Current Status of Bottom-Up Fabrication Approaches for $Cu(In,Ga)Se_2$ Micro-Concentrator Solar Cells

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Abstract. $Cu(In,Ga)Se_2$ solar cells have reached a record efficiency of 23.35% and are established as a renewable energy technology. However, future large-scale fabrication might be hindered by the availability and high cost of raw materials. To reduce the amount of solar cell material, strong efforts have been devoted to the development of the micro-concentrator photovoltaics concept for $Cu(In,Ga)Se_2$ thin-film solar cells, which combines the well stablished concentrator photovoltaics (CPV) technology with the miniaturization of the solar cells. In this work, we review different bottom-up approaches for the fabrication of $Cu(In,Ga)Se_2$ micro solar cells, that potentially allow the reduction of raw materials, and we present the latest results on a magnetron sputtering based method for $Cu(In,Ga)Se_2$ micro solar cells.

INTRODUCTION

In concentrator photovoltaics (CPV) the solar radiation is collected via an optical system and concentrated on small solar cells. Intensive research through the last years has been devoted to downscaling CPV to the micro-scale, typically stacking an array of micro lenses with the solar cell array [1]. Since the size reduction of the solar cells is proportional to the concentration factor, solar cells can be reduced by employing lenses with high magnification. This strategy largely benefits from significant materials and energy savings, by reducing the usage of active solar cell materials and therefore the production costs. Several theoretical studies have proposed that reducing the solar cell size below the mm scale leads to several benefits such as a better thermal management, lower series resistance, and, in general, better efficiency [1]–[9]. In particular, a strong research effort has been devoted to establishing the micro-concentrator PV concept also for thin-film solar cells based on $Cu(In,Ga)Se_2$ (CIGSe) as absorber material [7]. For regular flat panel CIGSe solar cells, remarkable efficiencies up to 23.35% have been achieved [10]. The miniaturization in CIGSe micro-concentrator devices would largely benefit the requirements for rare materials (In and Ga are considered critical raw materials).

The micro-concentrator concept has been successfully demonstrated for CIGSe solar cells by the so-called top-down fabrication, where micro-sized CIGSe solar cells are isolated starting from a large-area solar cell, either by shadowing, by selective contact deposition strategies [11], or by isolation strategies [12]. For such top-down fabrication of CIGSe micro solar cells, an efficiency of 21.3% under 475X concentration has been achieved [13], demonstrating the viability of the concept and previously predicted behaviors such as the dependency of the open-circuit voltage and the cell area [12]. However, these fabrication approaches do not enable any reduction in usage of critical raw materials and therefore might not be economically viable. Thus, suitable bottom-up approaches for the fabrication of the micro solar cells are required, that allow the reduction of raw materials usage. Different approaches are reviewed in this contribution, however, competitive efficiencies are yet to be achieved. Furthermore, the latest results on a magnetron sputtering method for the fabrication of CIGSe micro solar cells are presented.

STATE OF THE ART

The need for an efficient fabrication method for CIGSe micro solar cells enabling materials savings has driven an intense research effort in the last decade [7]. Typical thin-film fabrication methods actually enable the deposition of CIGSe micro solar cells directly in the desired locations on a substrate or module. With the goal of locally growing the absorber in the defined areas and interconnect them, multiple strategies have been explored, including electrodeposition on pre-patterned substrates [8],[14]–[16], the local growth via physical deposition techniques on pre-treated substrates [17], and the locally-controlled transfer from a donor film via a laser pulse [18]. Figure 1 schematically illustrates these approaches.

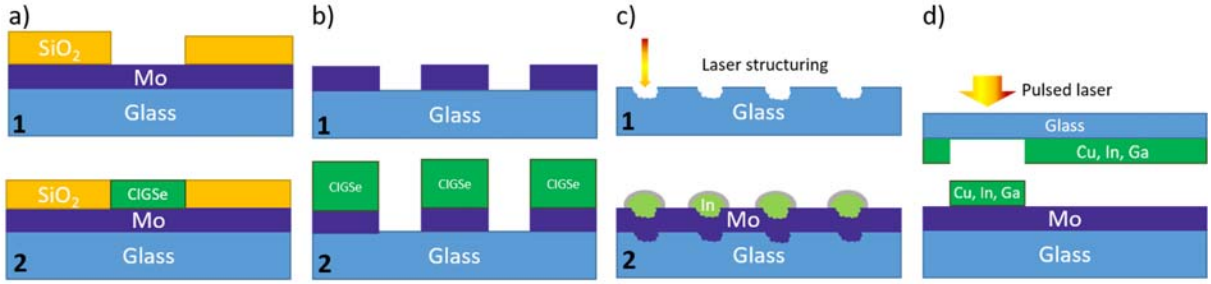

FIGURE 1. Schematic illustration of different approaches for the bottom-up fabrication of CIGSe micro solar cells. Electrodeposition (a) into pre-patterned insulator substrates [8] and (b) onto pre-patterned Mo back contacts [15]. (c) Structuring of the Mo back contact by pulsed femtosecond laser and subsequent selective evaporation of In, which is then converted to $CuInSe_2$ by evaporation of Cu-Se [19], [20]. (d) Laser-induced forward transfer (LIFT) of a Cu-In-Ga precursor layer onto a Mo/glass substrate, followed by selenization [18].

Figure 2 shows the efficiency values and open-circuit voltage gain for micro solar cells under concentration, achieved so far for these bottom-up approaches (left), differentiated by the approach. The experimentally observed V_{OC} gains follow rather well the expected behavior (gray dashed line), calculated based on the typical logarithmic V_{OC} dependence on the concentration factor [7].

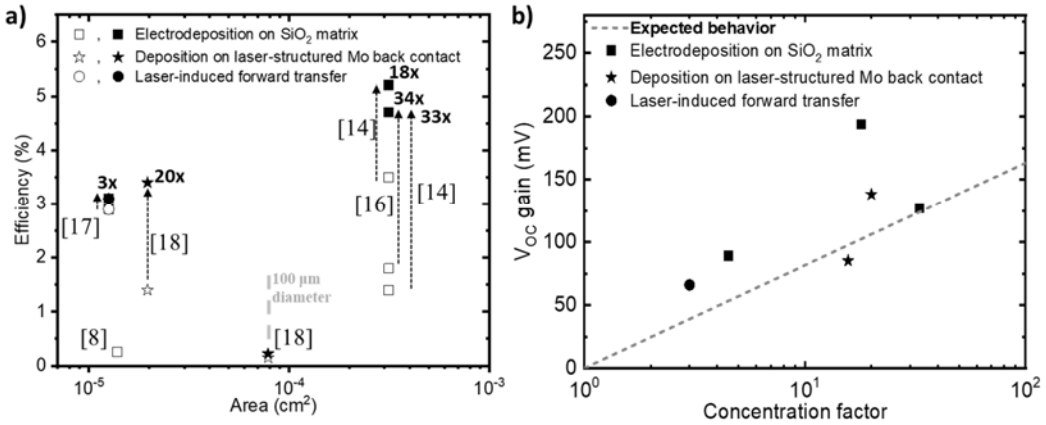

FIGURE 2. (a) Efficiency values under 1 sun and under concentrated illumination and (b) V_{OC} gain for bottom-up fabricated CIGSe micro solar cells. The dashed line in (b) corresponds to the expected dependence of V_{OC} under concentration for a high-efficiency CIGSe thin-film solar cell with CdS as a buffer layer [21].

Even though the devices fabricated by bottom-up approaches are still not competitive with those from top-down fabrication, partially due to the difference in absorber quality, impressive increases in efficiencies have been observed

for remarkably small islands (note that a 100 µm diameter solar cell corresponds to an area of ~8×10^{-5} cm^2), as shown in Figure 2a). Up to date, the best efficiency obtained for a micro-CIGSe solar cell by a bottom-up approach is 7.46% under 1 sun [15], where CIGSe was electrodeposited onto patterned Mo lines and subsequently completed by a CdS buffer layer and a ZnO/ZnO:Al window bilayer. The lines have a width of 105 µm, however, their length is ~1 cm, leading to a quite large area of ~0.01 cm^2. The fabrication of micro solar cells by area-selective electrodeposition was presented by Sadewasser et al .[6], who used an insulating matrix on top of a conductive Mo back contact. A schematic cross section view is shown in Figure 3a). A SiO_2 layer is patterned via direct-writer laser (DWL) lithography and etched down to the Mo layer by reactive ion etching. The CIGSe absorbers are then electrodeposited and subsequently reacted at 450ºC in Se atmosphere. The devices were finished by a KCN etching process, a CdS layer deposited via chemical bath deposition (CBD), and an intrinsic ZnO and Al-doped ZnO bilayer by magnetron sputtering. A similar approach was employed by Siopa et al. who electrodeposited only the metals within the SiO_2 template and formed the CIGSe via a gas phase reaction with Se [14]. SEM top-view and cross-section images of this process (Figure 3 c-d) show high quality films, without any visible holes that could act as pinholes. Measurements of the devices at one sun and under concentrated light show remarkable V_{OC} gains, with a record V_{OC} increase reaching 525 mV under 18X concentration for a 1500 nm thick CIGSe absorber.

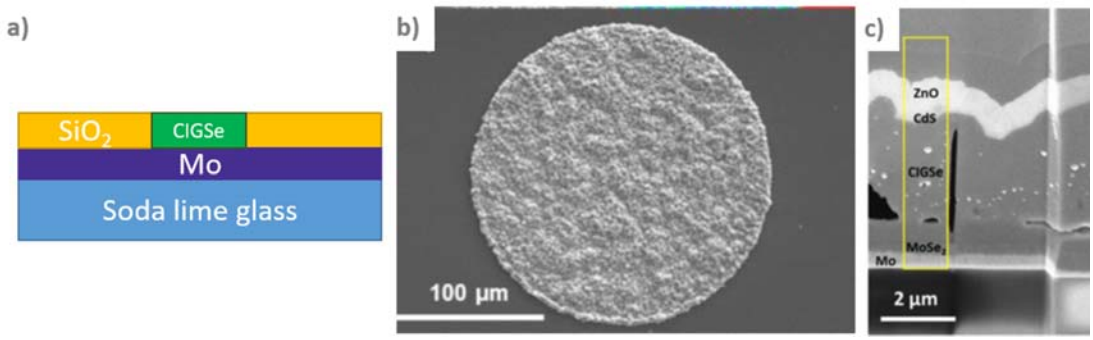

FIGURE 3. a) Schematic cross section of the electrodeposited CIGSe absorbers within an insulating SiO_2 matrix on a glass/Mo substrate. b) SEM top view of a 200 µm diameter fabricated absorber and c) high angular annular dark field image of the fabricated solar cell stack. Images reproduced from reference [14] under Creative Commons CC BY license.

CIGSe MICRO SOLAR CELLS BY SPUTTERING

Different methods can be employed for the deposition of the CIGSe absorber, with magnetron sputtering producing the highest efficiency devices to date [21], [22]. Here, we present a novel approach for the fabrication of CIGSe micro solar cells, in which the metals are deposited by direct-current magnetron sputtering from a mixed Cu-In-Ga target.

As in the selective-area electrodeposition approach presented above (Figure 1 a), we employ an insulating SiO_2 matrix. The process is illustrated in Figure 4. A 1 or 2 µm thick SiO_2 layer is deposited by chemical vapor deposition on a Mo-coated soda-lime glass substrate. Using photolithography, a regular pattern of evenly-spaced circular micro-areas is exposed in a photoresist. After development, reactive ion etching is used to etch the SiO_2 layer until the Mo back contact is reached (Figure 4-1). In this work, the diameter of the holes in the SiO_2 layer was varied from 10 to 500 µm. These pre-structured substrates, in which the layer of resist is still present, are introduced in the CIGSe sputter-deposition system (STAR: SpuTering for Advanced Research [23]), where the deposition of Cu-In-Ga by DC magnetron sputtering is performed (Figure 4-2). A lift-off of the photoresist leaves the patterned SiO_2 matrix with the deposited CIG in the holes behind (Figure 4-2). The lifted-off CIG material can be recovered and recycled to fabricate new CIG sputter targets. Subsequently, the samples are reacted in a tube furnace by selenization process, which leads to the formation of CIGSe in the holes, while the SiO_2 remains unchanged upon this process (Figure 4-3). Finally, the cells are completed by a KCN etching step, coating with a CdS buffer layer by CBD, and sputtering of a i-ZnO/ZnO:Al window layer.

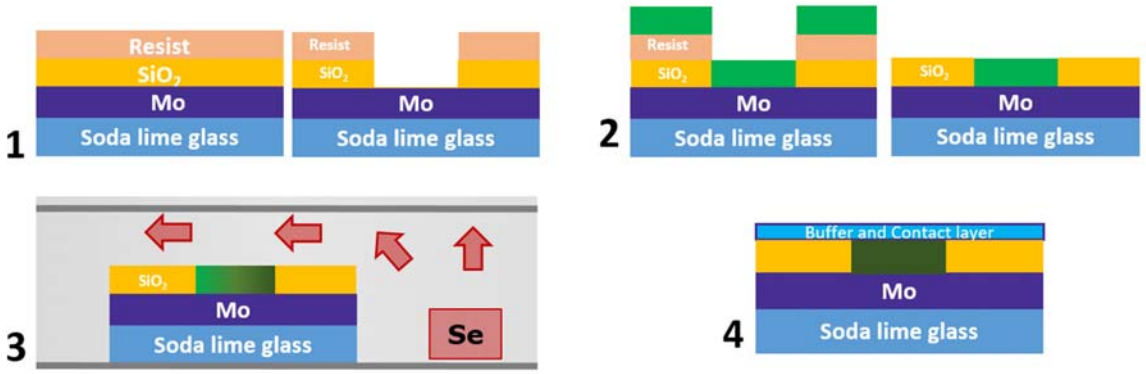

FIGURE 4. Schematics of the fabrication process of micro-CIGSe solar cells embedded in a SiO_2 micro patterned matrix.

A SEM cross section of the CIG sputtered layer can be seen in Figure 5a), which shows how CIG fills the etched holes in the SiO_2, remaining electrically and mechanically isolated from the rest. Figure 5b) shows a SEM top view of a CIGSe absorber, after the selenization process in the tube furnace at 480ºC, which converts the metallic CIG precursor into the polycrystalline CIGSe semiconductor with the typical grain size of around 1 µm. This selenization process is carried out by placing the sample in a graphite box inside the CVD, which is kept in Se atmosphere under an Ar flux. The whole process must undergo a careful screening, since the target temperature and the amount of Se employed are critical factors in order to preserve the integrity of the absorbers and the insulating matrix. As can be observed in the images c) and d) in Figure 5, the SiO_2 can be severely damaged and the CIGSe absorbers can *pop-out* from the holes in the matrix, which is more pronounced when higher amounts of Se are present.

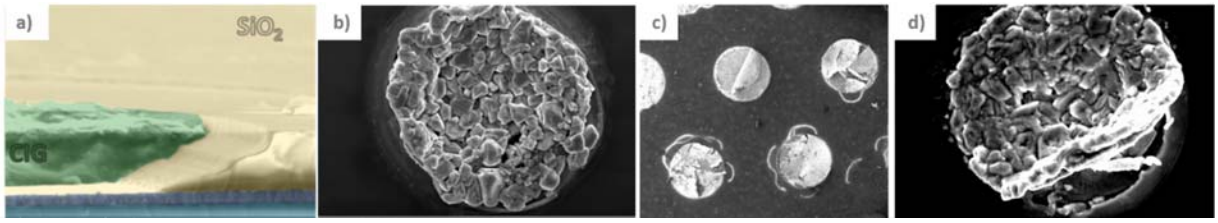

FIGURE 5. a) Cross-sectional SEM image of a 500 µm CIG island in the SiO_2 matrix. Top-view SEM images of (b, d) 30 µm and (c) 200 µm CIGSe absorbers after the selenization process at 480ºC (b) and 490ºC (c-d).

Different approaches have been tested to maintain the integrity of the absorbers. Figure 6 shows the effect of pre-annealing the CIG precursor material deposited in a 1 µm thick SiO_2 matrix before selenization. For both absorbers shown in Figure 6, an annealing process in Se atmosphere in a tube furnace was performed. However, for the absorber in Figure 6b) a pre-annealing [24] process at 440ºC in N_2 for 20 min was done, leading to the preservation of 60% of the micro-absorbers. A remarkable difference, with a clear inflation of the absorber with heights up to 22 µm is observed in Figure 6a) compared to the smoother and more homogeneous surface shown in Figure 6b). These results show that the integrity of the CIGSe absorbers strongly depends on the presence and amount of Se and on the temperature ramp of the annealing/selenization process.

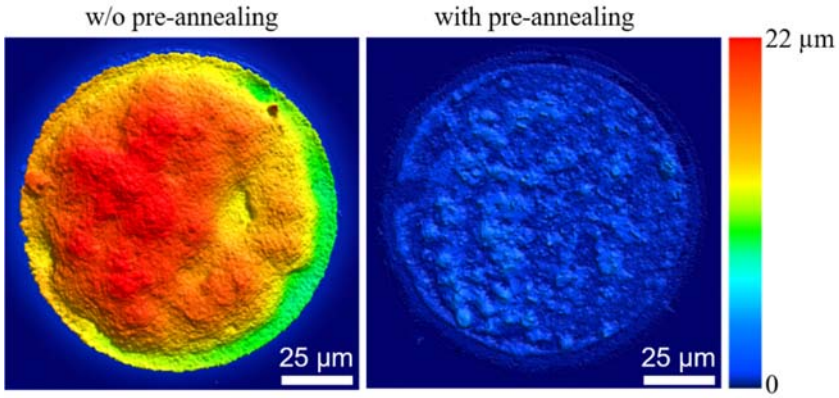

FIGURE 6. Topography image of 100 µm diameter absorbers without (a) and with (b) a pre-annealing in N_2 at 440ºC.

CONCLUSION

Different methods have been explored for the fabrication of CIGSe micro solar cells. The effort dedicated to the optimization of the CIG deposition and post-selenization processes for the micro absorbers has allowed us to identify multiple challenges related with high-temperature treatment in an insulating matrix. Although a complete device is yet to be fabricated, a material saving physical deposition method alternative to electrodeposition is presented, which allows for different structures and geometries, easily tunable through the DWL lithography.

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