TAILORING CHEMICALLY SPRAYED Cu$_X$S FILMS CRYSTALLINITY

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Relative dense, homogenous and uniform films of Cu$_x$S (x = 1.8-1.96), with 400–700 nm thickness and exhibiting electric resistance behavior were prepared by robotic spray pyrolysis technique, at T = 300 ºC, using 60–90 spraying sequences, from water:ethanol:glycerol= 7:2:1 (in volumes) solutions with molar ratios Cu:S = 1:2.5-3.5. Increasing the sulfur content in precursors' solution, the crystal nucleation is favored, while crystal growth is the limiting step in the formation of films deposited with 60–80 spraying sequences from solutions with Cu^{2+} concentration higher than 0.3 mol/L. Films containing Cu$_2$S as predominant phase and showing *p*-type semiconductor electrical behavior were grown by annealing in air, at 350 ºC, for 30 minutes, the films deposited from precursors' solutions with Cu:S= 1:3.5 at Cu^{2+} concentration of 0.25 mol/L.

INTRODUCTION

Copper sulfides (Cu$_x$S, x = 1-2) thin films are recognized as promising materials with applications in superconductors,[1] gas sensors,[2] photocatalysts,[3] solar radiation control coatings[4] and photovoltaic devices,[5, 6,7,8] such as Solide State Solar Cells (SSSC): Extremely Thin Absorber (ETA) and nanocomposite (3 D) solar cells. The optimum photovoltaic efficiency (about 6%) is obtained when digenite (Cu$_{1.8}$S) is used as p-type semiconductor and visible absorbing layer in a 3D solar cell,[6] in junction with TiO$_2$. Depending on the deposition conditions, copper sulfides (Cu$_x$S, x = 1.8 – 2) show mixed electronic-ionic conduction, with predominant electronic conductivity. The p-type conduction is the result of crystalline point defects (free holes from acceptors levels of copper vacancies), while ionic conduction is due to the Cu$^+$ ions mobility within the crystal lattice.[9] Moreover, the band gap energy of Cu$_x$S films, E$_g$ = 1.2 - 2.74 eV,[1,6,9,10,11] is favorable for light absorption under sunlight illumination.

Copper sulfides have distinct compositions (Cu$_x$S, *x* = 1-2) with different stoichiometry, up today at least eight crystalline phases are known,[9,12,13] ranging from the "copper-rich" phase Cu$_2$S (chalcocite, *x* = 2) to the "copper-poor" phase CuS$_2$ (copper disulphide, *x* = 0.5). Among these, only five phases are stable at room temperature: Cu$_2$S, Cu$_{1.96}$S (djurleite), Cu$_{1.8}$S (digenite), Cu$_{1.75}$S (anilite) and CuS (covellite). The change from one crystalline phase to another depends on the temperature and on the composition of the atmosphere above. The structural, optical and electrical properties of Cu$_x$S films may be tailored by varying the composition that, in turn, is dependent on the deposition parameters and after-deposition thermal treatment.

In the present work, the structural and the electrical properties of Cu$_x$S films prepared by Robotic Spray Pyrolysis Deposition (RSPD), a relatively simple, low-cost and up-scalable technique, were tailored by varying the deposition parameters and annealing. The crystalline structure (crystal lattice and crystallite size) and the surface morphology (average roughness) of the as-deposited and air annealed Cu$_x$S layers are correlated, giving important information on the ratio of the nucleation and growth reactions.

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EXPERIMENTAL

The Cu_xS films (S1-S5) were obtained from solutions containing $CuCl_2·2H_2O$ (99%, Scharlau Chemie SA) and thiourea (H_2NCSNH_2, 99%, Scharlau Chemie SA) dissolved in a mixture of water:ethanol:glycerol = 7:2:1, in volumes. The Cu:S molar ratio in the precursors' solutions was varied from 1:2.5 up to 1:3.5 and the Cu^{2+} concentration was in range 0.25-0.35 mol/L. As solvents, deionized water (W), absolute ethanol (Et, 99.2%, SC PAM Corporation SRL, Bucuresti) and glycerol (Gl, 99.5%, Scharlau Chemie SA) were used.

The Cu_xS layers were deposited onto transparent conductive SnO_2:F glass (FTO, 25 mm x 25 mm x 0.5 mm, TEC 8, Pilkington), previously cleaned by successive immersion in ethanol, in a ultrasonic bath, and dried in air flow. The films were deposited onto pre-heated FTO glass substrate by RSPD, at 300°C, with the pressure of carrier gas (air) at 1.2 bar. The distance between the spraying nozzle and the substrate was fixed at 15 cm. The number of spraying sequences (n_{sp}) was varied from 60-100, with 20 seconds breaks between two pulses and a pulse duration of 10 seconds. All the deposition parameters were previously optimized.[14] After deposition, the films were annealed in air at 350 °C, for 30 minutes.

The crystalline structure and composition analysis of the as-deposited and air annealed Cu_xS layers were investigated by X-ray Diffraction (XRD, Bruker D8 Discover Diffractometer that uses Cu-$K\alpha_1$ radiation). The surface morphology was studied via Atomic Force Microscopy (AFM, /STM NTEGRA Probe Nanolaboratory). Optical absorption measurements were carried out with a UV-VIS Spectrophotometer (Perkin Elmer Lambda 25) and electrical measurements (Current-Voltage in dark conditions) with a DC Source Meter (VSP, Princeton Applied Research) connected to a PC interface. The samples current-voltage curves were registered in dark conditions using the sandwich type structure $FTO/CU_XS/Graphite$, with FTO and graphite as ohmic contacts.

RESULTS AND DISCUSSION

Relatively homogenous and uniform thin films of Cu_xS (x = 1-2), with E_g = 2.46-3.1 eV and resistance or diode behaviours, were obtained by our group[14,15] using Spray Pyrolysis Deposition (SPD) method, and varying the deposition parameters: precursors' composition (Cu:S molar ratio, Cu^{2+} concentration), temperature (T) and number of spraying sequences (n_{sp}). The influence of the deposition temperature on the formation (crystal nucleation/growth) of Cu_2S thin films obtained by SPD is already reported.[16] The porous morphology and smaller crystallite sizes suggest that crystal nucleation is the limiting step in the films deposition, at lower temperatures (T = 235-280°C), while at higher temperatures (T > 280°C), the deposition of dense films with large crystallites/aggregates is favored, suggesting that crystal growth is the limiting step when water:alcohol mixtures are used as solvents in precursors' solution. The present study reports the influence of precursors' solution composition, number of spraying sequences and annealing on the Cu_xS (x = 1.8 - 2) films structural properties, presented in Table 1, and

therefore on the nucleation/growth steps during the films deposition.

The average value of crystallite size (D) was calculated using Debye-Scherrer formula.[16] The average films thickness (*t*) was calculated based on the absorption spectra registered in the wavelength range 200-800 nm, considering the value of refractive index n = 2.1[14] for Cu_xS (x = 1.8-2).

The XRD spectra (Fig. 1) recorded for the Cu_xS layers on the FTO substrate show that the as-deposited films contain digenite ($Cu_{1.8}S$, rhombohedral crystalline structure) and djurleite ($Cu_{1.96}S$, tetragonal crystalline lattice) as single or predominante crystalline phases. The air annealed films are mixtures of low chalcocite (Cu_2S, orthorombic crystalline structure) and djurleite ($Cu_{1.96}S$), in which Cu_2S is the predominant phase: 60.4 % in S3_100* and 90.8 % in S4_100*.

The composition of the films is influenced by the variation of precursors' solution composition (especially molar ratio Cu:S) and annealing in air. Increasing the sulfur content in the precursors' solution favours the mixtures in which $Cu_{1.8}S$ crystalline phase is predominant (96.6 % in sample S2), when at lower sulfur concentration $Cu_{1.96}S$ phase is predominant (66.4 % in S1). Interesting is that film S1 contain as secondary phase chalcocyanite ($CuSO_4$, 24.3 %, orthorhombic structure), compound obtained, at deposition temperature (T = 300 °C), from the oxidation of $Cu_{1.96}S$ and/or Cu_2S (also contained in S1 film) to Cu_2O which reacts with SO_2 obtained by oxidation of sulfur precursor, in agreement with literature.[17] By annealing in air, the composition of the as-deposited films is changed (Cu_2S is obtained as predominant phase), therefore the films properties are improved, especially electrical properties. Among Cu_xS (x = 1.8 -2), Cu_2S is considered the copper sulfide with the best photovoltaic activity.[7]

The variation of precursors' solution concentration in the spraying solutions and the variation of spraying sequences number have not a significant influence on the composition, but on the crystallinity, morphology and thickness of tested films. It has to be mentioned that by increasing the number of spraying sequences, the film is kept a longer period of time at the deposition temperature and a change between the content of $Cu_{1.8}S$ and $Cu_{1.96}S$ phases in the analysed films is observed.

The AFM images of the Cu_xS films, Fig. 2, show that sample surface has relatively good uniformity and homogeneity, with the average roughness decreasing from 47.5 nm (S1) to 16.3 nm (S3 and S4_100).

Table 1

The correlation between deposition parameters, crystalline phases composition, crystallinity (average crystallite size, D), morphology (average roughness, S$_a$) and average thickness (*t*) of Cu$_x$S films obtained by RSPD

Sample	Cu:S	$C_{Cu^{2+}}$ [mol/L]	n$_{sp}$	Crystalline structure	D [nm]	S$_a$ [nm]	t [nm]
S1	1:2.5	0.25	100	**Cu$_{1.96}$S, tetragonal (66.4 %)** Cu$_2$S, orthorhombic (9.3%) CuSO$_4$, orthorhombic (24.3 %)	**23.2** 28.8 27.4	47.5	715
S2	1:3	0.25	100	**Cu$_{1.8}$S, rhombohedral (96,6 %)** CuS, hexagonal (3,4 %)	**19.2** 3,9	18.4	595
S3	1:3.5	0.25	100	Cu$_{1.96}$S, tetragonal (42.7 %) **Cu$_{1.8}$S, rhombohedral (57,3 %)**	5.3 **16.3**	16.3	576
S3_100*			100*	**Cu$_2$S, orthorhombic (60.4%)** Cu$_{1.96}$S, tetragonal (39.6 %)	**20.1** 4.7	18.9	675
S4_60	1:3	0.3	60	**Cu$_{1.8}$S, rhombohedral (100 %)**	**16.7**	16.5	238
S4_70			70	**Cu$_{1.8}$S, rhombohedral (100 %)**	**17.8**	16	251
S4_80			80	Cu$_{1.8}$S, rhombohedral (22,6 %) **Cu$_{1.96}$S, tetragonal (77.4 %)**	17 **10.3**	18.7	290
S4_90			90	**Cu$_{1.96}$S, tetragonal (100 %)**	**9.8**	17.2	351
S4_100			100	**Cu$_{1.8}$S, rhombohedral (76.8 %)** Cu$_{1.96}$S, tetragonal (23.2 %)	**16.9** 6.91	16.3	412
S4_100*			100*	**Cu$_2$S, orthorhombic (90.8%)** Cu$_{1.96}$S, tetragonal (9.2 %)	21.92	36.4	498
S5	1:3	0.35	100	**Cu$_{1.8}$S, rhombohedral (96.5 %)** CuS, hexagonal (3,5 %)	**26.4** 4.4	23.3	586

* Samples S3 and S4 annealed in air, at 350 °C, for 30 minutes.

FTO (SnO$_2$, PDF 01-077-0452)   *** Cu$_2$S (PDF 00-023-0961)

* Cu$_{1.8}$S (PDF 00-047-1748)   + CuS (PDF 03-065-3931)

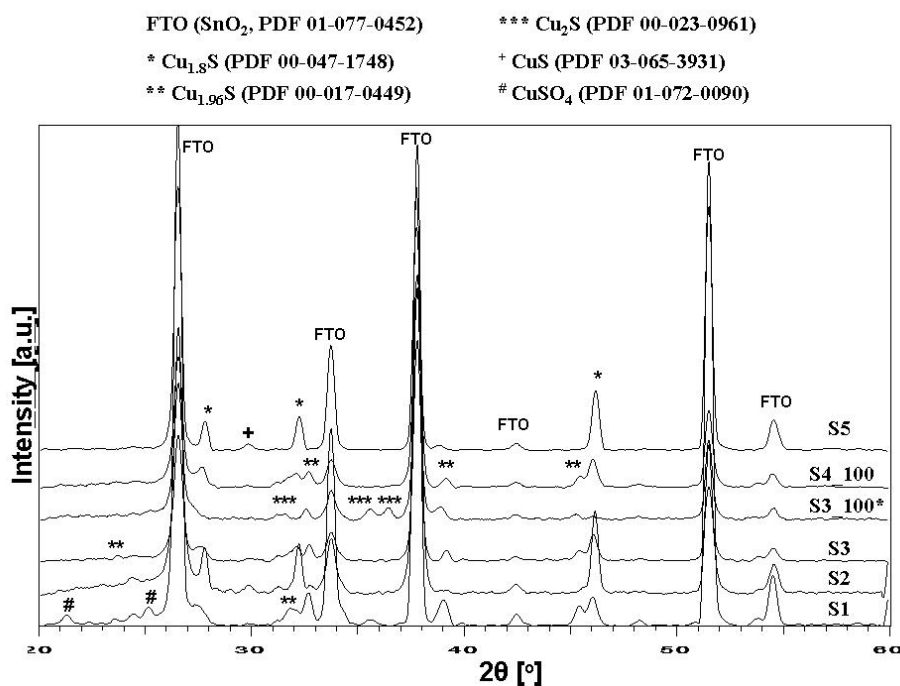** Cu$_{1.96}$S (PDF 00-017-0449)   # CuSO$_4$ (PDF 01-072-0090)

Fig. 1 – XRD patterns of as-deposited (S1-S5) and air annealed (S3_100*) Cu$_x$S layers deposited by RSPD onto FTO substrates.
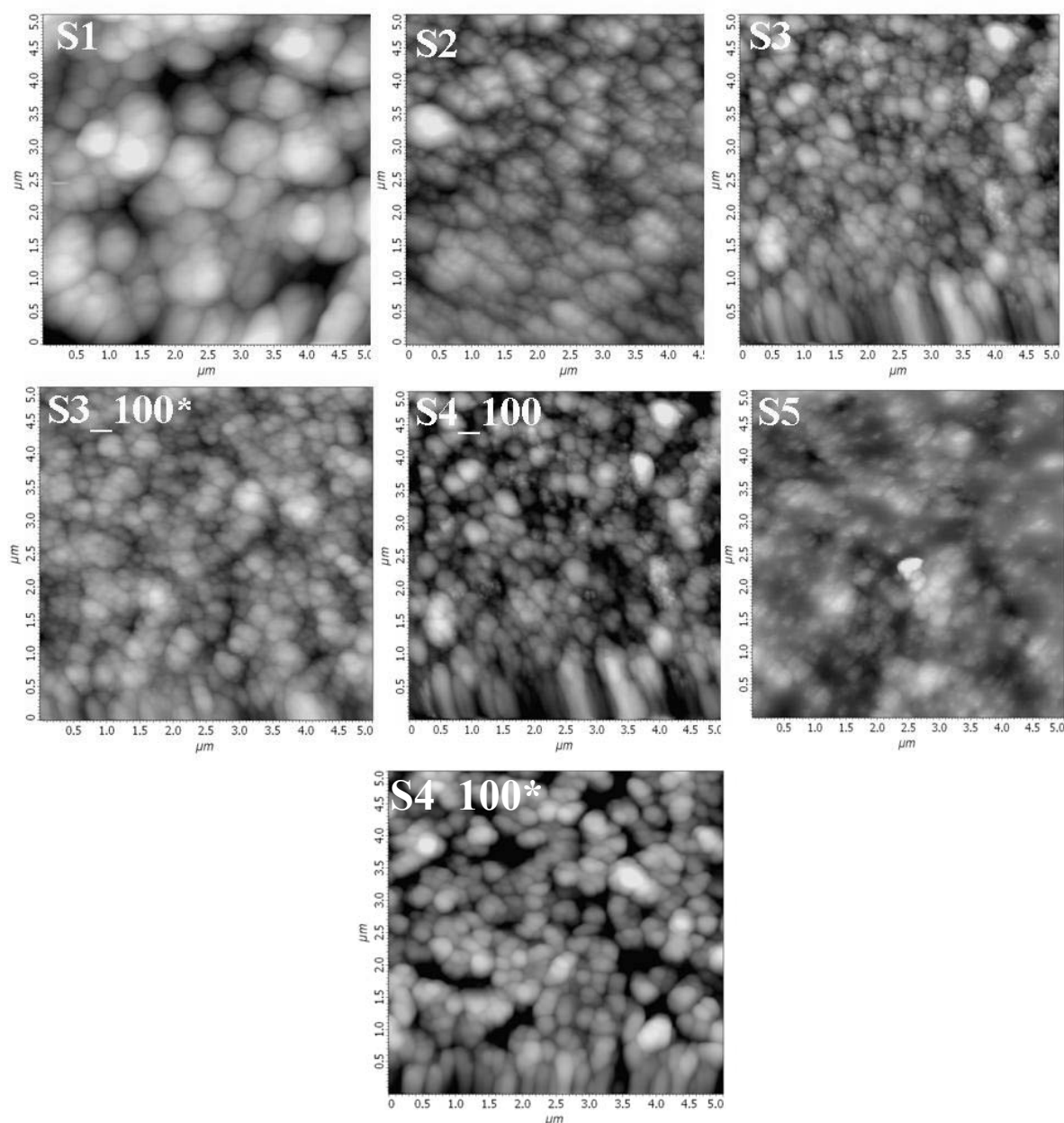
Fig. 2 – AFM images of as-deposited (S1-S5) and air annealed (S3_100*, S4_100*) Cu_xS
layers deposited by RSPD onto FTO substrates.

By increasing the sulfur precursor content in the spraying solution, a change in the morphology of S1, S2 and S3 films is observed, the average roughness of the films showing a significant decreasing of about 65 %, from 47.5 nm (S1) to 16.3 nm (S3). This suggests that the crystal nucleation is the limiting step in the films formation, confirmed either by the decreasing (about 30 %) of average crystallite sizes of $Cu_{1.8}S$ or by layers thickness variation, which decreases from S1 (715 nm) to S3 (575 nm). The Cu^{2+} concentration increase favours the $Cu_{1.8}S$ crystals nucleation, at lower Cu:S molar ratio (Cu:S = 1: 2.5 – 3), and crystals growth, of about 56 % in average crystallite size and about 43 % in average roughness, at Cu:S = 3 – 3.5 in precursors' solutions.

The increasing of spraying sequences number from 60 to 80 has as result a slowly increase of $Cu_{1.8}S$ crystallite sizes and films roughness, suggesting that crystals growth is the limiting step in the films formation. In the Cu_xS layers deposited with $n_{sp} > 80$, the nucleation of $Cu_{1.8}S$ and $Cu_{1.96}S$ crystals is favoured, the average roughness decreasing from 18.7 nm (S4_80) to 16.3 nm

(S4_100). The thickness of the films increases with n$_{sp}$ increase (n$_{sp}$ = 60-80), as consequence of the films growth, and seems to be not influenced by the composition and crystallinity of the films deposited with higher spraying sequences.

Annealing in air of as-deposited films favours the Cu$_x$S crystals growth, the average roughness increasing from the same value (16.3 nm for as-deposited films) to higher values, with a calculated increase of about 123 % for the film S4_100*. Temperature and the duration of thermal treatment are important control parameters on Cu$_x$S film composition and crystallinity changes, and therefore on its properties.

The electrical properties (current-potential curves in dark conditions) show that in all the samples the resistive behavior is predominant, excepting the film S3 annealed in air (S3_100*). The dark I-V curve registered for film S3_100* (Fig. 3) confirm the diode behavior and characteristic *p*-type semiconductor properties. These are in good agreement with film composition (mixture of Cu$_2$S and Cu$_{1.96}$S crystalline phases, with predominant Cu$_2$S orthorhombic structure phase), crystallinity (D = 20.1 nm for Cu$_2$S), and morphology (relative uniform and dense film). Further work will focus on tailoring Cu$_x$S mainly the electrical properties, by optimizing the thermal treatment conditions for the films deposited by RSPD.

Fig. 3 – I-V curve registered in dark for annealed (S3_100*) Cu$_x$S layers deposited by RSPD onto FTO substrates.
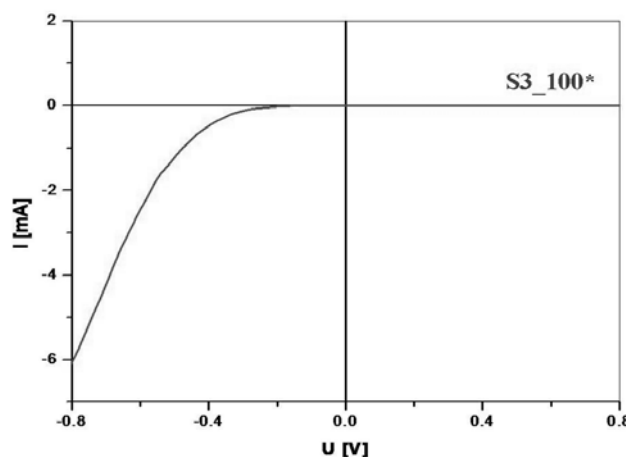
CONCLUSIONS

Films of Cu$_x$S (*x* = 1.8-2), with controlled composition, crystallinity, morphology and electrical properties required for *p*-type absorber materials in a Solide State Solar Cell (SSSC), are obtained by RSPD technique, at T = 300 ^{o}C from water:ethanol:glycerol (7:2:1 in volumes) solutions with molar ratio Cu:S = 1:2.5-3.5.

The composition of Cu$_x$S films may be controlled by varying the Cu:S molar ratio in precursors' solutions and by annealing conditions. Increasing the sulfur concentration in precursors' solutions, Cu$_x$S films with different stoichiometry (*x* = 1.8 - 1.96) are obtained. Annealing in air strongly influences the composition of the as-deposited Cu$_x$S (*x* = 1.8) films, when "copper-rich' phase Cu$_2$S is obtained as predominant crystalline phase in mixture wit djurleite (Cu$_{1.96}$S).

The crystallinity, surface morphology and thickness of the Cu$_x$S films can be tailored by modifying the precursors' solutions composition, the number of spraying sequences and by annealing:

a. increasing the sulfur precursor content in spraying solution favors the obtaining of thin dense films, suggesting that crystal nucleation is the limiting step in the as-deposited Cu$_x$S films formation, while the crystals growth is favored in films obtained from precursors' containing a higher Cu^{2+} concentration (0.35 mol/L);

b. increasing the number of spraying sequences from 60 to 80, a slow increase of Cu$_x$S films thickness is observed, associated with the crystallites growth; for films obtained with higher spraying sequences (n$_{sp}$ > 80), the thickness increase is not a consequence of the crystallinity (the crystal nucleation is favored) but probably to the composition (mixed phases) and chemical reactions which take places at prolonged time on the heated substrates;

c. annealing in air of as-deposited Cu$_x$S films strongly influences the morphology, suggesting that higher growth rates favors the films formation.

The electrical measuremets showed that film, deposited at 300 ^{o}C using 100 spraying sequences, from solution with Cu:S = 1:3.5 and then annealed in air, at 350 °C, for 30 minutes, exhibits *p*-type semiconductor behaviour. Further work will be focused on the integration of this layer in a SSSC, in junction with an adequate *n*- type semiconductor material (thin films of TiO$_2$, ZnO).

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