Copper Sulfide (CuₓS) Thin Films as Possible p-Type Absorbers in 3D Solar Cells

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Abstract

Films of CuₓS with 217-502 nm thickness were deposited by Automatic Spray Pyrolysis technique, at T = 275-325 ºC, from water:ethanol:glycerol= 7:2:1 (in volumes) solutions with molar ratio Cu:S = 1:2.5-3.5. Relative dense, homogenous and uniform films of CuₓS (x = 1-2), containing copper-rich phase digenite (single, predominant or secondary crystalline phase), with Eₚ = 2.41-3.1 eV and exhibiting electric resistance behavior were obtained. The optimized CuₓS layers were integrated in 3D solar cells which show the diode behavior but the photovoltaic response is very low, in the experimental conditions.

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Keywords: Copper sulfides; thin films; p-type absorbers; solid state solar cells; automatic spray pyrolysis

1. Introduction

Nowadays Solid State Solar Cells (SSSC), such as Extremely Thin Absorber (ETA) and 3D (nano-structured) solar cells, are promising alternatives to the silicon based photovoltaic (PV) cells/modules. The first ETA cell was developed by Kaiser et al. [1] as a stack of three thin layers: n-type semiconductor/light absorber/p-type semiconductor, following the observation that diffusion length of charge carriers within the absorber materials is a limiting property in the efficiency of solar cells. The ETA concept was further advanced by replacing the absorber with one of the partner semiconductors, usually the p-type one, in the 3 D or nano-structured solar cells, firstly reported by Goossens et al. [2, 3]. A nano-structured solar cell consists of a n-type semiconductor thin film (nanoporous TiO₂ anatase) and an absorber p-type semiconductor layer (Cu₂S [2], CuInS₂ [3], CuSbS₂ [4]) mixed together at nanometer scale to form an interpenetrating network. The best solar conversion efficiency of almost 6% was reported for the 3D cell using Cu₂S as absorber layer. The development of 3D solar cells with enhanced efficiency was obtained in the cells using buffer layers (InₓS₃ and/or Al₂O₃) between the n-type semiconductor and the p-type semiconductor/absorber layers [3]. Lenzman et al. [5] developed the first nano-structured solid state solar cell with TiO₂/Al₂O₃/InₓS₃/CuInS₂ structure and an overall conversion efficiency of almost 3%. It was shown that the photovoltaic characteristics of this type of cell could be substantially enhanced by using of Al₂O₃ tunnel barrier coating and InₓS₃ buffer layer at the interface between nano-structured TiO₂ and CuInS₂ films. The fundamental

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research in the SSSC field is mainly based on the thoroughgoing studies regarding the correlation between the properties (tailored by deposition parameters) of cell components (thin films) and the solar cell output (photovoltaic response). In the past years, the deposition and characterization of inorganic materials (new or already known), as components in a SSSC, attracted much interest, offering the possibility to develop efficient SSSC using up-scalable deposition techniques and low-cost materials (precursors). Among these materials, copper sulfides (Cu$_x$S, $x=1.8-2$), are promising candidates as absorbers and/or p-type semiconductors for SSSC, because of their structural, optical and electrical properties. The p-type conduction in Cu$_x$S is attributed to free holes from acceptor levels of copper vacancies [6], the electrical conductivity decreasing from Cu$_{1.8}$S to Cu$_2$S. The bandgap energy of Cu$_x$S thin films, ranging from 1.2 eV to 2.53 eV [2, 3, 6-9], is favorable for light absorption under sunlight illumination.

The present work is focused on the structural, morphological, optical and electrical characterization of Cu$_x$S thin films deposited onto FTO (SnO$_2$:F) substrates, at different temperatures ($T = 275-325$ °C), by Automatic Spray Pyrolysis (ASPD). As precursors, aqueous and alcoholic solutions of copper(II) chloride and thiourea with molar ratio Cu:S=1:3 have been used. The influence of the deposition parameters (precursors’ solution concentration, temperature and number of spraying sequences) on the optical ($E_g$) and electrical (I-V curves in dark conditions) properties of the deposited films are correlated with their chemical composition, crystalline structure and morphology. The optimized Cu$_x$S thin films were tested in a 3D solar cell with the structure: FTO/TiO$_2$(dense and nanoporous)/In$_2$S$_3$/Cu$_x$S/graphite and the photovoltaic response is presented. All cell components (TiO$_2$, In$_2$S$_3$, and Cu$_x$S) are deposited using ASPD as single technique.

2. Experimental

2.1. Cu$_x$S thin film deposition and characterization

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, were used as precursors for Cu$_x$S thin films (S1-S7) deposition. The Cu:S molar ratio in the precursors’ solutions was varied from 0.285 to 0.4, at a constant Cu$^{2+}$ concentration (0.3 mol/L). The Cu$^{2+}$ concentration in the precursors’ solutions was varied from 0.25 to 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 thin films 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 ASPD technique, at temperatures in the range of 275-325°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, as previously optimized [10]. The number of spraying sequences ($n_{sp}$) was varied from 15 to 35, with 20 seconds breaks between two pulses with pulse duration of 10 seconds.

The crystalline structure and composition analysis of the as-deposited 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.

2.2. Nano-structured (3D) solar cells development and characterization

Three solid state solar cell structures (SSSC) were developed, containing different Cu$_x$S thin films (S1, S2, S4) as absorber:

1. SSSC-S1: FTO/TiO$_2$(dense and nanoporous)/In$_2$S$_3$/S1/graphite,
2. SSSC-S2: FTO/TiO$_2$(dense and nanoporous)/In$_2$S$_3$/S2/graphite,
3. SSSC-S4: FTO/TiO$_2$(dense and nanoporous)/In$_2$S$_3$/S4/graphite.

All the thin films (TiO$_2$, In$_2$S$_3$, and Cu$_x$S) in the cell are deposited by ASPD technique:

a. the n-type TiO$_2$ anatase thin films (dense and nanoporous): solutions of 0.05 M of TiCl$_4$ (99.8%, Alfa Aesar) dissolved in a mixture of water:ethanol = 7:3 (in volumes), were used as precursors; the TiO$_2$ dense layers were deposited at 500°C, using 20 spraying sequences; the porous TiO$_2$ layers were deposited on the top of TiO$_2$ dense layers, at 400°C, after a number of 35 spraying sequences; the carrier gas (air) pressure was...
maintained at 1.2 bars and the deposition distance was 15 cm; after deposition, the samples (TiO₂ dense and TiO₂ dense and nanoporous) were cooled at room temperature and then annealed at 500 °C for 5 h [11].

b. the p-type absorber Cu₂S thin films (S1, S2, S4): as above described (see 2.1.) and at a fixed number of spraying sequences (10) for each of the copper sulfides.

c. The In₂S₃ buffer layers: solutions of InCl₃ (99.99%, Alfa Aesar) and thiourea (H₂NCSNH₂, 99%, Scharlau Chemie SA) dissolved in a mixture of water:ethanol = 1:1 (in volumes), were used as precursors; the In:S molar ratio in the precursors’ solutions was 0.133 at a concentration of In³⁺ ions of 0.03 mol/L; the films were deposited by ASPD at 250 °C [10], between the n and p type semiconductors, with the pressure of carrier gas (air) at 1.2 bar; the distance between the spraying nozzle and the substrate was maintained at 15 cm and the number of spraying sequences (n_sp) was 15, with breaks between two pulses of 20 seconds.

The PV cells were analyzed by current-voltage measurements, under illumination using a monochromator (Acton, SpectraPro 2150i) and a UV-VIS light source (300W, Oriel, model 7123). Graphite paste (graphite conductive adhesive aqueous based, Alfa Aesar) is used for contacts.

3. Results and discussion

Dense, relative homogenous and uniform films of Cu₂S, with composition close to chalcocite (Cu₂S) or to a mixture of copper-rich phases and with diode behavior, can be deposited at 285 °C, from aqueous alcoholic precursors’ solutions with molar ratio Cu:S of 1:3 [12, 13]. The present study presents new correlations between the properties of the Cu₂S thin layers (crystallinity, morphology, optical and electrical properties) and the photovoltaic response of a 3D solar cell involving these layers. The films with absorber properties, suitable to a SSSC are also tested in solar cells, to evaluate the photovoltaic response. The effect of precursors’ solution composition (Cu:S molar ratio, Cu²⁺ concentration) and the deposition parameters (temperature, T, number of spraying sequences, n_sp) on the structural and optical properties of Cu₂S thin films obtained in this study is presented in Table 1.

The average value of crystallite size (D) was calculated using Debye-Scherrer formula [13]. The average films thickness (t) and the bandgap energy (E_g) were calculated based on the absorption spectra registered in the wavelength range 200-1100 nm. The thickness of the films was calculated with the well-known formula [14]:

$$t = \frac{\lambda_1 \lambda_2}{2n(\lambda_1 - \lambda_2)}$$

where n is the film refractive index (the average value n = 2.1 is considered for Cu₂S [15], and n = 1.45 for CuS [16]) and \(\lambda_1\) and \(\lambda_2\) are the wavelengths of two successive interferences minima. The E_g values were obtained by extrapolation of the linear regions on the energy axis from the \((ahv)^2\) versus \((hv)\) graphs.

3.1. Cu₂S thin films composition and morphology

The XRD spectra (Figure 1) recorded for the Cu₂S thin films on the FTO substrate show that the films contain either single phase digenite (Cu₉S₅, samples S2 and S3), with rhomboedric structure, or mixtures of digenite with chalcosite high (Cu₂S, films S1, S2, S4_25) or with copper sulphide (CuS, S3 and S7), in which either digenite or copper sulphide is the predominant phase.

The composition of the films is influenced by the variation of precursors’ solution composition (especially molar ratio Cu:S) and deposition temperature. Increasing the sulphur concentration in the precursors’ solution favours the mixtures in which copper-poor phase CuS is predominant (65.15% CuS in sample S7). Lowering the sulphur content results in films containing copper-rich phases (Cu₂S and/or Cu₁.₃S): S1 (97.03% Cu₁.₃S), and S4_25 (97.76% Cu₁.₃S). The same effect is registered at higher deposition temperature (T = 300-325°C, samples S4 and S5).

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. Since this parameter did not influence the films composition, we could assume that the defects concentration is rather small.

The AFM images of the Cu₂S films, Figure 2, show sample surface with relative uniformity and homogeneity, with the average roughness decreasing from 182.5 nm (S7) to 115 nm (S2). The average roughness of the films
deposited at different temperatures \((T = 275-325^\circ)\) are higher (163 nm), for the films S3 (less homogenous in composition) and S5 (no uniform and thin, 258 nm), comparing to the S4 25 film (134 nm). The surface morphology is in good agreement with the composition and crystallinity of the films, which in turn are influenced by the deposition parameters. Uniform and low roughness, characterizing dense films, can play a key role in the reciprocal infiltration of the n-type TiO\(_2\) with the p-type Cu\(_x\)S and will further influence the PV cell properties.

The average crystallite sizes of copper-rich phases (Cu\(_1.8\)S predominant in films S1 and S4 25) decrease from 29.8 nm (S1) to 19 nm (S7) and have lower values in comparison with average crystallites sizes of secondary phases Cu\(_2\)S (38 nm in S1) or CuS (59 nm in S7). The crystalline aggregates sizes, estimated from AFM images, increase from 150-250 nm (S1) 250-450 nm (S7), suggesting that growth rate of Cu\(_x\)S crystallites is higher when lower molar ratio Cu:S are used in precursors’ solution, favouring the growth of secondary copper-poor phase (CuS). As a consequence of the films growth is the thickness which also increases from 266 nm (S1) to 483 nm (S7).

Table 1. The correlation between deposition parameters, crystallinity (average crystallite size, \(D\)), average thickness \((t)\) and optical properties \((E_g)\) of Cu\(_x\)S thin films

| Sample | Cu:S molar ratio | Cu\(^{2+}\) [mol/L] | \(T\) [°C] | \(n_{sp}\) | Crystalline structure          | \(D\) [nm] | \(t\) [nm] | \(E_g\) [eV] |
|--------|------------------|----------------------|-----------|----------|-------------------------------|------------|----------|----------|
| S1     | 1:2.5            | 0.3                  | 300       | 25       | Digenite, rhombohedral (97.03%) | 30         | 266      | 2.67     |
|        |                  |                      |           |          | Chalcosite high, hexagonal (2.97%) | 38         |          |          |
| S2     | 1:3              | 0.25                 | 300       | 25       | Digenite, rhombohedral (100%) | 23         | 287      | 2.69     |
| S3     | 1:3              | 0.3                  | 275       | 25       | Digenite, rhombohedral (11.79%) | 19         | 502      | 2.59     |
|        |                  |                      |           |          | Copper sulfide, hexagonal (88.21%) | 44         |          |          |
| S4_15  | 1:3              | 0.3                  | 300       | 15       | Digenite, rhombohedral (97.76%) | 22         | 217      | 3.01     |
| S4_25  |                  |                      |           | 25       | Chalcosite high, hexagonal (2.24%) | 31         | 275      | 2.73     |
| S4_35  |                  |                      |           | 35       |                                |            | 289      | 2.53     |
| S5     | 1:3              | 0.3                  | 325       | 25       | Digenite, rhombohedral (100%) | 24         | 258      | 3.1      |
| S6     | 1:3              | 0.35                 | 300       | 25       | Digenite, rhombohedral (98.25%) | 20         | 321      | 2.68     |
|        |                  |                      |           |          | Chalcosite high, hexagonal (1.75%) | 37         |          |          |
| S7     | 1:3.5            | 0.3                  | 300       | 25       | Digenite, rhombohedral (34.85%) | 19         | 483      | 2.46     |
|        |                  |                      |           |          | Copper sulfide, hexagonal (65.15%) | 59         |          |          |
Variations in the deposition temperature mainly influence the composition than the morphology of the Cu$_x$S thin films, especially related to their homogeneity. Increasing the deposition temperature, a significant increasing of the average digenite crystallite size, from 19 nm (S3, T = 275°C) to 24.37 nm (S5, T = 325°C), is observed. This suggests that the crystal growth is the limiting step for the film deposited at higher temperature.

Figure 1. XRD patterns of as-deposited Cu$_x$S thin films obtained by ASPD onto FTO substrates

Figure 2. AFM images of Cu$_x$S thin films obtained by ASPD onto FTO substrates
3.2. Cu\textsubscript{x}S thin films optical properties

The bandgap energy values of the as-deposited Cu\textsubscript{x}S layers are in the range 2.46-3.1 eV (Table 1), close to those reported in literature ($E_g = 1.3-2.53$ eV), and depending on the films composition and crystallinity.

The optical bandgaps of films, Figure 3, containing single or predominant copper-rich phase Cu\textsubscript{1.8}S (samples S1, S2, S4\_25, S5, S6) are higher ($E_g = 2.67-3.1$ eV) than those of films containing predominant copper-poor phase CuS (samples S3, S7, $E_g = 2.46-2.49$ eV). Conveyable values ($2.67$ eV) are obtained for films of digenite (single or predominant phase) with thickness varying from 266 nm (S1) to 321 nm (S6). The data prove that by increasing the number of sprayings (and thus the time spent at the deposition temperature) the films are getting denser and the decrease in the band gap value can be the result of lattice reorganisation (with defects or non-stoichiometric compounds formation). For the films obtained in the same deposition conditions, with different spraying sequences number, the lowest value of $2.53$ eV corresponds to the film S4\_35, with thickness of 289 nm, while the highest $E_g$ values corresponds to the very thin film S4\_15 ($t = 217$ nm) and may be due to the transparency and or reflection of the film.

![Figure 3. $(e^h\nu)_2$ vs. $\nu$ plot for as-deposited Cu\textsubscript{x}S thin films (S1, S2, S4\_25)](image)

3.3. Cu\textsubscript{x}S thin films electrical properties

The electrical measurements (current-potential curves) of the films are registered in dark conditions and are shown in Figure 4.

![Figure 4. (a) Current density vs. Potential, (b) Current density vs. Potential](image)
Figure 4. I-V curves registered in dark for Cu_xS thin films obtained by ASPD using different (a) Cu:S molar ratio, (b) Cu^{2+} molar concentrations, (c) deposition temperature and (d) number of spraying sequences.

For all the samples, the resistive behaviour is predominant, the electrical resistance decreases with increasing the Cu:S molar ratio and the spraying sequences number (film thickness). The sample S4_25 shows the highest electrical resistance (17.5 \( \Omega \)), and was further tested in a 3 D cell.

Due to their composition (digenite or mixtures of digenite and chalcosite high), morphology and optical properties (relative good \( E_g \) values), films S1, S2 and S4_25 were integrated in 3D solar cells with general structure: SSSC-S: FTO/TiO_2(dense and nanoporous)/In_2S_3/Cu_xS (S)/graphite. The results (Figure 5) prove the diode behavior of the cells (SSSC-S1) but the photovoltaic response is very low, in the experimental conditions.

Figure 5. I-V curves registered under illumination for SSSC-S1 and SSSC-S2 cells.

4. Conclusions

In order to obtain thin films with morphology, structural, optical and electrical properties, required for p-type absorbers in 3D solar cells, films of Cu_xS (217-502 nm thickness) were deposited by ASPD technique, at \( T = 275-325 \) °C, from water:ethanol:glycerol (7:2:1) solutions with molar ratio Cu:S = 1:2.5-3.5. The control of the precursors’ solution composition, the deposition temperature and the spraying sequences number allows the obtaining of relative dense, homogenous and uniform films of Cu_xS (x = 1-2), with \( E_g = 2.41-3.1 \) eV and exhibiting electric resistance behavior.

The Cu_xS films composition is influenced by the Cu:S molar ratio and deposition temperature: films containing copper-rich phases (Cu_2S and/or Cu_{1.8}S, as single or predominant crystalline phase) were obtained when the deposition were take place at higher temperatures (T = 300-325 °C), from precursors’ solutions with Cu:S = 1:2.5, respectively Cu:S = 1:3.

The surface morphology is in good agreement with the composition and crystallinity of the Cu_xS films, relative uniform and dense films with roughness increases from 115 nm to 182 nm. The crystalline aggregates sizes increase in the films obtained from solutions with lower Cu:S molar ratio, suggesting that the growth of copper-poor phase
CuS is favored. Increasing the deposition temperature, a significant increasing of the average copper-rich phase Cu$_{1.8}$S is observed, proving that the Cu$_{1.8}$S crystals growth is preferentially developed at higher temperatures (T = 300-325 ºC).

The bandgap energy values of the Cu$_x$S films ($E_g = 2.41-3.1$ eV) are depending on the films composition and thickness: lower values are obtained for samples containing CuS as predominant crystalline phase, with significant thickness.

The electrical measurements showed that all the layers have predominant resistive behavior, the highest electrical resistance (17.5 ´) was registered for sample deposited at 300 ºC using 25 spraying sequences, from solution with Cu:S = 1:3. This layer was integrated in a 3D solar cell and low conversion efficiency was obtained. Further work will be focused to the enhancement of the n/p interface in 3 D solar cell with Cu$_x$S p-type absorbers.

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