A comparison of different selenisation approaches for solution-processed Cu(In,Ga)(S,Se)$_2$ solar cells

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Abstract

Hydrazine-free Cu(In,Ga)Se$_2$ (CIGS) absorbers were fabricated using a low-cost atmospheric deposition method. The structural and electrical properties of thin film absorbers and the resulting solar cells processed using two different selenisation approaches were compared. A double selenisation process showed improved crystal structure compared to a single selenisation step, resulting in improved absorption throughout the spectrum and conversion efficiencies reaching 9.3%.

Introduction

The chalcopyrite semiconductor Cu(In,Ga)Se$_2$ (CIGS) is currently the best performing polycrystalline thin film solar cell technology reporting a record power conversion efficiency (PCE) of 22.6% (ZSW) [1]. The most efficient devices so far are typically fabricated by expensive vacuum-based techniques such as co-evaporation and sputtering. Atmospheric processing of CIGS solar cells becomes an attractive alternative to the vacuum-based techniques due to its lower production costs and the compatibility with roll-to-roll processing [2]. The best true solution-based device reached PCE of 17.3% using the extremely hazardous and toxic solvent hydrazine [3]. Recently, a much safer solvent mixture of 1,2-ethylenediamine and 1,2-ethanedithiol was found to successfully dissolve nine bulk V$_2$VI$_3$ chalcogenide semiconductors [4]. In our previous work, the same solvent mixture was used to effectively dissolve copper sulphide, indium sulphide and gallium in the presence of excess selenium for thin film chalcopyrite solar cell applications. Solar cells deposited by spray-coating of these precursors followed by selenisation exhibited PCEs of 8% for CIS and 9.8% for CIGS [5]. The performance of the final photovoltaic device is closely related to the grain size and the film quality (cracks, voids and adhesion), therefore selenisation is a critical step in the absorber formation. The resulting film quality is dependent on the selenisation reactor configuration and the parameters used, such as the temperature, pressure and heating duration [6].

The purpose of this work is to study the effect of selenisation approaches on the morphological and electrical properties of the sprayed CIGS absorber films. Typically, the solution processed absorbers suffer from incomplete recrystallization upon selenisation [7]. With the aim to fully recrystallize the absorber, an alternative double selenisation method was applied and compared to the baseline process, which is a single selenisation step.

Experimental

The CIGS absorber films were prepared by a two-step process, consisting of spraying the precursor solutions onto a Mo-coated substrate and post-deposition selenisation. The solution preparation and deposition procedure were identical as in our previous work [5]. The Cu$_{0.9}$In$_{0.7}$Ga$_{0.3}$Se$_2$ precursor solution was deposited in atmospheric conditions using a chromatography atomizer. The final film consisted of 6 sprayed layers in total. In between each spraying a drying step was performed to evaporate excess solvents. The as-deposited films were then thermally annealed in Se atmosphere to recrystallise the absorber. Two different selenisation approaches were performed using a tube furnace with two separately heated zones. The sample was positioned inside a partially closed graphite box containing Se pellets. The graphite box was then placed in the one zone of the furnace heated at 540°C for 50 min, including the ramping (~40°C/min). The working tube was purged with nitrogen three times prior to the annealing and the starting pressure was set to 400 Torr. "Single selenisation" is the case where the

film is selenised after depositing 6 separate layers. For the "double selenisation", a thinner absorber layer (3 sprayed layers) was selenised using the same starting conditions, then the spraying and selenisation was repeated [8]. The first and the second selenisation lasted for 30 and 40 min respectively. The devices were completed with the chemical bath deposition of CdS followed by intrinsic ZnO and Al doped ZnO (AZO) deposited by RF magnetron sputtering.

The grain structure of the absorber films was characterised using a JEOL JSM-7800F Field Emission Scanning Electron Microscope (FE-SEM). The electrical characterisation includes JV measurements under 1000 W/m^2 illumination. A Multi-laser LBIC (Laser-Beam Induced Current) measurement system using 11 diode lasers covering wavelengths ranging from violet (405nm) to the near infrared region (1060nm) was used to investigate the local spectral response and external quantum efficiency (EQE) of the device [9].

Results and Discussion

The SEM cross-sections of the two devices processed by single and double selenisation are shown in Fig. 1.
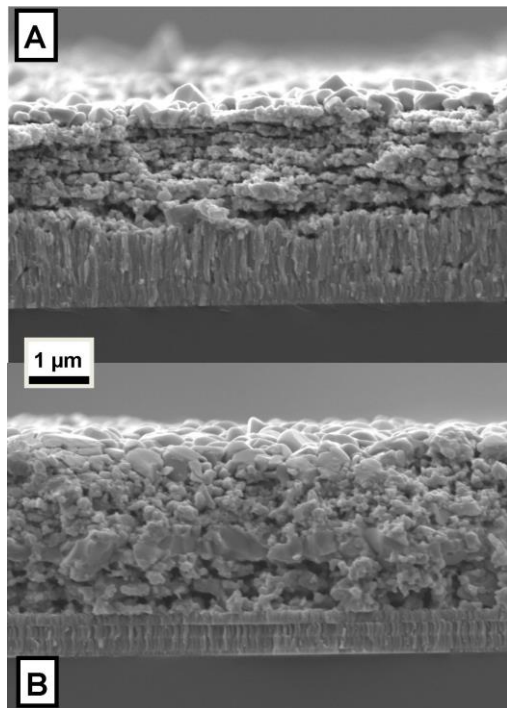

Figure 1 *SEM cross-sections of a) single b) double selenised CIGS absorber*

The single-time selenised absorber is incompletely-crystallised with slightly bigger grains on the top and a relatively porous bulk, where the individual sprayed layers can clearly be seen. Variation of selenisation conditions in terms of temperature, pressure and duration conditions for this selenisation configuration did not significantly improve crystallisation. Instead, the fine-grained layer persisted with the same thickness underneath the crystallised top layer. Moreover, the higher starting pressures result in excessively thick MoSe$_2$ layer contributing to the high series resistance (R$_S$) of the device and occasionally causing delamination. In the cross-section of the double selenised absorber, the first deposited stack of layers is clearly distinguished from the second. The large grains, normally visible on the top of a selenised stack, are now present in the middle of the absorber (top of the first selenised stack of layers), as well as on the top surface. The presence of large grains in the bulk and not only on the surface is expected to improve carrier collection. Therefore this selenisation approach seems to improve the absorber grain structure and it is expected that it will have an effect on the device electrical properties. However, the absorber is still incompletely crystallised. In addition, the back contact in this device shows only a thin MoSe$_2$ layer. This is due to a Mo/MoN$_X$/Mo multilayer that was used instead of a bare Mo, in order to prevent delamination due to a very thick MoSe$_2$ layer, which would form for selenisation times longer than 70 min. MoN$_X$ is acting as a barrier layer to the Se diffusion and hence limiting the MoSe$_2$ formation [10].
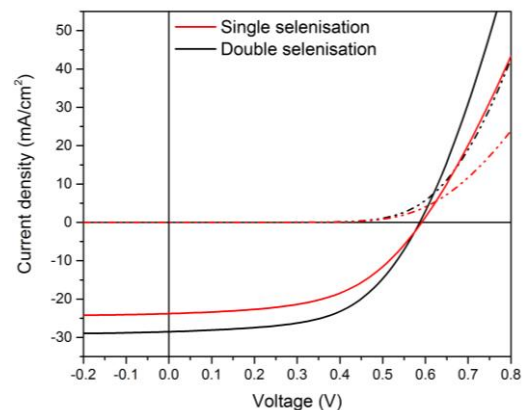

Figure 2 *JV curves for different selenisation configurations*

The light and dark JV characteristics for the samples processed with each selenisation approach are displayed in Fig. 2. The fundamental PV parameters e.g.

open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF) and efficiency are shown (Table 1).

Table 1 *Electrical performance of the three types of selenisation*

	V_{OC} (V)	FF (%)	J_{SC} (mA/cm^2)	Eff (%)
Single	0.591	52.5	23.8	7.38
Double	0.586	55.7	28.5	9.30

The box plots of the key performance indicators measured on six adjacent cells of each device are shown in Fig. 3.
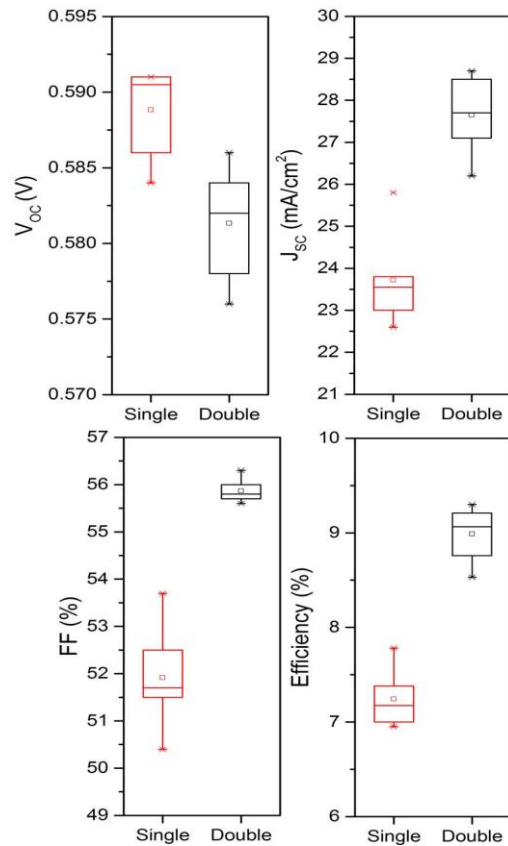

Figure 3 *Box plots showing the key performance indicators of the solar cells obtained using the two selenisation approaches*

The cells processed with the single selenisation step show a slightly better V_{OC}. However the J_{SC} and FF are significantly increased for the double selenisation step, leading to efficiencies up to 2% higher than the single selenised absorber. The MoN$_X$ barrier layer at the back contact can play a part in the improvement of the R_S seen on the JV curves; however it could also be responsible for the lower voltage. In fact, when the barrier layer was combined with a single selenised absorber, it resulted in

low V_{OC} of 460 mV. The overall improved electrical performance of the device with double selenised absorber is in agreement with the SEM cross-section showing improved crystallisation in the bulk. To test the absorption properties of both devices, a multi-laser LBIC measurement was performed on the same cell. The EQE spectra measured on each point of the cell was mapped and is displayed at four different wavelengths for both solar cells in Fig. 4.
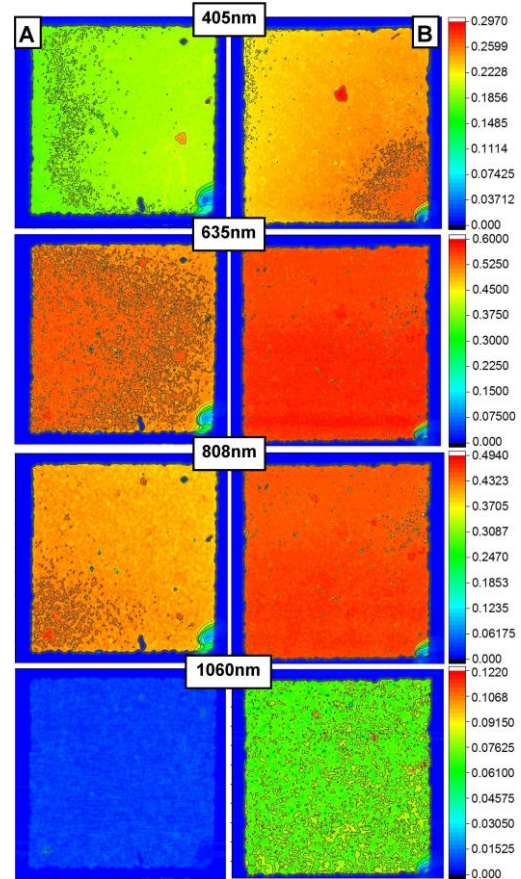

Figure 4 *Spectral response of a) single selenised, b) double selenised sample at four wavelength using multi-laser LBIC system*

The 405nm laser shows the absorption near the surface and the 1060nm laser the absorption near the back contact region. The double selenised device generates more current than the single selenised device throughout the whole thickness of the device. This improved absorption can be related to improved quality of the absorber, owing to bigger grains, as seen in the cross-section in Fig. 1. Moreover, both cells look relatively homogeneous over the whole cell area with only few dark spots or pinholes that might have been caused by accidental scratching or manipulation during the measurements.
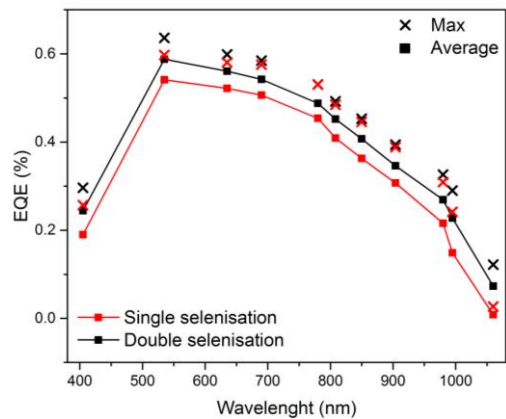
Figure 5 *Average EQE from all the points of the cell area and maximum values*

Fig. 5 shows the EQE values extracted from the LBIC data from 11 lasers. An average curve for all the points at the surface (>2,200 pt/mm^2) of the cell are plotted for both selenisation approaches as well as the maximum value reached at each wavelength. The average and maximum points of the EQE are higher for the double selenised cell. The absorption seems to be improved similarly in the front and in the back of the device. However, the maximum value is only slightly higher than 60%, which is still relatively low. The EQE drops gradually at long wavelengths (>700nm). This can be attributed to the recombination at the back, where the absorber is still poorly crystallised.

Conclusion

In this work, two selenisation approaches were investigated for hydrazine-free, solution-processed CIGS absorber layers. The first, "single selenisation" consisted of selenisation of the entire absorber at the end of the deposition. In the second approach, "double selenisation", half of the absorber thickness was selenised prior to the deposition and selenisation of the second half. It was shown that the double selenisation improves the grain structure of the absorber resulting in higher generated current and better absorption in the entire spectrum. Consequently, the double selenised cells reached PCEs up to 2% higher than the single selenised absorber. However, the progressive decay of the EQE curve at long wavelengths suggests that the selenisation step could be further improved to reduce the recombination in the bulk. In order to do so, repeating the spraying-selenisation steps multiple times on even thinner sprayed precursor layers may aid in the complete recrystallisation of the whole film thickness.

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