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Fabrication of semi-transparent $Cu(In,Ga)Se_2$ solar cells aided by Bromine etching

Pedro Santos [a,*], Pedro Anacleto [a], Daniel Brito [a], Shilpi Shital [b], Ricardo G. Poeira [b], Alice Debot [b], Phillip J. Dale [b], Sascha Sadewasser [a]

[a] *International Iberian Nanotechnology Laboratory, Avenida Mestre José Veiga s/n, Braga 4715-330, Portugal*
[b] *Department of Physics and Materials Sciences, 41, rue du Brill, Belvaux L-4422, Luxembourg*

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ABSTRACT

This study introduces a straightforward and reproducible fabrication method to achieve micro-structured semi-transparent $Cu(In,Ga)Se_2$ (CIGSe) solar cells by lithography and wet etch techniques. We fabricated a segmented micro-structured solar cell by selective etching of an opaque CIGSe solar cell with bromine and bleach solutions and obtained an array of micro lines from 200 μm to 1000 μm in width separated by transparent spaces, resulting in an overall semi-transparent structure. The CIGSe solar cell lines exhibit a maximum power conversion efficiency of 12.4 % for 1000 μm width, which reduces to 6.8 % for 200 μm wide lines. The obtained values are among the highest reported in the literature for similarly architected devices. Our results are a promising step towards the implementation of building integrated CIGSe photovoltaics as windows.

1. Introduction

Semi-transparent solar cells have gathered significant attention in the photovoltaic industry as they allow the implementation of photovoltaics (PV) in buildings as windows. According to the International Energy Agency, buildings represent a third of the global energy consumption and available land area can pose a significant challenge for PV installation [1]. Thus, achieving self-sustainable buildings is desirable. A viable solution to reduce buildings' carbon footprint is the implementation of building-integrated photovoltaics on rooftops and building facades/windows. PV systems that also function as windows require the fabrication of semi-transparent PV systems. $Cu(In,Ga)Se_2$ (CIGSe) photovoltaics are a promising option for the semi-transparent PV industry due to their high power conversion efficiency [2], low production cost, and high stability upon exposure to external environmental conditions [3].

Semi-transparent CIGSe solar cells can be achieved using two distinct approaches. One involves the deposition of ultra-thin wide-gap CIGSe layers on top of transparent conductive oxide (TCO) back contacts. The thickness of the CIGSe absorber layer needs to be reduced to sub-micron values to acquire the transparency characteristic [4]. The CIGSe layer thickness reduction and the use of high temperatures during the deposition are known to lead to increased shunt paths, reduced open-circuit voltages (V_{OC}), and reduced short-circuit current densities (J_{sc}) [5,6]. Besides the efficiency losses, further disadvantages arise from the use of ultra-thin CIGSe solar cells. Due to the different light absorption within the ultra-thin solar cell stack layers, the transmitted light is not color neutral. The perceived color changes from dark red to light yellow as the thickness of the CIGSe absorber is thinned [7], which is undesirable. Thus, new fabrication approaches are being explored.

An alternative approach to achieving semi-transparent CIGSe photovoltaics consists of micro-patterning a full-thickness solar cell stack in different shapes on a transparent substrate, thus achieving color-neutral devices. In these devices, some areas of the substrate have the complete solar cell stack, while the remaining regions don't have solar cell material, giving it the transparency characteristic. This approach makes it possible to control the average visual transparency by changing the area covered by the solar cell material. Furthermore, by micro-patterning a full solar cell stack, the use of a TCO back contact is unnecessary, which benefits the solar cell performance. There are few reports about micro-structured semi-transparent solar cells in the literature, fabricated either directly by area-selective electrodeposition [8] or by removing unwanted CIGSe material by laser scribing [9]. The former study has the advantage of being a material and energy-efficient synthesis, but the current disadvantage of relatively low device efficiency. The latter approach ablates potentially toxic nanomaterials into the atmosphere

* Corresponding author.
E-mail address: pedro.h.2111@hotmail.com (P. Santos).

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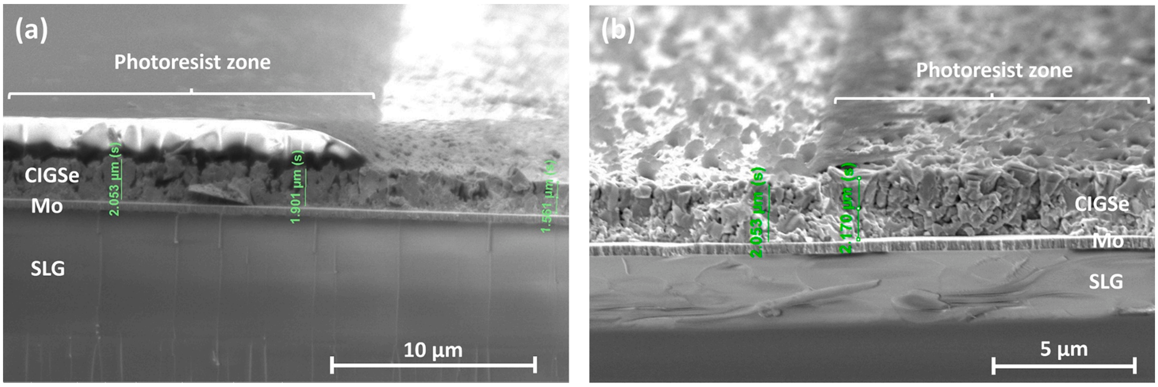

Fig. 1. SEM cross-section image of SLG/Mo/CIGSe stacks etched with a bromine:methanol solution with a concentration of (a) 0.02 mol/L (photoresist is on the left side of the image), and (b) 0.1 mol/L (damaged photoresist is on the right side of the image).

and needs careful control of the laser power to sufficiently remove material without damaging the remaining solar cell.

Here, we investigate a micro-structuring approach, where an opaque CIGSe solar cell is spatially segmented into micro-sized line-shaped solar cells aided by lithography techniques. To remove the unwanted material, a bromine wet-etch process was developed to etch the window and the CIGSe layer, followed by a bleach etch to remove the opaque molybdenum back contact. Several bromine solutions using methanol and water as solvents with different concentrations were investigated, and preliminary solar cell I-V results were obtained.

2. Experimental

Mo/CIGSe stacks were deposited on a soda-lime glass (SLG) substrate using a magnetron sputtering system called STAR (**S**pu**T**tering for **A**dvanced **R**esearch) [10]. The CIGSe deposition process followed the 2-step process described in a previous study [11]. The SLG/Mo/CIGSe stacks were coated with AZP-4110 positive photoresist, and stripes with widths ranging from 200 - 1000 µm were patterned using a direct-write laser system.

We prepared several bromine solutions with varying concentrations and solvents, to evaluate the impact of the different bromine solutions on the photoresist and CIGSe layers. The first set of solutions used for the chemical etching was bromine:methanol, with concentrations of 0.02 mol/L, 0.05 mol/L, and 0.1 mol/L. The second set of solutions was aqueous bromine, with concentrations of 0.02 mol/L and 0.1 mol/L. The Mo/CIGSe stacks were fully immersed in the different bromine solutions. Following the bromine etching step, a sodium hypochlorite (commercial bleach) solution was used to remove the molybdenum back contact [12]. We then fabricated complete CIGSe solar cells in STAR to evaluate the effect of the etching process on the window layer.

The different samples were analyzed by scanning electron microscopy (SEM) in an FEI Quanta FEG SEM microscope equipped with energy-dispersive X-ray spectroscopy (EDS). Cross-sectional views were obtained at 5 keV, and compositional analyses were carried out at 30 keV. Confocal microscope analyses were conducted in a Keyence VK-X1000 system, equipped with a 404 nm laser, using 5X, 20X, and 150X objectives. Once the optimal etching process was determined, complete solar cell devices were fabricated using commercially available SLG/Mo/CIGSe/CdS stacks provided by NICE Solar Energy. The window layer (20 nm ZnMgO and 300 nm ZnO:Al) was radio-frequency sputtered in STAR. The electrical properties of the devices were measured in a solar simulator (Oriel Sol3A class AAA) under AM 1.5 illumination.

3. Results and discussion

The first set of solutions used to perform the chemical etching were bromine:methanol solutions. The etching performed with 0.02 mol/L lasted 30 min, while for the solution with 0.1 mol/L, it took only 20 seconds. The etched samples were observed by SEM to study the effectiveness of the different solutions. Fig. 1 shows a cross-section view measured at the photoresist border zone (i.e., the intersection zone between the area protected by the photoresist and the unprotected area). For a concentration of 0.02 mol/L (Fig.1a), an average etch rate of 16.7 nm/min was determined, meaning that a long etch of nearly 2 h would be required to completely remove the 2 µm CIGSe layer. Moreover, due to the highly volatile nature of bromine, the solution loses etching efficacy with time [13], meaning that several etching steps would be necessary. For higher bromine concentrations of 0.1 mol/L (Fig.1b), the photoresist was severely damaged and almost completely etched away. Similar results were obtained for the solution with 0.05 ml/L, where the

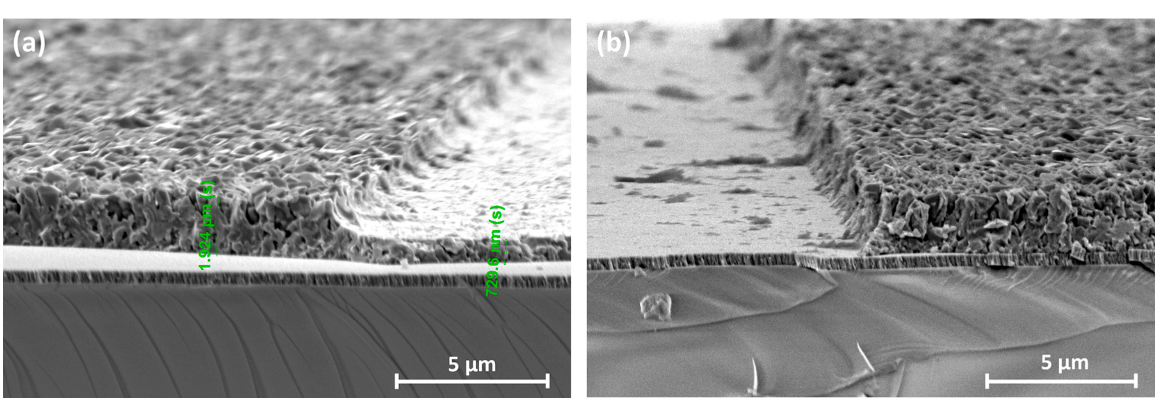

Fig. 2. SEM cross-section image of SLG/Mo/CIGSe stacks etched with an aqueous bromine solution with a concentration of (a) 0.02 mol/L, and (b) 0.1 mol/L.

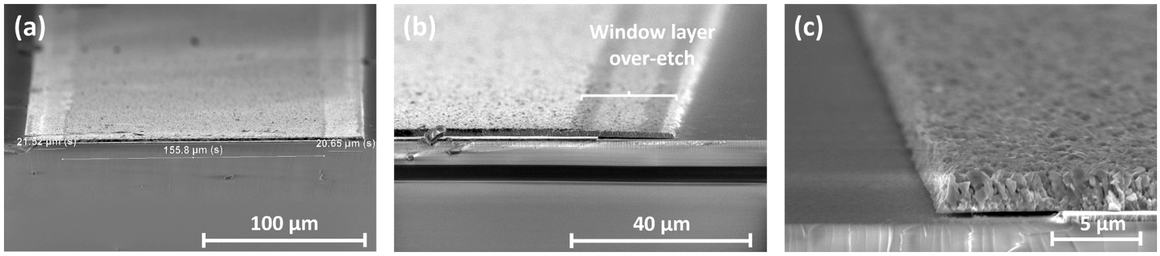

Fig. 3. SEM cross-section image of complete CIGSe solar cell stacks etched with an aqueous bromine solution with a concentration of 0.1 mol/L. (a) 200 µm wide line solar cell, (b) close-up view showing the window layer over-etch, and (c) close-up view of the molybdenum over-etch below the CIGSe layer.

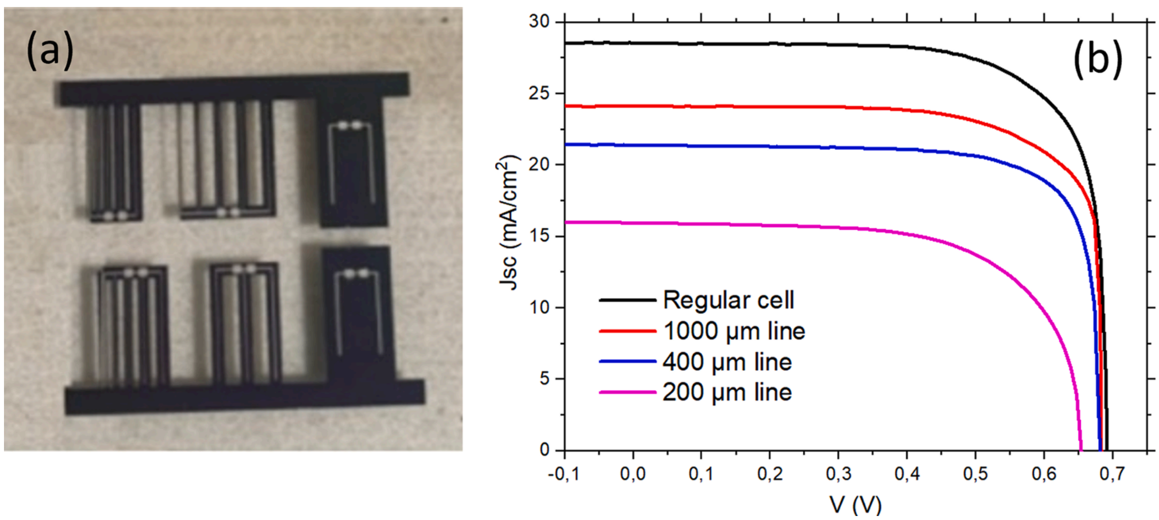

Fig. 4. (a) Photo of the fabricated devices. (b) Current-voltage characteristics of a regular solar cell and 1000 µm, 400 µm, and 200 µm wide line solar cells.

photoresist did not survive the etching step. Therefore, we conclude that using methanol as a solvent is not viable.

As an alternative option to bromine methanol solutions, we use an aqueous bromine solution. Two different aqueous bromine solutions with concentrations of 0.02 mol/L and 0.1 mol/L were studied, for which the etching processes lasted 30 min and 13 min, respectively. Unlike the bromine:methanol solution, these aqueous bromine solutions do not damage the photoresist during the etching-process.Fig. 2 shows cross-section SEM images of two samples after the etching step and subsequent photoresist removal with acetone. For a bromine concentration of 0.02 mol/L, the aqueous solution etch rate is 43 nm/min (Fig. 2a), more than double the value obtained for the bromine:methanol solution with equal concentration. However, due to the volatile nature of bromine, multiple etching steps would be required to perform the complete etch of the CIGSe layer, which is undesired.

Using a solution with a concentration of 0.1 mol/L, we managed to etch the complete CIGSe layer with a etch rate of approximately 153 nm/min (Fig. 2b). We observe that the sidewalls are inclined, in agreement with previous reports [14], which indicates the isotropic nature of the bromine etching. Moreover, the high-concentration solution attacks the molybdenum back contact, which facilitates its subsequent removal using a bleach solution.

To evaluate if the bromine solution affects the window layer, complete solar cells were fabricated and submitted to the optimized wet-etch process. Following the bromine etch step, the sample was dipped in a sodium hypochlorite (commercial bleach) solution for 30 seconds to remove the molybdenum layer. A cross-section view of a 200 µm wide line can be seen in Fig. 3. We observe that the bromine solution removes both the window and buffer layers, as well as the CIGSe layer. We also observed an over-etching of the window layer (confirmed by EDS and confocal microscopy) of approximately 20 µm on each side of the stripe, which occurs due to the lateral direction etching beneath the photoresist. This undesired over-etch reduces the active area available for photocurrent collection. In addition, the Mo etch with bleach solution leads to an undercut of approximately 5 µm on each side of the stripe.

Table 1
Photovoltaics parameters of a reference solar cell, and the best performing solar cell stripes with widths of 1000 µm, 400 µm, and 200 µm.

	Efficiency(%)	J_{sc}(mA/cm^2)	FF(%)	V_{oc}(mV)
Reference cell	14.7	29	75	691
1000 µm line	12.4	24	76	683
400 µm line	11.2	21	78	681
200 µm line	6.8	16	66	653

To assess the impact of the fabrication process on the device performance, a reference solar cell, and 0.8 cm long lines with 1000 µm, 400 µm, and 200 µm width were fabricated using industry-level CIGSe/CdS layers onto which the window layer was deposited in STAR (Fig. 4a). Its current-voltage characteristics were measured in the solar simulator and are shown in Fig. 4b and Table 1.

As expected, the reference solar cell exhibits the best performance, achieving an efficiency of 14.7%, with a J_{sc} of 29 mA/cm^2, fill factor (FF) of 76 %, and V_{oc} of 691 mV. We observe a decrease in efficiency with decreasing line width, mainly attributed to a reduction in J_{sc}. Efficiencies of 12.4 %, 11.2 %, and 6.8 % were obtained for lines with 1000 µm, 400 µm, and 200 µm of width, respectively. The window layer over-etch, estimated to have a total width of around 40 µm, is dead area, where due to the low diffusion length of charge carriers in CIGSe [15] the generated current cannot be effectively collected. The impact of this dead area is more significant for narrower lines, leading to lower short-circuit current densities. The open-circuit voltage also decreased slightly with the smaller line width, which we attribute to damages to the PN-junction during the etching. The FF for the 1000 and 400 μm lines showed minimal change after the etching process. The slight deviations may be attributed to small inhomogeneities in the window layer thickness, as no sample rotation was used during its depositions. The reduced FF of the 200 μm line suggests the presence of shunt-related issues, possibly arising from edge-recombination, which also negatively impacts the current collection.

4. Conclusion

We introduced a wet-etch process to fabricate semi-transparent solar cell devices. Several bromine solutions with different concentrations and different solvents were studied. We show that methanol is not a viable solvent due to its high aggressiveness towards the photoresist at high bromine concentrations, while at low concentrations it leads to a low etching rate. Similar results were obtained for low bromine concentrations using water as the solvent, where the etching rate was very low. However, using an aqueous bromine solution with high bromine concentrations enabled the complete etching of both the window and the CIGSe layers. The molybdenum back contact was etched with a bleach solution. This method introduces a straightforward and reproducible way to fabricate semi-transparent solar cell devices, without losing significant performance. Our solar cell device results suggest excellent suitability of the process for the fabrication of high-performance semi-transparent CIGSe photovoltaics.

CRediT authorship contribution statement

Pedro Santos: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing. **Pedro Anacleto:** Conceptualization, Methodology, Validation, Investigation, Writing – review & editing. **Daniel Brito:** Methodology, Investigation, Writing – review & editing. **Shilpi Shital:** Methodology, Investigation, Writing – review & editing. **Ricardo G. Poeira:** Methodology, Investigation, Writing – review & editing. **Alice Debot:** Methodology, Investigation, Writing – review & editing. **Phillip J. Dale:** Conceptualization, Methodology, Validation, Investigation, Writing – review & editing. **Sascha Sadewasser:** Conceptualization, Methodology, Validation, Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Data availability

Data will be made available on request.

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