INFLUENCE OF SULPHUR MOLAR CONCENTRATION ON STRUCTURAL AND OPTICAL PROPERTIES OF TIN SULPHIDE TIN FILMS

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The sulphur concentration plays an important role on the stoichiometry of sulphur based thin films due to its volatility. In the present work tin sulphide (SnS) thin film have been prepared by ultrasonic spray pyrolysis method on glass substrates. In order to optimize the sulphur molarity, it was varied in the range 0.01 to 0.09M in the starting solution, while the other deposition parameters are maintained constant. The films structural and optical properties were studied as a function of the molar concentration of sulphur. The results indicated that tin sulphide films grown at low molar concentration exhibit a single phase of SnS orthorhombic structure increasing the sulphur molar concentration above 0.07M is accompanied by the emergence of Sn_2S_3 secondary phase. The film thickness and average of films crystallite size value increases the sulphur concentration. We inferred that 0.07 M is the optimal condition leading to film sitable for solar cell production.

1. Introduction

Making solar energy viable and a long-term attracting alternative requires high efficient solar cells production through low cost effective techniques. At present, SnS thin film is a promising material, it is enrolled as good candidate as absorber layer, it is a cheap and eco-friendly material. SnS thin films can be considered as an alternative of CdTe and GaAs materials. SnS is a p-type semiconductor, it has a direct optical band gaps ranged from 1.2 to 1.5 eV which matches with the solar spectrum, it is also characterized by its high absorption coefficient in the visible region ($\alpha \geq 10^5$ cm^{-1}) [1, 2]. Thus making SnS thin film a serious candidate for solar cell production.

SnS semiconductor compound has been prepared by several methods, such as: chemical bath [3], thermal evaporation [4], SILAR [5], electrodeposition [6], spray pyrolysis [7] and electron beam evaporation [8], etc. Among these techniques ultrasonic spray pyrolysis is a simple and inexpensive technique, it does not require any vacuum vessels, and it is suitable for large surface substrate coating. The deposition technique is based on the precursor solution atomization on a heated substrate [9]. The sprayed solution is generally prepared by metallic precursor dissolution in an adequate solvent. The commonly used solvents are: distilled water, alcohol or their mixture are used.

Several researchers have been deposited tin sulphide thin films by spray pyrolysis where they investigated the influences of different deposition parameters on films structural, morphological and optoelectronic properties such as: tin concentration [10], deposition time, [11], substrate temperature [12], solution solvent [13], Sn source [14] and substrate nature [15]

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However, very few studies [10] were carried on the sulphur molarity effect. In the present work, we investigated the influence of sulphur molarity on SnS thin films prepared by ultrasonic spray pyrolysis technique.

2. Experimental procedure

Tin sulphide thin films were grown at different thiourea molar concentrations onto glass substrates by ultrasonic spray pyrolysis method. Fig. 1 is a schematic drawn of the home made deposition system. The used precursors are ($SnCl_2.2H_2O$) and thiourea ($SC(NH_2)_2$) as source of Sn and S elements respectively, they are dissolved in 40 ml of distilled water. The thiourea molarity was varied from 0.01 to 0.09 M with a step of 0.02M, while the molar concentration of tin salt was kept constant at 0.05 M. The substrate temperature was fixed at 350 °C and the distance between spray nozzle and substrate was fixed at 5 cm.
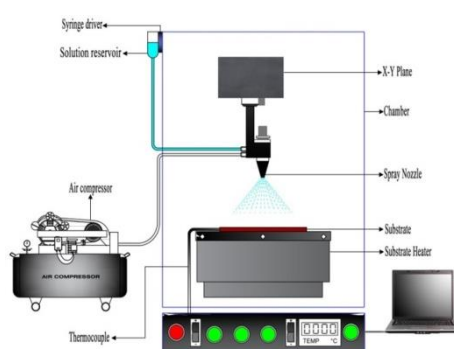

Fig. 1. Schematic diagram of the home made spray pyrolysis system set up.

The films structural properties were determined by X rays diffraction (XRD) using Philips PW 1774, X'Pert diffractometer using CuK_α rays (λ= 1.5418 Å) with an acceleration voltage of 40 KV and a current of 40 mA. Films morphology was analysed using scanning electron microscope (JEOL JSM 6301F). The films optical characterization was achieved by means of transmittance measurement using a spectrophotometer of the type (UV-3101 PC-Shimadzu), with double beams, working in the UV-Visible range from 300-3000 nm.

3. Results and discussions

3.1. Structural properties
Fig. 2 shows the XRD spectra of SnS thin films grown with different molar concentration of sulphur. At low molar concentrations from 0.01 to 0.05M, the films have a single-phase SnS structure. The films are polycrystalline with patterns composed of three relatively intense diffraction peaks located at the angles 27.31°, 31.24° and 31.92° assigned respectively to (021), (111) and (400) planes of SnS orthorhombic structure [16]. In accordance with JCPDS card N°. 39-0354. With increasing molar concentration of sulphur from 0.07 and 0.09M, we noticed beside the SnS related peaks, the emergence of peaks located at the angles 33.26°, 40.24° and 52.8° assigned to (105), (015) and (220) planes of Sn_2S_3 phase (JCPDS card N°. 75-2183) phase as secondary phase. Increasing thiourea molarity in the starting solution causes the availability of large amount of sulphur species in the solution, thus leading to the formation of Sn_2S_3 secondary phase with needs a large amount of sulphur to be formed. Indeed, several authors have claimed that SnS thin films is generally accompanied by secondary phases such as SnS_2, Sn_2S_3 [10, 17]. Due to the various oxidation states of Sn (0, +2 and +4), Sn, SnS_2 or Sn_2S_3 secondary phases can be formed along with SnS phase [18, 19].
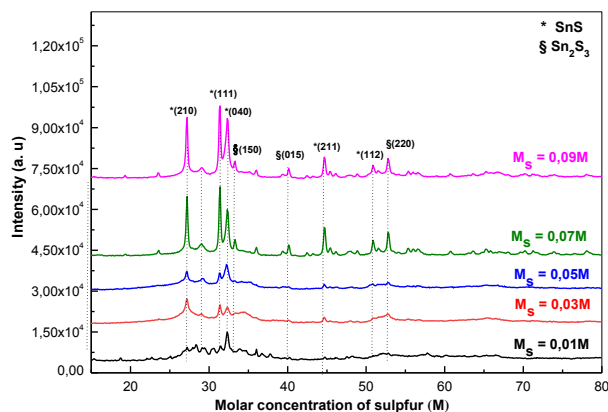
Fig. 2. XDR patterns of SnS thin films deposited by spray pyrolysis at different molar concentration of sulphur.

In Fig. 3 are plotted the intensities variation of the most peak related to each phase, namely the peak (110) of SnS phase and the peak (200) of the Sn_2S_3 secondary phase. As shown in figs. 2 and 3, the XRD peaks intensities rise with the sulphur molarity, this might be due to the film thickness increase. As reported in Table 1, and Fig. 4 the films thickness varies almost linearly from 130 to 1420 nm with increasing the sulphur molarity.

Table 1. Thickness, grain size and band gaps of SnS films prepared at different molar concentrations of sulphur.

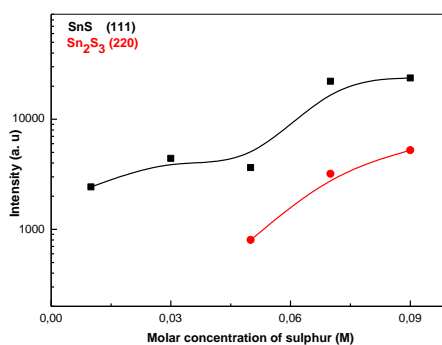| Molar concentration of sulphur (M)	Thickness (nm)	Crystallite (nm)	Band gaps (eV)
0.01	130	27	1.05
0.03	520	51	1.14
0.05	705	46	1.21
0.07	830	63	1.51
0.09	1420	56	1.35

Fig. 3. Variation of the intensities of most intense peak of SnS and Sn_2S_3 phases as a function of sulphur concentration.
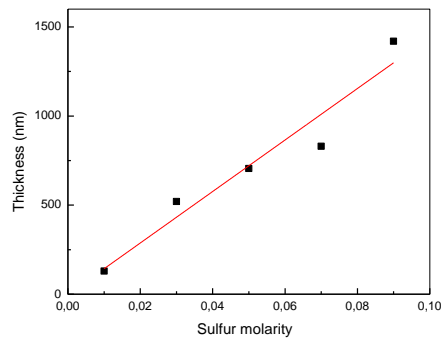
Fig. 4. SnS film thickness variation versus sulfur molarity.

The average crystallite sizes (D) of tin sulphide thin films were calculated using Debye Scherer's relation [20].

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

where λ is the XRD wavelength, k a constant, β is the FWHM, and θ is the diffraction angle.

The crystallite size average results are regrouped in the Table 1, they   vary in the range from 27 nm to 63 nm with the increase molar concentration of sulphur.

3.2. Morphological properties

Fig. 5 shows the SEM of SnS thin films grown at different molar concentration of sulphur. Films deposited at 0.01 M, 0.03M and 0.05M is rough, compact and granular with the presence of bumps structure of about 20 μm.
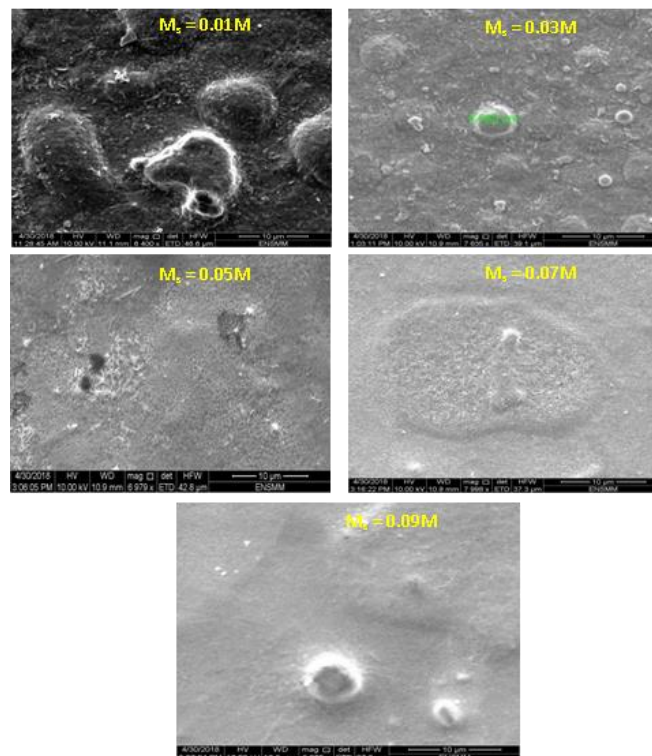

Fig. 5. Scanning electron microscope (SEM) images of SnS thin films prepared
with different sulphur concentrations.

In a previous work we have explained the bumps and bubble formation in terms of gas formation and sulphur volatility during films growth [13, 21]. The formed bulb might be due to the gas exo-diffusion during film growth. This suggests that the sub-layer beneath the film surface is dynamic. However, increasing the sulphur molar concentration from 0.07M and 0.09M leads to the change in the films morphology. As can be seen, films are compact and uniform with no bumps. The absence of bumps at large sulphur molarity indicates that the sulphur excess is involved to the formation of the secondary Sn_2S_3 rather than to exo-diffuse.

3.3. Optical properties

Optical transmittance spectra, in the wavelength range from 400 to 1200 nm, of films prepared by spray pyrolysis ultrasonic were shown in Fig. 6. Films transmittance is in the range of 10-50 %, it is reduced with the sulphur molarity increasing. This is due to the increase in film thickness. The films band gape is determine from the Tauc's plot of the values $(\alpha h\nu)^2$ as a function of photons energy as shown in Fig. 7. The direct optical band Eg, corresponds to the intercept of the straight portion of the graph with the photon energy axis [22].
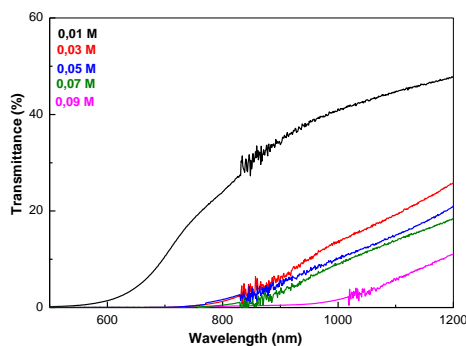

Fig. 6. Optical transmittance spectra of SnS films grown at different sulphur concentration.
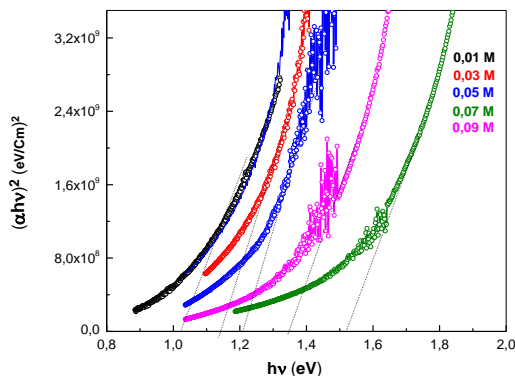

Fig. 7. Plot of $(\alpha h\nu)^2$ versus photon's energy for the optical band gap determination of SnS films deposited with different sulphur concentrations.

The optical band gap values of SnS thin films, as regrouped in Table 1, are found to be ranged from 1.05 to 1.51 eV with as increasing in molar concentration of sulphur. These values are within the range of SnS thin films optical band gap reported in the literature [23-25]. Gao et al [19] have reported an optical band gape in the same range from 1.0 to 1.3 eV in SnS thin films prepared by chemical bath deposition. While, Reddy et al [10], have reported a band gap range of 1.03 to 1.4 eV measured in SnS films prepared by spray pyrolysis method.

4. Conclusion

In this study, tin sulphide thin films have been synthetized by spray pyrolysis ultrasonic. In order to investigate the sulphur molar concentration effect on films properties, sulphur salt molarity have been varied from 0.01M to 0.09M. The DRX analysis reveals the growth of SnS orthorhombic monophasic at low molarities. However, increasing sulphur molarity above 0.07M leads to the formation of Sn_2S_3 secondary phase. The size crystallite average of SnS thin films and thickness increase with sulphur concentration. The molarity of 0.07 M seems to be optimal, it yields to a SnS thin film with a direct band gaps of 1.35 eV and high absorption coefficient superior at 105 cm^{-1} suggesting its application as absorber layer in thin film solar cells.

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