Hydrazine-free metal chalcogenide precursor solutions for sprayed CuIn(S,Se)$_2$ thin film solar cells

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Abstract

CuIn(S,Se)$_2$ (CIS) absorbers have been prepared by dissolving copper and indium sulphides in a hydrazine-free mixture of solvents, followed by spray deposition of the solution on molybdenum coated glass substrates. It was found that the choice of the solvent for dilution of the precursor solution can have an influence on the absorber quality and consequently, the device performance. The sprayed absorbers were implemented in solar cell devices, resulting in power conversion efficiencies (PCE) exceeding 7%.

Introduction

The chalcopyrite semiconductor CuInGaSe$_2$ (CIGS) is a promising material for thin film solar cells. CIGS is currently the best performing polycrystalline thin film solar cell technology reporting a record efficiency of 22.3% (Solar Frontier) when deposited by sputtering [1]. Despite the high efficiencies achieved by co-evaporation or sputtering approach, vacuum-based deposition techniques require high capital investment. Atmospheric solution processing of CIGS absorber layers offers a number of potential advantages, including lower capital costs.

Solution processing of semi-conductors allows easy control of the composition of the film. Beneficial dopants can also be added to the starting solution in a straight-forward way, which makes this method extremely versatile and controllable [2]. Solution processing is also suitable for large area roll to roll processing adding to its economic value, as well as rapid combinatorial analysis, allowing for fast materials development at an R&D level [3]. The most successful pure solution approach to date in terms of PCE is a hydrazine-based technique developed at IBM T.J.Watson Research Center. This method involves the dissolution of metal chalcogenides in hydrazine and spin-coating of the solution, yielding 15.2% efficiency [4]. Whilst the method has extreme promise, the use of hydrazine makes this process difficult at the industrial scale because of the toxic, explosive and carcinogenic nature of the solvent [5]. Hydrazine has been the only solvent until recently, to successfully dissolve metal chalcogenides. Recently an alternative technique has been developed, using non-hydrazine solvents (1,2-ethanedithiol/1,2-ethylenediamine) to effectively dissolve metal chalcogenides into solution as the starting precursors for CIGS deposition [6].

The purpose of this work is to further develop a hydrazine-free, environmentally friendly method for CIGS absorber fabrication using metal chalcogenide precursor solutions. As a solution based approach, all components (precursors, solvents, additives) and selenisation conditions (temperature, pressure) need to be carefully selected in order to achieve a final film with good opto-electronic characteristics.

Experimental

Metal chalcogenides are used as the starting material since they are free of detrimental impurities (such as carbon, oxygen or halogens) which can be incorporated into the film, deteriorating the device electronic properties or impede grain growth [2]. In our previous work, copper and indium sulphides (Cu_2S and In_2S_3) have been successfully dissolved in 1,2-ethanedithiol/1,2-ethylenediamine in a 1:10 volumetric ratio and pure solutions were obtained that remained stable for several days. This binary solvent mixture was developed by Webber et al. [7] and it has been used as a low-toxicity alternative to the hydrazine route for the preparation of CuIn(S,Se)$_2$ (CIS) films [6]. Here solutions have been prepared with a final precursor concentration of 0.1M and a copper poor composition (Cu/In ratio of 0.8). The solution was prepared in a nitrogen purged vial and was further diluted with polar aprotic solvents, such as ethyl acetate (EA), dimethyl sulfoxide (DMSO) or methyl ethyl ketone (MEK) with a solution to solvent ratio of 2:1. After the dilution, the solution was sprayed (using a chromatography atomiser) onto a molybdenum (Mo) coated soda-lime glass (SLG) substrates. Two 5x5 cm^2 substrates were placed on a preheated hot-plate, maintained at 310°C. The final solution of approximately 5 mL was filtered (0.45 µm PTFE) and then sprayed in air, onto the substrate. In order to obtain the desired absorber thickness, several layers are sprayed with a drying step in between, to allow excess solvent to evaporate. Once all the precursor layers are deposited, a post-deposition annealing treatment in a selenium atmosphere is performed inside a tube furnace. The amount of selenium used (initially in the form of pellets) was 0.25-0.3 g for a 2.5x5 cm^2 sample inside a graphite box. The selenisation is performed for 50 min (including the ramp from room temperature), with a final temperature of 540°C and a starting pressure of 400 Torr. The CIS device was completed with the chemical bath deposition of CdS, followed by the intrinsic ZnO and Al doped ZnO (AZO) by RF magnetron sputtering. Mechanical scribing delimited cells to an area of 0.25 cm^2. The microstructure of the films was analysed using a JEOL JSM-7800F Field Emission Scanning Electron Microscope (FE-SEM). The device performance was evaluated using a solar simulator to perform light and dark current-voltage measurements under 1000 W/m^2 illumination.

Results and Discussion

The choice of the appropriate solvent is one of the key elements to consider in solution-based approaches for CIS/CIGS. First, the precursors have to be successfully dissolved in the solvent, so they are mixed on a molecular level, forming a stable solution at room temperature. In the case of chalcogenides, this is extremely challenging, because this class of materials have strong covalent bonds and as a consequence, their solubility in commonly used organic solvents is limited. Secondly, the deposited film should be uniform, forming a good interface with the Mo layer. Solvent evaporation occurs during the spraying and drying steps after contact with the heated substrate. Depending on the solvent, impurities can be introduced into the inorganic semiconductor film, such as residual carbon or oxygen contamination. Finally, the final film needs to preserve its integrity (no cracks/delamination) even after the post-deposition selenisation treatment. Therefore, a number of solvent characteristics, such as polarity, surface tension, boiling point, vapour pressure, viscosity, reactivity and toxicity must be considered when choosing a solvent. The physical properties of three different solvents used to dilute the precursor solution in this study, are summarised in Table 1. All three solvents used in this work are aprotic solvents (with no O-H, N-H bonds and cannot donate H^+) with varying polarities (dielectric constant varying from 6 to 47). In our previous work, such solvents have been shown to effectively dilute the amine-thiol solution without causing the complex to crash out of solution. Such solvents have desirable characteristics for solvating and stabilising cationic species. Moreover they are non-hazardous, easy to handle and have relatively low boiling points.

Table 1 *Physical properties of the solvents used*

(At 20°C)	**EA**	**MEK**	**DMSO**
Boiling point (°C)	77	80	189
Dielectric constant	6	18.5	47
Density (g/mL)	0.90	0.81	1.1
Viscosity (cP)	0.45	0.43	1.99
Surface tension (dyn/cm)	23.9	24.6	43.5

The selenised absorber layers were fractured for the SEM cross-section images. These are displayed in Fig. 1 for each type of dilution. For all samples, successive layers of Mo, molybdenum selenide ($MoSe_2$) and CIS absorber can be clearly seen on the SLG substrate. The absorber film consists of relatively large, well-defined grains on the surface and a very poorly crystallised film underneath (<80%). Occasionally, large grains have grown in the middle of this ‘fine-grained’ layer. The formation of a similar fine grain/large grain bilayer has been previously reported in the literature for another solution-based approach [8]. Overall, the best crystallisation seems to be obtained for the EA treated film. The thickness of the absorber layer varies by up to 2 µm according to the different diluents used for the same amount of solution sprayed. This can mostly be due to the manual nature of the deposition technique, but also due to the nature of the diluting solvent. The thickness of the formed $MoSe_2$ interface layer is significant in each case and may be responsible for resistive losses at the back contact.

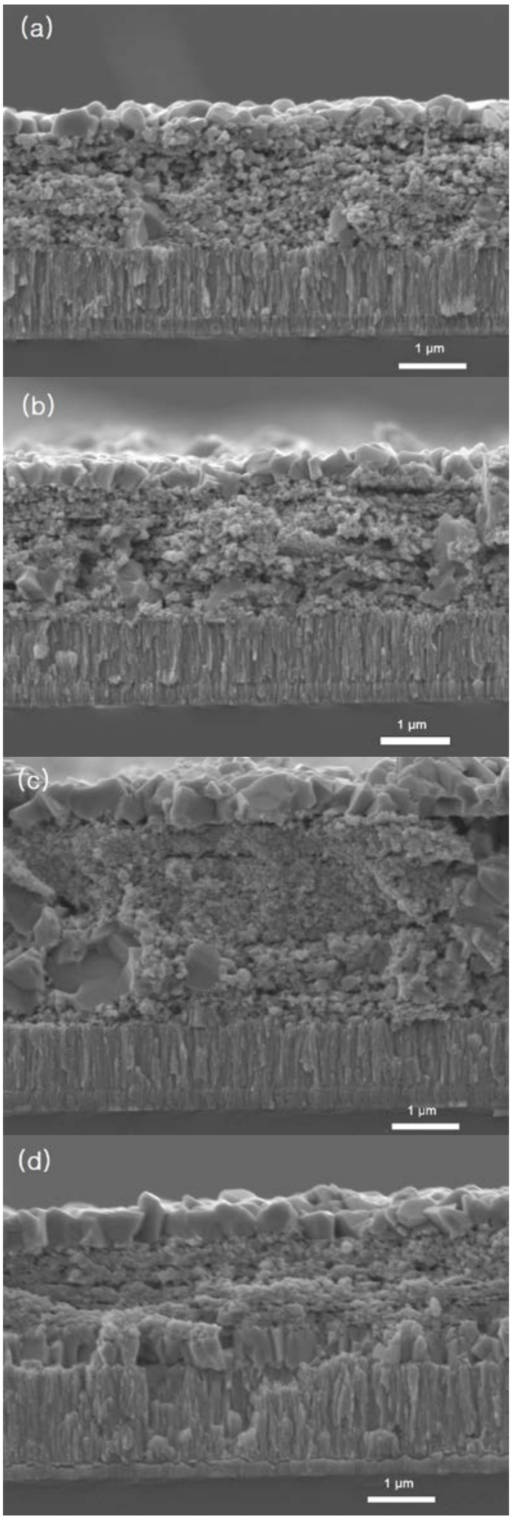

Figure 1 *SEM cross-sections of selenised absorber films deposited on Mo coated SLG for different solvents: (a) ethyl acetate (b) DMSO (c) without dilution (d) MEK*

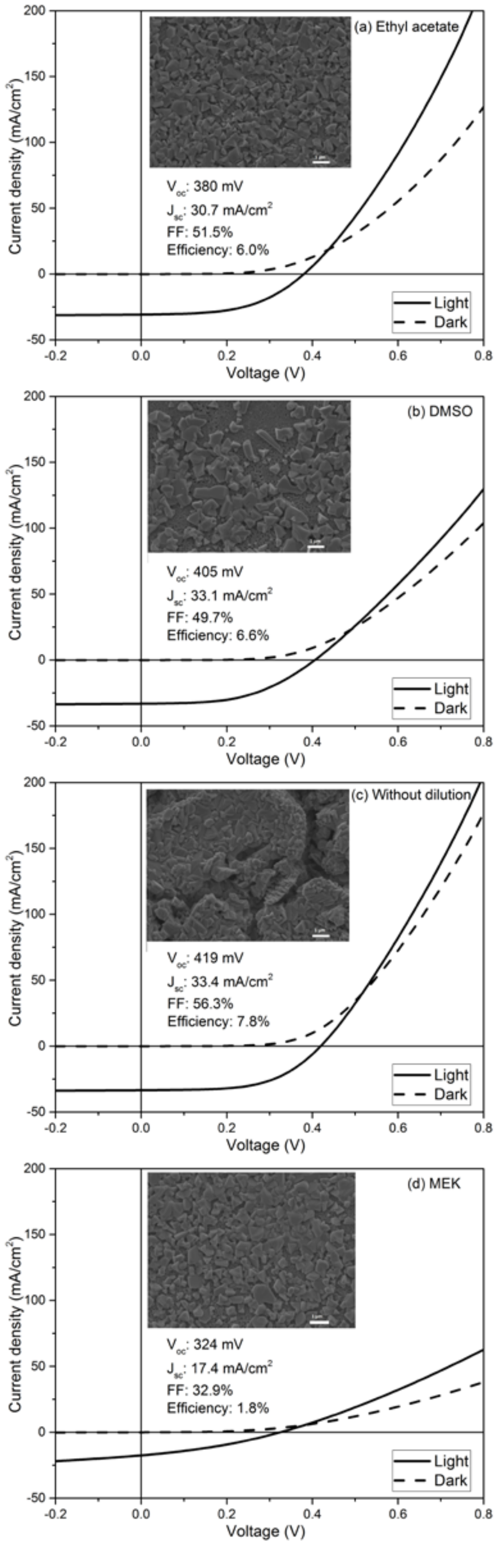

Figure 2 *J-V curves for different dilutions: (a) ethyl acetate (b) DMSO (c) without dilution (d) MEK. Inset: SEM images of the surface of selenised CIS film*

The $MoSe_2$ thickness seems to be even more significant for the MEK treated film, which is expected, since the absorber film is slightly thinner compared to the rest of the samples and more selenium can go through to react with Mo to form $MoSe_2$. Moreover, an unusual crystalline layer is formed at the interface between the back contact and the absorber layer in the MEK processed sample. An X-ray diffraction (XRD) or Energy dispersive spectroscopy (EDS) mapping is required to confirm the nature of the layer. The light and dark JV curves of a representative device from each dilution method are shown in Fig. 2. The inset of Fig. 2 shows the surface morphology of the selenised film, observed using SEM. The best performing device was deposited with a solution which was not diluted, and had a PCE of 7.8%. This is due to the relatively high fill factor of 56.3% and improved series resistance (R_S) compared to the other devices. The higher performance might also originate from the large thickness of the absorber layer, preventing shunting, which might otherwise occur in the porous, fine-grained layer. On the contrary, the lowest performing device was obtained when MEK was used for dilution. The obtained efficiency was only 1.8%, mostly due to the low short circuit current (J_{SC}) and a very high R_S possibly because the absorber film was too thin and $MoSe_2$ too thick. The top surface of the selenised layers looks very smooth, for the samples processed with dilution. The surface of the undiluted film has grains with a comparable size to the grains at the surface of the diluted samples, but is very rough with big agglomerates on the top. The film surface is not fully covered with large grains for DMSO or MEK treated films, which may explain the higher R_S compared to the other two devices with the top surface fully crystallised.

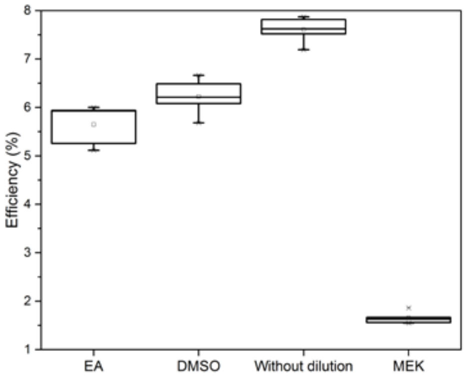

Figure 3 *Box plot showing variation of efficiencies with the type of dilution*

Fig. 3 shows the distribution of efficiencies measured on a set of 5 cells of each device. The difference in the performance between the DMSO and EA devices originate from the higher open circuit voltage (V_{OC}) of the DMSO processed device.

Conclusion

All of the CIS devices presented here have a relatively high series resistance, which limits the FF and hence, the efficiency. This may be caused by various reasons: imperfectly crystallised absorber, non-optimised back contact with too thick $MoSe_2$ layer or non-optimised TCO properties. Further optimisation of the top and back contact deposition processes is required for eliminating these problems, which is currently under investigation. This study shows that the choice of solvent is critical for the device performance, as there is an effect on the crystal quality of the films. However the solvent physical properties alone are insufficient to conclude on the choice of the solvent and further investigations are required.

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