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Influence of treatment conditions on chalcopyrite films deposited at atmospheric pressure

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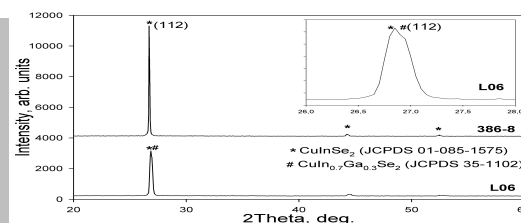
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Spin-coating technique was used to deposit precursor layers for chalcopyrite films of the series CuInX_2 and $\text{Cu}(\text{In,Ga})\text{X}_2$ where $\text{X}=\text{S}$ or Se or (S,Se) . The influence of different parameters of the process, such as solution composition, air pre-treatment and chalcogenation treatment is discussed with respect of film applicability in photovoltaic devices. Layer morphology, stoichiometry and crystalline structure varied widely with the different compositions and treatments.

Highly oriented CuInSe_2 and $\text{Cu}(\text{In,Ga})\text{Se}_2$ films were obtained.



X-ray diffraction patterns of highly oriented selenide materials prepared in this work.

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1 Introduction

Compound thin-film solar cells technologies are expected to lead to lower processing costs while maintaining high efficiency, making photovoltaics competitive with traditional means of energy production [1-3]. Nevertheless, the vacuum equipment that is currently used for state of art technology requires large capital investments. This is the reason why low-cost methods for chalcopyrite films deposition have been extensively studied [4-6]. So far, nanoparticle precursors have been one of the most successful alternative routes [7].

In previous works we described a soft-chemistry route for in situ synthesis of compact nanoparticulate CuInO_x films which were successfully converted to CuInS_2 through a relatively safe and environmentally friendly treatment yielding films with adequate morphology and optical properties for photovoltaic applications [8, 9]. Single phase layers with band gap of 1.48 eV were obtained.

The materials used in state of art devices usually are not stoichiometric i.e. copper-deficient selenides and copper-rich sulfides are used [10]. Similar elemental ratios were selected in the present study.

In this work we study different pre-chalcogenation treatments, such as industrially desirable lower working temperatures during the air pretreatments, reduction pretreatments and prepare selenide materials with and without gallium incorporation.

2 Experimental

2.1 Sample preparation The precursor solutions were prepared by forming copper, indium and, in some cases, gallium triethanolamine (TEA) or diethanolamine (DEA) complexes in ethanol solution. Typically, 3mmol of the complexant were dissolved in 1.2g of ethanol to which copper (II) acetate monohydrate and indium (III) acetate

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were added, using the ratios indicated in table 1, maintaining the amount of indium fixed (0.666 mmol). The substrates are spin-coated at 1500rpm and fired at 250 or 380°C on a hot plate for 4 minutes repeating this cycle 2-3 times. The chalcogenation treatment was carried out in a glass tube inserted in tubular oven at maximum temperature 550°C, typically with elemental sulfur or selenium vapour either in 5% H₂/N₂ or N₂ enriched with ethanol vapour.

Detailed description of the process as well as the reactor can be found elsewhere [8].

Different treatment parameters were investigated:

- Precursor ratios
- Air pretreatment temperature 250 or 380°C
- The influence of pre-chalcogenation reduction treatment with 5% H₂/N₂.
- The type of chalcogenation treatment.

Table 1 Sample description.

SAMPLE	COMPL. AGENT	Cu/In RATIO	PRE-TREATMENT	TREATMENT
369-2	TEA	1.8	250°C air+ reduction	-
369-8	TEA	1.8	250°C air+ reduction	Sulfurized
368-8	TEA	1.8	250°C air+ reduction	Selenized
370-3	DEA	1.8	250°C air+ reduction	Sulfurized
392-4	DEA	1.7	380°C air	Sulfurized
386-8	DEA	0.92	380°C air	Selenized
L06	DEA	0.92+30% Ga/(In+Ga)	380°C air	Selenized

2.2 Characterization The crystal structure of the films was monitored by X-ray powder diffraction (XRD) with a SIEMENS D5000D diffractometer equipped with a Cu-K α radiation source and "SIEMENS DIFFRACT PLUS" software which also determined diffraction peak positions and intensities. Data were collected by step-scanning from 20 to 60° 2 θ with a step size of 0.05 °2 θ and 1s counting time per step. The instrument was calibrated using an external Si standard which served also as a reference for grain-size determination.

Diferential thermal analysis/Thermogravimetry of precursor solutions was carried out in with Mettler-Toledo using platinum crucible air flux and heating rate of 5°C/min. Before the analysis, the solutions were let to dry in air at room temperature for 1 h.

Film morphology and composition were determined by Scanning Electron Microscopy (SEM) using a scanning electron microscope (Leica Leo 440) equipped with a

spectrometer for energy dispersive X-ray microanalysis(EDX) using the following operating parameters: acceleration voltage 20 kV, measuring time 100s, working distance 25 mm, counting rate 1.2 kcps. The samples for microstructure and microanalysis determination were introduced using an aluminum holder with graphite adhesive tape. The thickness of the films was estimated from micrographs of film cross sections.

3 Results and discussion

3.1 Pre-treatment During the air anneal the films passed through two transformations: below 250 and 350°C, both evidenced by black followed by transparent appearance. These were confirmed by thermal analysis exothermal peaks and can be related to combustion of organic material.

Films treated at lower temperature showed greater tendency to delaminate during the firing of the second or third layer than the samples treated at 350°C, which permitted the deposition of up to 3, 4 or 5 layers (yielding 1-2 μ m chalcopyrite thickness). The delamination of the films treated at 250°C can be attributed to higher thermal expansion coefficient of the film than glass, together with still insufficient sintering at lower temperature. Reduction treatment with H₂/N₂ of each layer at 550°C permitted the deposition of larger number of layers with no delamination. This extra processing step is technologically less practical than firing at 350°C, although permitting the deposition of thicker (well above 2 μ m) films.

3.2 X-ray diffraction All air-pretreated films had amorphous nature while the reduced showed mixed metallic phases (Fig.1a).

Surprisingly, it was impossible to sulfurize completely films based on TEA after a low-temperature treatment or treatment with subsequent reduction. Indium-rich phases formed as a top layer during the sulfurization treatment (confirmed also by EDX analysis), acting as an extremely efficient diffusion barrier which prevented the reaction of the bottom layers even after 20 min at 550°C in sulfur-rich atmosphere. Such behavior has not been reported for precursors with Cu/In ratio as high as 1.8. A screening test of identical sample was carried out with selenium vapor and resulted in complete reaction (Fig.1a).

DEA-based films were successfully sulfurized after both high-temperature air pretreatment and low-temperature one followed by reduction and yielded materials with good crystallinity (Fig 1, b).

Precursors pretreated in air at 380°C with elemental ratios Cu/In=0.92 and Cu/(In+Ga)=0.92 where Ga/(In+Ga)=0.3 were used for the selenization treatments. Figure 1c shows highly (112) oriented chalcopyrite materials, CuInSe₂ and CuIn_{0.7}Ga_{0.3}Se₂, in the last case showing asymmetric broadening which could be attributed to composition grading with higher gallium concentration at the bottom, often found in CIGS films used for device fabrication.

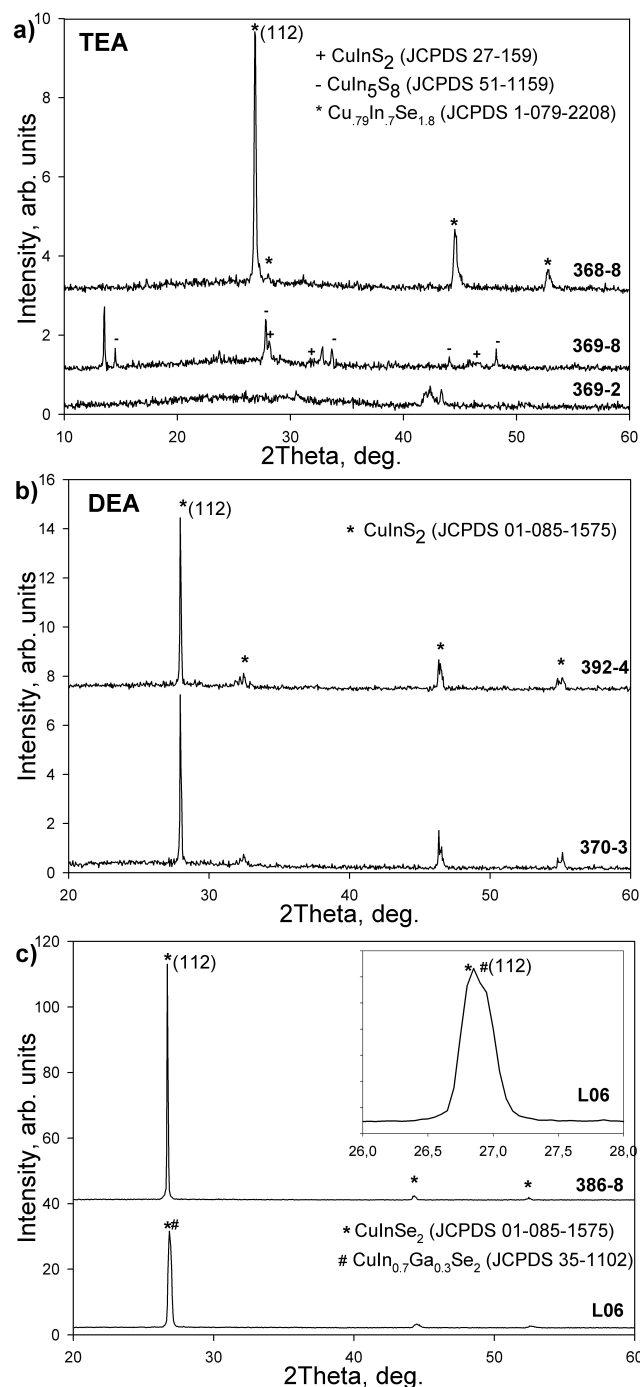


Figure 1 X-ray diffraction patterns of samples prepared in this work: reduced, sulfurized and selenized copper-rich TEA-based precursor pretreated at 250°C(a); sulfurized DEA precursor treated at 380 and 250°C with reduction(b); Selenides prepared from DEA precursors pre-treated at 380°C (c).

3.2 Scanning electron microscopy Figure 3 shows micrographs of samples sulfurized after 250°C air pre-treatment and reduction. In the case of TEA-based

precursors, as observed by XRD, incomplete reaction is manifested by layers with different composition: an indium-rich overlayer and a very copper-rich (almost indium-free), sulphur deficient bottom layer. This is not a typical behaviour for copper rich films, where in case of copper sulphide segregation the ordering of the layers is inverse [10].

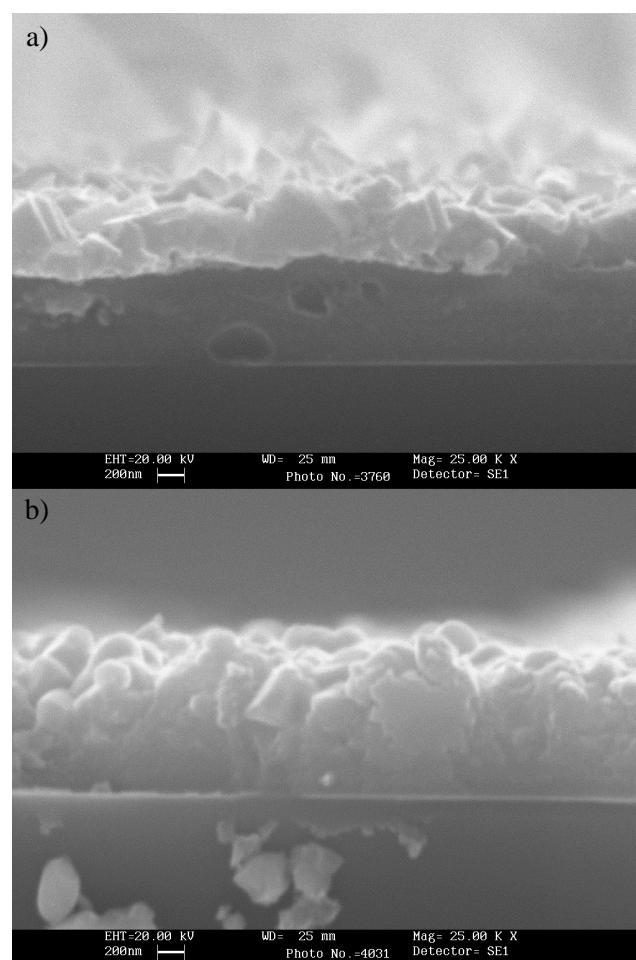


Figure 2 SEM micrographs of samples sulfurized after 250°C pre-treatment with reduction using TEA(a) and DEA(b).

The use of DEA-based precursors under the same conditions yielded more homogeneous and better sulfurized material, confirmed by the XRD data. Nevertheless, the concentration of copper at the bottom again was slightly higher than at the top.

This problem was not present when air pretreatment at higher temperature was used, as in our previous studies [9]. The reason for this may be related to the higher degree of elimination of the organic materials which, in the case of a low-temperature pretreatment could give place to carbon contamination, possibly blocking the interdiffusion of elements and preventing the completion of the reaction. This speculation was not supported by a screening test carried out with elemental selenium, which lead to

complete selenization. Nevertheless, this does not discard the above hypothesis as the materials and their intermediate phases are different.

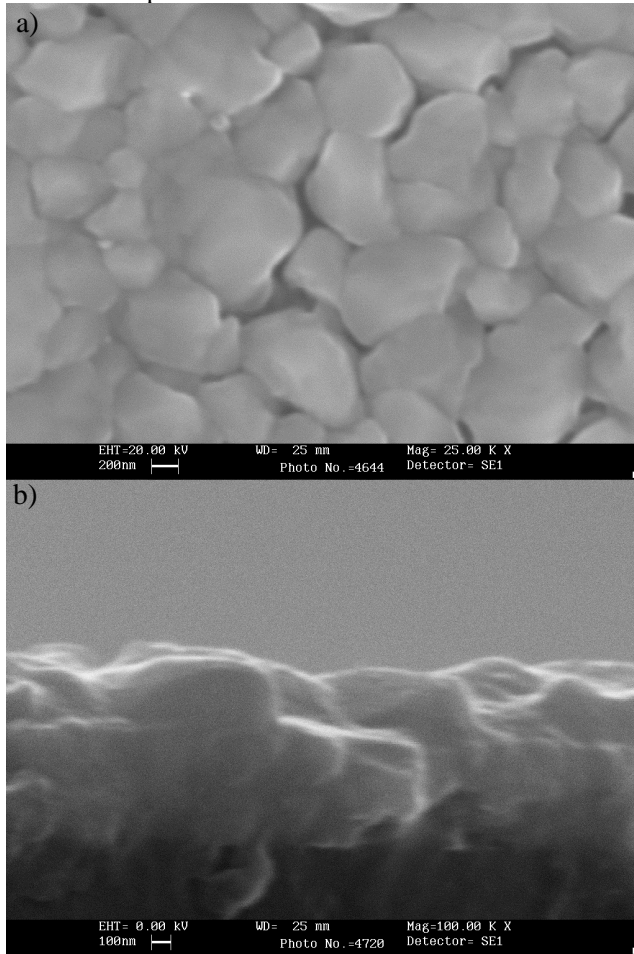


Figure 3 Selenized samples pretreated in air with elemental ratios $\text{Cu/In}=0.92$ (a) and $\text{Cu}/(\text{In}+\text{Ga})=0.92$ where $\text{Ga}/(\text{In}+\text{Ga})=0.3$ (b)

Selenized samples (figure 3) showed large grains and, in the case of CuInSe_2 homogeneous composition. The gallium containing samples showed higher gallium content at the bottom of the film, as predicted by the XRD data. The high crystalline orientation observed by XRD was not evident in the SEM micrographs.

4 Conclusion Lower temperature air pre-treatment lead to poor adhesion. Thickness limitations due to this were overcome by use of subsequent reduction treatment, nevertheless yielding incompletely sulfurized films. Air pretreatments at 380°C permitted full conversion of the precursor layers. Selenization was carried out successfully in all cases. Copper poor Cu-In and Cu-In-Ga precursors yielded highly (112) oriented films.

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