Locally-confined electrodeposition of $Cu(In,Ga)Se_2$ micro islands for micro-concentrator solar cells

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***Abstract* — The thin-film micro-concentrator solar cell concept promises to significantly reduce the consumption of the critical raw materials In and Ga by using a micro lens array to illuminate a regular array of $Cu(In,Ga)Se_2$ micro solar cells. We present the materials-efficient fabrication of micro solar cells by electrodeposition into holes inside a SiO_2 insulating matrix. The electrodeposition process shows a strong dependence on the hole size due to lateral diffusion in the solution, leading to faster deposition at the circumference of the holes. A calibration curve for the deposited $CuInSe_2$ thickness as a function of hole size is deduced. $Cu(In,Ga)Se_2$ micro solar cells were fabricated by sequential deposition of Cu and In-Ga, followed by a selenization process, leading to devices with 4.6% efficiency under 34 suns. Using finite element simulations, the heat transport in the micro-concentrator solar cells is shown to be beneficial.**

Keywords – photovoltaic cells; CIGS; concentration, electrodeposition

I. Introduction

The availability of critical raw materials such as In and Ga has been suggested as a potential limitation to the large scale deployment of $Cu(In,Ga)Se_2$ (CIGSe) photovoltaics technology [1]. To overcome this concern, different approaches are currently being explored. Replacing In and Ga completely is possible through the kesterite compound family $Cu_2ZnSn(S,Se)_4$; however, efficiencies have so far been limited [2]. On the other hand, the use of In and Ga can be reduced by making the absorber thinner. However, back contact recombination becomes relevant and requires the introduction of appropriate passivation layers [3-5]. Another approach to reduce costly or critical raw materials is the use of concentrated solar cells, which is widely applied for III-V multi-junction solar cells. More recently, CIGSe concentrator solar cells have been proposed and realized [6-7]. This micro-concentrator solar cell concept aims at using micrometer-sized CIGSe solar cells arranged in a regular array and then using a micro lens array to focus impinging light onto the micro solar cells. Due to the micrometer size scale the thickness of such a micro-concentrator solar cell can be similar to a regular CIGSe solar module. Compared to the reduction of the CIGSe thickness, which allows for materials savings on the order of 10 times, for the micro-concentrator solar cell concept the materials savings depend on the selected concentration factor and can be much higher, e.g. a few 100 times. In addition to materials savings, also higher light to power conversion efficiencies are possible due to the expected increase in the open-circuit voltage when concentrated sunlight is used [6].

Initial proof-of-concept studies have used complete CIGSe thin film solar cells and subsequent etching, scratching, or shadowing to define the micro solar cells [7,8]. Only recently, work has been presented that demonstrates CIGSe micro-solar cells using a materials-efficient deposition process. Line-shaped [9] and island-shaped [10] micro solar cells have been realized where the CI(G)Se absorber layer was grown using area-selective electrodeposition onto a structured Mo back contact or holes inside a SiO_2 insulating layer, respectively.

In this work, we present results showing that the electrodeposition process of $CuInSe_2$ (CISe) into holes of a SiO_2 layer depends on the hole size. We present efficiency data as a function of concentration for a 200 μm diameter micro solar cell. Finally, finite element simulations show that the heat management in micro-concentrator solar cells is superior to regular cm-sized concentrator solar cells and that passive cooling is sufficient to avoid a detrimental effect of the cell temperature on the power conversion efficiency.

II. Experimental

CI(G)Se micro solar cells were fabricated by electrodeposition. To provide for an area-selective deposition, we used pre-structured substrates consisting of a SiO_2 insulating layer (2 μm thickness) on top of a standard Mo/glass substrate. Photolithography and reactive ion etching (RIE) were used to produce circular holes of different sizes into the SiO_2 layer down to the Mo back contact [10].

Two approaches were used for the electrodeposition of the CI(G)Se absorber layer. For the study of the hole-size dependence, the co-deposition of $CuInSe_2$ was performed in a solution of 4.0 mM SeO_2, 3.89 mM $In_2(SO_4)_3 \cdot H_2O$, 2 mM $CuSO_4 \cdot 5H_2O$, and 0.26 M $Li_2SO_4 \cdot H_2O$ [11], and using a three-electrode setup with a saturated calomel reference electrode and a voltage of -0.55 V.

$Cu(In,Ga)Se_2$ was deposited into the holes in the SiO_2 layer using a sequential deposition of Cu, followed by In and Ga. Cu was deposited using a rotating disk electrode (RDE), a basic Cu solution (3.0 mol/l NaOH, 0.2 mol/l sorbitol, and 0.1 mol/l $CuSO_4 \cdot 7H_2O$), and a voltage of -1.15 V vs. a Ag/AgCl

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reference electrode. Subsequently, In and Ga were deposited in an In-Ga electrolyte (50 mmol/l $InCl_3$ and 29 mmol/l $GaCl_3$ in reline), at 60ºC inside a N_2-filled glovebox.

To obtain suitable CI(G)Se absorber material, the samples were annealed in a tube furnace in Se atmosphere. The CISe absorber was annealed at 500 ºC for ~15 min, while for the Cu-In-Ga stack, a pre-anneal (30 min at 100 ºC) was followed by a selenization step (20 min at 450 ºC). In both cases, Se was evaporated from an elemental Se precursor.

Complete solar cell devices were fabricated performing a KCN etch to remove $Cu_{2-x}Se$ phases, followed by a standard CdS chemical bath deposition (50-70 nm) and sputtering of a i-ZnO (90 nm) and ZnO:Al (350 nm) double layer [12].

Finite element method (FEM) simulations were carried out to study the size and concentration factor dependent temperature of the micro solar cells. A 3D geometry was analyzed, consisting of a soda-lime glass substrate (2 mm) and a Mo back contact (1 µm). A square-shaped $CuInSe_2$ micro island (2 µm thick) was embedded in an insulating SiO_2 layer (2 µm thick). A single ZnO layer (1 µm thickness) for the front contact was followed by a quartz layer (1 mm thick) to mimic the optical lens. The $CuInSe_2$ is considered as a homogeneous heat source corresponding to AM1.5 illumination multiplied by the concentration factor. Convective cooling is applied at the top and bottom of the cell (10 W/m^2).

III. RESULTS

Fig. 1 shows scanning electron microscopy (SEM) images of $CuInSe_2$ absorber material (prior to selenization) deposited into holes in SiO_2 with different diameters, realized in the same deposition process (20 min). A clear dependence of the deposit on the hole size is noticed, where for smaller holes a ring-like structure with irregular edges appears, while for larger holes a nicely defined circular CISe deposit is obtained. The thickness of the deposited CISe material was determined by profilometry and the results are shown in Fig. 2 (open circles). The deposited CISe thickness decreases with increasing hole size. In the literature, such an effect has been reported for the electrodeposition of a single species [13], and has been interpreted as a lateral diffusion of species in the solution, from areas where no deposition can take place to those where deposition occurs. The current governing the electrodeposition was described as:

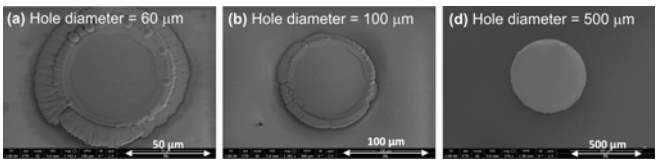

Fig. 1. Electrodeposited $CuInSe_2$ micro islands inside a SiO_2 matrix with different hole sizes. All micro islands were deposited in the same deposition process.

$$I = i \cdot n = 4 r z F D C n , \quad (1)$$

where I is the total current, i the current per micro hole, n the number of holes, z the number of electrons transferred, F the Faraday constant, D the diffusion coefficient, and C the concentration of the solution. For a recessed hole of depth L, a correction factor of $\pi r/(4L+\pi r)$ needs to be applied [13].

For the present case of the co-deposition of Cu, In, and Se, we consider the sum of the individual currents for Cu, In, and Se deposition. To model the deposition current, we consider a single diffusion coefficient of $D = 6.5\times10^{-6}$ cm^2s^{-1} (a typical value for electrodeposition of Cu), and the sum of the weighted (by the number of transferred electrons) molar concentrations of Cu, In, and Se. Considering the duration of the deposition (20 min), the density of $CuInSe_2$ and the area of each hole, the thickness of the deposited CISe layer was computed (red line, Fig. 2). The thickness from the simple model reasonably describes the trend of the hole-size dependence of the deposited CISe. However, the model overestimates the thickness by a factor of about 4. We attribute this discrepancy to several issues: (i) over-simplification of the model by using only one diffusion coefficient, (ii) the thickness was measured at the center of the hole, and (iii) neglecting the ring-like CISe deposit at the circumference. In fact, the deposition process in the smaller holes changes throughout the deposition, where initially deposition in a recessed hole according to Eq. (1) with the respective correction is considered. When the thickness reaches 2 µm, deposition on a flat electrode occurs, and when the thickness exceeds 2 µm, lateral growth occurs, leading to the CISe deposits with an irregular edge (see Fig. 1). Therefore, Eq. (1) is insufficient to describe the results of Fig. 1 and 2. Nevertheless, the experimental data of Fig. 2 can be used as a calibration curve to estimate the deposition time required to deposit a desired thickness of CISe into the SiO_2 hole matrix, which would ideally the same thickness as that of

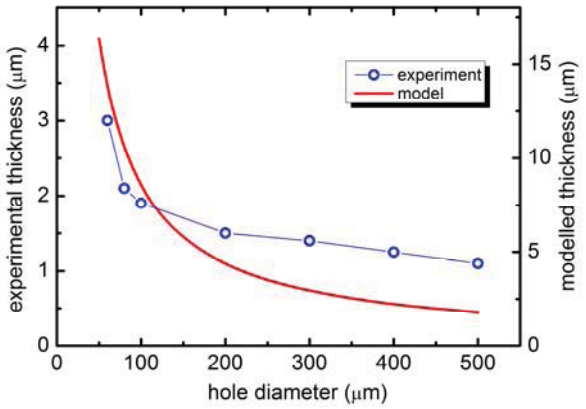

Fig. 2. Thickness of electrodeposited CISe micro islands in holes in a SiO_2 matrix depending on the hole diameter after 20 min deposition time. Experimental data (open circles) are compared to a model (Eq. (1) including the correction for recessed holes) reproducing the trend reasonably well.

the SiO_2 matrix, i.e. 2000 nm in the present case. Additionally, for the micro-concentrator solar cell application, a regular array with holes of the same size is used.

To test the micro-concentrator concept, we prepared micro solar cell devices with a diameter of 200 µm by the sequential electrodeposition of first Cu and then In-Ga, which were subsequently selenized to form CIGSe. Current-voltage curves were measured with a red laser at different intensities emulating concentrated illumination. The efficiency (Fig. 3) increases logarithmically with concentration, with a deviation from this dependency for concentrations higher than 30x, which could be due to resistive losses in the window layer or cell overheating.

From conventional concentrator photovoltaics it is well known that the temperature of the solar cell under concentrated illumination can increase quite significantly, requiring special (active or passive) cooling efforts. To analyze the micro-concentrator solar cell concept in terms of heat management, we conducted FEM simulations. Fig. 4 (a) shows the temperature of the solar cell as a function of the cell size for an intermediate (49x) and a high (400x) concentration factor. Larger cells are more strongly affected by heat-up, than smaller ones, where the heat can be effectively dissipated on the micrometer length scale to the surrounding SiO_2 matrix. Using typical values for the temperature coefficient of the efficiency (-0.4%/K) and the efficiency increase with concentration (+2%/decade), we estimate the size dependence of the efficiency (Fig. 4b). These results clearly demonstrate that it is beneficial to reduce the size of the micro solar cell to below 100-200 µm and use concentration factors lower than 400x.

IV. Conclusions

We fabricated CI(G)Se micro solar cells using two different electrodepostion processes by deposition inside holes in a SiO_2 matrix. For the co-deposition of $CuInSe_2$, we observed a hole-size-dependent deposition process, which follows the trends predicted for electrochemical processes in micro-electrodes. CIGSe micro solar cell devices were fabricated and exhibit an absolute efficiency increase from below ~2% to ~4.6% when increasing the concentration of the illumination from 1 to 35 suns. Finally, FEM simulations show that the temperature increase due to the concentrated illumination can be kept reasonably small for micro solar cells below about 100 – 200 µm.

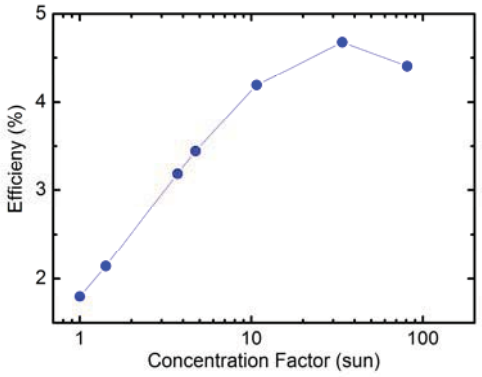

Fig. 3. Efficiency of a 200 µm micro solar cell.

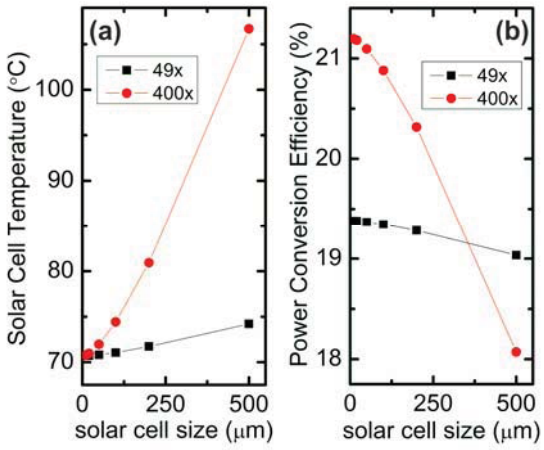

Fig. 4. (a) Simulated temperature and (b) estimated efficiency of the micro solar cells as a function of size and for two concentration factors.

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