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Opto-electrical characterisation of In-doped SnS thin films for photovoltaic applications

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ABSTRACT

Spray pyrolised SnS thin films doped with indium were studied using various optical and electrical techniques. Structural analysis shows that all films crystallise in an orthorhombic structure with (111) as a preferential direction, without secondary phases. The doping of SnS layers with indium results in better morphology with increased grain size. Absorption measurements indicate a dominant direct transition with energy decreasing from around 1.7 eV to 1.5 eV with increased indium supply. Apart from the direct transition, an indirect one, of energy of around 1.05 eV, independent of indium doping, was identified. The photoluminescence study revealed two donors to acceptor transitions between two deep defect levels and one shallower one, with an energy of around 90 meV. The observed transitions did not depend significantly on In concentration. The conductivity measurements reveal thermal activation of conductivity with energy decreasing from around 165 meV to 145 meV with increased In content.

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1. Introduction

Thin film photovoltaics are nowadays dominated by CdTe- and Cu(In,Ga)Se_2-based technologies [1,2]. However, the supply issues of In, Ga and Te as well as the toxicity and disposal requirements of Cd have stimulated the search for other photovoltaic materials. Therefore, more simple, binary and Earth-abundant compounds like SnS [3], FeS_2 [4] and Cu_2S [5] have recently received interest in the photovoltaic community. SnS has high optical absorption of photons with energies above 1,3 eV [3,6], which is in the range of 1–1.5 eV considered as the bandgap energy boundaries for an optimum absorber in solar cells [7]. SnS shows an intrinsic p-type conductivity due to the formation of tin vacancies V_{Sn} [3,6] with carrier concentrations above 10^{15} cm^{-3} [3]. Despite these promising electrical and optical parameters, the efficiencies of SnS-based solar cells are far from satisfactory, with a record efficiency of 4,36% [8]. Moreover, this record has been achieved using Atomic Layer Deposition, which is not a well scalable technique considering solar cell production beyond the laboratory scale. Here we investigated SnS thin films made by spray pyrolysis [9,10]: a simple, inexpensive and versatile technique suitable for industrial-scale production. In this case, the efficiencies obtained so far are below 2% [3]. This could be due to the intrinsic limitations of the material or due to the lack of proper material growth and device optimisation. One of the most important issues for an absorber material is control of its carrier concentration by either appropriate doping or growth parameters. Theoretical calculations [11] predict that an antisite defect In_{Sn} has low formation energy (around 1 eV) under S-rich growth conditions, and should act as a shallow acceptor introducing holes into material. The defect concentration n_s can be estimated as

$$n_S \approx N_{Sn} \exp\left(\frac{H_S}{k_B T}\right) \quad (1)$$

where N_{Sn} is the concentration of Sn atoms, H_s is the In_{Sn} formation enthalpy k_B is the Boltzmann constant and T is the temperature. Based on the formation enthalpy we can estimate the number of defects at 350 °C, which was the growth temperature to be around $3.4*10^{16}$ cm^{-3}. Even though this defect concentration is too low to be detected by most of the techniques it is a typical value of hole concentrations in semiconductors and can significantly affect its electrical parameters. Here, we prepared In-doped SnS thin films by spray pyrolysis [12,13] and studied their basic optical and electrical properties.

2. Experimental

2.1. Thin film preparation

The SnS films were prepared using an aqueous solution containing tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$) and thiourea ($SC(NH_2)_2$). The

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molarities of both solutes were 0,104 M. Indium chloride ($InCl_3$ 99,999% purity) was directly added to the solution at different concentrations ([In]/[Sn] = 0; 0,03; 0,06, and 0,09). To avoid the milky solution resulting of the dissolution of $SnCl_2 \cdot 2H_2O$ in bi-distilled water, it is required to dissolve the stannous chloride dihydrate with chloride acid (37%) before mixed it in sulfur solution. The solution was sprayed at a 1,5 mL/min rate for 4 min on the glass substrate keeping the constant substrate temperature of 350 °C. The pressure of the carrier gas was 0,7 bar and the distance nozzle-substrate was 25 cm. To avoid growth of Sn_2S_3 and SnS_2 phases, Sn (II) instead of Sn(IV) was used [14]. The SnS growth receipt was adapted from the previous work concerning spray pyrolised SnS thin films [15]. Based on it we estimated the [Sn]/[S] ratio to be close to 1 and the thicknesses of the layers to be around 1 μm. To obtain clean and stain-free substrates, an ultrasonic bath was used, and the substrates were cleaned by acetone, distilled water, ethanol and distilled water.

2.2. Thin film characterisation

The X-Ray Diffraction (XRD) measurements were made using a Rigaku Ultima IV diffractometer at the Bragg-Brentano (θ–2θ) configuration and with Cu:Kα radiation (1,5418 Å). Atomic Force Microscopy (AFM) analysis was carried out using an NT-MDT NTEGRA PRIMA microscope in semi-contact mode. The optical properties, including transmittance and reflectance, were measured using Bentham PVE300 setup in the 300–1800 nm range of light wavelength using a halogen and wolfram light source and Ge and Si photodetectors. The reflectance was measured in the diffused standard. The photoluminescence (PL) was evaluated using the lock-in technique. The samples were excited with 514,5 nm chopped Ar + laser light in the laser power output range from 4 to 500 mW, which corresponds to the excitation density roughly from 100 mW/cm^2 to 12,5 W/cm^2. The PL signal was collected with an iHR550 grating monochromator and detected with a liquid nitrogen-cooled germanium detector. The samples were cooled down to low temperatures in the helium closed-cycle setup and analysed in the 10–100 K temperature range. To perform electrical measurements, Al electrodes were evaporated on SnS film in planar configuration. The conductivity was then measured in a nitrogen-cooled cryostat in the 80–330 K temperature range.

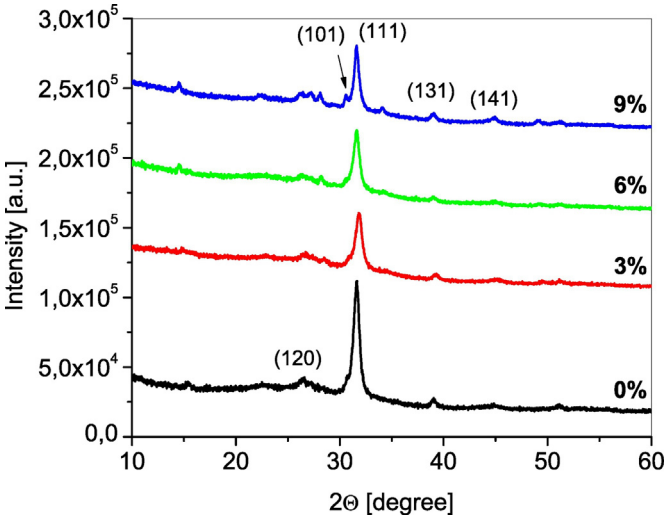

Fig. 1. XRD spectra for SnS samples with different In concentrations in the sprayed solution. Preferential crystallographic directions are also shown.

3. Results and discussion

3.1. XRD analysis and AFM measurements

To investigate the crystalline properties of the synthesised films, XRD measurements were carried out, together with AFM imaging. The diffraction spectra of all four SnS thin films are presented in Fig. 1.

All films are polycrystalline and the XRD peaks are in good agreement with standard data for SnS orthorhombic phase (JCPDS #39-0354) with (111) as the preferential crystallographic direction. The peaks are broad, which indicates high disorder in the material, as well as point into small crystallite sizes. The intensity of the (111) main peak decreases with increasing amount of In. The crystallite size of SnS thin film doped with indium for the main (111) XRD peak can be calculated using the Scherrer formula: $D = k\lambda/\beta\cos\theta$. Here D is the crystalline size, k is a crystallite shape factor being in the range of 0,62–2,08 [16] (k = 0.9 was used), λ = 1,5418 Å is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the Gaussian peak fitted to the data, and θ is the Bragg angle of diffraction. To determine θ and FWHM parameters, we used the X'Pert HighScore software. The calculated crystallite sizes are presented in Table 1. The size of the crystallites in the investigated samples is in the range 116–125 Å, and does not depend significantly on the amount of indium supplied during growth.

Fig. 2 presents AFM images of two investigated SnS thin films – the undoped one and the one with 9% of indium concentration in the solution. The scan area was 8 μm × 8 μm with 512 × 512 resolution. The films have an irregular structure with longitudinal type of grains, which has already been observed in spray pyrolised SnS thin films [10]. The average grain size and the average roughness height are presented in Table 1. The presence of indium during growth generally increases the mean grain size from around 38 nm to around 60 nm as well as the roughness of the film. However, there is no further increase of grain size when more indium is added. The average grain size is also larger than the average crystallite size obtained from XRD. This might be the result of the different physical meaning of the calculated size parameters between the XRD and AFM analyses. The Scherrer equation gives the minimum crystallite size and the analysis of AFM provides the mean grain size. Taking into account that the grains are clearly longitudinal, we might expect higher average grain sizes then the minimum crystallite width. The second reason might be the fact that the grains could actually consist of few smaller crystallites indistinguishable by AFM analysis.

3.2. Absorbance

According to basic semiconductor equations, the absorption coefficient, in the case of direct transitions, is proportional to:

$$\alpha \propto \frac{1}{h\upsilon}\left(h\upsilon - E_g\right)^{1/2} \tag{2}$$

where h is Planck's constant, ν is the frequency of incident photons and E_g is the bandgap energy. In the case of indirect allowed transitions, the absorption coefficient is proportional to:

$$\alpha \propto \frac{1}{h\upsilon}\left(h\upsilon - E_g \pm E_{ph}\right)^2 \tag{3}$$

Table 1
Size of crystallites calculated from XRD spectra and grain parameters calculated based on the AFM images.

sample	crystallite size (Å)	mean grain size (nm)	mean roughness height (nm)
SnS: undoped	125	37,7 ± 3,8	155 ± 27
SnS: In 3%	116	61,0 ± 9,2	193 ± 25
SnS: In 6%	125	62,6 ± 6,8	196 ± 20
SnS: In 9%	119	58,6 ± 6,5	203 ± 38

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