Solar Energy Materials & Solar Cells 115 (2013) 86–92

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

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

Chalcopyrite thin-film solar cells by industry-compatible ink-based process

F. Roux [a,*], S. Amtablian [a], M. Anton [a], G. Besnard [a], L. Bilhaut [b], P. Bommersbach [a], J. Braillon [a], C. Cayron [a], A. Disdier [a], H. Fournier [a], J. Garnier [b], A. Jannaud [a], J. Jouhannaud [a], A. Kaminski [c], N. Karst [a], S. Noël [a], S. Perraud [a], O. Poncelet [a], O. Raccurt [a], D. Rapisarda [a], A. Ricaud [b], D. Rouchon [d], M. Roumanie [a], E. Rouviere [a], O. Sicardy [a], F. Sonier [a], K. Tarasov [a], F. Tardif [a], M. Tomassini [e], J. Villanova [f]

[a] *CEA, LITEN, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*
[b] *Screen Solar, la Petite Maison ZEN, 390 route de la traverse, 73000 Montagnole, France*
[c] *IMEP-LAHC-Minatec, 3 rue Parvis Louis Néel, BP 257, 38016 Grenoble Cedex 1, France*
[d] *CEA, LETI, Minatec Campus, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*
[e] *Institut des Matériaux Jean Rouxel (IMN), UMR 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes, France*
[f] *ESRF, 6 rue Jules Horowitz, BP 220, 38043 Grenoble Cedex 9, France*

ARTICLE INFO

Article history:
Received 18 May 2012
Received in revised form
8 February 2013
Accepted 25 March 2013
Available online 21 April 2013

Keywords:
CIS
CIGS
Non-vacuum
Doctor blading
Ink
Formulation

ABSTRACT

We developed a new industry-compatible ink-based process to produce efficient chalcopyrite $CuIn_{1-x}Ga_xSe_2$ thin-film solar cells. Metallic In and Ga nanoparticles were produced by purely physical methods, using a low-cost and non-explosive solvent. The solvent acts as a protection against oxidation and can be removed without leaving carbon contamination. We formulated inks that can be safely coated in air by doctor blading. The precursors were converted into a functional absorber after annealing under Se vapors in a primary vacuum. This simple two-step process led to chalcopyrite $CuIn_{1-x}Ga_xSe_2$ thin-films with strong mechanical adhesion, and power conversion efficiency higher than 7%.

1. Introduction

Chalcopyrite-based thin-film solar cells made by vacuum deposition techniques have recently proven that they are serious candidates to compete with crystalline silicon technology, which is still dominating the market in the photovoltaic industry: in the laboratory, power conversion efficiency of 14.5% (0.447 cm²) [1] has been reached for $CuInSe_2$ (CIS) absorber, and 20.3% (0.5 cm²) [2] for $Cu(In,Ga)Se_2$ (CIGS) absorber. However, to beneficiate from economy of scale, large volume production still has to be developed; in 2011, only 3 CIGS manufacturers ranked among the top 10 thin-film manufacturers in terms of production: Solar Frontier (525 MW), Solibro (70 MW), and Miasole (60 MW).

In this context, non-vacuum deposition techniques, particularly ink-based ones, like doctor blading, spraying, or screen printing, are seen as promising alternative tools, as they offer a number of combined advantages to lower the manufacturing costs: reduced machine investments, lower maintenance costs, and faster coating capabilities over larger areas, compatibility with roll-to-roll processes for high throughput production, and patterning possibilities for semi-transparent devices. Moreover, in an ink-based process, the material utilization can be as high as 95% [3], which has a special interest in the case of scarce metals like In and Ga. Additionally, the precursors can be mixed at a sub-micrometer (or even molecular) level, and the stoichiometry can be maintained constant over virtually any substrate size.

Very recently, high quality chalcopyrite devices have been made through these low-cost ink-based processes, as nanosolar claimed a 17.1% efficiency (area not given) [4], and IBM demonstrated with more details a 15.2% efficiency (0.454 cm²) [5], both related to a CIGS absorber. When Ga is not incorporated in the absorber, lower but still significant performances have been achieved: using a CIS absorber, IBM demonstrated a 12.2% efficiency (0.450 cm²) with sulfur addition [6], ISET a 10.56% efficiency (0.100 cm²) [7], and KIT and ZSW a 7.0% efficiency (area not given) [8].

Nevertheless, to remain industrially compatible, an ink-based process should meet some essential criterions such as: neither toxic nor explosive solvents or gases, low-cost synthesis of

---

[*] Corresponding author. Tel.: +33 0 438781463.
E-mail address: frederic.roux@cea.fr (F. Roux).

0927-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.solmat.2013.03.029

precursors, limited number of steps. Additionally, the choice of the precursors and solvents should lead to a minimum carbon or ion contamination. For example, a very reductive agent such as hydrazine cannot be safely processed in large volume because it is highly explosive and toxic [6]. Toxicity has also to be carefully managed when selenization processes using H_2Se gas are employed [7]. For the choice of precursors, alloyed nanoparticles of $Cu_{11}In_9$ have been successfully used, but the Cu rich composition of these particles leads to parasitic copper selenide phases that need an additional step of etching with very toxic KCN solutions [8].

Taking these criterions into account, we developed a process in an industrial perspective. First, we formulated an ink containing metallic Cu and In particles. The In particles were made by purely physical and very low-cost methods, avoiding contamination and chemical synthesis. The solvent, which can be safely processed in air, acts as a protection against oxidation. Once coated, the precursors were directly converted into an active CIS layer under Se vapors annealing. We achieved a 7.2% power conversion efficiency over a 1 cm² area. Then, in order to increase this efficiency, we formulated an ink containing metallic Ga particles with the same methods. This first attempt led to a power conversion efficiency of 8.1% over a 0.25 cm² area. Both devices were extensively characterized.

2. Materials and methods

2.1. Characterization tools

The viscosity of the inks was measured on a MCR 300 rheometer from Anton Paar, at 25 °C with the following procedure: rapid increase of shear rate from $0\ s^{-1}$ to $1000\ s^{-1}$, stabilization plateau at $1000\ s^{-1}$, and measurement of viscosity from $1000\ s^{-1}$ to $0\ s^{-1}$.

A Hitachi S4000 scanning electron microscope (SEM) was used to examine the morphology of the layers on cleaved samples. A Zeiss LEO1530 SEM equipped with a Brucker silicon drift detector was used for chemical energy dispersive spectroscopy (EDS) analyses on polished cross-section samples. Crystallographic properties were investigated by means of X-ray diffraction (XRD) and micro-Raman spectroscopy. For the XRD, a Cu X-Ray tube was used on a D8 Advance Bruker AXS goniometer in the theta–2theta configuration. For Raman characterization, we used an Ar laser with an excitation wavelength of 514.5 nm and an output power of 0.2 mW. After focalization, the spot size was 0.7 μm. Power conversion efficiencies were measured through current–voltage (I–V) measurements under simulated AM 1.5 global solar irradiation at $100\ mW\ cm^{-2}$, at 25 °C. An external quantum efficiency (EQE) set-up was used for gap determination.

For Suns-V_{oc} measurements, we used a Flash Cell Tester from Sinton Instrument (FCT-350). The cell was lighted by a flash lamp from a class AAA solar simulator. The flash intensity decreases from 1.2 Suns to 0 in 12 ms. The open-circuit voltage (V_{oc}) and the light intensity are monitored as a function of time during the decay of the flash. The light intensity is measured by an external photodiode calibrated in Suns and is converted to a current defined as $I=I_{sc}$ (1-Sun), where I_{sc} is the short-circuit current measured under 1 Sun by I–V measurement, and Suns is the light intensity normalized to $100\ mW\ cm^{-2}$. Plotting I as a function of V_{oc} yields a pseudo I–V curve obtained in an open-circuit configuration, thus eliminating the effects of series resistance [9].

Adhesion test was performed in order to evaluate the mechanical adhesion of the CIS layer to the Mo substrate. We followed the normalized procedure described by the ISO NF 2409 standards. We used a tool kit from Elcometer (Elcometer 1542 Cross Hatch Tester Kit) complying with the ISO NF 2409 standards. Two series of perpendicular strips, 1 mm spaced, were mechanically scribed into the bare absorber. The dusts were removed by a smooth pencil. A scotch ribbon was then applied on the surface, and stripped back with a constant angle of 60°.

2.2. Ink formulation

Metallic In particles were directly obtained by a patented method [WO 2012/025893 A1]: we started by melting In chunks (5 N purity) in an alkanethiol solvent, and then, dispersed the liquid metal by applying an ultrasonic treatment. Once cooled at room temperature, we directly got a stable In ink, with a typical particle size of 500 nm (Fig. 1a). This method can easily be scaled up to large volumes, as continuous ultrasonic reactors are frequently used in the industry. Alkanethiols are non expensive and commercially available products, and can be safely processed under ambient air conditions, which make them compatible with an industrial production. They have boiling points high enough to have a limited evaporation rate at room temperature, but low enough to be removed at moderate temperature. Moreover, the thiol group acts as a protection against oxidation of metallic particles. Indeed, alkanethiols are known to form stable self-assembled monolayers (SAM) on metal surfaces, protecting them against oxidation and corrosion [10,11]. For copper and silver surfaces for example, it has been shown that chemisorbed alkanethiol molecules remain anchored to the metal surface up to temperatures of 400 K, while at higher temperatures the sulfur–carbon bond cleaves, giving rise to the desorption of alkyl chains and the formation of sulfur thin layer on the metal surfaces [12–14]. This avoids the reduction step usually needed for oxide nanoparticles. Furthermore, alkanethiols have a good wetability on Mo substrates. For Cu particles preparation, we used classical reduction reactions of $CuSO_4$ (4 N purity), leading to typically 300 nm particles (Fig. 1b). After washing and centrifugation, the Cu particles were dispersed in an alkanethiol solvent.

The Cu and In inks were finally gathered in a single ink, with a slightly Cu poor composition of Cu:In = 0.98:1, as measured by inductively coupled plasma mass spectrometry (ICPMS). Thus no KCN etching was used after selenization. The suspension is stable over weeks, and can be easily redispersed by ultrasonic treatment if needed.

To formulate an ink containing Ga, we used the same straightforward method as for the In nanoparticles. We started by melting Ga chunks (5 N purity) in an alkanethiol solvent, and then, dispersed the liquid metal by applying an ultrasonic treatment. Ga has a much less elevated melting point (29 °C) than In (156 °C). Thus, much less heat and ultrasonic power density is needed, which makes the synthesis even more cost effective. We obtained directly Ga nanoparticles with typically the same size and dispersion as for the In nanoparticles (Fig. 1c). Our first attempts to mix directly Cu, In, and Ga nanoparticles in a single ink led to unstable suspensions, with aggregates of several tens of micrometers. In order to avoid binder or stabilizing agent addition, that could introduce carbon contamination, we decided to first deposit a 250 nm thick Cu layer by electron beam evaporation on a Mo/glass substrate. Note that the Cu layer can possibly be deposited by non-vacuum methods, such as electroless or electrodeposition. Then we gathered the In and Ga particles to obtain an ink with a stoichiometry of In:Ga = 0.70:0.30, as measured by ICPMS. The ink containing only In and Ga in an alkanethiol solvent is much more stable and does not contain aggregates. The non stability of an ink containing Cu, In and Ga particles is currently under investigation.

2.3. Coating step

The Cu–In ink and the In–Ga ink were both coated by doctor blading at room temperature, on a laboratory film applicator from