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Annealing influence over structural and optical properties of sprayed SnS thin films

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ABSTRACT

A systematic investigation of the effect of annealing temperature on the structural and opto-electrical properties of spray deposited SnS thin films has been presented. As received $SnCl_2{\cdot}2H_2O$ and thiourea were used for Sn^{2+} and S^{2-} ion sources, respectively in the solution without any complexing agent. Following the deposition, films were annealed in a tubular quartz furnace at different temperature in the range of 300–500 °C for 30 min and cooled down to room temperature under flowing Argon atmosphere. The surface morphology and crystallite size were modified by the annealing temperature. Structural characterization revealed nano-crystalline nature of the deposited film. The XRD spectra showed deposited films were orthorhombic-SnS with preferential (1 1 1) orientation and better phase purity, which was further improved by increasing annealing temperature to 500 °C. The effect of annealing temperature on the optical and electrical properties of SnS films was also investigated using UV–vis spectroscopy, Photo-electrochemical response and Hall Effect. The increase of annealing temperature up to 500 °C induced a substantial increase in the absorption coefficient and electrical conductivity.

1. Introduction

Tin sulfide (SnS) is a semiconductor with direct optical band gap E_g = 1.3 eV [1] and 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] and has emerged as one of the simple, non-toxic and affordable material for thin films solar cells since a decade [3]. According to the Shockley–Queisser criteria, a maximum efficiency up to 33% could be achievable for the material having E_g of 1.3 eV [4]. However, maximum efficiency of 2.04% (pulsed CVD [5]) and 1.3% (sprayed [3] and sputtered [6]) were reported for SnS based thin film solar cells till the date. In a computation and experimental studies, Vidal et al. [7] have shown in details that the structural defects of layered SnS leads to a moderation of electronic band structure and results a low efficiency of SnS-based solar cells. According to their observations the intrinsic p-type conductivity of SnS is due to the Sn-vacancies which act as shallow acceptors. Whereas, Sn on S antisites or S-vacancy defects act as donor states and play a detrimental role to photovoltaic properties. However, such defect formation can be avoided under the S rich growth condition [7]. In this context, the synthesis condition of SnS, especially the post-annealing where tin loss and residual strain play important role, would be crucial in controlling its structure and properties.

The SnS thin films have been synthesized by various techniques such as, vacuum evaporation [8–10], sputtering [6], atomic layer deposition (ALD) [11], molecular beam epitaxy (MBE) [12], pulsed laser deposition (PLD) [7], hot wall vacuum deposition method (HWVD) [13], plasma-enhanced chemical vapor deposition (PECVD) [14], electron beam evaporation [1], multilayer-based solid-state reaction [15], electro deposition (ED) [16–20], successive ionic layer adsorption and reaction (SILAR) [21–23], chemical bath deposition (CBD) [24–31], brush plating [32] and atmospheric pressure chemical spray pyrolysis (CSP) [3,33–42]. The post-processing such as annealing of the deposited SnS thin films has been found to improve its material properties [8,43], where Ristov et al. demonstrated that, an annealing of the SnS films for a shorter duration above 280 °C could change the conductivity to n-type without detectable change in the composition and for longer time (over 24 h) changes the composition to SnS_2 [43]. The SnS films oxidize and change composition to SnO_2 by annealing at higher temperature of 300–400 °C in open air [43,44] and 400–450 °C during spray [33]. However, to the best of our knowledge, a systematic investigation of the effect of annealing over structure and opto-electronic properties of SnS has been lacking. The thin films of any material normally contain residual internal stress during the condensation on the substrate. Internal stress could also affect the physical properties similar to externally applied stress [45]. The additional strain can be induced by annealing which in turn can alter associated properties of the film. In this work the effect of annealing temperature on the structure, optical and electrical properties of

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spray deposited SnS films were investigated for its application in solar cells.

2. Experimental

Thin films of tin (II) sulfide were prepared by the spray pyrolysis technique using aqueous solution of as received $SnCl_2{\cdot}2H_2O$ (SC) (>96% from Merck) and Thiourea (TU) (>99% from Merck), used as a tin and sulfur source, respectively. Few drops of HCl were added to enhance the solubility of SC. Excess concentration of TU was taken to compensate for the sulphur loss during the deposition process. The substrates 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 [46] provided that the temperature of the glass substrates was maintained at 375 ± 5 °C in the present study. 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 sky light transmission. The films were annealed in an indigenously developed tubular quartz vacuum furnace as shown in Fig. 1. Thermocouple was inserted through a stainless steel tube sample holder and kept just below the film to precisely measure the temperature. Temperature was increased at the ramp of 30 °C min^{-1} and then maintained for 30 min at 300, 400 and 500 °C under flowing Argon atmosphere.

The structural characterization of the SnS thin films was carried out by X-ray diffractometer from PANalytical (model, X'Pert Powder) using Cu $K\alpha_1$ (λ = 1.540598 Å) with the PIXcel detector. The thickness and average surface roughness of the deposited SnS thin films were characterized by a surface profiler of Vecco (model, Dektak 150). The surface morphology and grain growth along the vertical direction were observed using a Hitachi scanning electron microscope, SEM (model, Hitachi-3400N). Optical characterization was carried out by a UV–vis spectrophotometer of Cyber Lab (model, UV-100) by recording the transmission spectra of the thin films in the range 200–1100 nm. The extrinsic nature of type of conductivity of the thin films was determined using the hot point probe method. The electrical resistivity and carrier mobility of the thin films was measured by the van der Pauw method at room temperature by a Hall effect measurement system from Lakeshore Cryotronics (model 7504).

The SnS-based photo electrochemical (PEC) cells were fabricated with spray deposited SnS over F:SnO_2 (FTO) glass substrate in same technique as described above, where 50 ml of 0.1 M aqueous solution of $Na_2S_2O_3$ was 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 the monochromatic blue LEDs from Nichia (product, NCSB119T, λ = 470 ± 10 nm) excited by a square wave of frequency 2 Hz.

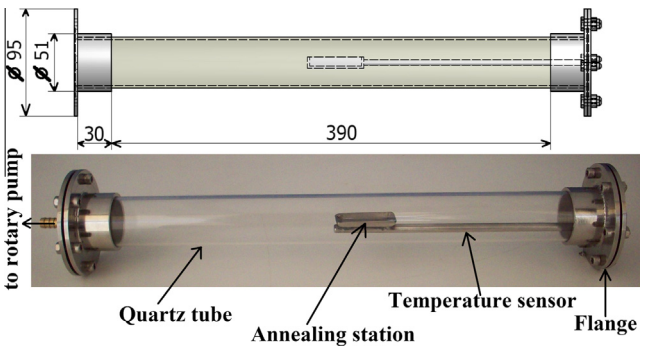

Fig. 1. Developed quartz tube vacuum furnace for annealing of the sprayed deposited thin films (dimensions are in mm).

3. Results and discussion

3.1. Structural properties

3.1.1. Structural and phase analysis

The XRD pattern of the sprayed SnS films without and with annealing is shown in Fig. 2. The observed XRD spectra are used to determine the phases, lattice parameters, space group and dimension of unit cells. Peak broadening of the characteristic phase is used to estimate the strain and crystallite size. According to the Crystallography Open Database-American Mineralogist Crystal Structure Database (COD-AMCSD) the SnS materials appear with two different orthorhombic symmetries, Cmcm (63) (COD-AMCSD 96-900-8296) and Pbnm (62) (COD-AMCSD, 96-900-8686) (Herzenbergite). In order to understand the structural aspect, we have employed the software, Diamond 3.1f for generating the SnS crystal structure. The XRD profile as shown in Fig. 2a was generated from the crystallographic information file by using the Pseudo-Voigt profile function having the full width half maxima (FWHM) of 0.36° with Lorentz and polarization factors for comparison with experimental XRD profiles of SnS thin films here. The phase details, crystal structure and reflection parameters for the obtained SnS crystal structure are shown in inset of Fig. 2a.

The XRD patterns of as deposited and the annealed SnS films are shown in Fig. 2b. The background-corrected XRD patterns of all the sprayed films after performing the phase analysis reveal peaks corresponding to the (1 1 0), (0 2 1), (0 4 0), (1 1 1), (1 3 0) and (1 3 1) planes of reflection, which are the characteristics of the SnS phase having the Cmcm orthorhombic symmetry. SnS_2 was observed as a secondary phase in all the sprayed SnS thin films [24,27,33,34,37,40,42], however, a larger fraction of SnS phase was found to grow at higher annealing temperature making the film less rich in SnS_2. At annealing temperature of 500 °C the sprayed SnS thin film was preferentially oriented in (1 1 1) direction and therefore a better phase purity of the SnS film could be achieved via annealing. In case of F:SnO_2/Glass substrate, beside the usual thermodynamic instability of Sn^{2+} (*i.e.* in SnS) state, the presence of coordinately unsaturated O^{2-} species in SnO_2, a kinetic competition would occur to convert unsaturated Sn^{2+} state into saturated Sn^{4+} state. Hence, the formation of SnS_2 over F:SnO_2/Glass substrate would likely to occur. On the other hand, the glass substrate contains saturated O^{2-} species in the form of silicates. So the Sn loss from SnS on glass substrate could only be due to thermodynamic instability, which would be possible only at higher temperatures. Therefore, the formation of SnS_2 by Sn loss during annealing would be easier in case of SnS on F:SnO_2/Glass than that on glass substrates.

The finite size of the crystallite causes a broadening of the diffraction lines which can be related to size by the Debye–Scherrer formula [47]. The microstrain ($\triangle$) of the films was obtained using the relation [48]. In thin films, the residual strain may occur at the scale of microstructure and crystal structure, which are, by necessity, balanced by stresses in the other locations or crystal planes within the material for an equilibrium configuration [49]. XRD data can determine the residual strain only at the level of crystal structure. The intergranual microstress can be determined by optical interferometric method. However, both types of strain measurement on same sample are rarely found [45].

The estimated *d*-spacing, crystallite size (t), dislocation density (δ) and residual strain ($\triangle$) for all the films are shown in Table 1. In