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Molar optimization of spray pyrolyzed SnS thin films for photoelectrochemical applications

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ABSTRACT

A systematic investigation of the effect of molar concentration ratio on the structural, morphological, optical and opto-electronic properties of spray deposited SnS thin films on F:SnO_2 coated glass substrate is presented. The as-deposited SnS was polycrystalline with orthorhombic crystal symmetry. The S atomic percentage of SnS film was found to be linear with respect to the molar concentration of thiourea for fixed concentration of $SnCl_2$. An optimum molar concentration ratio of S^{2-}/Sn^{2+} in the range of 1.3–1.4 was found superior for photoelectrochemical applications.

1. Introduction

Tin sulphide (SnS) is a semiconductor with direct optical band gap E_g = 1.3 eV [1] and has absorption coefficient above 10^4 cm^{-1} for photon energies above 1.3 eV. It is a *p*-type semiconductor whose electrical properties can be tailored by doping and structural modification [2,3]. It is one of the simplest, non-toxic and affordable material for thin film solar cells. According to the Shockley–Queisser criteria, the spectroscopic limited maximum efficiency up to 33% could be achieved for the material having E_g of 1.3 eV [4]. However, a maximum efficiency of 2.04% (pulsed CVD [5]) and 1.3% (sprayed [6] and sputtered [7]) has been recorded so far. Owing to its easy solution processability, SnS thin films have been fabricated by chemical spray pyrolysis by many groups. The first SnS thin films was prepared by Lopez et al. [8], where the effect of glass substrate temperature was studied. The effect of temperature of corning glass substrate on the structural and optical properties of sprayed SnS films was studied by Reddy et al. [9,10] by taking the equal molar concentration of Sn and S. The SnS films, deposited by glass made double nozzle sprayer were studied by Thangaraju et al. [11], where films were found to have *n*-type conductivity on glass and FTO substrates. The polycrystalline, single phase and nearly stoichiometric SnS films can be grown using the CSP technique when the glass substrate temperature is maintained between 300 and 360 °C [12]. Later it was optimized for the Sb:SnO_2 coated glass substrate as well [13]. A high electrical resistivity of as deposited sprayed SnS thin film on glass was found to be reduced by ex-situ tin diffusion [14]. An optimization of parameters of CSP technique to get *n* and *p*-type layers of SnS on the glass substrate was reported by Sajeesh et al. [15]. The effect of precursors concentration on the photoconductivity and thermoelectric properties of Sn_xS_y films on glass substrate was studied by Fadavieslam [16].

In a previous investigation on the effect of post annealing of the sprayed SnS thin film [17], it was reported that the optical properties of the film can be tailored by post annealing temperature. To the best of our knowledge, there is no report on the influence of precursor molar ratio on the structural, physical, optical and opto-electronic properties of SnS films on the F:SnO_2 coated glass substrate. In this paper, we report a systematic investigation on the influence of the precursor molar ratio on the structural, physical, optical and opto-electronic properties of SnS film grown by the chemical spray pyrolysis without using any complexing agent. The photoelectrochemical properties of spray deposited SnS film for constructed photoelectrochemical cell with configuration Pt |0.1 M $Na_2S_2O_3$| SnS/FTO is discussed.

2. Experimental

Thin film of tin (II) sulfide was prepared by the spray pyrolysis technique using aqueous solution of as received $SnCl_2$ (SC) (>99% from Sigma Aldrich) and Thiourea (TU) (>99% from Sigma Aldrich). The molar concentration of 0.05 M of SC was maintained throughout the study. Few drops of HCl were added to enhance the solubility

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of SC. The F:SnO_2 (FTO) coated glass substrates (15 Ω/□, 1 cm × 1.5 cm area, 2.2 mm thick, from Sigma Aldrich) were thoroughly cleaned sequentially in trychloro ethylene, acetone and Milli-Q water in an ultrasonic bath for 10 min each. Prepared aqueous chemical solution was transported to the spray nozzle from a syringe pusher and sprayed on the glass substrate in ambient atmosphere. The process parameters and details of CSP are described elsewhere [18] provided the temperature of the glass substrates was maintained at 375 ± 5 °C during the spray. After the spray, the substrate was naturally cooled down to 50 °C and then removed from the spray station. The films appeared to be dark red in day light transmission.

The structural characterization of the SnS thin film was carried out by X-ray diffractometer from PANalytical (model, X'Pert Powder) with Cu Kα radiation, $\lambda_{K\alpha}$ = 1.540598 Å, step size = 0.05°, and time/step size = 2 s/step. The thickness and average surface roughness of the deposited SnS thin film were characterized by a surface profiler of Vecco (model, Dektak 150). The planar surface morphology were analyzed by field emission scanning electron microscope (FESEM) of Zeiss (model, Ultra 55) with 5 kV of field voltage using inlens detector. The elemental composition of the as-prepared film was determined by energy dispersive spectroscopy (EDS) attached to the SEM. Optical characterization was carried out by a UV–vis spectrophotometer of Shimadzu (model, UV-2600) by recording the transmission spectra of the thin films in the range 320–1400 nm. The extrinsic nature of type of conductivity of the thin films was determined using the hot point probe method.

The SnS-based photoelectrochemical (PEC) cells were fabricated with spray deposited SnS over F:SnO_2 (FTO) glass substrate, where 50 ml of 0.1 M aqueous solution of $Na_2S_2O_3$ has been used as electrolyte. A PEC solar cell having configuration Pt (2 cm^2) |0.1 M $Na_2S_2O_3$ |SnS (1 cm^2)/FTO was constructed. The current voltage profile under chopped light illumination condition was recorded by CHI 660D potentiostat galvanostat using Ag/AgCl as reference electrode. The film surface inside the PEC cell was illuminated by monochromatic amber LED from Nichia (model, NS6A183T, λ = 600 ± 10 nm) excited by a square wave of frequency 2 Hz using the function generator by GW INSTEK (model, SFG-1013).

3. Results and discussion

3.1. Structural properties

The XRD pattern of the sprayed SnS films on F:SnO_2 coated glass substrates, with various molar concentration ratio of Sn/S precursors are shown in Fig. 1. It includes the XRD pattern of the FTO coated glass substrate as well. The peaks corresponding to the FTO and SnS are presented as down and up right arrows, respectively. The peaks corresponding to the FTO substrate was masked during the analysis. The observed XRD spectra are used to determine the phases, lattice parameters, space group and dimension of unit cells, as described elsewhere [18,17]. The effect of the molar concentration ratio over the sprayed SnS thin films on FTO substrates was clearly observed from the XRD data. The details of the batch distribution for the various molar concentration of $SnCl_2$ to thiourea are provided in Table 1. The dominating peak corresponding to (1 1 1) planes was more intense as the Sn/S precursor ratio was varied from 1/1 to 1/1.3. The phase analysis reveals peaks corresponding to the (1 1 0), (1 0 1), (1 1 1) and (0 4 0) planes of

Table 1
The estimated elemental atomic percentage of as deposited SnS thin films on FTO coated glass substrate.

Sample code	Molar ratio $SnCl_2$/thiourea	Atomic percentage (%)			
		Sn	S	Cl	O
A	1/1	20.22	5.21	0.5	55
B	1/1.15	22.11	6.88	0.41	48.8
C	1/1.3	24.32	11.67	0.74	41.3
D	1/1.45	25.52	12.85	1.03	39.1
E	1/1.6	26.21	13.15	1.39	34.5
F	1/1.75	22.39	14.54	1.03	39.6

reflection at Bragg angle of 22.78°, 30.8°, 31.5° and 32.5°, respectively and they are the characteristics of the SnS phase with mixed space groups. The planes (1 1 0) and (1 1 1) correspond to the space groups *C m c m* (63) with lattice volume of 198.9 $Å^3$ (COD-9008295, Fig. S1), while (1 0 1) and (0 4 0) correspond to the space group *P b n m* (62) with lattice volume of 192.67 $Å^3$ (COD-9008785, Fig. S2). Both the space groups represent the orthorhombic crystal system. For the Sn and S precursor ratio of 1/1.45, the SnS of *C m c m* (63) was dominating over the *P b n m* (62). In this case, it was observed that the *C m c m* phase was dominated over the *P b n m* phase by an increase in S precursor concentration. With the help of first principle techniques, the phase transition from *P b n m* to *C m c m* of SnS is already reported under the high pressure condition [19,20]. According to Chattopadhyay et al. it was a second order phase transition in the SnS system caused by the continuous movement of the Sn and S atoms mainly along [1 0 0] direction [21]. In our present case, a crystal volume change was noticed by increased S-precursor concentration, which may be considered as a stress developed due to non-hydrostatic pressure. Ke et al. also showed that, the total energy of unit cells of *C m c m* remains lower than that of *P b n m* phase after a certain crystal volume. The growth of *C m c m* can therefore be expected at higher S-precursor concentration. The possibility of secondary phases, such as Sn_2S_3, SnO_2 and residual $SnCl_2$ cannot be ruled out due to uncontrolled synthesis condition during the pyrolysis process of Sn^{+2} and S^{-2} precursors at high temperature. However, SnS remaining as a predominant component, has dictated all macroscopic responses, such as optical absorption and flat band condition.

3.2. Microstructure analysis

The surface morphology of the as prepared SnS thin films for different molar ratio of $SnCl_2$/thiourea ranging from 1/1 to 1/2

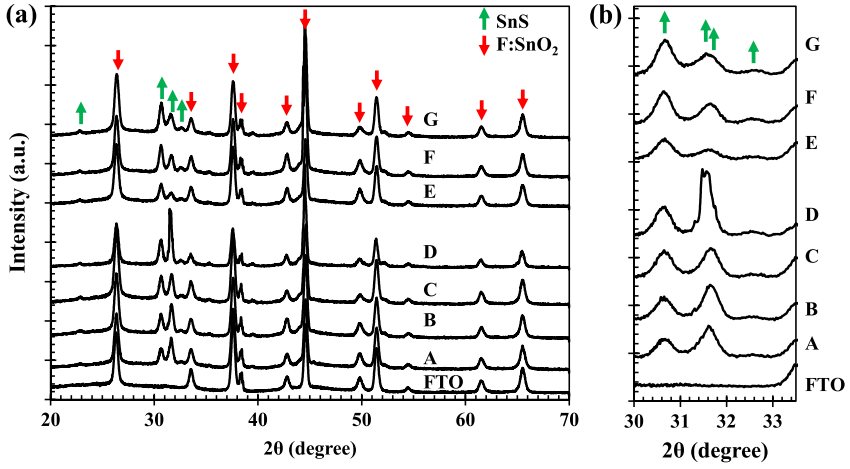

Fig. 1. X-ray diffractograms of spray pyrolyzed SnS thin films on FTO coated glass substrate (a) for 2θ 20–70° and (b) 30–33.5°. The XRD of FTO substrates is included here and shown at the bottom.