

Tailoring copper sulfide thin films morphology using spray pyrolysis deposition technique

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Thin films of Cu_xS ($x = 1-2$) were deposited onto TCO ($\text{SnO}_2:\text{F}$) glass by spray pyrolysis. As precursors, aqueous and water:alcohol solutions of copper(II) chloride, copper(II) acetate and thiourea with different compositions have been used. The substrate temperature was varied from 235 °C to 285 °C. The morphology and the composition of the as-deposited films have been carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Relatively uniform with low homogeneity films are obtained when higher copper precursor concentration in spraying solution is used. The solvent (deionized water or water:alcohol mixture) used in spraying solution strongly influences the morphology of Cu_xS thin films. The films obtained from precursors' solutions containing mixtures of water: alcohol(s) (1-propanol, ethanol, glycerine) as solvents are denser than those obtained from aqueous precursors' solutions. The substrate temperature influences more the composition than the morphology of the sulfide layers: increasing the deposition temperature, from 235 °C to 285 °C, films containing a mixture of Cu_xS phases (CuS , Cu_2S , $\text{Cu}_{1.8}\text{S}$) with predominant phase digenite ($\text{Cu}_{1.8}\text{S}$) are obtained. Increasing the number of spraying sequences, the average grains/aggregates size of Cu_xS deposited at 285 °C also increases.

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1. Introduction

Among metal chalcogenides, copper sulfides (Cu_xS , $x = 0.5-2$) are characterized by various crystalline phases, determined by the variation of composition or Cu:S (x) combination ratio. Moreover, Cu_xS are relatively easy obtained as powders, [1, 2], or thin films, [3-7]. Due to their optical and electrical properties, Cu_xS thin films are considered attractive materials with application in optoelectronics, photovoltaic cells, solar selective coatings and solid-state based gas sensors, [8-11].

Copper sulfides thin films can be deposited onto different substrates (e.g. glass, quartz glass, TCO glass, metals, polymers) by various techniques: metal-organic vapour deposition (MOCVD), [12], chemical bath deposition (CBD), [4,5,10,13], electrodeposition (ED), [14], and spray pyrolysis deposition (SPD), [7,8,12, 15,16].

During the last decades, spray pyrolysis deposition is considered one of the simplest, low-cost and up-scalable techniques used for preparation of nano-, mezzo- or micro-structured layers with controlled properties (morphology, composition, crystallinity). Despite its simplicity, SPD has a number of advantages; the main of these is the obtaining of homogenous layers with high uniformity in particle size and composition, on surfaces with different geometries and areas. Other advantages are, [17-18]:

- no special restrictions regarding substrate material, dimension or its surface profile;
- no special technological conditions: higher deposition temperatures, higher or lower carrier gas pressure;

- an extremely easy way to dope layers with virtually any element in any proportions and to prepare multilayered structures;
- the possibility to control (tailor) the layer thickness and properties by changing the precursors' solution composition and deposition parameters.

The SPD process consists of spraying a finely atomised solution (precursors' solution) onto a heated substrate where, after chemical reactions, the product is deposited as a thin film. The mechanism of the process is detailed elsewhere, [19].

In this paper, the influence of precursors' solution composition (copper precursor concentration, solvent) and deposition parameters (substrate temperature, spraying sequences number) on the morphology and composition of Cu_xS thin films, prepared by SPD technique, is studied.

2. Experimental

The Cu_xS thin films were deposited from aqueous and water(W):alcohol(s) (ethanol, Et, 1-propanol, Pr, glycerine, Gl) solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99.9%, Merck), respectively $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (99.9%, Merck), and H_2NCSNH_2 (99.9%, Sigma Aldrich), with molar ratio Cu:S = 0.25-0.33. The concentration of Cu^{2+} ions in the precursors' solution was varied from 0.1 to 0.25 mol/L. The acid pH (3) of the precursors' solution was insured by adding 10 mL of CH_3COOH 2N in a volume ratio of 1:5. The alcohol solutions contained, in volumes, mixtures of W:Pr (Et) = 4:1 (Pr, 99%, J.T Baker; Et, 99.8%, J.T. Baker) and W:Et:Gl = 7:2:1 (Gl, 99%, J.T Baker).

Slides (25 mm x 25 mm) of transparent conductive SnO₂:F glass (TCO, Libbey Owens Ford, TEC15/2.3 mm), were used as substrates for Cu_xS films deposition.

A Camag nozzle, a ceramic hot plate (CERAN 500 ± 1°C) and N₂ as carrier gas were used for the deposition of Cu_xS thin films by spray pyrolysis. During spraying, the substrate temperature (T) was varied from 235°C to 285°C. The pressure of the carrier gas was maintained at 1-1.2 bar and the distance between the spraying nozzle and the heater was varied from 25 cm to 30 cm. The spraying sequences number (n_{sp}) was varied from 20 (aqueous solutions) to 100 (W:Pr solutions) with breaks between two sequences of 10 to 50 seconds.

The as-deposited Cu_xS thin films were characterised by scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM analysis was performed using a Jeol JSM-5800LV scanning microscope. XRD patterns of the films were registered by a Bruker D8 Advance Diffractometer with Cu-Kα₁ radiation.

3. Results and discussion

Previous studies, [11,15,16], have shown that structural and electrical properties of chalcocite (Cu₂S) and covellite (CuS) thin films obtained by SPD, can be tailored by changing precursors' solution composition (Cu:S molar ratio, solvent type) and deposition parameters (substrate temperature). It was observed that Cu:S molar ratio and substrate temperature variation influences more the composition and crystallinity than the films morphology.

In the present study, the effect of the precursors' solution composition (copper precursor concentration, type of solvent) and deposition parameters (substrate temperature, spraying sequences number) on the Cu_xS thin films morphology (average grain/aggregate size, *d*) is reported (Table 1).

Table 1. The influence of precursors' solution composition and deposition parameters on Cu_xS thin films morphology.

Test	Cu ²⁺ mol/L	Solvent W:Et/Pr W:Et:Gl	T °C	n _{sp}	\bar{d} * nm
S1	0.2	10:0	285	20	250-300
S2	0.25	10:0	285	20	500
S3	0.1	4:1(Pr)	285	100	300-350
S4	0.1	4:1(Et)	285	100	300-500
S5	0.2	7:2:1	235	65	300
S6	0.2	7:2:1	265	65	200-300
S7	0.2	7:2:1	285	65	250-350
S8	0.1	4:1(Pr)	285	55	250

* Based on SEM images

The XRD spectra (Figure 1), recorded for the S2, S5 and S6 films deposited on TCO substrate, show that the films contain two (S5) or three (S2 and S6) phases of Cu_xS. In S5 film, the predominant phase is CuS (84.6%), while S2 and S6 films are mixtures of CuS, Cu₂S and Cu_{1.8}S, with predominant phase Cu_{1.8}S: 63.1% in S2 and 68.68% in S6. These results confirm that at substrate temperatures higher than 265 °C, the deposition of "copper-rich" phases (Cu_{1.8}S, Cu₂S) is favoured, while lower temperatures (235 °C) allow the formation of "copper-poor" phase CuS as predominant phase.

When the deposition is performed at 285 °C, from aqueous solutions containing Cu(CH₃COO)₂ and thiourea, with different concentrations and Cu:S = 1:3, relatively uniform and porous Cu_xS thin films with low homogeneity are obtained (Figure 2). These films are formed from large crystalline aggregates, with average size increasing from 250-300 nm (S1) to 500 nm (S2), in the same way with the increasing of copper precursor concentration in spraying solution, from 0.2 mol/L to 0.25 mol/L. The lower homogeneity of S2 film, in comparison with S1, is probably due to the different composition of the films, S2 containing three Cu_xS phase (CuS, Cu₂S and Cu_{1.8}S) with different crystalline structures.

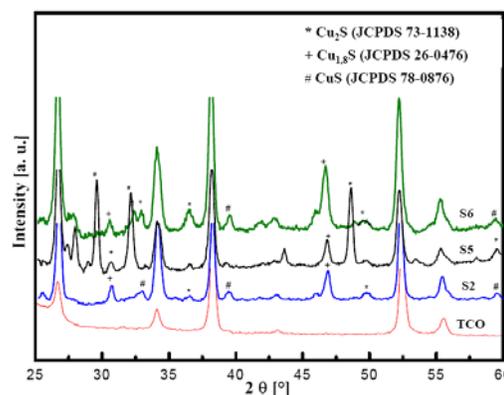


Fig. 1. XRD patterns of Cu_xS thin films deposited on TCO substrates.

According with SEM pictures (Fig. 2), relatively uniform and low homogenous Cu_xS thin films are deposited at 285 °C, from precursors' solutions containing mixtures of water-propanol (S3) and water:ethanol (S4), in the same volume ratios (4:1). The low homogeneity of the films can be associated with the presence of two or more Cu_xS phases, with the same (polymorphs)/different compositions or a mixture of polymorph phases with different x values.

The layers deposited at different temperatures (T = 235 - 285 °C), from precursors' solutions containing mixture of W:Et:Gl as solvent, are uniform, dense and relatively homogenous, with average grains/aggregates size ranging from 200 nm (in film S6) to 350 nm (in film S7). It is observed that the substrate temperature has not a significant influence on the films morphology (the

grains/aggregates size slowly increases with temperature), but influence the films composition (Figure 1). It can be also observed, that the low homogeneity of S6 film is attributed to the three different Cu_xS phases (CuS -10.32%, Cu_2S -21% and $\text{Cu}_{1.8}\text{S}$ -68.68%), which contain crystallites with different sizes and geometries.

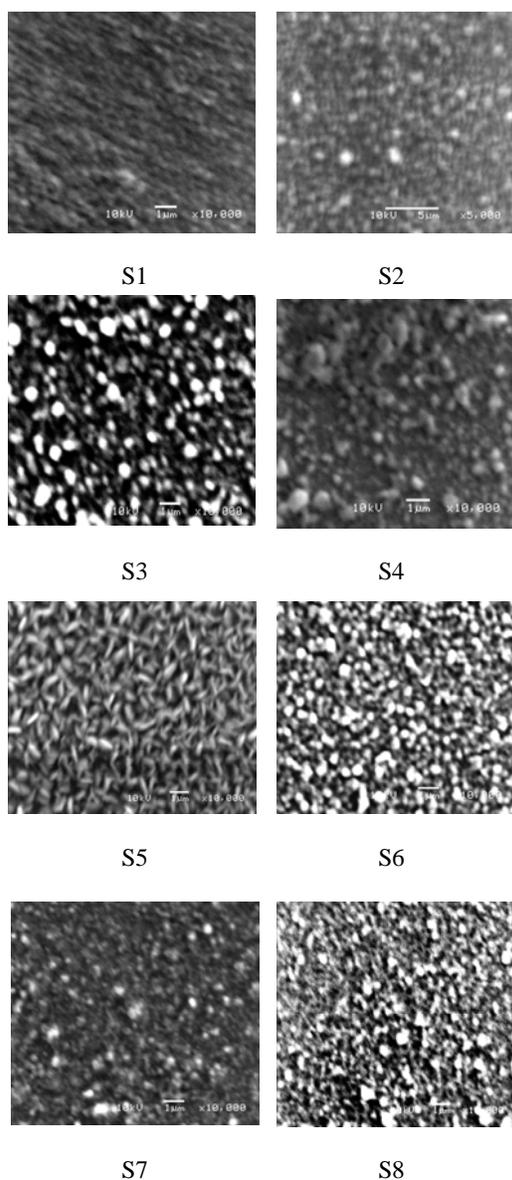


Fig. 2. SEM images of Cu_xS deposited on TCO substrates.

The mono-layered film S8, obtained by 55 spraying sequences, from precursors solution in water:propanol (4:1) mixture, is uniform, dens and homogenous (Figure 2). The average grains/aggregates size is about 250 nm, suggesting that the film contains the same phases with different crystal lattices. The double-layered S3 film, deposited after 100 spraying sequences, is uniform, dens and inhomogeneous, containing aggregates with $d = 300$ -

350 nm. This variation can be attributed to monophasic (the same phase, with different crystalline structures) or polyphasic composition of the S3 film. It is observed that the average crystalline aggregate sizes increase, from 250 nm (S8 film) to 350 nm (S3 film), with the increasing of spraying sequences number.

The variation of other deposition parameters (spraying distance, carrier gas nature and pressure) may also influence the morphology of the Cu_xS thin film prepared by SPD. This will be the subject of a future study.

4. Conclusions

Thin films of copper sulfides (Cu_xS , $x = 1-2$) with different morphology and composition are deposited at temperatures varying from 235 °C to 285 °C, by chemical spray pyrolysis, from aqueous and water:alcohol(s) solutions containing CuCl_2 , $\text{Cu}(\text{CH}_3\text{COO})_2$ and thiourea as precursors. These properties strongly depend on the deposition process parameters: precursors' solution composition, substrate temperature and spraying sequences number.

Increasing the copper precursor concentration in spraying solution, the average grains/aggregates size increases and relatively uniform with low homogeneity Cu_xS thin films are obtained. The homogeneity of the films is determined by the films composition.

To improve the Cu_xS films morphology, in order to obtain denser and uniform films, mixtures of water:alcohol(s) (ethanol, propanol, glycerine) are used as solvents in precursors' solutions. Dens, uniform and homogenous Cu_xS thin films are deposited at 285 °C, from precursors' solution, with W:Et:Gl = 7:2:1 and Cu:S = 1:3.

Increasing the substrate temperature, from 235 °C to 285 °C, films containing three different phases (CuS , Cu_2S and $\text{Cu}_{1.8}\text{S}$), with different crystalline structures, are obtained, with influence on the films homogeneity.

Increasing the number of spraying sequences, from 55 to 100, the average grains/aggregates size of Cu_xS from films deposited at 285 °C also increases.

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