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


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We developed a new industry-compatible ink-based process to produce efficient chalcopyrite CuIn$_{1-x}$Ga$_x$Se$_2$ 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$_x$Se$_2$ thin-films with strong mechanical adhesion, and power conversion efficiency higher than 7%.

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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 cm$^2$) [1] has been reached for CuInSe$_2$ (CIS) absorber, and 20.3% (0.5 cm$^2$) [2] for Cu(In,Ga)$_2$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), Sollibro (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 cm$^2$) [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 cm$^2$) with sulfur addition [6], ISET a 10.56% efficiency (0.100 cm$^2$) [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 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 also has to be carefully managed when selenization processes using H₂Se gas are employed [7]. For the choice of precursors, alloyed nanoparticles of Cu₂-xInₓ 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 criteria 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–Vₘₚ 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 (Vₘₚ) 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 soc (1-Sun), where I soc 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 [WO2012/025893 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 wettability on Mo substrates. For Cu particles preparation, we used classical reduction reactions of CuSO₄ (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 Elcometer (Elcometer 4340 Automatic Film Applicator) on 5 × 4 cm² substrates (Mo/glass for the Cu–In ink, or Cu/Mo/glass for the In–Ga
Doctor blading has the advantage to be compatible with roll-to-roll production, contrary to other techniques like spin-coating [15].

For the Cu–In ink, we used a coating speed of 5 cm s\(^{-1}\), and a height blade of 150 \(\mu\)m, corresponding to a shear rate of 330 s\(^{-1}\). The viscosity of the ink exhibits a non-Newtonian behavior up to shear rates of 1000 s\(^{-1}\) (Fig. 1c). For the shear rate employed, we measured a viscosity of 120 mPa s, which lies in the typical range encountered for inks designed to be coated by doctor blading[15]. These conditions, together with the metallic load of the ink (\(\text{Cu} \geq 5\%\) by weight) were convenient to get a final CIS absorber of 2–3 \(\mu\)m.

Once coated, the layer was dried on the doctor blading table at 125°C, 30 min, in order to partially remove the solvent (this step is needed to transfer the sample from the doctor blading table to the selenization furnace). Under these conditions, no metal oxide was detected by XRD (Fig. 2a).

The In–Ga ink also exhibits a non-Newtonian behavior, and its viscosity (10 mPa s at a shear rate of 330 s\(^{-1}\)) is much lower than the viscosity of the Cu–In ink described above, but it still can be coated by doctor blading at room temperature. Given the initial amount of Cu brought by the pre-deposited Cu layer, we adjusted the metallic load of the ink (\(\text{Cu} \geq 4\%\) by weight) and the coating conditions (height blade of 145 \(\mu\)m, speed of 5 cm s\(^{-1}\)) to target a Cu poor composition. Indeed, the Cu/III atomic ratio was measured to be 0.84 by ICPMS, after selenization. Once coated, the In–Ga ink was dried in the same conditions as the Cu–In ink.

2.4. Selenization and device fabrication

We used a single zone tubular furnace to convert the precursor layers (Cu–In and Cu–In–Ga) into chalcopyrite absorbers (CIS and CIGS respectively). Although \(\text{H}_2\text{Se}\) can be used at an industrial scale, the high toxicity of this gas makes it complicated to process. Se vapors are much less toxic. Se pellets were evaporated at the entrance of the furnace, and the vapors were carried by a nitrogen flux at 20 mbar. The sample was positioned at the center of the furnace, ramped up at 9 °C/min to reach a temperature of 570 °C, and maintained at this value for 1 h. Because of the strong gradient of temperature at the entrance of the furnace, the Se pellets started to evaporate only when the temperature of the sample was around 400 °C. At this temperature, all the solvent has been removed from the precursor layers. After selenization, the chalcopyrite layers were completed with a 50 nm CdS buffer layer deposited by chemical bath deposition, and a ZnO:i(50 nm)/ZnO:Al(450 nm) stack was deposited by sputtering. No antireflective layer was used. For CIS absorbers, a Ni(50 nm)/Al(500 nm) grid was finally evaporated on top, shading 11.05% of the surface of each cell of 1 cm\(^2\), that were isolated by mechanical scribing. For CIGS absorbers, only 5 \(\times\) 5 mm\(^2\) cells were isolated, thus no grid was used. For \(I–V\) measurements in this case, the current is directly collected by contacting a tip on the ZnO:Al layer.

3. Results and discussion

3.1. CIS absorber

Fig. 2b shows a cross sectional SEM image of the CIS absorber. As it is frequently observed for CIS and CIGS layers made by a reactive two steps process [8,16–18], two different types of crystallization can be seen: an upper layer well crystallized and a layer near the Mo poorly crystallized. Ashlswede et al. showed that a dense upper layer is formed at the earliest stages of the selenization process [16]. This could act as a barrier limiting the diffusion of Se through the layer. In our case, this assumption is confirmed by the fact that no MoSe\(_2\) is observed by XRD (Fig. 2a). The diffraction pattern shows all the characteristic peaks of a Cu\(_{0.938}\)InSe\(_2\) phase ([JCPDS 01-07-2001]. The sharpness of the peaks indicates a good crystallinity: from the Scherrer relation, the full width at half maximum of the main peak can be used to estimate the typical size of the diffracting domains to 60 nm, which is of the same order of magnitude as the typical size of the diffracting...
domains for a CIS absorber deposited by sputtering [19]. The cross sectional SEM image on Fig. 2b also shows that no carbon residual layer is formed, as it frequently observed with organic solvent like ethyl cellulose [20].

The layer has a thickness of roughly 3 μm, which is comparable to the thickness of CIS absorbers of same level of efficiency made by other groups [8]. For CIS absorbers, the correlation between absorber thickness and efficiency is not so clear, as high quality CIS solar cells have been made with much higher absorber thickness [7]. Nonetheless, from an industrial point of view, it is obvious that thinner absorbers are preferable to minimize the utilization of In. Also, reducing the thickness could help in limiting the formation of the poorly crystallized layer near the Mo. As mentioned by Ahlsvede et al. [8], the role of this poorly crystallized layer is not well established so far.

The mechanical adhesion of the absorber to the underlying Mo layer has been studied with the standard procedure described in Section 2.1. The results are classified on a semi-quantitative scale between 0 (strong adhesion, no peeling at all) and 5 (no adhesion, complete peeling). The CIS layer obtained a mark of 1, showing that our fabrication process leads to a very good adhesion of the absorber. This point is rarely reported in the literature, but is critical in the scope of an industrial production.

The surface of the absorber was also investigated by micro-Raman scattering (Fig. 2c and d). At the excitation wavelength employed (514.5 nm), the absorption depth is about 100 nm; thus only the well crystallized upper part is probed. A first analysis is performed locally, with a scan of the scattered frequencies between 125 cm⁻¹ and 350 cm⁻¹. From the spectrum shown on Fig. 2c, only a pure CIS phase is detected, with a sharp peak at 176 cm⁻¹ assigned to the A1 vibration mode of the CIS lattice, and a broader peak at 215 cm⁻¹ attributed to the B2-E vibration mode of the CIS lattice. Cu₂₋₋₅Se compounds, known to be highly conductive phases, have a strong vibration frequency at 260 cm⁻¹ (A1 vibration mode) [21]. As expected, because of the Cu-poor stoichiometry, these parasitic phases are not present at the absorber surface. The frequency of the A1 vibration of the CIS is shifted by roughly +2 cm⁻¹ compared to values usually reported of 174 cm⁻¹ [22]. As assumed by Rzepka et al. [23], this is probably due to a residual stress in the structure. To have a better idea of the frequency dispersion of the A1 vibration mode of the CIS lattice, a frequency mapping around 176 cm⁻¹ is performed on a 20 × 20 μm² area. The data are plotted as a frequency histogram (Fig. 2d). From these data, the mean value of the A1 vibration mode is found at 175.93 ± 0.33 cm⁻¹. This very weak dispersion shows that the crystalline structure of the CIS remains very homogeneous over a 20 × 20 μm² area.

Typically, nine CIS solar cells, each with an area of 1 cm², were fabricated on the same 5 × 4 cm² substrate, and measured power conversion efficiencies were higher than 5%.

Fig. 3 shows the I-V curve of the best CIS solar cell: the power conversion efficiency is 7.2% on 1 cm² under simulated AM 1.5 global solar irradiation at 100 mW cm⁻², the short-circuit current density (Isc) is 32 mA cm⁻², the open circuit voltage (Voc) is 420 mV and the fill-factor (FF) is 53.5%. Taking into account the inactive area under the grid (11.05% of the surface), one can correct the Isc to a value of 36 mA cm⁻², and estimate a power conversion efficiency of 8.1%. As mentioned above, the morphology of the absorber shows a poorly crystallized layer near the back electrode. This could increase the series resistance of the cell and be one of the reasons to explain the low FF measured. In order to experimentally estimate what could be the performance of the cell in the ideal case of no series resistance, we performed Suns-Voc measurements, as shown in Fig. 3. With these Suns-Voc measurements, the Voc is found to be slightly higher (429 mV) because the temperature was of 20 °C, instead of the 25 °C used for the I-V measurements (for chalcopyrite solar cells, the variation of the Voc with the temperature is typically 2 mV/°C, as measured by Parisi [24]). This has no incidence on the Isc (32 mA cm⁻²). The FF jumps to an ideal value of 70.6%. Thus, for such a device, one could expect an ideal power conversion efficiency of 9.7% on 1 cm².
Finally, from the external quantum efficiency curve (Fig. 4a), the current density (36 mA cm\(^{-2}\)) is confirmed, and the absorption threshold determined to be 0.98 eV (Fig. 4b). This low value compared to CIS optical bandgap (1.04 eV) may be explained by absorption due to defects located in the bandgap.

3.2. Integration of gallium

Chalcopyrite thin-film solar cells have shown much higher efficiencies when Ga is fully integrated in the absorber. We made a first attempt to integrate Ga in the ink, as described in Section 2.2. Fig. 5a shows a cross sectional SEM image of the CIGS absorber. Note that the thickness is significantly reduced (2 \(\mu\)m) compared to the thickness of the CIS absorber (Fig. 2b). This could be done because the In–Ga ink can be processed with smaller metallic loads, thus bringing less material on the substrate. As mentioned above, the reduced thickness may also limit the formation of the poorly crystallized layer near the Mo, observed for the CIS absorber. Indeed, only a very thin layer of smaller grains can be seen near the Mo electrode. As it is well known, Ga incorporation comes only at the end of the reactional pathways leading to the formation of a 30% at. Ga containing CIGS phase. Thus, during the selenization process, Ga tends to segregates toward the Mo back contact.

The Ga gradient and the morphology can also be correlated to a careful XRD analysis (Fig. 5b) performed around the main peak of the diffraction pattern. The shape of the diffraction signal could be interpreted in terms of three chalcopyrite phases with different Ga compositions. To make this analysis, we assumed that the Cu stoichiometry does not modify the \(a\) and \(c\) parameters of the tetragonal structure of the chalcopyrite phase. Indeed, this is the case for all the CuInSe\(_2\) tetragonal centered phases found in the JCPDS database. Then, for the XRD analysis, we assumed a Cu/III ratio of 1. When In atoms are partially replaced by Ga atoms, the diffraction peaks shift toward higher angles, following Vegard’s law. We found that the two sharp peaks at 26.63° and 26.70° correspond respectively to a CuIn\(_{0.98}\)Ga\(_{0.02}\)Se\(_2\) phase and a CuIn\(_{0.94}\)Ga\(_{0.06}\)Se\(_2\) phase. The broad peak at 27.42° corresponds to a CuIn\(_{0.23}\)Ga\(_{0.77}\)Se\(_2\) phase. This is coherent with the morphology observed on Fig. 5a, with a well crystallized layer (close to a CIS phase), and the small grains located near the Mo electrode (close to a CGS phase). These observations are also coherent with grazing XRD measurements (not shown): the broad peak attributed to a Ga rich phase, poorly crystallized, is quenched when the angle of the incident beam is weak enough to probe only the surface. This Ga gradient is confirmed by EDS measurements performed on the cross section (Fig. 6): Ga is only present in the lower half of the absorber. Note that Cu, initially deposited as a separate precursor layer, has completely diffused into the whole absorber. In and Se are also homogeneously distributed. Also, the SEM
image (Fig. 6) of the polished cross section reveals a much more porous morphology than observed by mechanically cleaving the sample.

Fig. 7 shows the I–V curve of our best CIGS solar cell: the efficiency is 8.1% on 0.25 cm² under simulated AM 1.5 global solar irradiation at 100 mW cm⁻², the I_{sc} is 33 mA cm⁻², the V_{oc} is 413 mV and the FF is 58%. The short-circuit current density is confirmed by EQE (Fig. 4a). Compared to the CIS absorber, we maintain a good current density, but we slightly lower the V_{oc}. From an electrical point of view, the Ga integration is yet not fully achieved. The bandgap, as determined by EQE measurement (Fig. 4b) shifts by 40 meV toward higher energies but remains to a low value compared to CIGS optical bandgap (1.2 eV). Again, this may be explained by absorption due to defects located in the bandgap. The most significant improvement is achieved for the FF, which raises the efficiency to 8.1%. This may be explained by a thinner and better crystallized absorber.

4. Conclusions

We developed an industry compatible ink-based process to produce thin-film CIS solar cells with efficiencies as high as 7.2% on 1 cm². The Cu–In ink could be coated on substrates as large as 5 × 4 cm², ensuring efficiencies higher than 5%. The formulation of the Cu–In ink is based on metallic In particles made by purely physical methods, that could be safely used at an industrial scale. With In–Ga inks, coated on Cu layers, we demonstrated an 8.1% efficiency on 0.25 cm². The incorporation of Ga particles together with Cu and In particles in a stable formulation is currently under investigation.

References


