Accepted Manuscript

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Reference code: G2ZLF

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Abstract

A pure solution-based approach is proposed for the fabrication of high quality CuIn(S,Se)$_2$ (CIS) thin films. This is an alternative procedure to the hydrazine-based route and involves the dissolution of metal chalcogenides in a safer solvent combination. The solvent mixture used in this work has the same advantages as hydrazine, such as good solubility of metal chalcogenides and clean decomposition, which is a prerequisite for high quality absorber layers. The solvents that are used are also much less toxic compared to hydrazine and can potentially result in a more feasibly industrially scalable deposition technology for CIS and the related alloys including Cu(In,Ga)(S,Se)$_2$ (CIGS). The characterization of the obtained thin film material verifies the presence of the CIS chalcopyrite phase with good crystal growth.

Keywords: Chalcopyrite, CIGS, Solar cell, Spin-coating, Solution processing

1. Introduction

The chalcopyrite semiconductor $CuIn(S,Se)_2$ (CIS) along with the related alloy $Cu(In,Ga)(S,Se)_2$ (CIGS), is a high performance photovoltaic material for thin film solar cells. This material has attracted considerable attention in the solar community, with a record efficiency of 20.8%, recently reported by ZSW [1].

High efficiency CIGS thin films are conventionally fabricated using a vacuum-based coevaporation approach. The use of such vacuum-based deposition techniques results in a high manufacturing cost, which is the major obstacle to the commercialization of CIGS. Recent research on high efficiency CIGS solar cells is focused on low-cost deposition techniques, without the necessity of vacuum processing. Various low cost techniques are under investigation which, depending on the nature of the precursor that is used, can be considered as solution or nanoparticle-based processes. Both approaches are attractive for cheaper, large-scale manufacturing and can involve deposition techniques such as printing. These techniques are already established in low cost manufacturing [2]. However, considering the two routes, the solution-based technique is more favourable as the synthetic and purification processes are simpler compared to the nanoparticle route. Also, the components of a pure solution are mixed on a molecular scale, which enables the formation of a compositionally uniform CIGS layer [3]. The chemical composition of the final layer can be directly associated with the precursor solution and this makes the process more controllable compared to the conventional vacuum techniques, which normally have multiple sources.

Various types of precursor compounds can be used for solution processing of CIGS thin films, including metal-organic precursors [4-5], metal salts [6-7] or chalcogenides

[8]. Among the different starting materials, solution processed chalcogenides have been used for solar cells, resulting in high performance [8]. The main advantage of this type of process is the avoidance of contamination in the thin film (such as carbon, oxygen or chlorine), since the precursors are free of these undesirable elements [9]. However, most metal chalcogenide semiconductors are insoluble in common solvents, whilst some metal chalcogenides, namely Cu_2S and In_2Se_3, can be dissolved in hydrazine in the presence of elemental chalcogen. It was reported that the dissolution of these compounds occurs via "dimensional reduction" [3] which is a solid-state reaction [10]. The mixing of hydrazine with metal chalcogenides results in the formation of metal chalcogenide anions and hydrazinium cations. The presence of excess chalcogen is required for the precursor to be dissolved, as the chalcogen breaks the metal chalcogenide framework, by dimensional reduction [3]. This process has led to the highest solar cell efficiency (15.2%) for the solution-based deposition techniques for CIGS [8]. Hydrazine can easily dissolve the chalcogenide precursors and the resulting precursor solution can be decomposed cleanly, without leaving impurities in the film. However, hydrazine is very toxic and explosive and therefore unsuitable for large scale production. A similar approach was also proposed, based on less toxic solvents (ethanolamine and dimethylsulfoxide), but the use of hydrazine was still required in the precursor preparation step [11]. A different methodology is required to eliminate completely the use of hydrazine and substitute it with a safer solvent, leading to high efficiency CIGS solar cells.

Consequently, the aim of this work is to develop a safer procedure for the deposition of the absorber layer in CIGS solar cells. We have substituted hydrazine with a safer, lower toxicity solvent mixture. Metal chalcogenides, including copper and indium

selenides and sulphides are easily dissolved in this solvent combination in air at room temperature and true solutions are obtained that remain stable for days.

2. Experimental Details

$CuIn(S,Se)_2$ thin films were deposited by spin coating, using a solvent mixture comprised of 1,2-ethanedithiol and 1,2-ethylenediamine [12]. The procedure consists of four stages: the precursor preparation, the deposition of the precursor, drying and the final post-annealing step.

2.1. Precursor preparation

Initially, the solutions of metal chalcogenides are prepared separately. Each chalcogenide, Cu_2S/Cu_2Se and In_2S_3/In_2Se_3, is dissolved separately in a mixture of 1:10 vol/vol 1,2-ethanedithiol/1,2-ethylenediamine at room temperature. The concentrations of the solutions used in this work varied from 0.05 M to 0.3 M. The dissolution of these compounds does not require the addition of elemental chalcogen, which is required for the dimensional reduction with hydrazine [13]. Evidence that true solutions are obtained in both cases, where chalcogen is present or absent in the precursor, is shown in Figure 1. Therefore, the final chalcogen composition in the absorber layer can be controlled directly, either in the solution preparation step (by adding excess chalcogen to the solution) or in the post-deposition annealing procedure (by adding excess chalcogen in the annealing step). Each individual solution of chalcogenide or a mixture of chalcogenide and chalcogen is prepared separately and is stirred at room temperature in air for 24 hours. First, a coloured suspension is formed, which is then converted to a transparent solution after stirring in a sealed vial. Figure 1 illustrates the suspension-like appearance of In_2Se_3 immediately after mixing with the solvents and the solution formation after stirring the

mixture at room temperature for 24 hours. Cu_2S and Cu_2Se form black solutions after a few hours of stirring with this solvent combination. The solutions are then mixed together in different ratios, according to the required stoichiometry of the final absorber layer. The mixed precursor solution is stirred for a few hours and it is used for the deposition stage.

2.2. Deposition process

The precursor is spin coated on molybdenum-coated soda-lime glass substrates. The solution is first coated at a low rotation speed of 500 revolutions per minute (rpm), followed by a faster rotation at 1000 rpm. Between each coating, the film is dried on a hot plate at 250 °C for 5 minutes. The coating and the drying steps are then repeated, to obtain the required thickness. The thickness of each coating depends on the concentrations of the precursor used. For 0.15 M, which was a standard concentration used in this work, five runs of precursor resulted in a 500 nm thickness. The deposition and the drying steps both occur in air, inside a fume hood.

2.3. Post-deposition annealing

The dried sample is annealed and/or selenized in nitrogen in a two temperature zone tube furnace controlled with proportional integral derivative (PID) controllers. Selenium (Se) pellets are used for the selenization process and the temperature of the Se source is 350-400 °C. The Se vapour is transported to the substrate using nitrogen as a carrier gas, using a working pressure of 1.1 MPa. The annealing was performed with and without the Se source, at various temperatures, annealing times, ramping rates and flow rates of nitrogen. The annealing duration used for the results presented here was 50 minutes including the ramping (40 °C/min). The annealing temperature was 550 °C. These parameters resulted in approximately 25 mg of selenium being used in each annealing treatment.

2.4. Characterization

The CIS absorber has been deposited on molybdenum coated and bare glass substrates, to facilitate the characterization of the samples. The molybdenum layer was deposited by direct current (DC) magnetron sputtering using two different working gas pressures. This causes the formation of a bilayer, which has been reported to improve the adhesion and electrical properties [14].

The surface morphology was analysed using a Carl Zeiss 1530 VP field emission gun scanning electron microscope (SEM). The aperture size was 30 μm and the operating voltage was 5 kV. Transmission electron microscopy (TEM) was carried out using a FEI Tecnai F20 (S)TEM equipped with a silicon drift detector, with an operating voltage of 200 kV. The TEM samples were prepared by Focused Ion Beam (FIB) milling and platinum was locally deposited as an over-layer.

For the thickness measurement, the cross section SEM images of fractured samples were analysed. Energy Dispersive X-ray spectroscopy (EDS) was used for the chemical characterization of the sample, with an aperture size of 60 μm and 20 kV operating voltage. A D2 phaser X-ray diffractometer by Bruker was used for the X-ray diffraction (XRD) analysis of the samples deposited on glass. The X-ray diffractometer was equipped with a Cu-Kα X-ray source and Lynxeye detector. The divergence slit was set at 1 mm and the antiscatter slit at 3 mm. The sample was rotated at 15 rpm. Thermogravimetric analysis (TGA) scans were performed using a TA Instruments Q5000IR system with flowing nitrogen atmosphere and a ramp rate of 5 °C/min, in a covered unsealed platinum pan.

3. Results and Discussion

3.1. Characterization of samples

The following results were obtained solely using the sulphide precursor combination. The selenide combination can be applied in a similar manner. The XRD pattern of a selenized sample deposited using the sulphide precursor combination (Cu_2S and In_2S_3) is shown in Figure 2. The spectrum verifies the presence of CuInSSe chalcopyrite phase (JCPDS 36–1311). The XRD analysis of the dried sample before annealing is also shown for a comparison. Three peaks with low intensity are evident which either correspond to the (112), (220) and (312) peaks of $CuInS_2$ (JCPDS 15-0681), or to a Cu_xS phase. It is evident that the crystallinity of the dried film is very low, but there is a significant crystallization after annealing at 550 °C.

TGA was carried out on the precursor residue after the prepared solution was evaporated using a rotary evaporator at 60 °C. For the precursor preparation, a solution of Cu_2S with excess S and a solution of In_2S_3 with excess S were mixed in an equimolar ratio, with a concentration of 0.14 M. The thermal decomposition pattern of the precursor is shown in the inset of Figure 2 and is consisted mainly of two steps in the weight loss regime. The first step at around 120 °C is associated with residual solvent evaporation, from solvent still present in the not fully dried sample. The second step in the weight loss curve occurs at around 200 °C and can be attributed to the dissociation of the complexes that are formed between the diamine/dithiol and the metal chalcogenides. This weight loss can also be partly related to the loss of excess chalcogen, as was previously reported for the hydrazine-based procedure [13]. The TGA analysis shows that the precursor is decomposed at fairly low temperatures (200 °C), which is verified by EDS measurements of samples dried at 250 °C that did not contain carbon (not shown). In this work, 250 °C was identified as the optimum drying temperature, as it is

sufficiently high for the removal of the organic species and it is low enough to eliminate molybdenum and precursor oxidation in air during the drying step.

The investigation of the film morphology with SEM shows that the material has good crystal growth with grains approaching 500 nm in size after annealing, as shown in Figure 3 (a). The SEM image was obtained from a sample with a thickness of 500 nm and therefore larger crystals are expected when thicker films are processed. However, the film is not sufficiently uniform and fully compact, with some cracks and voids present. This is due to the rapid evaporation of the solvent during the drying step and will be fully optimized in future work.

The crystal growth of the material is also evident in the cross-sectional TEM image, shown in Figure 3 (b). The image was taken for a sample deposited on molybdenum. The crystalline CIS layer is shown on the surface of the molybdenum with a grain size approaching 500 nm. The final surface layer is the platinum over-layer. The intermediate layer at the Mo/CIS interface was identified to be molybdenum oxide, using EDS measurements. The molybdenum is partly oxidized due to a leak in the selenization furnace.

3.2. Comparison with the hydrazine route

The development of the hydrazine-based route was a breakthrough for the low cost deposition of CIGS. Hydrazine, as a solvent for CIGS deposition has many advantages; it coordinates weakly, it is decomposed cleanly without leaving carbon or oxygen impurities and it is a strong reducing agent. However, it is explosive, highly toxic and carcinogenic, which makes the commercialization of the process unlikely. An alternative approach is required which will eliminate completely the use of hydrazine, which will be safer and more scalable.

In this work, hydrazine is substituted by an alternative solvent combination, comprised of a dithiol and a diamine. The solvents are neither explosive nor carcinogenic and they are relatively non-toxic. This allows us to eliminate the use of a glove box for the process and therefore the experiments are carried out in air. The elimination of the necessity for an inert atmosphere simplifies the scale-up of this deposition technique.

The addition of an equimolar amount of elemental chalcogen is a prerequisite for the dissolution of the chalcogen compounds in hydrazine [13]. Conversely, the dithiol/diamine mixture can dissolve the metal chalcogenides without the addition of sulphur or selenium, which provides an increased flexibility for the precursor preparation. In this case, the elemental chalcogen can be dissolved separately and the quantity of the chalcogenide solution used can be directly associated with the chemical composition of the absorber.

One of the main advantages of the hydrazine-based route is the avoidance of a post-deposition selenization step [15]. In our approach, we have not yet eliminated completely the selenization step, due to the incomplete optimization of the process. Our aim is to eliminate the selenization step in future work.

The proposed methodology is promising for the preparation of sufficiently high quality absorber layers for a thin film photovoltaic device. True solutions are obtained by using a safer solvent than hydrazine and are cleanly decomposed forming the CIS chalcopyrite phase. These preliminary results are therefore very encouraging for the development of an alternative solution-based technique.

4. Conclusions

A pure solution-based deposition procedure for CIS has been proposed by using an alternative solvent combination to hydrazine. The avoidance of hydrazine makes the process safer and more production-friendly. Metal chalcogenides are dissolved at room temperature in the solvent combination and the precursor solution is decomposed cleanly, leading to crystalline films of CIS without impurities. Even though the process requires further improvement, the presence of CIS chalcopyrite phase with good crystal growth is evident. This methodology has the potential to result in a more cost-effective and safer production of thin film photovoltaics.

Acknowledgements

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Figure Captions

Figure 1: Images of the In_2Se_3 precursor show that clear solutions are obtained. The mixture is initially in the form of suspension (a) but it becomes transparent after stirring at room temperature for 24 hours (b).

Figure 2: XRD pattern of a selenized sample deposited using the sulphide precursor combination (Cu_2S and In_2S_3). The XRD of the dried sample before annealing is also shown for a comparison. Inset: TGA data of the precursor mixture of sulphides, evaporated using a rotary evaporator.

Figure 3: (a) An SEM image of the surface of a film deposited on bare glass showing that the material is crystalline. (b) A cross-sectional TEM image of a sample deposited on molybdenum, showing good crystal growth, with grains ~500 nm in size.
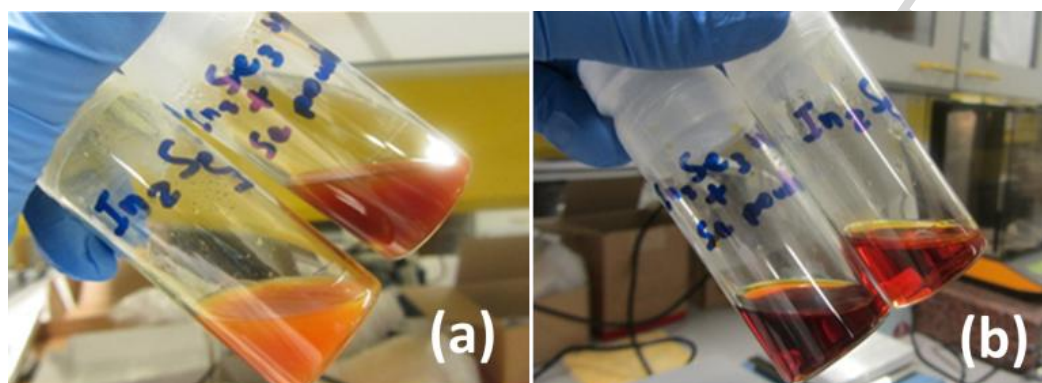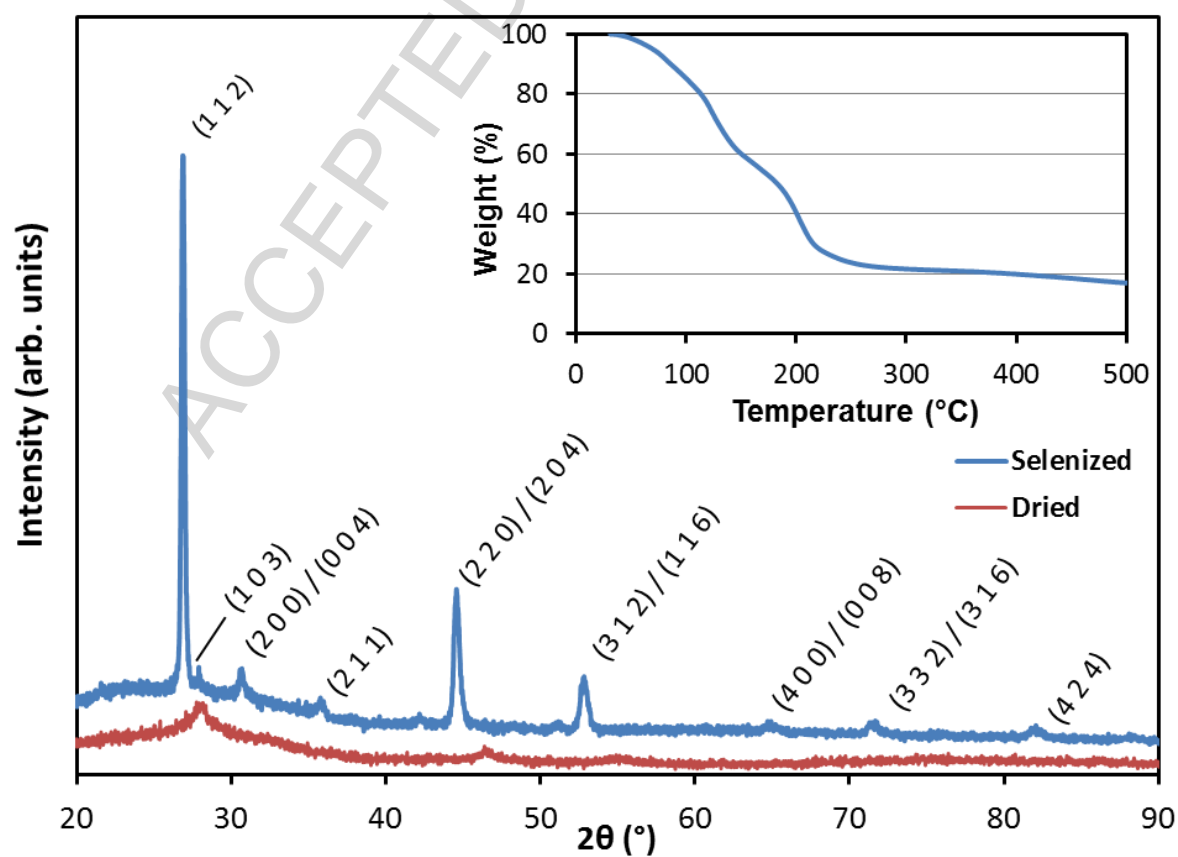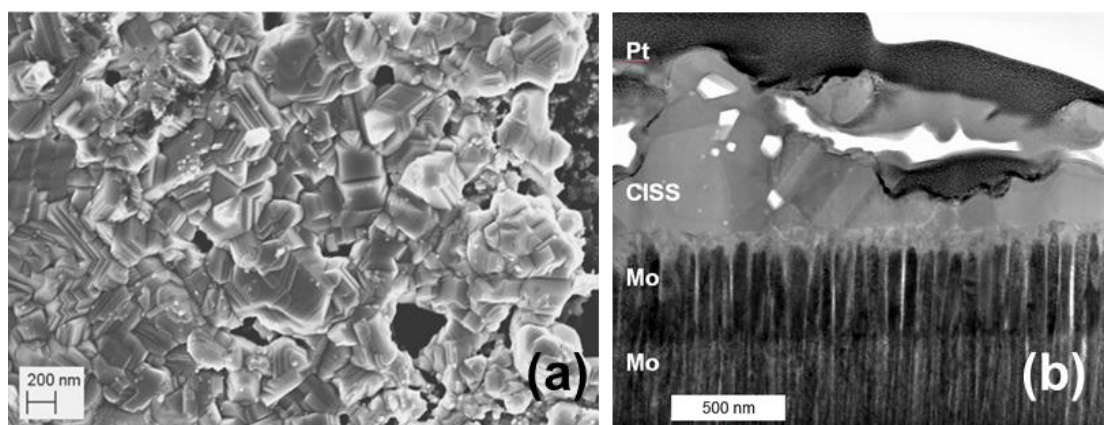
Figures

Figure 1

Figure 2

Figure 3

Highlights

- Pure solution-based approach for CIS from metal chalcogenides.
- Safer, alternative solvent to hydrazine.
- CuIn(S,Se)$_2$ chalcopyrite phase with good crystal growth.