15% efficient Cu(In,Ga)Se2 solar cells obtained by low-temperature pulsed electron deposition

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15% efficient Cu(In,Ga)Se$_2$ solar cells obtained by low-temperature pulsed electron deposition


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An approach to low-cost production of Cu(In,Ga)Se$_2$ (CIGS) solar cells based on pulsed electron deposition (PED) has achieved a crucial milestone. Lab-scale solar cells with efficiencies exceeding 15% were obtained by depositing CIGS from a stoichiometric quaternary target at 270°C and without any post-growth treatment. An effective control of the p-doping level in CIGS was achieved by starting the PED deposition with a layer of NaF tailored to generate the optimum Na diffusion. These results show that PED is a promising technology for the development of a competitive low-cost production process for CIGS solar cells. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4755772]

Polycrystalline Cu(In,Ga)Se$_2$ (CIGS) has emerged as one of the most promising light absorbing materials for low-cost and high-quality thin film solar cells, because of its tunable bandgap (1.04–1.68 eV), high absorption coefficient ($\alpha > 10^5$ cm$^{-1}$), high-tolerance to stoichiometry defects and impurities, as well as high conversion efficiencies exceeding 20% at laboratory scale. A variety of different deposition processes have been developed for the production of CIGS solar cells among which thermal co-evaporation, sputtering/seleinzation, and electrodeposition have so far emerged as the preferred candidates for industrial scale-up. However, all these techniques still present serious limitations and drawbacks which are delaying the industrial take-off of CIGS solar cells. Multi-stage co-evaporation, by which the current 20.3% lab-record efficiency was achieved, is generally considered to be unsuitable for mass production because of its complexity and poor composition reproducibility in large manufacturing systems. Sputtering of metal precursors followed by a post-growth selenization step appears to be a more feasible route for industrial scale up but the unavoidable selenization stage is a major issue in terms of environmental impact (highly toxic H$_2$Se is usually used) as well as the operation costs linked to high temperature processing. In order to overcome the limitations associated with multi-stage deposition, several single-stage processes based on sputtering and co-evaporation have been proposed as more cost-effective alternatives. Reported efficiencies for lab-scale cells are typically lower than 12.5% with the most striking exception of 18% achieved by an in-line co-evaporation process at a substrate temperature, $T_{\text{sub}} = 550\,^\circ\text{C}$. In this paper, we report the achievement of efficiencies exceeding 15% in lab-scale CIGS solar cells by using a low-temperature single-stage production process based on pulsed electron deposition (PED). Three out of four of the cell active layers were deposited by PED at a maximum $T_{\text{sub}} = 270\,^\circ\text{C}$. PED is a thin film deposition technique based on high-power electron-beam ablation of a bulk material (target) having the desired composition and stoichiometry. Electron beam pulses of about 100 ns dissipate a power density of the order of $10^8$ W/cm$^2$ within a depth of the order of 1 μm from the target surface. This causes a rapid non-equilibrium evaporation of all the elemental components of the target and the formation of a plume of ions having a large average kinetic energy. As a result, the deposition of good quality films occurs at a much lower substrate temperature compared to sputtering or single-stage co-evaporation. The effectiveness of PED as an alternative single-stage deposition technique was discussed in our earlier publication reporting how the stoichiometry of CIGS films can be controlled by properly matching the key physical parameters influencing target ablation and film deposition. 7.2% efficient solar cells where CIGS was grown at $T_{\text{sub}} = 500\,^\circ\text{C}$ were obtained at that early stage before any attempts were made to optimise the production process and the device performance. At the current stage of the optimisation work, the ratio between cell efficiency and substrate temperature has been improved to the extent that this process can now be considered a promising option to achieve significant reductions in both production costs and energy payback time of CIGS photovoltaic modules, with respect to more mature industrial processes. PED deposition on flexible low-melting-point substrates has also become a viable option. The two key process parameters whose optimisation allowed us to more than double the efficiency of our cells are Na doping and quality of the targets used for PED deposition. The control of the p-type doping of CIGS films is a crucial process step to optimize the solar cells performance and it is now widely accepted that the level of doping is mainly controlled by the Na concentration and diffusion profile. In our low-temperature deposition process, the desired doping profile is provided by a sodium fluoride (NaF) layer deposited by PED between the Mo back contact and the absorber. As the properties of PED-deposited films crucially depend on the target morphology and composition, the recipe for the synthesis of each target was the result of a thorough optimization process. CIGS targets were obtained by a...
boron-oxide-encapsulated synthesis process starting from elemental species (Cu, In, Ga, and Se with 5 N purity). This process, previously developed for the synthesis of high-purity polycrystalline targets of CdTe\(^{15}\) and other III-V/II-VI semiconductors, is capable of preserving the starting stoichiometry in the target because molten boron-oxide encapsulation and high inert gas counter pressure (30 \(\div\) 40 bar Ar) inhibit Se evaporation. Moreover morphology and density of CIGS targets can be optimised for clean and efficient PED ablation. In the case of the targets used for this work, a deposition rate of 0.25 nm/pulse over a 3 square-inch substrate area was achieved without the formation of large (>0.1 \(\mu\)m) particulates whose detrimental effect on the film quality is a well known problem of both PED and pulsed laser deposition.\(^{16}\) High-density cylindrical targets of NaF were prepared by cold pressing followed by powder sintering at 900 \(^\circ\)C for 12 h. Finally, ZnO and 2 wt. \%-\(\text{Al}_2\text{O}_3\) powders were mixed and pressed and then treated at 1000 \(^\circ\)C for 8 h to obtain the ZnO:Al targets for depositing the transparent conductive oxide (TCO).

The solar cells presented in this paper were prepared as follows. Soda-lime glass (SLG) substrates (25 \(\times\) 25 mm\(^2\) wide and 1 mm thick) were cleaned by sonicating in soap and deionised water, rinsed in hot acetone and ethanol, and finally dried in nitrogen flux. A 500 nm-thick Mo back contact was then deposited on glass by DC sputtering at room temperature using a bilayer structure similar to the one proposed in Ref.\(^{17}\). Mo-coated glasses were then transferred to the PED chamber for the deposition of the optically active layers of the solar cells at a process pressure of about 10\(^{-3}\) mbar starting with a 30 nm-thick precursor film of NaF grown at \(T_{\text{sub}} = 80\ \degree\text{C}\). CIGS films were deposited in the same chamber at \(T_{\text{sub}} = 270\ \degree\text{C}\) as measured by a thermocouple placed on the deposition surface. Accelerating voltage and repetition rate were set to 16 kV and 10 Hz, respectively. The other PED process parameters were chosen in order to obtain a p-type Cu-poor CIGS film with a Ga/[In + Ga] atomic ratio of about 0.30 as described in Ref.\(^{13}\). The total thickness of the CIGS film is about 1.6 \(\mu\)m. The formation of the light-absorbing layer was completed with an annealing treatment for 20 min at 300 \(^\circ\)C in order to finalize the Na diffusion from the NaF layer into the CIGS film. After the growth of a 70 nm-thick buffer layer of CdS by chemical bath deposition technique, the samples were transferred to a second PED chamber for the deposition of a 250 nm-thick TCO of ZnO:Al. No undoped ZnO was deposited between CIGS and TCO. Finally, test solar cell devices were fabricated by evaporating 1.5 mm diameter circular Al top contacts through a shadow mask. The cell size (0.15 cm\(^2\)) was defined by mechanical scribing and no antireflection coating was applied. The solar cell architecture is displayed in Figure 1.

The atomic content of Cu, In, Ga, and Se in the films, measured by energy-dispersed x-ray spectroscopy, is 20.0\%, 19.8\%, 7.6\%, and 52.6\%, respectively. From the structural point of view, CIGS films crystallize in the tetragonal chalcopyrite phase, and the grains are fully oriented along the (112) direction. No secondary phases, such as Cu\(_2\)Se and (In,Ga)\(_2\)Se\(_3\), are noticed in the \(\theta/2\theta\) x-ray diffraction pattern. The net carrier density in the CIGS light-absorbing layer was estimated from the capacitance-voltage (C-V) characterization of the solar cell structure. Figure 2 shows the C-V profile at 120 K obtained by using an AC test signal with 25 mV amplitude at a frequency of 1 MHz. At this temperature, only free carriers are expected to respond to the test signal\(^{18}\) and the "freeze out" of the majority carriers should be negligible.\(^{19}\) Furthermore, to avoid metastability effects, the sample was cooled down with no applied voltage after being kept in the dark for 1 h at 330 K.\(^{20}\) The experimental profile exhibits the typical U-shape reported in the literature\(^{18}\)–\(^{20}\) with a minimum corresponding to a depletion layer width of about 350 nm. Following the procedure proposed by Cwil et al.,\(^{18}\) the net acceptor concentration \(N_A\) is estimated at the minimum of the C-V profile and turns out to be about \(6.2 \times 10^{15}\) cm\(^{-3}\). The apparent increase of the doping level towards the back contact (depletion layer width > 400 nm) could be attributed to the accumulation of static charge in deep acceptors present in concentrations much higher than

![FIG. 1. Representative scheme of the solar cell architecture: the thickness of the constituent layers, together with their growth temperature and the respective deposition technique are indicated.](image)

![FIG. 2. C-V profile obtained on the full solar cell stack; the applied DC bias goes from +0.5 to −1 V, the area of the investigated junction is 0.15 cm\(^2\).](image)
Apart from a slightly lower $N_A$ value, the observed C-V characteristic is qualitatively similar to those reported in the literature for high efficiency CIGS solar cells prepared by more conventional growth techniques.

Solar cells were tested by measuring current–density vs. voltage (J–V) characteristics with a Keithley 2635 system under a ABET SUN 2000 solar simulator at standard test conditions (AM1.5 G at 25°C).

Figure 3 shows the typical J–V characteristics of the best of our laboratory cells alongside with a control device grown at the same temperature with no intentional Na doping. The comparison of the two curves highlights the dramatic improvement of the photovoltaic efficiency obtained by tuning and optimising thickness and growth conditions of the NaF layer.

The relevant photovoltaic parameters are reported in Table I. It is worth noting that our typical $J_{SC}$ values are comparable to the best CIGS cells reported in the literature, while the $V_{OC}$ is smaller but comparable to the typical values obtained with Na-doped CIGS grown by single-stage thermal co-evaporation.

A quantitative electron beam induced current (EBIC) analysis was carried out in a scanning electron microscope fitted with a current amplifier and a high-resolution digital image acquisition system. A sequence of 11 digital maps of the EBIC signal generated by the electron beam while scanning the solar cell top surface were collected at different beam accelerating voltages between 7.5 kV and 32.5 kV at a constant beam current of 30 pA. Each image was processed to obtain a statistical distribution of the EBIC gain (= generated current/beam current) over the $2048 \times 1536$ pixels of the map. All the histograms exhibit a narrow gaussian peak with a FWHM between 6.5% and 10% of the peak EBIC gain. By fitting the peak EBIC gain data to the number of e-h pairs generated by the scanning beam as computed by a Monte Carlo simulation, a step-profile of the charge collection efficiency was obtained as a function of depth from the top surface of the cell. The profile shown in Figure 4 includes the contribution of both diffusive and depletion regions whose width was estimated to be $\sim 350$ nm from the C-V measurements. The collection efficiency is negligible on the n side of the junction and reaches a maximum just short of 90% at a distance of about $500$ nm below the interface between CIGS and CdS. This result not only provides evidence that the CdS/CIGS physical interface acts as a strong carrier recombination centre but also indicates that the actual depletion region is located well inside the CIGS layer.

The results presented in this paper suggest that pulsed electron deposition is a viable candidate to complement or even replace co-evaporation and sputtering in TFSC production processes. There are three main reasons supporting this statement:

1. Homogeneous CIGS films can be deposited by PED at much lower temperatures ($< 300 ^\circ C$) compared to other physical techniques. In particular, PED-deposited CIGS films are essentially free of secondary phases like (In,Ga)$_2$Se$_3$ and Cu$_2$Se, observed in CIGS films deposited by single- and three-stage thermal co-evaporation at $T_{sub} < 350 ^\circ C$. They are also not affected by (In,Ga)$_2$Se$_3$ surface segregation and incomplete Se vacancy recovery occurring when sputtered Cu-In-Ga precursors are selenized below $300 ^\circ C$. In fact, thanks to the high internal energy of PED ablated species, films with a single Cu(In,Ga)Se$_2$ crystalline phase can be grown even at temperatures as low as $T_{sub} = 200 ^\circ C$.

2. PED deposition of CIGS is carried out in a single stage, without any further treatments to adjust the Cu/(In + Ga) ratio nor selenization steps after the deposition. This is due to the good control and reproducibility of the film stoichiometry delivered by PED when the target structural and compositional properties are properly matched with the ablation conditions. In particular, the formation of Se-rich films (>50%) directly from a

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**TABLE I.** Photovoltaic parameters of CIGS-based cells fabricated at $T_{sub} < 300 ^\circ C$ with (Device A) and without (Device B) NaF layer. The top metal contacts are excluded from the estimation of the illuminated area.

<table>
<thead>
<tr>
<th>Device</th>
<th>NaF layer</th>
<th>$V_{OC} \text{(mV)}$</th>
<th>$J_{SC} \text{(mA/cm^2)}$</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>with</td>
<td>584</td>
<td>37.5</td>
<td>69.4</td>
<td>15.2</td>
</tr>
<tr>
<td>B</td>
<td>without</td>
<td>350</td>
<td>18.4</td>
<td>34.3</td>
<td>2.7</td>
</tr>
</tbody>
</table>

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**FIG. 3.** Current-voltage characteristics of CIGS solar cells with (A) and without (B) NaF precursor layer, measured at 25°C under AM 1.5 G (100 mW/cm$^2$) illumination.

**FIG. 4.** Average charge collection efficiency as a function of distance from the top surface of the cell as obtained from EBIC.
Cu(In,Ga)Se$_2$ target is a prerogative of PED which other growth techniques might not be able to reproduce because of the low sticking coefficient of Se vapours on a CIGS surface.\textsuperscript{26} For example, a Se flow at least 4-5 times larger than the metal species is needed to achieve stoichiometric films of CIGS by thermal co-evaporation,\textsuperscript{27} which require substrate temperatures of the order of 500 °C or higher for effective Se incorporation. The growth of CIGS films by single stage sputtering also requires a significant Se enrichment of the CIGS targets to achieve 50% Se content in the film.\textsuperscript{28} In the case of PED, the Se sticking probability is effectively enhanced by the large average kinetic energy of the species in the plasma generated by the ablation (reaching tens of eV}\textsuperscript{29} rather than by the substrate temperature or by the Se over-flux.

(3) This work is an important step towards the implementation of a CIGS solar cell production process entirely based on a single deposition technique. At present, three out of four layers of the cell structure (NaF, CIGS and ZnO:Al) are grown by PED in the same deposition chamber simply by using a rotating multi-target carousel.

In conclusion, we have shown that laboratory-scale solar cells based on CIGS grown with a single-stage deposition technique at $T_{\text{sub}} < 300$ °C can achieve efficiencies as large as 15%. This result is to be compared to the 18% efficiency achieved by single-stage co-evaporation but at $T_{\text{sub}} = 550$ °C and in the presence of a large Se over-flux.\textsuperscript{11–30} Techniques based on single quaternary targets, besides requiring substrate temperatures larger than 450 °C, are still limited to top efficiencies of the order of 10%.\textsuperscript{28} We are currently developing a process step to extend the use of PED to the deposition of the buffer layer and demonstrate the production of the whole active structure of a CIGS solar cell with a single low-cost deposition technique.

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