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Growth and Characterization of $\text{Cu}_2\text{MnSnS}_4$ Thin Films Synthesized by Spray Pyrolysis under Air Atmosphere

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Abstract: The direct synthesis of chalcopyrite $\text{Cu}_2\text{MnSnS}_4$ (CMTS) thin films by a spray pyrolysis technique on glass substrates under oxidative conditions (ambient atmosphere and using compressed air as a carrier gas instead of nitrogen) was studied. The effect of the deposition temperature on the structural, chemical composition, and optical and electrical properties of thin films has been assessed. X-ray diffraction study reveals that the tetragonal stannite structure crystallizes with a [112] preferential orientation from 280 up to 360 °C, with its crystallinity correlated with the substrate temperature. However, in addition to its crystallization, traces of secondary phases are observed: a mixture of SnO and CuO at 360 °C prevails on the formation of CuS at 320 °C. Above 360 °C, the oxidant conditions combined with the loss in sulfur lead to the crystallization of only the tenorite CuO. The crystallization of sulfides by spray pyrolysis under air is possible only at relatively low deposition temperature for which the oxidation rate is inefficient compared to the sulfidation rate. Further optical studies of stannite films indicate a high absorption coefficient toward the visible range ($>10^4 \text{ cm}^{-1}$) and an optical band gap of about 1.64–1.85 eV, also depending on the substrate temperature. The CMTS thin films deposited below 360 °C exhibit a moderate electrical resistivity of about $\Omega\cdot\text{cm}$ at room temperature. The properties of the stannite films synthesized using a spray pyrolysis technique in ambient air are comparable to those of films obtained by spray pyrolysis with nitrogen carrier gas despite the presence of oxides traces, an increase in the deposition temperature improving the microstructure, and its related optical and electrical properties.

Keywords: $\text{Cu}_2\text{MnSnS}_4$; thin films; effect substrate temperature; spray pyrolysis; photovoltaic applications

1. Introduction

The growth of environmental problems related to the overexploitation of fossil resources is forcing research groups to focus their research on new renewable and clean energies. Solar energy is one of the most important demand of today. A standard photovoltaic device consists in a films stack, from bottom to the top: a Mo back contact layer ($\sim 0.5\text{--}1 \mu\text{m}$), a thick p-type absorber ($\sim 1\text{--}2.5 \mu\text{m}$), thin n-type buffer layer ($\sim 0.1 \mu\text{m}$), and a transparent conductive oxide contact layer ($< \sim 0.5 \mu\text{m}$) [1]. The electrical contacts on the top and on the back are necessary to harvest the electrical charges generated by the adsorption of

photons. The p–n junction formed by the contact of the n or p doped materials facilitates the separation of electron and holes charges in avoiding their fast recombination after their excitation [2].

One of the major challenges lies in the production of sufficient and inexpensive solar energy while respecting environmental standards. Traditionally, the absorber is based on CuInSe₂ (CIS), CuInGa(S,Se)₂ (CIGS), or CdTe compounds. The toxicity and the rarity of some elements composing it make crucial the definition of other material. To overcome this problem, recent researches have been focused on absorber composed of earth abundant elements, low-cost to extract and to transform, and non-toxic [3,4]. In this frame, the quaternary diluted magnetic semiconductors sulphides (Cu_{2-x}M_xSnS₄ with M = Mn, Fe, Co, Ni, Zn, etc.) derivate from the chalcopyrite family. The quaternary sulfides exhibit different polymorphs (tetragonal kesterite $\bar{1}\bar{4}$, tetragonal stannite $\bar{1}42m$, and cubic F43m ...) according to the cation distribution in the tetrahedral site, temperature, or technical synthesis [5,6]. They exhibit interesting photoelectric characteristics relatively close to those of the CIGS reference material [7,8]. Modeling analysis are also reported in view to gain insight into the thermal stability [9]. Among them, copper manganese tin sulfide Cu₂MnSnS₄ (CMTS) is one of the most promising. Each component of CMTS is abundant in the earth's crust (Cu: 68 ppm, Mn: 1100 ppm, Sn: 2.2 ppm, S: 420 ppm) [4]. This compound does not exhibit high recombination contrary to the CZTS compound [10]. Further, a direct band gap energy between 1 and 1.5 eV has been reported [11,12] and a large absorption coefficient higher than 10⁴ cm⁻¹ [13]. A power conversion efficiency of 0.76%–0.83% has been achieved recently for CMTS based solar cells [4,14]. In addition, this compound exhibits high radiation stability contrary to the first generation of solar cells for which the application was limited to terrestrial applications [15].

A variety of methods have been used recently to synthesize CMTS, including spray pyrolysis [16,17], sol gel [18,19], direct liquid coating [13], spin coating [20], thermal evaporation [21,22], and electrodeposition [23]. The advantage of the spray pyrolysis technique compared to those mentioned above is its simplicity, its ability to deposit on large areas at lower costs and it is environmentally friendly [24]. The structure and microstructure of the CMTS film depend on the crystallization temperature, and hence strongly influence the efficiency of quaternary chalcogenide thin film solar cells [16,25]. The objective of the present work is to study the direct deposition of CMTS thin films under ambient atmosphere by spray pyrolysis technique using a compressed air as a carrier gas instead of nitrogen. A complete compressed air system meets modern demands in terms of budget, accessibility and respect for the environment and is coherent with cheap photovoltaic industry (low-cost raw materials and production). No supplementary step of sulfurization treatment leading to variable results was used to synthesize crystallized phase [26,27]. Furthermore, researches have dealt with the sulfidation of oxides at 300 °C [28,29], and a previous study on the optical properties of CMTS has already demonstrated the feasibility to deposit this phase by spray pyrolysis under a relatively oxidant atmosphere without providing more detailed information [30]. Because of the potential influence of the synthesis temperature on the structure and the microstructure, the deposition temperature was varied from 280 to 400 °C, and the structural, chemical composition, optical, and electrical characteristics were then assessed.

2. Materials and Methods

2.1. Elaboration

Cu₂MnSnS₄ (CMTS) thin films have been successfully grown, in our laboratory, using a chemical spray technique on glass substrates in ambient atmosphere using one step-method without post-sulfurization. The experimental setup that was utilized to spray CMTS thin films consists of a substrate heating system and a spray head moving in the *x*–*y* plane parallel to the substrate surface in order to achieve a uniform coating on the heated substrates. Before the deposition, the glass substrates with dimension of 2 × 2 cm² were cleaned with a detergent, washed with 3% nitric acid, rinsed in succession with distilled water and acetone, and finally dried in an oven at 120 °C for 15 min.

For deposition, the starting solutions were prepared in four different glass bottles consisting of $\text{SC}(\text{NH}_2)_2$ (32 mmol), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2 mmol), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (4 mmol), respectively, by dissolving in distilled water as the solvent agent. The solutions were then mixed in a beaker under magnetic stirring for a few second. HCl (0.5 mL) was also added in order to obtain a homogenous, colorless, and transparent solution. The precursors were taken in stoichiometric composition of CMTS except of thiourea, which, due to its volatility, was taken in excess to prevent any deficiency of sulfur during the spraying. Compressed air was used as a carrier gas. In order to optimize the deposition temperature, the CMTS solution (100 mL) was sprayed onto a heated glass substrate at 280, 320, 360, and 400 °C with a fixed deposition time of 30 min in air. Other deposition parameters of the spraying system including the spray deposition rate, the gas flow rate, the distance nozzle-substrate and the hot plate rotation speed were set at: 3×10^{-3} L/min, 10 L/min, 20 cm, and 14 rpm, respectively. After deposition, the final samples were naturally cooled down at room temperature.

The first step of the formation mechanism of CMTS films corresponds to the dissolution of the precursors in the solvent according to these chemical equations as also reported in CCTS thin films by Maldar et al. [31]:

Then, once spraying onto the glass substrates, the formation of CMTS thin films under thermal decomposition can be explained by the following overall equation:

2.2. Characterization

The structural features of the coatings were investigated by using X-ray diffraction (XRD, Philips X'Pert diffractometer, El manar, Tunisia) with $\text{Cu-K}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$) operated in the scanning angle 2θ from 20° to 70° . The operation voltage and current for the XRD patterns were 40 kV and 30 mA, respectively. The chemical composition of the film deposited on glass substrates was estimated by energy dispersive spectroscopy (EDS, Quantax Bruker with XFlash 6|30, Bruker nano, Berlin, Germany). The total transmittance and reflectance of the coatings were measured with a double beam UV-VIS-NIR spectrophotometer (Shimadzu 3100 S, El manar, Tunisia) equipped by integrating sphere (LISR3200, El manar, Tunisia) in the wavelength range of 300–1800 nm in order to determine the optical parameters such as the absorption coefficient and the band gap energy. Resistivity measurements were made on the CMTS film deposited on glass substrates, at room temperature by the four-probe technique. The device is composed by a certified Jandel cell (Multi height probe, Jandel Engineering Limited, Lindslade, UK), the factor form is well known, and it is connected with an HP 3458A multimeter (Agilent, Massy, France) to measure electrical parameters.

3. Results and Discussion

3.1. Structural Characterization

Figure 1 shows the XRD patterns of the as-sprayed films deposited at different substrate temperatures. For the films deposited at substrate temperatures of 280 up to 360 °C, four major peaks can be noted corresponding to the reflections (112), (200), (204), and (303) of the CMTS phase (JCPDS card no. 89-1952), respectively. The CMTS crystallizes in the tetragonal stannite structure with the space group $\bar{1}42m$. As the substrate temperature increases from 280 to 360 °C, the intensity and the sharpness of the CMTS peaks increase, showing an improvement of the crystalline quality.

Figure 1. X-ray diffractograms of CMTS thin films grown at different substrate temperatures.

Since the CMTS is a quaternary compound, the crystallization of secondary phases is possible. Taking into account that the deposition occurs in ambient air on heated substrate using a compressed air as a carrier gas and in agreement with the values of the standard Gibb's energies of formation of simple oxides or sulfides in the corresponding range of temperature, the crystallization of oxides could prevail on that of sulfide compounds. At 280 °C, no trace of impurity phases is X-ray detected, but it is still probable that a small proportion of amorphous oxide could be present. With a further increase at 320 °C, traces of tenorite copper oxide and copper sulfide (CuS) is observed in addition to CMTS phases. At 360 °C, only oxide secondary phases (SnO and CuO) are detected. For further increase of the substrate temperature (T_s) up to 400 °C, the instable SnO is no more observable, and the crystallization of the tenorite CuO prevails over the sulfide crystallization [32,33].

The structural parameters like reticular distance (d_{hkl}), lattice parameters (a , b and c), full-width-at-half-maximum (β), the average crystallite size (D_{av}), microstrain (ϵ), and dislocation density (δ) were determined. By using the main peak of (112), the inter reticular distance d_{hkl} values were calculated according to the Bragg equation [34]:

$$N\lambda = 2d_{hkl}\sin\theta \quad (6)$$

As mentioned above, the CMTS thin films represent a tetragonal stannite structure which leads to ($a = b \neq c$). Therefore, the lattice parameters were determined by using the reticular distance formula:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2 \frac{a^2}{c^2}}} \quad (7)$$

The average crystallite size (D_{av}) was calculated using the Scherrer formula [35]:

$$D_{av} = \frac{k\lambda}{\beta \cos\theta} \quad (8)$$

where k is the shape factor ($k = 0.9$) assuming spherical shape for which the crystallite size is independent of the crystallographic direction, λ is the X-ray wavelength (1.5406 Å), β is the full-width-at-half-maximum (FWHM), and θ is the Bragg diffraction angle.

The microstrain (ϵ) can be expressed as follows [36]:

$$\epsilon = \frac{\beta}{4\tan\theta} \quad (9)$$

The dislocation density (δ) can be evaluated by Williamson and Smallman's formula [37]:

$$\delta = \frac{1}{D^2} \quad (10)$$

The detailed data, involving the main structural parameters of the stannite CMTS phase, are listed in Table 1. The average crystallite size (D_{av}) grows significantly from 5.45 to 12.05 nm with increasing substrate temperature from 280 to 360 °C. This effect associated with the increase of the relative intensity of the diffraction peaks and with the progressive decrease of the microstrain and dislocation density demonstrate an improvement of the crystalline quality with the increase of the substrate temperature in agreement with other reported study [19]. The interplanar spacing is almost constant of all CMTS thin films. The lattice constants a and c (Table 1) are in good agreement with the reported values [19]. The evaluation of ratios of lattice parameters ($\eta = c/2a$) of the CMTS thin films is almost constant and they are found to be less than unity, which confirms the stannite structure. This result is consistent with those cited in literature [38]. The constancy of the lattice parameters and the crystallization of minor oxide phases would suggest that the growing CMTS phase does not contain oxygen.

Table 1. Lattice constants of the CMTS thin films deposited at different substrate temperatures.

T_s (°C)	FWHM of (112) Peak (Degree)	Interplanar Spacing of (112) (Å)	Lattice Constant a (Å)	Lattice Constant c (Å)	$\eta=c/2a$	Crystallite Size D (nm)	ϵ (10^{-1})	δ (10^{-2} nm^{-2})
280	1.508	3.13	5.49	10.72	0.97	5.45	1.48	3.36
320	1.211	3.09	5.48	10.74	0.97	6.79	1.17	2.16
360	0.684	3.09	5.44	10.55	0.96	12.05	0.66	0.68

3.2. Chemical Composition Characterization

Table 2 lists the composition ratios of the CMTS thin films deposited at different substrate temperatures. All the CMTS thin films show a near stoichiometry metal atomic ratio but with a deficiency of S. However, as observed from this table, the rise of substrate temperature leads to a slight increase of the Cu relatively to the Mn and Sn atoms, and to a slight decrease of Sn content relatively to the Mn and Cu contents. In addition, the S/metals ratio decreases drastically when increasing the substrate temperature above 320 °C, probably due to the higher volatility of sulfur at elevated temperatures, despite the excess of thiourea in the precursor solution [31], and also because of the crystallization of oxides with temperature. The strong loss in sulfur (>50%) combined with the slight change in the stoichiometry of the metal elements at 400 °C explain the non-crystallization of the CMTS phase and the presence of the oxide phase only. In spite of the rather poor accuracy of the EDS technique to measure the oxygen content, it is worth of noting, based on XRD results, that the proportion of oxide phases in CMTS films is increasing with the rise of the substrate temperature. Then an increase of the oxygen content with the deposition temperature is expecting, which contributes to the prevention of sulfurization of the growing films. In agreement with XRD results, the crystallization of sulfides by spray pyrolysis under air is possible only at a relatively low deposition temperature for which the sulfidation conditions remains more efficient than the oxidation.

Table 2. Composition ratios of the CMTS thin films deposited at different substrate temperatures.

T_s (°C)	Composition Ratios		
	Cu/(Sn + Mn)	Mn/Sn	S/Metals
280	0.95	0.97	0.76
320	1.05	1.22	0.75
360	1.04	1.18	0.54
400	1.09	1.05	0.29

3.3. Optical Characterization

The optical properties including the measurement of the absorption coefficient and the band gap energy of CMTS thin films were investigated by using UV-Vis spectroscopy. Indeed, the absorption coefficients and the band gap energies were determined from the experimental transmittance (T) and reflectance (R) spectra using these equations, neglecting scattering phenomena [39,40]:

$$\alpha = \left(\frac{1}{d}\right) * \ln\left(\frac{(1-R)^2}{T}\right) \quad (11)$$

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (12)$$

where α and E_g characterize the absorption coefficient and the band gap energy, respectively, d is the coating thickness, A is a constant, h is the Planck's constant, ν is the incident light frequency, and n is equal to $1/2$ for the direct band gap material. The Figure 2a,b shows the variations of the absorption coefficient (α) and the $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$), respectively. From Figure 2a, all the films exhibit absorption coefficients higher than 10^4 cm^{-1} towards the visible light region. However, the absorption coefficient of the film deposited at 400°C corresponding to the CuO phase strongly decreases to $2 \times 10^3 \text{ cm}^{-1}$ in the infrared ($\lambda > 1600 \text{ nm}$), due to the non-crystallization of the tetragonal CMTS phase. These high absorption coefficients are consistent with other reports [41,42] and are considered as suitable absorber layer in thin film solar cell.

Figure 2. (a) Variation of absorption coefficient (α), and (b) variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of CMTS thin films grown at different substrate temperatures.

Referring to Figure 2b, the band gap energies of the films were deduced by extrapolating the linear portion of the plots to the photon energies axis. The extracted band gap energies of all the films deposited at 280, 320, 360, and 400°C are found to be 1.85, 1.75, 1.64, and 2.2 eV, respectively. For the films crystallizing with the tetragonal phase with only minor phases, one can observe a decrease of the band gap when increasing the substrate temperature. However, these values are slightly higher than that those reported in literature ($E_g \sim 1.23\text{--}1.45 \text{ eV}$) [25,43]. The crystallization of secondary phases having higher band gap values than that of the CMTS phase explain the higher observed band gap energy range of the films deposited from 280 to 360°C . Indeed, the possibility to tune the optical band gap as a function of the proportion of phases in composite film has already been reported [44]. Nie et al. have also observed an increase of the band gap energy in CMTS films due to the crystallization of sulfide impurity which exhibits a band gap energy of about 2 eV as deposited [16]. Furthermore, the decrease of the optical band gap with the deposition temperature is coherent with the crystallization of secondary phases having an increasingly smaller band gap energy with the elevation of the deposition temperature (e.g., CuS $\sim 3.5\text{--}3.8 \text{ eV}$ [45], SnO $\sim 2.5\text{--}2.9 \text{ eV}$ [46], CuO $\sim 1.2\text{--}2.2 \text{ eV}$ [47,48]). In addition, other factors could also contribute to the observed bandgap decrease: the Cu enrichment of the tetragonal phase associated with the sulfur loss, as observed by EDS, could change the degree of

hybridization [25,49], and the improvement of crystalline quality of the main CMTS phase would lead to a lower number of structural defects and grain boundaries in agreement with XRD results.

It is worth of noting that an increase of the deposition temperature at 360 °C leads to a superior absorption coefficient in the visible range due, on the one hand, to the lower band gap energy resulting in a widening of the spectral window, and on the other hand, to the enhancement of the crystallinity.

3.4. Electrical Characterization

The electrical resistivity at room temperature of the CMTS thin films has been measured using a four-probe method. As presented in Table 3, the resistivity of CMTS thin films slowly decreases from 3.38 to 1.14 $\Omega\cdot\text{cm}$ as the substrate temperature increases from 280 to 360 °C, and then increases significantly to $9.53 \times 10^4 \Omega\cdot\text{cm}$ with further prolonging substrate temperature to 400 °C which is ascribed to the presence of the CuO phase. This value is rather coherent with other electrical resistivities of copper oxide previously reported [50,51]. The electrical resistivity values of the optimum CMTS thin films are near to the values of CZTS thin films doped Al obtained by Gadallah et al. [52]. The slow decrease of the electrical resistivity is favored by the crystallinity improvement such as the crystallite growth [53], and also by the higher metal enrichment due to the sulfur loss with the temperature increases.

Table 3. Electrical resistivity of the CMTS thin films deposited at different substrate temperatures.

T_s (°C)	R (Ω)	Resistivity ($\Omega\cdot\text{cm}$)
280	2.92×10^3	3.38
320	9.91×10^3	3.33
360	1.99×10^3	1.14
400	1.58×10^8	9.53×10^4

4. Conclusions

The tetragonal structured CMTS thin films have been elaborated by a spray pyrolysis technique on a heated glass substrate in air atmosphere and using a compressed air as a carrier gas. Despite rather oxidative conditions, it was shown that the tetragonal CMTS crystallizes as a dominant phase with a preferential orientation [112] for a moderate deposition temperature (<400 °C). The improvement in the crystalline quality of the CMTS thin films is correlated with the substrate temperature. With the increase of the deposition temperature, a small and progressive oxidation of the growing film occurs, leading to the formation of oxides traces at elevated temperatures prevailing over the formation of sulfides at lower temperatures. The crystalline quality improvement with the deposition temperature increase at 360 °C results in a high absorption coefficient ($<10^4 \text{ cm}^{-1}$) in the visible range, and a rather low electrical resistivity of about $\Omega\cdot\text{cm}$. The bandgap energy is close to 1.64 eV. It is demonstrated that these properties are suitable as a solar absorber in low-cost solar cells, even if impurity traces can crystallize. Further analyses, such as TEM, XPS, EPMA, EELS, and photoelectrical response could be useful to gain a deeper insight into the properties of the material studied, but they are beyond the scope of the present analysis. From an engineering point of view, the deposition of sulfide under air atmosphere can be an asset to facilitate a cheap solar cell process. The stacks could be strengthened by the oxides crystallization to promote the mechanical adhesion when implementing a chemical gradient, or in tuning the spectral sensitivity in a multiple junction solar cell.

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