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# Earth-abundant absorber based solar cells onto low weight stainless steel substrate



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## ABSTRACT

In this paper we demonstrate the potentiality to produce solar cells based in earth abundant materials deposited onto low weight and flexible stainless steel substrates. Due to the increasing interest of kesterite absorbers like those formed by Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub>, we deposited Cu<sub>2</sub>ZnSnSe<sub>4</sub> layers by a two stage method onto stainless steel substrates coated with a Chromium diffusion barrier, a Mo back contact and a ZnO intermediate layer as substrate configuration, obtaining photovoltaic grade absorbers. First preliminary results, using thermal treatments optimized for glass substrates, lead to a 3.5% efficiency solar cell. This is a promising result, showing the potentiality of this low cost technology for the development of devices onto flexible and low weight substrates, compatible with roll-to-roll industrial implementation.

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## 1. Introduction

Thin films photovoltaic devices deposited onto low weight and flexible substrates, is a very promising way to reach the grid parity between the electricity produced by solar modules and classical non-renewable energies [1–3]. It brings the advantages to provide “green energy” at low prices, with the possibility of being easily integrated in a wide type of buildings and structures. Also, flexible substrates can be used in roll-to-roll processes, which are extremely attractive from the fabrication point of view, allowing for a continuous and cheap production of solar modules [1]. Recently, very encouraging results have been obtained in the development of CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (CIGS) based solar cells onto low weight substrates, in particular deposited onto polymers and metal foils, with efficiencies in the same order of the best results obtained for the technology developed onto classical soda lime glass substrate (SLG) [2–5]. Considering that the production throughput is usually higher for flexible substrates, their advantages are clear.

Among the possible flexible substrates, CIGS solar cells have been prepared onto polymers [2,3,6–8], stainless steel [5,9–11], aluminum [12], zirconia sheets [13], etc. Within these options stainless steel is

clearly one of the most promising because it fulfils all the requirements necessary to be a good substrate attractive for the PV industry: good chemical, mechanical and thermal stability, widely used in the industry, relatively cheap material, easily available in thin foils (50 to 300 μm) and with very low surface roughness. As was previously highlighted, efficiencies obtained with these substrates (principally stainless steel and polymers) are in the order of those obtained on classical SLG substrates. Two particular issues have to be addressed in order to allow for high efficiency values: the incorporation of Na and the development of chemical barriers to avoid the diffusion of impurities from the substrate. The importance of the incorporation of Na in this type of technology has been extensively analyzed and in general, a NaF layer deposited by e-beam at the back or front region of the absorber is used to control the concentration of this important element [3,6,7,14]. Additionally, different types of barriers have been employed with success, like: Al<sub>2</sub>O<sub>3</sub> [15], ZnO [16], SiO<sub>2</sub> [17] and Cr [18]. The effectiveness of all these materials has been demonstrated, and advantages from one to other are not clear, but Cr has the advantage of matching better the thermal expansion coefficient of Mo (for example: CTE<sub>Mo</sub> 4.8 × 10<sup>-6</sup> K<sup>-1</sup>, CTE<sub>Cr</sub> 4.9 × 10<sup>-6</sup> K<sup>-1</sup>, CTE<sub>Al<sub>2</sub>O<sub>3</sub></sub> 6–8 × 10<sup>-6</sup> K<sup>-1</sup>, CTE<sub>SiO<sub>2</sub></sub> 1–9 × 10<sup>-6</sup> K<sup>-1</sup>) [19,20].

It is important to note that CIGS based technology has as a major drawback the In and Ga scarcity, which can hinder the future mass deployment of photovoltaic modules based on this

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material [21]. In this sense, many efforts are focused on the development of new earth abundant and low toxic materials, which can meet the increasing demand of electricity produced with solar energy. Among the absorbers under study, a family of compounds generally called kesterites ( $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  –CZTSSe–,  $\text{Cu}_2\text{ZnSnSe}_4$ –CZTSe– and  $\text{Cu}_2\text{ZnSnS}_4$ –CZTS–), are attracting a considerable interest, because they fulfill all the properties required to be a good photovoltaic absorber: direct band gap with values between 1.0 eV and 1.50 eV, high light absorption coefficient and p-type conductivity [20–25]. Also, these materials are formed only by earth abundant and/or low toxic elements. Photovoltaic devices produced with these materials have shown so far efficiencies exceeding 10% onto classical Glass/Mo substrates, becoming a real alternative to the most mature CIGS and CdTe technologies [22]. Typically, CZTSSe has to be prepared under Zn-rich and Cu-poor composition to obtain high efficiencies as one of the most remarkable peculiarities of this family of materials [22–27].

So far, kesterite solar cells have been prepared onto classical soda lime glass substrates, covered by Mo as back contact, and using the same technology developed for its close cousin material: CIGS [22–27]. But recently, a detrimental reaction between kesterite and Mo has been demonstrated questioning the viability of this type of substrate [27]. Nevertheless, a facile solution has been proposed based in the use of a very thin intermediate layer between the Mo and CZTS, which prevents the contact between both materials and in consequence the decomposition reaction [28]. As intermediate layer, a 10 nm in thickness ZnO film seems to be enough to prevent the decomposition. In this work we present an extension of the CZTSSe based technology to flexible and low weight substrates, demonstrating its higher potentiality for the production of low cost, high throughput and eco-friendly devices. We implement a special back contact configuration including Cr as diffusion layer for the substrate, Mo as back contact and ZnO as intermediate layer, in order to avoid the decomposition of kesterite when is in direct contact with Mo as was previously commented [28]. By using a two stage process consisting in the deposition of metallic stacks by DC-magnetron sputtering, followed by a reactive thermal annealing under Se or S atmosphere, we obtain a photovoltaic grade material with efficiency exceeding 3% in a first optimization of the complete device.

## 2. Material and methods

Austenitic stainless steel (SS) foils (0.05 mm in thickness) were used as substrate. The substrates were mechanically polished to obtain a very smooth surface (average roughness lower than 20 nm), and then carefully cleaned with a basic soap and rinsed with deionized water (18 M $\Omega$ ). Immediately after, they were submitted to an ultrasonic bath cleaning process with the following organic solvent sequence: acetone, methanol and isopropyl alcohol. The time of the ultrasonic treatment for each solvent was 10 min at a temperature of 55 °C. Finally, the substrates were rinsed with deionized water (18 M $\Omega$ ) and dried at 60 °C with a nitrogen flux. Previous to the chemical barrier and back contact deposition, they were submitted to an additional surface treatment using radiofrequency (RF) plasma (100 W,  $2 \times 10^{-3}$  mbar Ar pressure, room temperature, 5 min). This last process does have any impact neither on the surface roughness, nor in the surface composition of the substrate.

As substrate, a three layers configuration was used: chemical barrier, back electrical contact and intermediate layer. The chemical barrier was a thin Cr layer (220 nm in thickness calibrated onto glass substrate by X-ray fluorescence – XRF Fisherscope XVD–), deposited by direct current magnetron sputtering (DC-Sp) (120 W,  $2 \times 10^{-3}$  mbar of Ar, room temperature, 15 min of time

deposition). An 800 nm in thickness Mo layer is used as back electrical contact and 10 nm in thickness ZnO as intermediate layer. The details of the deposition of Mo and ZnO intermediate layer were published elsewhere [28]. The substrate size is  $2.5 \times 2.5 \text{ cm}^2$  in area in all cases.

To synthesize the CZTSe absorbers, we employed a two stage process consisting in the deposition of metallic stacks followed by a reactive annealing process. The structure of the metallic stack precursor was the following: Cu(3 nm)/Sn(333 nm)/Cu(140 nm)/Zn(220 nm); all the metallic layers were deposited by DC-Sp (see Refs. [25,28] for detailed description of the deposition process). The thicknesses were selected in order to have the following final composition, further confirmed by XRF using calibration samples grown onto glass:  $[\text{Cu}]/([\text{Zn}] + [\text{Sn}]) = 0.75$  and  $[\text{Zn}]/[\text{Sn}] = 1.25$ . The annealing process is carried out in a three zones tubular furnace, using a graphite box (23.5 cm<sup>3</sup> in volume). Two different thermal treatments have been investigated: (i) a one step thermal process at 450 °C during 45 min (heating ramp 20 °C/min, total Ar pressure of 1 mbar, 50 mg of Se, 5 mg of Sn, natural cooling down); (ii) a two step thermal process consisting in a first treatment at 400 °C during 30 min (heating ramp 20 °C/min, total Ar pressure of 1 mbar) and a subsequent second treatment at 550 °C during 15 min (heating ramp 20 °C/min, total Ar pressure of 1 bar). Both treatments were sequentially carried out, using 50 mg of Se and 5 mg of Sn, with a natural cooling down to room temperature. It is important to note that the lowest temperature, 450 °C, will lead to lower crystalline quality when compared with higher temperatures. Nevertheless, this temperature regime will certainly minimize diffusion of contaminants from the absorber and will also reduce the induced thermal stresses during the cooling process. In contrast, the temperature of 550 °C will certainly lead to bigger grain size and higher crystalline quality, usually tight to high devices efficiency, but as it was stated above, higher thermal stresses could affect the final quality of the absorber. Therefore, the investigation of these temperatures, which values (or similar to) are widely reported in the literature for kesterite synthesis, are an interesting subject of study for this work [25,28–31].

Se concentration is close to 50% for both annealing temperatures, as is already expected for this material.

The samples were characterized using a FEI NovaTM NanoSEM 230 microscope, an atomic force microscopy AFM in tapping and contact modes (Park Systems XE-100), X-ray diffraction using a Bruker D8 Advance equipment and Auger spectroscopy (Phi 670 scanning Auger nanoprobe).

The as-annealed layers are submitted to a chemical etching in acidic  $\text{KMnO}_4$  solution followed by a  $\text{Na}_2\text{S}$  etching (see Ref. [30] for detailed description of the etching process). Immediately after, and with the aim to complete the solar cells, a CdS layer is deposited by chemical bath deposition (60 nm in thickness), i-ZnO (50 nm) and ZnO:Al (450 nm, 25  $\Omega/\square$ ) both by pulsed DC-Sp.  $3 \times 3 \text{ mm}^2$  cells are scribed using a micro-diamond scribe (MR200 OEG) and then the IV-dark and illuminated curves (AM1.5 illumination conditions) are obtained using a pre-calibrated Sun 3000 Class AAA solar simulator from Abet Technologies. The spectral response is measured in a pre-calibrated Bentham PVE300 system, allowing us to obtain the external quantum efficiency (EQE) of the cells.

## 3. Results and discussion

The deposition of photovoltaic grade absorbers onto non classical substrates (i.e. onto substrates different than SGL), present many challenges as was already investigated and demonstrated for other thin films technologies like CIGS and CdTe [1–17,32,33]. Among them, the surface status (roughness, composition, cleaning), the thermal properties of the material, the possible

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