Solar Energy Materials & Solar Cells 139 (2015) 101–107

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Impact of Cu–Au type domains in high current density $CuInS_2$ solar cells

Antonin Moreau [a,b,*], Cristina Insignares-Cuello [c], Ludovic Escoubas [a], Jean-Jaques Simon [a], Verónica Bermúdez [b,1], Alejandro Pérez-Rodríguez [c,d], Víctor Izquierdo-Roca [c], Carmen M. Ruiz [a]

[a] Aix Marseille Université, CNRS, Université de Toulon, IM2NP UMR 7334, 13397 Marseille, France
[b] NEXCIS, 190 avenue Célestin Coq, 13790 Rousset, France
[c] IREC, Catalonia Institute for Energy Research, Jardins de les Dones de Negre 1, 2ª, 08930 Sant Adrià del Besòs, Spain
[d] IN²UB, Departament d'Electrònica, Universitat de Barcelona, C. Martí i Franquès 1, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 16 October 2014
Received in revised form
3 February 2015
Accepted 11 March 2015
Available online 3 April 2015

Keywords:
CIS
Raman scattering
Photoreflectance
Flexible solar cells
Cu–Au phase

ABSTRACT

In this work, a series of stain steel 15 × 15 cm² $CuInS_2$ solar cells with efficiencies close to the record one for this kind of devices, are analyzed. Through a careful and comprehensive study of the structural and electronic properties of the $CuInS_2$ layer, we show that in a general fashion the strain originated by the thermal annealing affects the energy band splitting and reduces the short circuit current. Then, through an innovative combination of photoreflectance and Raman scattering analysis, we demonstrate that the presence of CuAu domains in the bulk layer of a $CuInS_2$ is directly related with this strain reduction contributing to the improvement of short circuit current. We propose that the presence Cu–Au phase domains reduce the strain within the $CuInS_2$ layer, and improve the quality of the CIS chalcopyrite crystals, leading to reduced carrier recombination while increasing carriers mobility. As a consequence we conclude that the presence of said domains improves the short circuit current in the studied devices.

1. Introduction

Chalcopyrite family $(Cu(In,Ga)(Se,S)_2$, CIGSSe), presents a big potential for developing a high efficiency and cost competitive solar devices. Fabrication methods allow depositing in large surfaces of a wide variety of substrates, from rigid glass up to lightweight (such as polymers or metallic ones [1]). While in laboratory scale CIGSSe has achieved a record value of 21.7% [2], chalcopyrite based technologies are yet in the stage of industrial demonstration, with module records of 16% [3].

In contrast to CIGSSe, CIS ($CuInS_2$, without Ga) based solar cells present a lower efficiency, although the expected theoretical V_{oc} is about 1.2 V. This high V_{oc} is very interesting for series connected devices, for high voltage output modules, or for top cells in tandem structures due to the large bandgap of the material. For instance, Stion (start up based in California) is developing a second generation of CIGSSe devices based in tandem structures where the top cell of the structure is a S based chalcopyrite CIS [4]. Also, sulfur based chalcopyrite materials with high band gap are potentially interesting for the development of third generation low cost intermediate band solar cells [5,6]. However, the efficiency of actual $CuInS_2$ solar cells is still far from the theoretical value, mainly due to V_{oc} losses that limit the performance of the devices. In this sense the best reported conversion efficiency for $CuInS_2$ cells is 12.7% [7,8].

Under Cu-poor conditions, Cu–Au ordered domains have been observed in $CuInS_2$ layers [9]. On the other hand, Cu rich conditions lead to the formation of Cu_xS and $CuIn_5S_8$ in rapid thermal annealing (RTA) samples [10,11]. In both cases, the presence of secondary phases leads to low efficiency devices, limiting the application of this material for general purpose modules or in band gap engineered devices such as tandem structures.

With the aim to understand the main parameters influencing the efficiency limitations in CIS devices, several examples of comprehensive characterization can be found in the literature [10,12–14]. In this paper we intend to demonstrate the strong correlation between the presence of secondary phases, the electronic quality and the device performance by deepening in the utilization of optical based characterization techniques (Raman scattering, photoreflectance spectroscopy) and their correlation with the optoelectronic characteristics of the cells on CIS devices that were made by electrodeposition processes on stainless steel

* Corresponding author at: Aix Marseille Université, CNRS, Université de Toulon, IM2NP UMR 7334, 13397 Marseille, France.
E-mail address: antonin.moreau@im2np.fr (A. Moreau).
[1] Present address: Institute de Recherche et Dévelopement sur l'Energie Photovoltaïque (IRDEP), 6, Quai Watier, 78401 Chatou Cedex, France.

http://dx.doi.org/10.1016/j.solmat.2015.03.008
0927-0248/

flexible substrates. Analyzed devices include cells with different efficiencies, being the highest efficiency values close to the record ones reported in the literature for $CuInS_2$ based solar cells (9.7% in this work, versus 11.4% reported in [15]). It is interesting to remark that the best efficiencies in this work are higher than the highest ones previously reported for cells fabricated on lightweight substrates alternative to glass [15].

Raman spectroscopy has proved its suitability for the very sensitive detection of these secondary phases [9,16–18]. Additionally, Photoreflectance spectroscopy (PR) provides valuable information about the electronic structure of semiconductor that directly impacts in the final performance [19]. Other authors have shown with PR the importance of external parameters such as strain in the electronic band structure [20].

2. Experimental setup

$CuInS_2$ (CIS) solar cells analyzed in this work were fabricated over 15×15 cm^2 stainless steel (SS) substrates. In order to avoid undesired impurity diffusions from the steel substrate, a chromium barrier was deposited before the device fabrication. For the formation of the absorber a two step process was followed as explained elsewhere [11]. Firstly, the copper rich metallic precursors, copper and indium, were electroplated on the molybdenum coated substrate. Then, the whole stack was subjected to a rapid thermal annealing (RTA) in a sulfur atmosphere. The resulting CIS_2 absorbers, still copper rich, are submitted to a KCN etching. After that, a buffer layer of CdS was deposited by Chemical Bath Deposition (CBD) with a thickness of 50 nm. Finally the transparent window is formed by the sputtering of successively intrinsic ZnO and Al-doped layers. Individual 0.5 cm^2 cells were then mechanically scribed at the center of the substrate, for avoiding border effects, and a aluminum grid was deposited at each cell. Total cell area was checked for each device to conform the desired size. For this study, a set of eleven cells manufactured in the same nominal conditions but leading to different efficiencies, related to thermal inhomogeneities in the RTA process, is studied with the aim in mind of identifying the origin of the main differences between the devices. All cells present efficiencies higher than 7.5% and J_{sc} above 19.5 mA/cm^2, with one particular cell with efficiency close to 10% and a current density of 22.1 mA/cm^2. These high J_{sc} values corroborate the high electronic and crystalline quality of the $CuInS_2$ synthesized layers, in spite of the difficulties to achieve an optimal annealing step on SS substrates without introduction of inhomogeneities leading to shunts in the devices. *J–V* curves were measured under AM1.5 conditions with an AAA solar simulator, and the electrical parameter assessment is completed with an External Quantum Efficiency (EQE) measurement in the range of 300–900 nm.

Photoreflectance (PR) is the contactless form of electro-modulation techniques. It permits the investigation of the electronic structure of a material. The principle lies in taking the derivative of the static optical spectrum (reflectance or transmittance) by modifying the electric field associated with the space charge regions (SCR) at surfaces and interfaces [21]. This is made possible by applying a modulated pump source that optically generates charge carriers in the SRC. The resulting PR curve is defined as relative change of the probe reflection [22] induced by the pump beam, where optical transitions are revealed by sharp derivative-like features in the spectrum.

PR experimental set-up consists of a tunable wavelength probe beam (QTH lamp, 250 W) for measuring the reflectance R by means of Si-photodiode. The pump source is a blue laser (at 447 nm, 10 mW), overlaps the probe beam on the surface of the device, defining a measurement area with a diameter of about 400 microns. Measurements are performed at room temperature (295 K) over the complete solar cell. To overcome luminescence perturbation and scattering issues due to surface roughness, dual frequency photoreflectance (DFPR) setup is used. In this double modulation approach, both probe and pump beams are chopped at respectively 500 and 600 Hz. An appropriate signal treatment using two lock-in amplifiers allows to properly extracting the quantity of interest ΔR. Complementary information about DFPR principle and setup can be found elsewhere [19,22,23].

Raman scattering measurements were made in backscattering configuration using a LabRam HR800-UV Horiba-Jobin Yvon spectrometer coupled with an Olympus metallographic microscope. The spectra were measured using the 532 nm line from an Nd:YAG solid state laser as excitation light, and excitation and light collection were made through the $50\times$ objective of the microscope (size of the laser spot on the sample is about 2 μm). At these conditions, penetration depth of scattered light in $CuInS_2$ is estimated to be of the order of 100 nm. In order to avoid microscopic inhomogeneity effects on the measurements, the laser spot was scanned over a 30×30 μm^2 surface on the samples. Several measurements over each cell were done for ascertaining the homogeneity of the samples. Excitation power density on the samples was kept ≤ 20 kW/cm^2, to avoid presence of thermal effects in the Raman spectra. Raman shift calibration was performed imposing the 520 cm^{-1} Raman shift for a silicon monocrystal reference sample performed after each measurement. For both Raman scattering and XRD, samples were etched in order to remove the effect on the signal of ZnO and CdS layers.

The XRD measurements for phase identification and stress analysis were performed with CuKα ($\lambda = 1.5418$ Å) radiation at 40 kV/40 mA in a four circles configuration. Parallel beam is provided by a 4-bounce Ge(220) Bragg reflection channel-cut crystal. Regarding the detection, optical elements include a 3-bounce Ge (220) analyzer with an acceptance angle of 0.003°.

3. Results

3.1. Electrical characterization

J–V curves under illumination were performed for all CIS solar cells, and corroborate the high quality of the cells developed. The efficiencies obtained are between 8% and 10%, relatively close to the record world efficiency for a $CuInS_2$ cell [8]. Results are presented in Fig. 1(b–d). Best lightweight CIS cells reported in literature are at 9%, to our knowledge [15]. In comparison with the bibliography, as summarized in Table 1, the cells presented in this work have J_{sc} comparables to the best reported on glass substrates

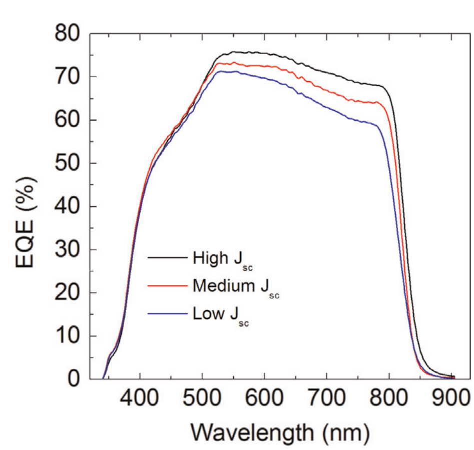

Fig. 1. EQE for some cells with different J_{sc} (high, medium and low),showing the decrease in carrier collection in the long wavelength range for the lower J_{sc} devices.