ELECTRICAL CONDUCTIVITY IN COPPER SULFIDES - INFLUENCE OF THE DEPOSITION PARAMETERS AND PRECURSOR'S CONCENTRATION

I. POPOVICI[1] **L. ISAC**[1] **A. DUȚĂ**[1]

Abstract: *Films of copper sulfides with various composition and properties were deposited on FTO (fluorine doped tin oxide) substrate using SPD (Spray pyrolysis deposition) as deposition technique, from aqueous and alcoholic solutions. The precursors' solutions of copper (II) chloride and thiourea, in different Cu:S ratios, were sprayed and the deposition parameters were varied. The present paper studies the electrical conductivity of the as-deposited films. The influence of temperature, film composition and film thickness was investigated. Electrical measurements (I-V curves) were registered in dark and were correlated with the film composition and structure, as obtained from the XRD patterns.*

Key words: *copper sulphide, thin films, Spray pyrolysis deposition.*

1. Introduction

It is known that Cu_xS are useful minerals therefore their mineralogical and technological properties were extensively studied. Recently, Cu_xS thin films have attracted the attention of researchers due to their optical and electrical properties. The optical spectra of Cu_xS films exhibit high transmission in the visible region and absorption throughout the near-infrared region (800-1500 nm) [5]. The compound exhibits fast ion conduction at higher temperatures and exists in a wide variety of compositions ranging from Cu_2S at copper-rich sites to CuS_2 at the copper-deficient sites such as CuS [1].

From the eight copper sulfides that have been discovered with different stoichiometries only five of them are stable at room temperature: CuS (covellite), $Cu_{1.75}S$ (anilite), $Cu_{1.8}S$ (digenite), $Cu_{1.96}S$ (djurleite), Cu_2S (chalcocite). Considering its pre-eminent role in thin film Cu_xS/CdS solar cells, copper sulphide has been investigated [2] in both bulk single-crystal and thin film form with regard to its structural, optical and electronic properties. These properties are largely determined by the composition of Cu_xS which, in turn, is governed by the preparation method and deposition conditions applied during growth.

Various processes for producing cuprous sulphide for solar cells have been investigated. These include evaporation of cuprous sulphide powder, flash evaporation of Cu_2S, sulphurization of copper foils and films, deposition from a slurry, spray techniques and chemiplating of CdS in CuCl solution [6-7]. All these methods have several limitations, most notably a

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[1] Centre "Product Design for Sustainable Development", *Transilvania* University of Brașov.

lack of process control which results in poor reproducibility and the coexistence of phases of Cu_xS other than chalcocite (Cu_2S) which is the optimum compound for highly efficient solar cells [4].

2. Experimental

Thin films of Cu_xS were obtained using the spray pyrolysis deposition technique (SPD) from an aqueous-alcoholic solution. Copper dichloride dehydrate $CuCl_2 \cdot 2H_2O$ (Scharlau, min 99%) and thiourea CH_4N_2S (Scharlau, min 99%) were used as copper and sulfur precursors.

Solutions with different Cu:S molar ratio were prepared: 1:2.5; 1:2.75 and 1:3 using a mixture of 30% ethanol and de-ionized water.

Conductive glass, with a layer of fluorine doped tin oxide (FTO) was used as substrate in the Cu_xS thin film deposition. The substrate was cut in slides of 25×25×0.8 mm, washed with de-ionized water and ultrasonically cleaned in ethanol, then dried in a compressed air flow. Using a hot plate the substrates were heated at the deposition temperature.

The deposition parameters such as the spraying distance from the nozzle to the substrate and the carrier gas pressure were set at previously optimized values [3]. Thus, the spraying distance was 25 cm and was kept constant for all depositions. The carrier gas pressure was fixed at a constant value of 1.5 bar. Also the optimal break between two consecutive spraying sequences was of 30”.

The temperature, the number of sprayed sequences and the Cu:S ratio were the three variables investigated in this study.

Temperature was varied from 240 to 315 °C (240, 250, 285, 300, 315 °C). Films obtained after 15, 20 and 25 spraying sequences, with 3 layers for each sequence, were obtained.

The as-deposited films were characterized using X-ray diffraction using an Advanced D8 Bruker diffractometer; the film thickness and energy bandgap were measured from the UV-Visible absorption spectra using a Perkin Elmer Lambda 25 photo-spectrometer, and the electrical properties were registered from I-V curves measured in the dark, using a Princeton Applied Research Potentiostat.

3. Results and Discussion

Thin layers of Cu_xS with direct bandgap ranging from 2.66 to 3 eV were obtained; the values are close to those presented in literature [4].

Film thickness ranging from 220 to 800 nm was measured for films obtained after 15, 20 and 25 deposition sequences.

Film thickness together with the energy bandgap show that these films can be used as potential absorbers in solid state solar cells.

Table 1

The influence of deposition temperature on crystallite size and phase composition

Deposition temperature [°C]	**Number of deposited layers**	**Cu:S molar ratio**	**Crystallite size (Scherrer) [Å]**	**Phase composition**	**Film thickness [nm]**
315	20	1:3	175-275	Digenite 27.13% Roxbyite 72.87%	372.14
300	20	1:3	206-271	Digenite 97.64% Roxbyite 2.36%	252.00
285	20	1:3	311.6	Covellite	220.78
250	20	1:3	323.4	Covellite	144.23

The XRD spectra, Figure 1, recorded for the Cu_xS films on FTO substrate show that films obtained at lower temperatures 250-285 °C consist mostly of CuS (Covellite JCPDS-03-065-0603) with a crystallite size calculated from the Scherrer equation of 311-323 Å. For films deposited at temperatures in the range 300° to 315 °C, the phase composition shows a mixture of two phases of Cu_xS with different stoichiometries (Cu_7S_4 - Roxbyite, JCPDS-00-023-0958, and Cu_9S_5 - Digenite, JCPDS-00-047-1748). The dominant phase in the film deposited at 300 °C is the Cu_7S_4-Roxbyite with 72.87% and a crystallite size of 274.14 Å. For the film obtained at 315 °C the dominant phase is Digenite Cu_9S_5 with 97.64% and a crystallite size of 206.2 Å.

From the X-ray diffraction pattern the phase composition and the crystallite size can be easily correlated with deposition temperature. This is important for further work in which we can tailor the composition of the film by varying the deposition temperature.

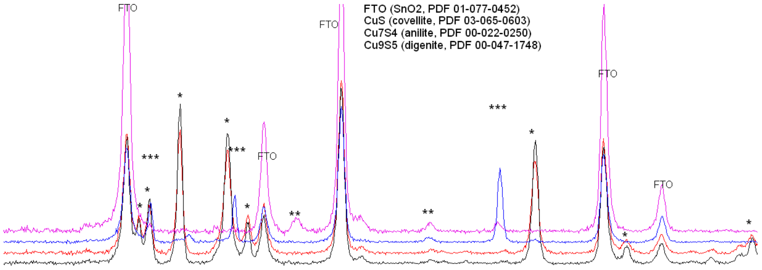

Fig. 1. *X-ray diffraction pattern of Cu_xS films deposited on TCO at 250-285-300-315 °C*

The electrical measurements (I-V curves) of the deposited films were registered in the dark (Figure 2). From the I-V curves, the electrical resistance of the films has been calculated and correlated with deposition parameters, precursor composition and film phase composition.

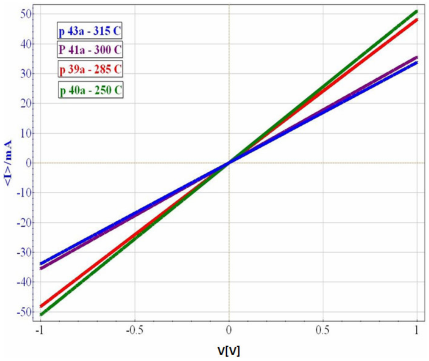

Fig. 2. *Dark I-V curves of Cu_xS films deposited at 250-285-300-315 °C*

Figure 3 presents the variation of the electrical resistance of the films with the deposition temperature.

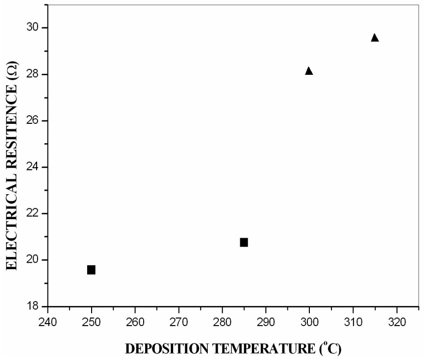

Fig. 3. *Dependence of electrical resistance with deposition temperature*

The resistive behaviour, with charge transport but no charge transfer, characterises all the films. There are two distinct domains in which the electric resistance varies. This is due to the presence of different Cu_xS phases. In the first region where CuS is the dominant phase the values for resistance are lower than in the second region where Cu_7S_4 and Cu_9S_5 are the dominant phases in the material.

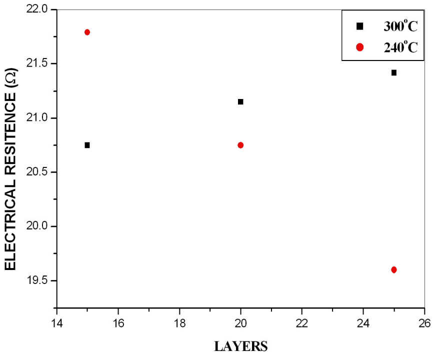

Fig. 4. *Resistance variation with number of layers for films deposited at 240 and 300 °C*

Figure 4 presents the variation of resistance with the number of layers deposited. For the films in which Covellite is the dominant phase in the film, electric resistance decreases with the number of layers due to the well known metallic behaviour of Covellite. For films in which Digenite and Roxbyite are the dominant phases electric resistance increases with the number of layers deposited, this can indicate a possible diode-like behaviour of this type of films [3].

4. Conclusions

Thin films of Cu_xS can be deposited on glass substrates using the SPD deposition technique.

Thin conductive films with thicknesses from 200 to 800 nm were deposited from aqueous and alcoholic solutions at different temperatures.

According to this study, the electrical properties of the films are closely related to the copper sulphide phases that are formed. This process can be controlled by the deposition parameters, in which temperature plays the most important role.

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