SnS THIN FILMS DEPOSITION BY SPRAY PYROLYSIS: SOLVENT INFLUENCE

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Tin monosulfide (SnS) films are a new generation of absorber layers for thin film heterojunction solar cell. The goal of the present study is the investigation of the role of the solvent on SnS thin films properties. Films were synthesized by ultrasonic spray pyrolysis technique. The used solution is a mixture of SnCl₂.2H₂O and thiourea (SC(NH₂)₂ precursors prepared with two different solvents: methanol and distilled water. X-ray diffraction (XRD) analysis reveals the SnS orthorhombic polycrystalline phase in different films. Using methanol as solvent leads to Sn₂S₃ secondary phase formation. While, film prepared with distilled water contains SnS₂ as secondary phase. Scanning electron microscopy (SEM) observations reveal that films deposited with the methanol are rough with the presence of craters bubbles on the surface due to gas exo-diffusion during film growth. However, the film deposited with distilled water has a smooth, uniform, homogeneous and pinholes free surface. The electrical measurements reveal that films are p-type semiconductors, the dark conductivity increases from 3.07×10^{-4} (Ω .cm)⁻¹ in film prepared with methanol to 5.15×10^{-3} (Ω .cm)⁻¹ when using distilled water. We inferred that using distilled water leads to films with better quality than methanol as solvent.

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1. Introduction

Tin monosulfide SnS belongs to IV–VI group of compounds, it has attracted much attention these last years, due to its interesting optical, electronic and structural properties. Indeed, SnS optical band gap is varying in the range of 1.2 to 1.5 eV, the transitions are direct with a high absorption coefficient of 10^4 cm⁻¹, it exhibits p-type electrical conductivity which can be controlled by using various dopants such as Al, Ag and Cl [1, 2], Beside this, SnS is composed of non-toxic, low cost and abundant elements compared to indium and selenium forming CIGS thin film solar cells. Thus making SnS material a serious candidate as absorbing layer for thin film solar cells [3]. The theoretical prediction of the solar cell efficiency prepared with SnS layer indicates that a value of 25% can be achieved [4].

There are several techniques to grow SnS semiconducting thin films such as: vacuum evaporation [5], sputtering [6], electrochemical deposition [7,8], atmospheric pressure chemical vapor deposition[9], plasma enhanced chemical vapor deposition [10], brush plating[11], dip deposition [12], chemical bath deposition (CBD)[13] and spray pyrolysis [14, 15]. 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 atomization of a precursor solution by ultrasound, on a heated substrate [16]. In spray pyrolysis technique, the sprayed solution is generally prepared by dissolution of the metallic precursor in an adequate solvent.

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Commonly the used solvent are distilled water, alcohol or a mixture of water and alcohol.Properties of films prepared by spray pyrolysis can be controlled by several parameters namely substrate temperature [16-19], solution concentration and nature [20-22], flow rate, and solvent. The first two parameters are intensively studied. However, solvent are less studied.

The present work deals with the investigation of the solvent nature effect on the physical properties of the SnS thin films. In this study we have studied two solvents: methanol and distilled water.

2. Materials and methods

Tin sulfide (SnS) thin films have been grown, by ultrasonic spray pyrolysis method, onto heated glass substrates at 350°C. The starting solution is formed of 0.05M SnCl₂.2H₂O and 0.005M thiourea (SC(NH₂))₂ as sources of Sn and S respectively. Two sets of films were prepared using two different solvents: methanol and distilled water. Fine droplets of 40 μ m size are generated by using an ultrasonic generator of 40 KHz frequency.

The structural properties were determined by XRD Marque (PAnalytical X'PERT PRO), using a source of radiation Cu-k α , having a wavelength of λ =1.5418 °A, with a condition of 30 KV voltage and a current of 40mA. The film surface morphology was analyzed by scanning electron microscopy (JEOL JSM 6301F). The optical properties of the SnS films were characterized using a spectrophotometer of the type (UV-3101 PC-Shimadzu) with double beams, working in the range UV-Visible from 300 to 3000 nm.

The absorption coefficient was used to determine the optical energy band gap (Eg). The latter was estimated using the Tauc formula [23] by assuming a direct transition between valence and conduction bands:

$$\left(\alpha h v\right)^{2} = \beta \left(h v - E_{g}\right) \tag{2}$$

 β is a constant and hv is the energy of photon. The optical band-gap was determined by extrapolating the straight line portion of the spectrum to dhv = 0.

The films electrical characterization were achieved by Hall Effect measurements, carried in dark and at room temperature, with Ecopia HMS-3000 Hall Measurement System

3. Results and discussion

All the obtained deposits are homogeneous and well adherent to the substrates. In Fig. 1 we have shown the XRD spectra of SnS thin films deposited using different solvents methanol and distilled water. The patterns of the film prepared with methanol solution, are little diffuse with broad peaks of low intensities. While, the pattern of the film prepared with the aqueous solution is composed with intense and sharper peaks. The difference in the peak intensities is probably due to the difference in the film thicknesses because the film prepared with distilled water has a thickness of the order of 5000 nm, while, the film prepared with methanol is thinner, with a thickness of 538 nm (ten times less thick). It has been reported that the increasing film thickness improve the SnS films crystallinity [24]. The film deposited with the aqueous solution (Fig. 1.a) has a polycrystalline structure, it is characterized by the emergence of several peaks assigned of (112), (201), (022), (023), (116) and (133) planes of orthorhombic SnS phases (according to JCPDS card number 79-2193). A small peak of the SnS₂ secondary phase is present in the pattern (according to JCPDS card number 23-0677).



Fig. 1. XRD diffraction patterns of SnS thin films deposited using (a) aqueous solution and (b) methanol.

As shown in Fig. 1.b, the film prepared with methanol as solvent is composed of a small peaks related to the (001), (112) and (116) planes assigned of the SnS phase. Secondary phase is present as indicated by the small peak assigned to Sn_2S_3 phase (according to JCPDS card number 75-2183). Due to multiple oxidation state of Sn (0,+2 and +4) secondary phases such as Sn, SnS₂ or Sn₂S₃ can be co-deposited along with SnS phase [25, 26].

Thereafter, one can conclude from XRD results that the film prepared with distilled water enjoys better crystallinity than the one prepared with methanol. This discrepancy in films structure might be due to the difference in the involved reactions during film growth.

Table 1 shows the crystallite sizes calculated for SnS thin films prepared with methanol and distilled water. The crystallite size are estimated from the most intense XRD peaks using Debye Scherer formula. As shown in Table 1, the film prepared with distilled water has a crystallite size equal to 40 nm. However, using alcohol leads to smaller crystallite size in the order of 8 nm.

Table 1. Optical band gap Eg, the thickness d, crystallite size D, electrical conductivity values and activation energy E_a of SnS thin films deposited with methanol and distilled water as solvents.

	$E_{g}\left(eV ight)$	d (nm)	D crystallite size(nm)	Conductivity (Ω.cm) ⁻¹	Mobility (V.cm ⁻¹ s ⁻¹)	Туре
Methanol	1.67	538	8.0	3.07 x 10 ⁻⁴	24	р
Distilled	1.20	4929	40.5	5.15x 10 ⁻³	$7x10^{2}$	p
Water						

Figs. 2(a) and 2(b), represents SEM images of film surfaces deposited with methanol (Fig. 2.a) and distilled water (Fig. 2.b). As can be seen, the surface of films deposited with methanol is

rough, it contains craters and bulbs. However, the films deposited with distilled water are dense, smooth, compact and homogeneous (Fig. 2.b).



Fig. 2. SEM images of SnS films prepared with (a) methanol, (b) distilled water.

The formed bulb and craters in film prepared with methanol is due to the gas exodiffusion during film growth, indicating that the sub-layer beneath the film surface is dynamic. Where the reactions continue to occurring accompanied by gas production. The produced gas might be due to the methanol combustion which accompanied by the exo-diffusion of CO, CO_2 , both gas are detected in the substrate surrounding during film growth together with H₂S. The produced gas can be also the sulfur due to its high volatility. The sulfur may diffuse from the bulk toward the surface especially in high temperature based deposition such as spray pyrolysis [28].

The spectral behavior of Uv visible transmittance $T(\lambda)$ of SnS films prepared with different solvents are shown in Fig. 3.a and 3.b respectively. Measurements of transmittance were carried in the range wavelengths 300-800 nm. Films deposited with methanol (Fig. 3.a) are more transparent than that prepared with distilled water (Fig. 3.b), the value of the transmission is about 35% and 5% respectively. This difference in transparency can be attributed to the differences in films thickness (see Table 1).



Fig. 3. UV-visible transmittance spectra of SnS films deposited using (a) methanol and (b) distilled water.

Figs. 4(a), 4(b), present the variation from $(\alpha h v)^2$ as a function of incident photon energy (hv) for both films. The extrapolation of the linear part of these curves yields to the band gap energy Eg. The calculated gap energy of films prepared with methanol and distilled water, are respectively of 1.67eV and 1.2eV, indicating that the optical gap of film deposited by methanol is broader than the films deposited by distilled water. Actually, the room temperature band gap energy of SnS thin film varies in a wide range from 1.1 to 1.87 eV [29-31]. The band gap variation

is close related to the deposition technique, the film composition, stoichiometry and the presence of secondary phases [32-35]. The band gap in crystal SnS is equal to 1.14 eV [36]. The film prepared by the distilled water has a band gap of 1.2eV, which is close to bulk value and near the required value for photovoltaic solar energy conversion and to SnS crystal value [37-39]. This can be ascribed to its good crystallinity as deduced from for XRD analysis. However, the broad band gap measured in film prepared with alcohol can be due to quantum effect due to the low crystallite size [40].



Fig. 4. Typical plot of $(\alpha h v)^2$ as a function of photon energy used for optical gap estimation for SnS films prepared with (a) methanol and (b) distilled water.

The Hall Effect measurements results are regrouped in table 2. Both films exhibit a p type conductivity. The measured conductivities are of 3.07×10^{-4} and $5.15 \times 10^{-3} (\Omega.cm)^{-1}$ for the film deposited with the methanol and aqueous solution, respectively. The films nobilities are respectively equal to 24 and 700 V.cm⁻¹s⁻¹. The superiority of film prepared with distilled water, i.e., larger conductivity and mobility is in agreement with the films good crystallinity as deduced from XRD analysis.

4. Conclusions

Tin monosulfide thin films were deposited by spray pyrolysis technique, onto heated glass substrates at 300°C. Two solvents, methanol and distilled water were used. The XRD analysis indicated that the films are mainly composed with SnS orthorhombic phase for two solutions with the presence of SnS_2 and Sn_2S_3 secondary phases. Film prepared with solvent methanol has an inferior crystallinity by comparison to the film prepared by distilled water.

The films surface morphology, analysed by SEM, reveals that the surfaces of the films deposited with methanol is rough and contains bubbles and craters due to the exodiffusion of the formed gases during film growth. However the films deposited by distilled water is smooth, compact and homogeneous. Moreover, the electrical measurements reveal that the film prepared with aqueous solvent has a larger conductivity and holes mobility than the film prepared by methanol. In conclusion using aqueous solution yields to films with better structural, optical and electrical properties which is more suitable candidate as absorber layer in thin films solar cells.

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