited microcells of different sizes.

where R_c is the light independent series resistance, R_{s0} the absorber resistance in dark condition, $R_{s0} = t/q\mu_p p_0$, with q the elementary charge, t the absorber thickness, μ_n (μ_p) the electron (hole) mobility, P_{light} the incident light power density, L_n the minority carrier diffusion length in the absorber, EQE the external quantum efficiency at 532 nm, kT/q the thermal voltage, and hν the energy of the incident photons. We can estimate that in electrodeposited samples the diffusion length is of the order of 0.4 μm, which is nearly one order of magnitude smaller than in co-evaporated samples. This is consistent with the lower crystallinity and higher defect concentration in electrodeposited absorbers. It can also stem from the fact that the Ga gradient in electrodeposited absorbers is not optimum, and thus, the effective diffusion length is not improved by grading, contrary to the co-evaporated samples with either V-shape or linear grading.

C. Temperature Effect

As we test the microcells under concentrated illumination, the temperature of the device can increase. This increase is linear with the incident light power, as thus the short-circuit current density: $T = T_0 + \kappa \times j_{\text{sc}}$, where T_0 is the temperature of the cell in the dark, or the ambient temperature, and κ is a proportionality factor. The consequence of this temperature elevation is the decrease of the open-circuit voltage at high concentration (see Fig. 1). Indeed, the V_{oc} can be expressed as a function of the short-circuit current density as [4]

$$V_{\text{oc}} = \frac{E_g}{q} - \frac{2kT_0}{q} \times \left(1 + \frac{\kappa}{T_0} J_{\text{sc}}\right) \times \ln\left(\frac{2J_{001}}{-J_{002} + \sqrt{J_{002}^2 + 4J_{001}J_{\text{sc}}}}\right) \quad (4)$$

where q is the elementary charge, and T_0 the temperature of the cell in the dark, Eg the absorber bandgap energy, and J_{001} and J_{002} the dark saturation current prefactors. By fitting the $V_{\text{oc}} - J_{\text{sc}}$ curve in this high illumination regime, we can evaluate κ and, thus, conclude on the thermal conduction properties

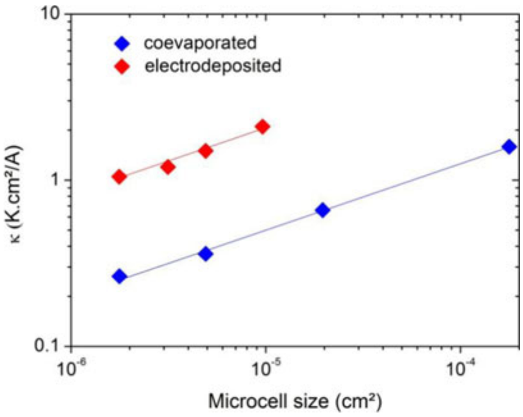

Fig. 5. Factor κ as a function of the cell size.

of the different cells (see Fig. 5). One can see that the factor κ increases with increasing cell size. This scale effect is easily explained as with increasing laser spot size, the heat evacuation is less efficient [4], [9]–[11]. Indeed, the ratio of volume heated over the surface for heat exchange is increased. One can also see that the factor tends to be more important on electrodeposited samples. The Mo back contact layer plays the role of a heat spreading layer in the Cu(In,Ga)Se$_2$ stack, because of its large thermal conductivity (1.37 W/cm/K [12]). In electrodeposited cells, the Mo layer is partly consumed and transformed in MoSe$_2$ by selenization, whose thermal conductivity is lower (i.e., $\sim 10^{-2}$W/cm/K [13]). This contributes to explain that these cells are more sensitive to temperature elevation than the co-evaporated ones. Other factors can also play a role in the temperature dependence of electrodeposited cells, such as the low density of Cu(In,Ga)Se$_2$ close to the molybdenum interface (see Fig. 3), that prevents an efficient thermal conduction between these two layers.

IV. CONCLUSION

By means of the pixelation of Cu(In,Ga)Se$_2$ solar cells, we were able to study co-evaporated and electrodeposited Cu(In,Ga)Se$_2$ solar cells. As expected, the electrodeposited cells are more inhomogeneous, in terms of resistivity, for example. Because of a higher concentration of defects, electrodeposited absorbers are also more sensitive to efficiency gains under concentration. The record electrodeposited microcell reaches 15% efficiency under 33 suns equivalent. It is very interesting in the perspective of using the Cu(In,Ga)Se$_2$ device under concentration. In the future, the pixelation could be used to couple different characterization techniques, and complement classic cartographic measurements, by providing the local electrical properties of the device.

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