

# Characterisation of ultrasonically sprayed $\text{In}_x\text{S}_y$ buffer layers for $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells

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Available online 19 December 2006

## Abstract

In order to replace chemical bath deposited (CBD) CdS buffer layers in  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) solar cells by an alternative material,  $\text{In}_x\text{S}_y$  thin-film buffer layers were prepared by ultrasonic spray pyrolysis at various substrate temperatures. X-ray Diffraction measurements confirmed that the films contained primarily the tetragonal  $\text{In}_2\text{S}_3$  phase. X-ray Photoelectron Spectroscopy measurements revealed a small concentration of chlorine impurity throughout the  $\text{In}_x\text{S}_y$  layer. By depositing the indium sulphide layer as buffer layer in the CIGS solar cell configuration, a maximum solar cell efficiency of 8.9% was achieved, whilst the reference cell with CdS/CIGS on a similar absorber exhibited 12.7% efficiency. Additionally, light soaking enhanced the efficiency of  $\text{In}_x\text{S}_y$ /CIGS cells primarily by improvements in fill factor and open circuit voltage.

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**Keywords:** Indium sulphide;  $\text{In}_2\text{S}_3$ ; Buffer layer; Thin film; Solar cells; Ultrasonic spray pyrolysis; CIGS

## 1. Introduction

The development of alternatives to CdS for CIGS solar cell buffer layers is currently attracting considerable attention [1].  $\text{In}_x\text{S}_y$  is an attractive alternative buffer material to substitute CdS because of its higher band gap energy of 2.4–2.8 eV [2,3], which makes it more transparent in the wavelength region of 350–500 nm.  $\text{In}_x\text{S}_y$  thin films have been grown by various techniques, such as physical vapour deposition (PVD) [4], atomic layer deposition (ALD) [2], metal-organic chemical vapour deposition (MOCVD) [5], chemical bath deposition (CBD) [6], ion layer gas reaction (ILGAR) [7] and spray pyrolysis [3,8]. So far only ALD and ILGAR have produced  $\text{In}_x\text{S}_y$ /CIGS cells comparable to CBD-CdS/CIGS cells, with efficiencies of 16.4% and 14.7%, respectively [1,2,7]. CBD, ILGAR and spray pyrolysis techniques are preferable for industrial applications because of the

economical, non-vacuum systems involved. The advantages of spray pyrolysis are that it is a fast, material-efficient, large-area scalable and simple method for growing thin-film layers.

In the ultrasonic spray pyrolysis (USP) system, an alcoholic solution containing the precursor-salts is nebulised by an ultrasonic actuator and then transported to a heated substrate. The advantage of USP over conventional pneumatic spraying is the better control of the spray flux with a soft carrier-gas flow, which allows the deposition of very thin layers with homogeneous thickness. This is important for thin buffer layers in CIGS solar cells, where the desired film thickness is 30–50 nm.

In this work, the optical and compositional properties of USP- $\text{In}_x\text{S}_y$  films deposited at various substrate temperatures are investigated and the characteristics of CIGS solar cells with USP- $\text{In}_x\text{S}_y$  buffer layers are compared to the conventional CIGS solar cells with CBD-CdS buffer layers.

## 2. Experimental details

$\text{In}_x\text{S}_y$  thin films were deposited on soda lime glass (SLG) substrates by spraying an alcoholic solution containing  $\text{InCl}_3$

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(0.005 M) and  $\text{SC}(\text{NH}_2)_2$  (0.015 M) with USP equipment provided by Solaronix SA, Switzerland. SLG substrates were cleaned with isopropanol and double deionised water, the CIGS surface was activated by etching with 10% KCN just before the USP deposition. Various heater temperatures were used to produce layers for spraying times of generally 20 min. In order to have a buffer-layer thickness smaller than 70 nm, on CIGS substrates at a heater temperature of 380 °C a spraying time of 10 min was used. The nitrogen carrier-gas flow rate was kept at 15 l/min corresponding to an average solution spray-rate of 30 ml/20 min.

The thickness of the  $\text{In}_x\text{S}_y$  layers was investigated with a stylus profilometer (DEKTAK 3030 from Sloan) and the optical properties were measured with a spectrophotometer (UV-160 from Shimadzu) over the wavelength range of 300–1100 nm. In X-ray Photoelectron Spectroscopy (XPS Quantum 2000 from PHI) for sputtering Ar at 4 kV was used to investigate the In to S ratio depth profile, the calibration was made on  $\text{SiO}_2$  and etching rate was 21.7 nm/min. X-ray Diffraction (XRD) was used to determine the chemical and structural phases of the  $\text{In}_x\text{S}_y$  films.

CIGS films used for the production of solar cells were co-evaporated onto Mo-coated SLG [9]. After buffer-layer deposition onto the CIGS, an i-ZnO/ZnO:Al window double layer was deposited by radio-frequency sputtering and a Ni/Al grid was evaporated. The solar cells were investigated by measurement of their current–voltage ( $I$ – $V$ ) characteristics under a simulated AM1.5 illumination ( $100 \text{ mW}/\text{cm}^2$ ) and by external quantum efficiency measurements (EQE).

### 3. Results and discussion

#### 3.1. Characterisation of $\text{In}_x\text{S}_y$ layers

Using heater temperatures ( $T_h$ ) lower than 300 °C yielded hardly any deposition. At  $T_h$  higher than 400 °C the resulting solar cells yielded only low solar cell efficiencies. Therefore,  $T_h$  was set to 310 °C, 345 °C and 380 °C, the absorber surface temperature was significantly (approximately 100 °C) lower than the heater temperature.

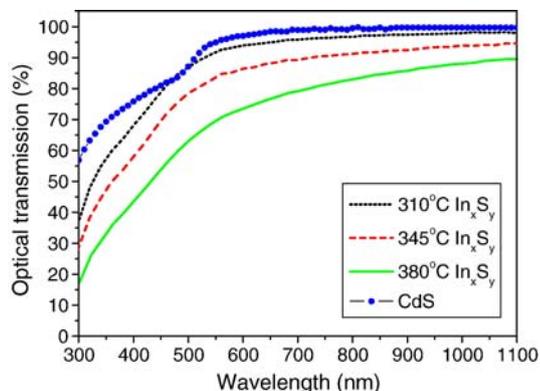


Fig. 1. Optical transmission in wavelength region 300–1100 nm for a standard CBD-CdS film and for  $\text{In}_x\text{S}_y$  films sprayed during 20 min at different heater temperatures.

Table 1

Average thicknesses and average optical transmissions (600–1100 nm) of  $\text{In}_x\text{S}_y$  films sprayed for 20 min at different heater temperatures and of a CdS film deposited for 15 min in a chemical bath

Buffer layer	Heater temperature (°C)	Film thickness (nm)	Optical transmission (%)
310 °C $\text{In}_x\text{S}_y$	310	35	96.8
345 °C $\text{In}_x\text{S}_y$	345	70	91.5
380 °C $\text{In}_x\text{S}_y$	380	120	83.5
CBD-CdS	70	30	99.2

Fig. 1 displays the optical transmission of films prepared at different heater temperatures in the wavelength region from 300 to 1100 nm. As the layer thicknesses are very thin, only a rough estimation of the band gap energies could be determined. However, it is clear that the absorption edge of CdS is in the 500–550 nm region while for  $\text{In}_x\text{S}_y$  it is in the 400–500 nm region, which corresponds well to theory.

The thickness and transmission of CBD-CdS films and of  $\text{In}_x\text{S}_y$  films sprayed at different temperatures for a fixed duration are given in Table 1. It can be seen that the film growth-rate increases with  $T_h$ . This is consistent with the lower optical transmission (600–1100 nm) observed for films deposited at higher  $T_h$  as compared to lower  $T_h$  (when the deposition duration was kept constant).

As can be seen from the XPS depth profile (Fig. 2), the indium and sulphur concentrations are uniform throughout the layer. At the surface, carbon and oxygen are seen due the adsorption and are simply surface contamination since both disappear after 1–2 sputter cycles. A chlorine impurity of around 1 at.%, resulting from the use of  $\text{InCl}_3$  salt, is present throughout the layer. The values of exact concentrations have not been calculated.

XRD measurements (Fig. 3) show that the USP- $\text{In}_x\text{S}_y$  films mainly consist of the tetragonal  $\text{In}_2\text{S}_3$  crystal phase [10,11]. No indium oxide peaks were detected [12].

The results of the structural and chemical characterisation suggest that the sprayed layers are pure indium sulphide.

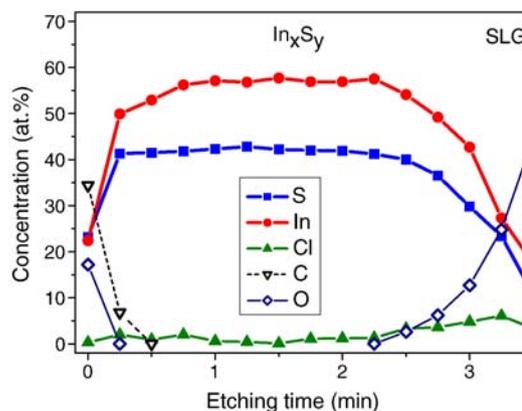


Fig. 2. XPS depth profile for USP- $\text{In}_x\text{S}_y$  film on SLG, sprayed at heater temperature 345 °C.

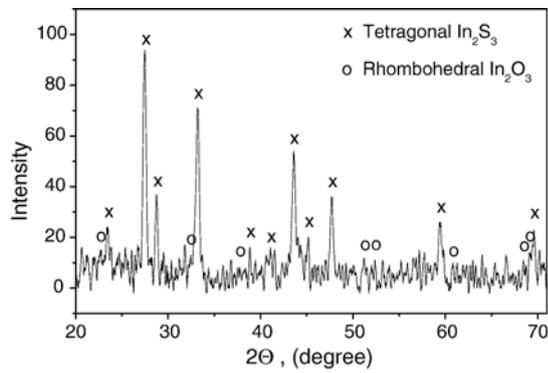


Fig. 3. XRD patterns for USP- $\text{In}_x\text{S}_y$  film on SLG, sprayed at heater temperature 345 °C, peaks marked as: (x) for indium sulphide and (o) for supposed indium oxide peaks.

Because of the uncertainty in the exact concentration ratio of In/S we use the expression  $\text{In}_x\text{S}_y$  throughout the paper.

### 3.2. Characterisation of solar cells

USP- $\text{In}_x\text{S}_y$  films deposited at 3 different heater temperatures and a reference CBD-CdS film grown at 70 °C bath temperature were used as buffer layers in CIGS solar cells. Table 2 displays  $I-V$  characteristics for the best solar cells, namely open circuit voltage ( $V_{OC}$ ), short-circuit current density ( $J_{SC}$ ), fill factor (FF) and efficiency ( $\eta$ ). The efficiency of the reference cell with CBD-CdS was 30% (relative) higher than the best efficiency obtained using  $\text{In}_x\text{S}_y$  buffer layer, mainly due to higher values of  $V_{OC}$  and FF. Examining the impact of substrate temperature,  $V_{OC}$  increased slightly and FF decreased with increasing substrate temperature, the latter being responsible for a drop in efficiency for the 380 °C USP- $\text{In}_x\text{S}_y$ /CIGS solar cell.

EQE measurements (Fig. 4a) reveal the impact of CdS and  $\text{In}_x\text{S}_y$  buffer layers on the solar cell light absorption and collection of photo generated carriers (Fig. 4b). The most pronounced differences in EQE occur in the wavelength region 350–700 nm. The EQE of the  $\text{In}_x\text{S}_y$ /CIGS cell is up to 15% higher in the 350–500 nm (UV and blue light) region whereas the EQE of the CdS/CIGS cell is up to 15% higher in the 500–700 nm (visible light) region. This effect is due to differences in the absorption characteristics of CBD-CdS and USP- $\text{In}_x\text{S}_y$ . The USP- $\text{In}_x\text{S}_y$  band gap is apparently higher, therefore more photons can pass through the buffer layer and reach to the absorber layer. It was found by Abou-Ras et al., that high substrate temperatures influence the interface between CIGS and  $\text{In}_x\text{S}_y$  and lead to the formation of an interfacial layer with defective structure and unfavourable

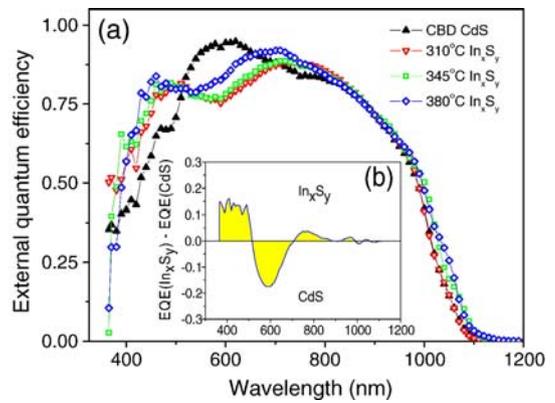


Fig. 4. (a) Quantum efficiency measurements of CIGS solar cells with different buffer layers; (b) differences in spectral responses between solar cells with 345 °C sprayed  $\text{In}_x\text{S}_y$  and CBD-CdS buffer layers.

electronic characteristics due to inter-diffusion of Cu and In [4]. Together, these effects resulted in a decrease in solar cell efficiency for cells with the buffer layer grown at high temperature (380 °C).

Light soaking under AM1.5 illumination conditions was used to evaluate  $\text{In}_x\text{S}_y$ /CIGS solar cell stability and the results are presented in Fig. 5. During 14 h of light soaking the solar cell's FF and to a slightly lesser extent its  $V_{OC}$  increased greatly (Fig. 5a), which resulted in the solar cell's efficiency increasing by approximately 16% (relative) (Fig. 5b). The high buffer-sensitivity to light soaking can be explained by enhancement in the  $\text{In}_x\text{S}_y$ /CIGS interface quality [13]. The increase in  $V_{OC}$  may be caused by an increase in effective carrier density [14]. The light-soaking effect was reversible, which means that after keeping the cell in dark ambient, its efficiency decreased to the initial level. A similar effect has been reported for CIGS solar cells with zinc-containing buffer layers, where the reversible improvement was made irreversible by using significantly higher irradiation intensities during the light soaking [13]. Some further investigations are needed to clarify the light-soaking effect and its potential for irreversibility in our structures.

Table 2  
Current–voltage characteristics for CIGS solar cells with different buffer layers

Buffer layer	$V_{OC}$ (V)	$J_{SC}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
CBD-CdS	0.609	28.4	73.2	12.7
310 °C $\text{In}_x\text{S}_y$	0.514	27.3	63.0	8.8
345 °C $\text{In}_x\text{S}_y$	0.523	27.9	60.9	8.9
380 °C $\text{In}_x\text{S}_y$	0.531	27.6	52.1	7.6

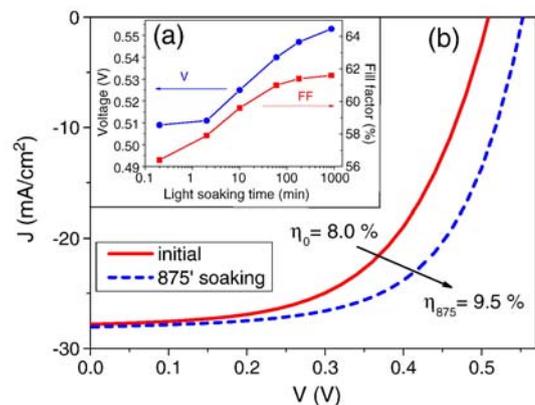


Fig. 5. (a) Light-soaking effects on the open circuit voltage and fill factor of an  $\text{In}_x\text{S}_y$ /CIGS solar cell; (b) current–voltage curves for a CIGS solar cell with 345 °C sprayed  $\text{In}_x\text{S}_y$  buffer layer before and after 875 min light soaking under AM1.5 illumination.

#### 4. Conclusion

Ultrasonic spray pyrolysis is a suitable method for producing  $\text{In}_x\text{S}_y$  buffer layers for CIGS absorber material. XPS measurements revealed a constant In to S ratio through the layer's depth, except in the presence of some surface contamination. XRD measurements indicated indium sulphide as the dominant phase in the film. Higher substrate temperatures resulted in greater thicknesses and lower transparencies for USP- $\text{In}_x\text{S}_y$  thin films. EQE measurements showed better quantum efficiency for solar cells with  $\text{In}_x\text{S}_y$  buffers than for standard CdS/CIGS solar cells in the 350–500 nm range.  $I$ – $V$  measurements on  $\text{In}_x\text{S}_y$ /CIGS solar cells gave efficiencies up to 8.9%, while standard CdS/CIGS cells yielded up to 12.7% efficiency. During light soaking, the  $\text{In}_x\text{S}_y$ /CIGS solar cell efficiency increased up to 9.5%, mainly caused by an increase in the solar cell fill factor. The light-soaking effect was reversible and further investigation is needed to clarify this effect. These results confirm that USP- $\text{In}_x\text{S}_y$  is a promising alternative buffer-layer material for CIGS due to a higher band gap value than CdS.

#### Acknowledgements

The authors would like to acknowledge the support of the EU project ATHLET-PV and Solaronix SA, Switzerland, for providing the USP equipment.

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