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Crystal order in Cu_2S thin films obtained by spray pyrolysis

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Thin films of Cu_2S (chalcocite) were obtained onto TCO (SnO_2:F) glass, by Spray Pyrolysis Deposition (SPD). As precursors, aqueous and water:ethanol:glyceryne solutions of copper(II) chloride and thiourea with molar ratio Cu:S = 1:3 have been used. The substrate temperature was maintained at 235 °C, respectively at 285 °C. The structural and the morphological characterisation of the films has been carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The deposited Cu_2S thin films may have tetragonal or monoclinic crystal structure built around two or three preferred orientation (*hkl*) planes, the (111) plane being the common one. The porous morphology and smaller crystallite sizes suggest that crystal germination is the limiting step in the films deposition, at 235°C, from precursor solution containing water or mixtures of water:ethanol:glycerine solvents. Increasing the substrate temperature at 285°C, the deposition of dense films with large crystallites/aggregates is favoured, suggesting that crystal growth is the limiting step when water:alcohol mixtures are used as solvents.

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1. Introduction

Copper sulfides ($Cu_{2-x}S$, x = 0-1) deposited as thin films onto different substrates are considered promising materials for solar energy conversion systems, such as photovoltaic cells, due to their structural, optical and electrical properties. Among these, Cu_2S (chalcocite) is recognised as the most suitable to be used as absorber and/or *p*-type semiconductor in a solid-state solar cell, [1-4].

Chalcocite, the copper-rich phase (79.85% Cu), is a black or blue-black crystalline solid compound with density around 5.6 g/cm^3, which crystallises in three distinct allotropic forms (α, β, χ), depending on temperature. The orthorhombic chalcocite (α-Cu_2S or low-chalcocite) is stable at low temperatures and shows a complex hexagonal close-packed crystal structure with a large unit cell containing 48 Cu_2S units, [5]. Copper and sulphur atoms mainly occupy triangular interstices, with 21 out of the 24 non-equivalent copper atoms, forming triangular CuS_3 groups, [6]. The lattice parameters are: a = 15.246 Å, b = 11.884 Å and c = 13.494 Å, [7]. The hexagonal chalcocite, β-Cu_2S, is stable between 103°C and 435°C. The crystalline lattice is hexagonal with the S atoms arranged in a nearly perfect close-packing and the Cu atoms distributed in the interstices in an almost fluid-like way. The lattice parameters are: a = 3.959Å and c = 6.784 Å, [5]. The cubic chalcocite, γ-Cu_2S or high-chalcocite, is stable at temperatures higher than 435°C and shows a face-centred cubic crystalline structure, which is assigned to antifluorite. This structure is a cubic close-packing arrangement of S atoms with Cu atoms in all the tetrahedral interstices, the unit cell containing 4 Cu_2S units. At 465°C, the lattice parameter a is equal to 5.725 Å, [5]. Within these compact structures, the copper ions (Cu^+) occupy the vacancies and are ordered, in low temperature phase (α-Cu_2S), or disordered (in high temperature phases: β-Cu_2S and γ-Cu_2S). Therefore, low-temperature phases crystallise in complex ordered superstructures, in which a week distortion of the sulphur framework is remarked. The high-temperature phases have structures with higher symmetries and usually smaller primitive unit cell parameters, [8].

Chalcocite, Cu_2S, is considered a mixed electronic-ionic conducting material, with predominant electronic conduction, attributed to free holes from acceptor levels of copper vacancies (p-type conduction), [9]. Cu_2S could be used as p-type semiconducting material in diode or photovoltaics, but also as absorber in solar cells, due to its optical properties, such as the energy bandgap, which ranges from 1.2 to 2.35 eV, and high absorption coefficients, [4, 9,10].

The aim of the present study is to characterise the formation (nucleation and growth reactions) of Cu_2S thin films by SPD, correlating the crystalline structure with the surface morphology, which strongly depend on the precursor solution composition and deposition parameters.

2. Experimental

The Cu_2S thin films were deposited from aqueous and water:ethanol (W-Et) precursor solutions containing

$CuCl_2 \cdot 2H_2O$ (99.9%, Merck), and H_2NCSNH_2 (99.9%, Sigma Aldrich), with molar ratio Cu:S = 1:3. The concentration of $CuCl_2 \cdot 2H_2O$ in the precursor solution was varied from 0.1 to 0.25 mol/L. The alcohol solutions contained, in volumes, 10% glycerine (Gl, 99%, J.T Baker) and 20-30% ethanol (Et, 99.8%, J.T. Baker) solved in deionized water (W).

Films were deposited onto transparent conductive SnO_2:F glass substrates (TCO, Libbey Owens Ford, TEC15/2.3 mm), which were ultrasonically cleaned by successive immersion in ethanol and acetone and dried under a nitrogen gas flow.

A Camag nozzle, a ceramic hot plate (CERAN 500 ± 1°C) and N_2 as carrier gas were used for the deposition of Cu_2S thin films by chemical spray pyrolysis from precursor solutions. During spraying, the substrate temperature (T) was 235°C, respectively 285 °C, the pressure of the carrier gas was maintained at 1 bar and the distance between the spraying nozzle and the heater was varied from 25 cm to 30 cm. The spraying times (t_{sp}) were varied from 20 minutes (aqueous solutions) to 40 minutes (W:Et solutions) and the breaks between two pulses varied from 10 to 60 seconds.

The as-deposited films were characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns of the films were registered by a Bruker D8 Advance Diffractometer with Cu-Kα_1 radiation. SEM analysis was performed using a Jeol JSM-5800LV scanning microscope.

3. Results and discussion

Previous studies, [11-13], have shown that the composition, morphology and electrical properties of $Cu_{2-x}S$ (x = 0-1) thin films, deposited by SPD, can be tailored by changing the composition of precursor solution and deposition parameters. Dense, relative homogenous and uniform films of Cu_2S, with diode behaviour, can be deposited at 285 °C from precursor solutions containing mixtures of water:ethanol:glycerine as solvents, with Cu:S molar ratio of 1:3. In the present study, the correlation of crystal structure (crystal lattice and crystallite size) with the surface morphology (average grain/aggregate size), depending on the composition of precursor solution and deposition temperature (Table 1) is reported.

Table 1. The chemical deposition parameters for obtaining of Cu_2S thin films via SPD.

Test	Solvent W:Et:$Gl_{(V)}$	$CuCl_2$ [mol/L]	T [°C]	t_{sp} [min]
A1	10:0:0	0.15	235	20
A2		0.2		
B	7:2:1	0.15	235	40
C1	6:3:1	0.25	285	35
C2		0.2		40

The XRD spectra recorded for the Cu_2S films deposited on the TCO substrates are shown in Fig. 1.

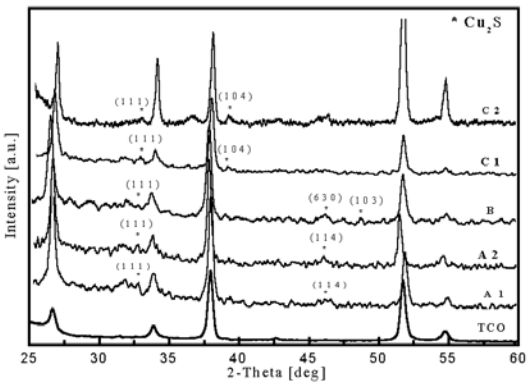

Fig. 1. XRD patterns of Cu_2S thin films deposited on TCO substrates at: a) 235 °C, W:Et:Gl = 10:0:0 (A1, A2) and W:Et:Gl = 7:2:1 (B); b) 285 °C , W:Et:Gl = 6:3:1 (C1, C2).

By comparison with the JCPDS-ICCD diffraction patterns, [7], films A1, A2, C1 and C2 contain single phase chalcocite (Cu_2S, JCPDS 72-1071) with tetragonal crystal structure and lattice parameters: a = 3.9962 Å, c = 11.287 Å. In the films A1 and A2, the tetragonal structure is built around two preferred orientations corresponding to (111) and (114) planes, while in C1 and C2 films the preferred orientation of the diffraction peaks corresponding to (111) and (104) planes. This difference can be attributed both to different precursor solution composition (aqueous and water:ethanol:glycerine solvent) and different substrate temperature (Table 1).

Table 2. The correlation of the crystal structure with surface morphology of the deposited Cu_2S thin films.

Test	Crystalline structure		Surface morphology	
	hkl	D[nm]	$\overline{d}$ [nm]	$\overline{N}$
A1	114	18.65	400	14
	111	**27.77**		
A2	114	20.64	350	16
	111	**21.26**		
B	103	24.18	250	7
	630	43.27		
	111	**36**		
C1	104	42.27	200	5
	111	**41.54**		
C2	104	21.10	300	7
	111	**41.54**		

According with the JCPDS 73-1138, film B contains Cu_2S phase with monoclinic crystal structure built around preferred orientations corresponding to (111), (630) and (103) planes. The lattice parameters are very close to those reported in literature, [5] for orthorhombic chalcocite (α-Cu_2S or low-chalcocite): a = 15.246 Å, b = 11.884 Å and c = 13.494 Å. It can be also observed that all Cu_2S crystallites have a preferential orientation to (111) plane.

The influence of the TCO substrate on this behaviour can be suspected.

The average crystallite size, D, was calculated by using the Scherrer's relation, [14]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of Cu-Kα_1 radiation (1.5406 Å), β is the broadening of diffraction line measured at half maximum intensity (in radians), and θ is the diffraction angle. The calculated average crystallite size in Cu_2S thin films are given in Table 2.

The SEM pictures of the Cu_2S films, Fig. 2, show that the films are homogenous and relative uniform, with the average aggregate/grain size decreasing from 400 nm (A1) to 200 nm (C1).

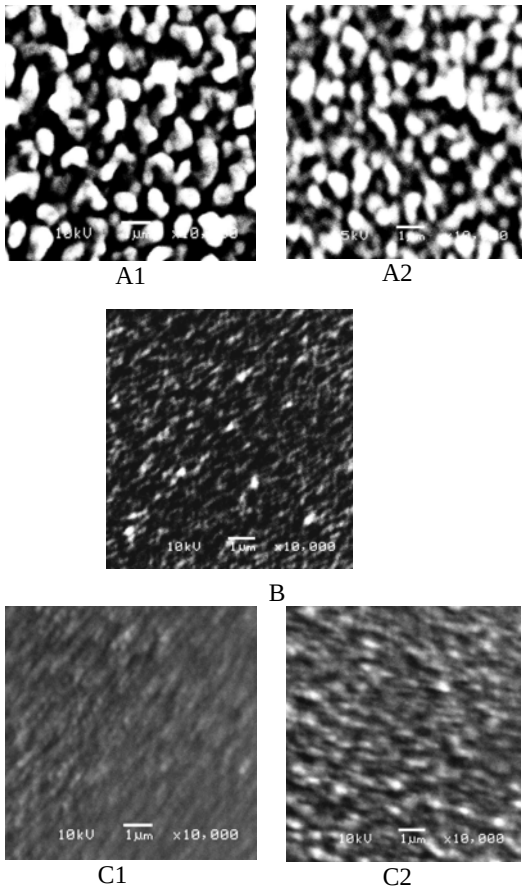

Fig. 2. SEM images of Cu_2S deposited on TCO substrates at: a) 235 ℃, W:Et:Gl = 10:0:0 (A1, A2) and W:Et:Gl = 7:2:1 (B); b) 285 ℃ , W:Et:Gl = 6:3:1 (C1, C2).

The films obtained from precursor solutions containing water:ethanol:glycerine solvents are denser then the films obtained from aqueous precursor solution. The alcohols in the solvent lower the surface tension and the dimensions of the precursor drops in the aerosol, allowing a fast solvent evaporation and a higher reaction rate.

The differences in surface morphology of the Cu_2S films obtained from precursor solutions containing aqueous and W:Et:Gl solvents, can be explained as a consequence of the increasing of crystal germination rate and obtaining of larger crystallites. The reaction rate in the germination step strongly depends on the stability of copper complexes formed with H_2O/alcohol or with thiourea. The addition of ethanol and glycerine solvents in aqueous precursor solution, determine the consumption of H_2O solvent favouring the decreasing of copper complexes stability, therefore a higher germination rate of the metal ion in precursor solution is obtained.

The second step in the formation of solid phase from a solution is the particle growth and the obtaining of thin films. The film growth can be controlled by adding alcohols in precursor solution and by increasing the substrate temperature.

By correlating the crystal structure and surface morphology of the Cu_2S thin films growth by chemically spray pyrolysis (Table 2) with the chemical composition of the precursor solutions and deposition parameters (Table 1), a dependence is observed: the average crystallite size for the orientation corresponding to (111) plane, common to all crystal structures, increases from 27.7 nm (film A1) to 41.54 nm (in films C1 and C2). This confirms that the addition of alcohol solvents in precursor solutions and the increasing of deposition temperature determine a growth in the crystallite size. The average number of crystallites ($\overline{N} = \overline{d}$ /D), grown on the (111) plane, decreases from 14-16 crystallites (films A1 and A2) to 5-7 crystallites (films C1, B and C2), suggesting that crystal germination is the limiting step for the films deposited at lower substrate temperatures (235 ℃) from aqueous precursor solution.The crystal growth is the limiting step for the formation of thin films from precursor solutions containing alcohol:water solvents, at higher temperatures (285 ℃).

4. Conclusions

Thin films of chalcocite (Cu_2S) with different crystalline structure and morphology are deposited at 235 °C, respectively at 285 °C, by chemical spray pyrolysis, from aqueous and alcohol solutions containing $CuCl_2$ and thiourea as precursors.

The crystal structure (crystal lattice and average crystallites size) correlated with the surface morphology (average grain/aggregate size) gives important information on ratio of the germination and growth reactions. These strongly depend on the composition of precursor solution and deposition temperature.

The addition of alcohols in aqueous precursor solution favours the obtaining of porous films with larger aggregates, suggesting that crystal germination is the limiting step, when the deposition temperature is lower. Increasing the substrate temperature, dense films with large crystallites are deposited by SPD from precursor

solution containing mixtures of water:alcohols. This suggests that the higher crystal growth rate favours the formation of thin films.

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