TAILORING CHEMICALLY SPRAYED Cu_xS FILMS CRYSTALLINITY

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Relative dense, homogenous and uniform films of Cu_xS (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_2S 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_xS, x = 1-2) thin films are recognized as promising materials with applications in superconductors,1 gas sensors,2 photocatalysts,3 solar radiation control coatings4 and photovoltaic devices,5,6,7 such as Solid 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 cell6 in junction with TiO_2. Depending on the deposition conditions, copper sulfides (Cu_xS, 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_xS 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_xS, 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_2S (chalcolite, 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_2S, 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_xS 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_xS 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_xS layers are correlated, giving important information on the ratio of the nucleation and growth reactions.

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EXPERIMENTAL

The Cu$_x$S films (S1-S5) were obtained from solutions containing CuCl$_2$·2H$_2$O (99%, Scharlau Chemie SA) and thiourea (H$_2$NCSNH$_2$, 99%, Scharlau Chemie SA) dissolved in a mixture of water:ethanol:glycerol = 7:2:1, in volumes. The Cu$_x$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$_x$S 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. 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$_x$S layers were investigated by X-ray Diffraction (XRD, Bruker D8 Discover Diffractometer that uses Cu-K$_{α1}$ 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$_x$S/Graphite, with FTO and graphite as ohmic contacts.

RESULTS AND DISCUSSION

Relatively homogenous and uniform thin films of Cu$_x$S (x = 1-2), with $E_g$ = 2.46-3.1 eV and resistance or diode behaviours, were obtained by our group using Spray Pyrolysis Deposition (SPD) method, and varying the deposition parameters: precursors’ composition (Cu$_x$S molar ratio, Cu$^{2+}$ concentration), temperature (T) and number of spraying sequences (n$_{sp}$). The influence of the deposition temperature on the formation (cristal nucleation/growth) of Cu$_x$S thin films obtained by SPD is already reported. 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$_x$S (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. 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 = 2.14 for Cu$_x$S (x = 1.8-2).

The XRD spectra (Fig. 1) recorded for the Cu$_x$S 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 predominant crystalline phases. The air annealed films are mixtures of low chalcocite (Cu$_{2}$S, orhotomic crystalline structure) and djurleite (Cu$_{1.96}$S), in which Cu$_2$S 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 %, orhotomic structure), compound obtained, at deposition temperature (T = 300°C), from the oxidation of Cu$_{1.8}$S and/or Cu$_2$S (also contained in S1 film) to Cu$_2$O which reacts with SO$_2$ obtained by oxidation of sulfur precursor, in agreement with literature. By annealing in air, the composition of the as-deposited films is changed (Cu$_x$S is obtained as predominant phase), therefore the films properties are improved, especially electrical properties. Among Cu$_x$S (x = 1.8 - 2), Cu$_2$S is considered the copper sulfide with the best photovoltaic activity.

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$_x$S 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu:S</th>
<th>$C_{Cu^{2+}}$ [mol/L]</th>
<th>$n_{sp}$</th>
<th>Crystalline structure</th>
<th>D [nm]</th>
<th>$S_a$ [nm]</th>
<th>$t$ [nm]</th>
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<tr>
<td>S1</td>
<td>1:2.5</td>
<td>0.25</td>
<td>100</td>
<td>Cu$_{1.96}$S, tetragonal (66.4%)</td>
<td>23.2</td>
<td>47.5</td>
<td>715</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu$_2$S, orthorhombic (9.3%)</td>
<td>28.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CuSO$_4$, orthorhombic (24.3%)</td>
<td>27.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>1:3</td>
<td>0.25</td>
<td>100</td>
<td>Cu$_{1.96}$S, rhombohedral (96.6%)</td>
<td>19.2</td>
<td>18.4</td>
<td>595</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu$_2$S, hexagonal (3.4%)</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>1:3.5</td>
<td>0.25</td>
<td>100</td>
<td>Cu$_{1.96}$S, tetragonal (42.7%)</td>
<td>5.3</td>
<td>16.3</td>
<td>576</td>
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<tr>
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<td></td>
<td></td>
<td>Cu$_2$S, rhombohedral (57.3%)</td>
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<tr>
<td>S3_100*</td>
<td></td>
<td>100*</td>
<td></td>
<td>Cu$_2$S, orthorhombic (60.4%)</td>
<td>20.1</td>
<td>18.9</td>
<td>675</td>
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<td></td>
<td></td>
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<td>Cu$_{1.96}$S, tetragonal (39.6%)</td>
<td>4.7</td>
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<td>S4_60</td>
<td>1:3</td>
<td>0.3</td>
<td>60</td>
<td>Cu$_{1.96}$S, rhombohedral (100%)</td>
<td>16.7</td>
<td>16.5</td>
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<td>S4_70</td>
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<td>70</td>
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<td>Cu$_{1.96}$S, rhombohedral (100%)</td>
<td>17.8</td>
<td>16</td>
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<td>S4_80</td>
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<td>80</td>
<td></td>
<td>Cu$_{1.96}$S, rhombohedral (22.6%)</td>
<td>17</td>
<td>18.7</td>
<td>290</td>
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<td>Cu$_{1.96}$S, tetragonal (77.4%)</td>
<td>10.3</td>
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<tr>
<td>S4_90</td>
<td></td>
<td>90</td>
<td></td>
<td>Cu$_{1.96}$S, tetragonal (100%)</td>
<td>9.8</td>
<td>17.2</td>
<td>351</td>
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<td>S4_100</td>
<td></td>
<td>100</td>
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<td>Cu$_{1.96}$S, rhombohedral (76.8%)</td>
<td>16.9</td>
<td>16.3</td>
<td>412</td>
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<td></td>
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<td></td>
<td>Cu$_{1.96}$S, tetragonal (23.2%)</td>
<td>6.91</td>
<td></td>
<td></td>
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<td>S4_100*</td>
<td></td>
<td>100*</td>
<td></td>
<td>Cu$_2$S, orthorhombic (90.8%)</td>
<td>21.92</td>
<td>36.4</td>
<td>498</td>
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<td></td>
<td></td>
<td>Cu$_{1.96}$S, tetragonal (9.2%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>1:3</td>
<td>0.35</td>
<td>100</td>
<td>Cu$_{1.96}$S, rhombohedral (96.5%)</td>
<td>26.4</td>
<td>23.3</td>
<td>586</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu$_2$S, hexagonal (3.5%)</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
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</table>

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

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

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**FTO (SnO$_2$ PDF 01-077-0452)**

**Cu$_2$S (PDF 90-023-0961)**

**Cu$_2$S (PDF 90-047-1748)**

**CuS (PDF 03-065-3931)**

**Cu$_{1.96}$S (PDF 09-017-0449)**

**CuSO$_4$ (PDF 01-072-0090)**
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$_x$S 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 nsp increase (nsp = 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 xS 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 xS 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 Cu2S and Cu1.96S crystalline phases, with predominant Cu2S orthorhombic structure phase), crystallinity (D = 20.1 nm for Cu2S), and morphology (relative uniform and dense film). Further work will focus on tailoring Cu xS mainly the electrical properties, by optimizing the thermal treatment conditions for the films deposited by RSPD.

**CONCLUSIONS**

Films of Cu xS (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 °C from water:ethanol:glycerol (7:2:1 in volumes) solutions with molar ratio Cu:Cu = 1:2.5-3.5.

The composition of Cu xS films may be controlled by varying the Cu:Cu molar ratio in precursors’ solutions and by annealing conditions. Increasing the sulfur concentration in precursors’ solutions, Cu xS films with different stoichiometry (x = 1.8 - 1.96) are obtained. Annealing in air strongly influences the composition of the as-deposited Cu xS (x = 1.8) films, when “copper-rich” phase Cu2S is obtained as predominant crystalline phase in mixture wit djurleite (Cu1.96S).

The crystallinity, surface morphology and thickness of the Cu xS films can be tailored by modifying the precursors’ solutions composition, the number of precursors’ solutions composition, 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 xS films formation, while the crystals growth is favored in films obtained from precursors’ containing a higher Cu2+ concentration (0.35 mol/L);

b. increasing the number of spraying sequences from 60 to 80, a slow increase of Cu xS films thickness is observed, associated with the crystallites growth; for films obtained with higher spraying sequences (nsp > 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 measurements showed that film, deposited at 300 °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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**REFERENCES**