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Solution processing of $\text{CuIn}(\text{S},\text{Se})_2$ and $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ thin film solar cells using metal chalcogenide precursors

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ABSTRACT

In order to realize the true low cost potential of $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ (CIGS) thin film solar cells, high performance needs to be combined with simple and easily controllable atmospheric-based deposition processes. A molecular solution-based approach for CIGS deposition is proposed, using metal chalcogenide precursors dissolved in an amine-thiol solvent combination. CIGS thin films were sprayed with varying Ga content and the sprayed films were incorporated into solar cells. The effect of the Ga content on the material and device properties is investigated. A champion power conversion efficiency of 9.8% (active area) was achieved, which highlights the potential of this methodology.

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1. Introduction

Thin film solar cells are a promising low cost alternative to wafer-based cells, due to materials savings. Among other advantages, these types of solar cells are compatible with low cost, atmospheric-based fabrication processes which can result in significant cost reductions. Such processes are also adaptable to roll-to-roll processing, which brings additional cost benefits [1].

One of the most promising thin film technologies is the chalcopyrite semiconductor CuInSe_2 and its alloys, commonly referred to as CIGS. CIGS has a broad single-phase composition range and a tuneable bandgap, by alloying CuInSe_2 with S or Ga. High performing devices are commonly obtained with a bandgap of around 1.1–1.3 eV, $\text{CGI} = [\text{Cu}]/([\text{Ga}] + [\text{In}])$ of 0.88–0.95 and $\text{GGI} = [\text{Ga}]/([\text{Ga}] + [\text{In}])$ of ~0.3 [2]. Usually, a graded bandgap as a function of depth is desirable, with higher Ga content towards the back of the absorber [3].

Although the highest performing CIGS devices to date are typically obtained by vacuum co-evaporation, high vacuum deposition equipment requires high capital investment [4]. CIGS can be more cost effective when atmospheric solution processes are used instead, while maintaining high performance. Atmospheric-based processes combine

the advantages of high material utilization, low capital investment and a high manufacturing throughput, and as a consequence they are an attractive alternative to vacuum techniques [5]. Pure solution-based approaches in particular offer additional advantages, such as straightforward compositional control simply by modifying the precursor solution [5].

The most promising solution-based approach for CIGS in terms of efficiency, involves the dissolution of metal chalcogenides (Cu_2S and In_2Se_3) and Ga metal in hydrazine [6]. Whilst these precursors are not easily dissolved in common solvents due to their strong covalent bonds, they can be effectively dissolved in hydrazine, in the presence of excess chalcogen [6]. However, the toxic and explosive nature of the solvent makes it difficult to scale up and commercially use this process. This fact has stimulated research on hydrazine-free approaches. For example, recently proposed molecular-based approaches use a combination of dimethyl sulfoxide, thiourea and chlorides [7], butyldithiocarbamic acid [8] or thioacetic acid [9] combined with metal oxides/hydroxides/acetylacetonates. Despite the success of these methods, metal salts and/or oxides are used, which contain impurities that can deteriorate device performance. An alternative molecular-based approach should ideally be developed to involve metal chalcogenides instead, in a similar manner as the hydrazine-based route, but by completely eliminating hydrazine from the process.

An alternative solvent combination of an alkanethiol and 1,2-ethylenediamine has recently been discovered by Brutchey et al. to

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dissolve a range of metals, metal oxides, and metal chalcogenides [10, 11]. This solvent mixture has also been used for $\text{CuIn}(\text{S}, \text{Se})_2$ thin film deposition by dissolving Cu_2S , Cu_2Se , In_2S_3 and In_2Se_3 [12]. However, no working devices were reported due to the high porosity of the spin coated films [12]. Other work suggests that the molecular species in the as-deposited and dried film are partly re-dissolved during the subsequent spinning step, which results in poor material quality [13]. Substitution of spin coating with spraying of the same metal chalcogenide precursor solutions used in our previous work [12], resulted in more densely packed $\text{CuIn}(\text{S}, \text{Se})_2$ absorber layers and power conversion efficiencies (PCE) up to 8% [14]. The alkanethiol – diamine solvent system was later used for fabrication of $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ solar cells with PCEs exceeding 7%, starting from metal oxides [15]. Pure Cu, In and Ga metals have also been dissolved in the same solvent mixture by heating the solutions for several hours, resulting in CIGS solar cells with PCEs of up to 9.5% [16]. In this work we further explore the potential of this solvent system for CIGS deposition, starting from metal sulphide solution precursors. The Ga content was also varied, in an effort to investigate the effect on the material and device properties.

A repeatable and easily controlled methodology is proposed that allows fine adjustment of the absorber composition. A champion PCE of 9.8% is obtained for a graded bandgap of GGI 0.2–0.3. These results highlight the potential of this approach and it is anticipated that further process optimization will result in higher performance.

2. Experimental details

2.1. Preparation of CIGS precursor solutions

The solutions were prepared targeting a Cu-poor film stoichiometry with varying Ga content. Each individual component solution (i.e., In_2S_3 , Cu_2S , Ga) was prepared by dissolution in a mixture of 1,2-ethylenediamine and 1,2-ethanedithiol (vol/vol = 10:1) with a targeted concentration of 0.2 M. The CIGS film composition was controlled by varying the amount of each component solution used. Ga was dissolved in the presence of Se (2 mmol Se per 1 mmol of Ga). It should be noted that no excess chalcogen is required for metal sulphide dissolution, which is the case in the hydrazine-based approach [6]. Hence, elemental Se was only added to the Ga stock solution. The three inks (initially in the form of suspension) were stirred overnight and were converted into optically transparent solutions that are stable for weeks. Cu_2S was converted into a brown solution; Ga stock solution was dark orange and the In_2S_3 solution was colourless. The precursor preparation was performed inside a fume hood, with a nitrogen-purged vial during dissolution. The three component solutions were mixed in certain ratios to form the CIGS precursor solution. The precursor solution was diluted with ethyl acetate (2:1 v/v) and was filtered (0.45 μm polytetrafluoroethylene) prior to the deposition step. After dilution, the precursor solution had a bright orange colour.

2.2. Film preparation and selenization

The spray deposition was performed in ambient atmospheric conditions within a fume hood using a glass chromatography atomizer. The films were sprayed on a molybdenum coated glass substrate placed on a hot plate, controlled at 310 °C. In-between each spray run there was a short drying step for 90 s at the same temperature. After the last deposition/drying cycle, a post-deposition selenization step was performed inside a tube furnace. Unless otherwise stated, there was no intentional bandgap grading in the films and the same solution was used for all the spray runs. In one case, a bandgap grading was attempted by first spraying 3 layers of the solution with GGI = 0.3, followed by two layers of the solution with GGI = 0.2.

For the selenization, two 2.5×2.5 cm samples were placed inside a graphite box with Se pellets. The tube was first purged with nitrogen, before setting the starting pressure to 53 kPa. The heating profile lasted

for 50 min including ramping (~ 35 °C/min), which resulted in the complete evaporation of the Se pellets in the box (~ 300 mg).

2.3. Fabrication of CIGS solar cells

The devices prepared in this work were deposited in the standard stack configuration of $\text{ZnO}:\text{Al}/\text{iZnO}/\text{CdS}/\text{CIGS}/\text{Mo}/\text{glass}$. The CdS layer (~ 60 nm thickness) was deposited by chemical bath deposition. The intrinsic ZnO and Al doped ZnO layers (~ 80 nm and 500 nm respectively) were both deposited using RF sputtering. Finally, a top contact grid and MgF_2 anti-reflective (AR) coating were evaporated. Mechanical scribing was performed to isolate each cell of ~ 0.25 cm² area. The grid (0.05 cm²) shades $\sim 20\%$ of the device area.

2.4. Characterization

Energy Dispersive X-ray spectroscopy (EDS) was used for compositional analysis, with an aperture size of 60 μm and 20 kV operating voltage. A Bruker D2 phaser X-ray diffractometer was used for X-ray diffraction (XRD) analysis, using a $\text{Cu-K}\alpha$ X-ray source and a Lynxeye detector. For the Raman measurements, a Jobin-Yvon LabRam HR system was used to collect un-polarised micro-Raman spectra using a $\times 50$ objective lens and a He-Ne laser ($\lambda = 632.817$ nm). The current density/voltage (J-V) characterization of the devices was performed using AM1.5G simulated sunlight from a dual source solar simulator (Wacom, Japan) under 100 mW cm⁻², using a calibrated Si reference cell. Prior to the J-V measurements, the cell area was measured using a digital microscope. The external quantum efficiency (EQE) spectra were acquired with chopped light using a Bentham PVE300 system with both Si and Ge reference diodes for calibration. The measurements were performed at 0 V bias with a spectral resolution of 5 nm.

3. Results and discussion

EDS analysis was performed on as-deposited and selenized samples. The chemical composition of the film was determined by averaging the data collected from 2 random points. Table 1 summarizes the composition of each selenized film, as the concentration of each element in relation to (In + Ga) content. The targeted film composition (based on the precursor solution) was $\text{Cu}_{0.9}\text{In}_{1-x}\text{Ga}_x\text{Se}_2$, with a constant CGI ratio and GGI varied from 0 to 0.4. It is assumed that S is fully displaced by Se during selenization, as previously observed for sulphide nanocrystal precursors [17]. We have also previously shown for Ga-free samples that S is mostly displaced by Se during the selenization step with comparable selenization conditions [14]. Overall, the atomic ratios of the cations in the films are retained. Previous work on spin coated CIGS films using the alkanethiol – diamine solvent system showed that there was a strong Cu loss during film deposition [13]. This problem is not evident

Table 1

The targeted film composition (based on the precursor solution) and the actual composition of each selenized CIGS sample, estimated with EDS analysis.

		Composition				
		Ga/(In + Ga)	Cu	In	Ga	S
0.0	Targeted	0.90	1.00	0.00	0.00	2.00
	Film	0.86	1.00	0.00	0.11	2.19
0.1	Targeted	0.90	0.90	0.10	0.00	2.00
	Film	0.88	0.92	0.08	0.08	2.41
0.2	Targeted	0.90	0.80	0.20	0.00	2.00
	Film	0.93	0.81	0.19	0.72	3.57
0.3	Targeted	0.90	0.70	0.30	0.00	2.00
	Film	0.88	0.72	0.28	0.19	2.04
0.4	Targeted	0.90	0.60	0.40	0.00	2.00
	Film	0.90	0.61	0.39	0.17	2.30

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