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Copper sulfides obtained by spray pyrolysis — Possible absorbers in solid-state solar cells

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Abstract

Copper sulfide (Cu_xS, $x=1.8$–2) thin films were deposited at 285 °C by spray pyrolysis from aqueous and alcoholic solutions of copper (II) chloride and thiourea with different Cu:S molar ratio. The XRD analysis showed that deposited films are chemically close to chalcocite (Cu_2S) or to mixtures of copper-rich phases (Cu_2S, $Cu_{1.8}S$, $Cu_{1.9375}S$) in which chalcocite or digenite ($Cu_{1.8}S$) is predominant. The films containing the single phase Cu_2S are denser and more homogenous than the films formed by two or more phases. The current–voltage (I–V) dark curves showed the diode behavior of the films, depending on the film thickness.

Keywords: Solar cells; Copper sulfides; Thin films; Spray Pyrolysis Deposition

1. Introduction

Solid-state solar cells, such as Extremely Thin Absorber (ETA) and nanocomposite (3 D) solar cells, are considered attractive devices for the next generation of photovoltaic (PV) cells. An ETA solar cell consists of an absorber film (CdTe, $CuInS_2$) with a thickness of just a few tenths of nanometers, between two interpenetrating transparent semiconductors, one n-type (TiO_2) and one p-type (CuSCN) [1]. The ETA concept is very attractive but presents some disadvantages, such as relatively slow electron transfer reactions at the interfaces, the recombination of the carrier charges with a concomitant loss of conversion efficiency [2]. The development of nanocomposite or so-called 3 D solar cells represents an alternative, firstly reported by Goossens and co-workers [3,4]. A nanocomposite solar cell consists of an n-type semiconductor film (TiO_2), a p-type semiconductor and an absorber film ($CuInS_2$ or Cu_2S), mixed together at nanometer scale to form an interpenetrating network. These solar cells showed energy conversion efficiency around 6% when Cu_2S is used [3].

Copper sulfide (Cu_xS, $x=1.8$–2) thin films, mainly Cu_2S, are considered promising materials for solar energy conversion systems, especially as p-type semiconductors and/or absorbers of visible light, due to their structural, electrical and optical properties. These properties are often determined by the composition of Cu_xS that, in turn, is dependent on the precursor solution composition and deposition parameters.

It is already reported [5] that the p-type conduction in Cu_xS is attributed to free holes from acceptor levels of copper vacancies. The density of copper vacancies increases with "x" value, from 1.8 to 2, with consequences on the electrical properties: it increases the sheet resistance (R_{sh}) [6,7] and decreases the electrical conductivity. The energy bandgap of Cu_xS, ranging from 1.2 to 2.35 eV [3–5,8–12] is favorable for light absorption under sunlight illumination. Moreover, transition band structure in Cu_xS provides high absorption coefficients ($\alpha=10^5$ cm^{-1} at 750 nm, for Cu_2S [3]) and therefore thin films are suitable forming in the design of low cost solid-state solar cells with satisfactory efficiency. A possible disadvantage in most of these devices can be their poor stability, considering here the problems encountered for the well-known Cu_2S/CdS solar cells [6,13]. This instability is mainly due to the diffusion of Cu^+ ions from Cu_2S into the CdS layer, reducing the semiconductor properties of the latter [3].

The aim of our work is to obtain dense, homogeneous and relative uniform thin films of chalcocite (Cu_2S) with specific structural and electrical properties, as absorber materials in

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solid-state solar cells. The films were obtained by Spray Pyrolysis Deposition (SPD), a relative simple and low cost deposition method, which is suitable for large area thin films deposition. The morphology, composition and electrical properties of the films deposited by SPD can be tailored by changing the composition of precursor solution and the deposition parameters.

2. Experimental

Aqueous and water:alcohol precursor solutions, containing $CuCl_2 \cdot 2H_2O$ (Merck), and $SC(NH_2)_2$ (Sigma Aldrich), are used for Cu_xS thin films deposition. The Cu:S molar ratio was varied from 0.33 to 0.5. Two concentrations of $CuCl_2 \cdot 2H_2O$ in the precursor solution were used: 0.2 or 0.25 mol/L. The alcohol solutions contain, in volumes, 10% glycerin (Gl — 99%, J.T. Baker) and 20%–30% ethanol (Et — 99.8%, J.T. Baker) solved in deionized water (W).

Transparent conductive SnO_2:F glass (TCO, Libbey Owens Ford, TEC 8/3 mm; TEC 15/2.3 mm) is used as substrate for Cu_xS thin films deposition. Slides of 25 mm × 25 mm × 0.5 mm were ultrasonically cleaned by successive immersion in ethanol and acetone and dried under nitrogen gas flow.

A Camag nozzle, a ceramic hot plate (CERAN 500 ± 1 °C) and N_2 as carrier gas are used for the deposition of Cu_xS thin films by chemical spray pyrolysis from precursor solutions.

The films were sprayed onto pre-heated TCO glass substrate at 285 °C, with the pressure of carrier gas at 1 bar. The distance between the spraying nozzle and the substrate was 30 cm or 25 cm. The spraying times were varied from 15 min (aqueous solutions) to 35 and 40 min (alcoholic solutions) and the breaks between two pulses varied from 10 to 60 s. Another set of samples was prepared by a 3 separate spraying sequences, each of 35 min.

The as-deposited films were studied via Scanning Electron Microscopy (SEM, Jeol JSM-5800LV model), X-ray diffraction (XRD, Bruker D8 Advance Diffractometer that uses Cu–Kα_1 radiation), and dark current–voltage measurements (EGG 273 potentiostat connected to a PC interface).

3. Results and discussion

The influence of the substrate temperature on the morphology and chemical composition of Cu_xS thin films, deposited from aqueous and alcoholic spraying solutions containing

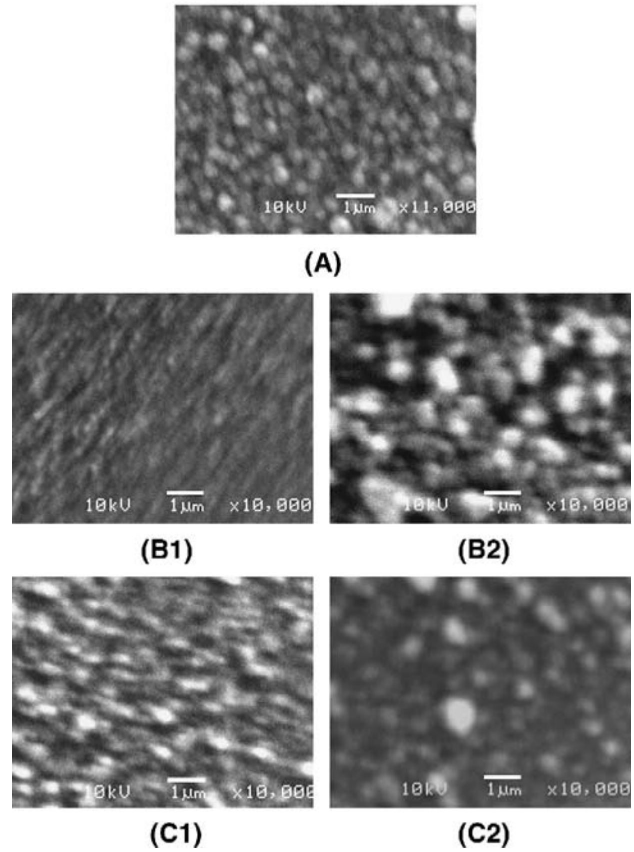

Fig. 1. SEM pictures of Cu_xS deposited at 285 °C.

$CuCl_2$ and thiourea in different Cu:S molar ratio, has been previously optimized. It was observed that the substrate temperature has more influence on the composition than on the morphology of the films. Generally, higher substrate temperatures (T = 260–330 °C) favor the obtaining of copper-rich phases (Cu_xS, x = 1.8–2), while temperatures lower than 260 °C allow the obtaining of copper-poor phases (Cu_xS, x = 1, 1.75). The substrate temperature of 285 °C was found to be the optimum for the Cu_2S thin films deposition by chemical spray

Table 1
The correlation between deposition parameters (distance and spraying time, t_{sp}), morphology (average grain size, d) and chemical composition of Cu_xS thin films

Tests	Solvent: W:Et:Gl$_{(v)}$	Cu:S	$CuCl_2$ [mol/L]	t_{sp} [min]	Phase composition	d [nm]
A*	1:0:0	1:2.28	0.2	15	Cu_2S + **$Cu_{1.8}S$** + $Cu_{1.9375}S$	300–350
B1**				35	Cu_2S	200
B2**	7:2:1	1:2.93	0.25	3 × 35	**Cu_2S** + $Cu_{1.8}S$	350–1000
C1*		1:3	0.2		Cu_2S	330
C2*	6:3:1	1:2.98	0.25	40	**Cu_2S** + $Cu_{1.8}S$	250–500

Spraying distance: 30 cm (*); 25 cm (**).
Data in bold correspond to the predominant phase in the Cu_2S phases mixture.

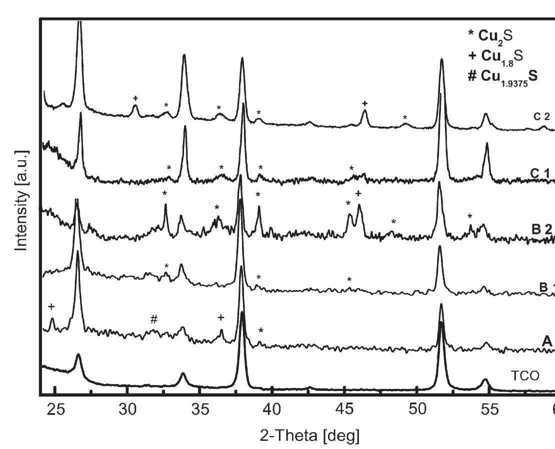

Fig. 2. X-ray diffraction patterns of Cu_xS deposited at 285 °C onto TCO substrate.