



# Raman spectroscopic study of $\text{In}_2\text{S}_3$ films prepared by spray pyrolysis



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## ABSTRACT

Indium sulfide ( $\text{In}_2\text{S}_3$ ) thin films are of interest as buffer layers in chalcopyrite absorber based solar cells; and as media providing two-photon absorption for intermediate-band solar cells. We investigated the suitability of chemical spray pyrolysis (CSP) for growing  $\text{In}_2\text{S}_3$  thin films in a structural order where indium atoms are preferentially in the octahedral sites. We sprayed aqueous or alcoholic solutions of indium chloride ( $\text{InCl}_3$ ) and thiourea ( $\text{SC}(\text{NH}_2)_2$ ) precursors onto a substrate with surface temperatures ( $T_s$ ) of 205, 230, 275 and 320 °C. The as-deposited films grown from aqueous solutions were annealed in 5%  $\text{H}_2\text{S}$  containing atmosphere at 500 °C. We used Raman spectroscopy, X-ray diffraction and Energy Dispersive X-ray spectroscopy to evaluate the effect of growth temperature and the effect of annealing on the film structure and stoichiometry. The use of alcoholic solvent instead of aqueous allows us to use much lower  $T_s$  while preserving the quality of the  $\beta\text{-In}_2\text{S}_3$  films obtained. Similarly, films with increased stoichiometry and quality are present at a higher  $T_s$ ; and when annealed. The annealing of the films grown at  $T_s$  of 205 °C results in a much higher gain of the crystal quality compared to the gain when annealing the films grown at  $T_s$  of 320 °C, although the quality remain higher when deposited at  $T_s$  of 320 °C. Simultaneously with the increase of the film quality, there is a sign of increased quality of the crystal ordering with indium in the octahedral sites. Such a crystal ordering favor the use of CSP deposited  $\text{In}_2\text{S}_3$  films in the intermediate band solar cells.

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## 1. Introduction

Indium sulfide ( $\text{In}_2\text{S}_3$ ) thin films are used as a substitute for cadmium sulfide (CdS) in solar cells that use chalcopyrite as an absorber material [1,2]. Additionally,  $\text{In}_2\text{S}_3$  itself can provide the active absorption medium in a new type of solar cells called intermediate band solar cells [3]. In such cells, when doped by a transition metal,  $\text{In}_2\text{S}_3$  allows an electron band-to-band excitation by absorbing two sub-bandgap photons. In the present work, we study if the chemical spray pyrolysis (CSP) deposition method in conjunction with thermal treatment in  $\text{H}_2\text{S}$  allows to prepare  $\text{In}_2\text{S}_3$  thin films that fulfill expectations for an intermediate band solar cell.

It has been shown that the preparation method dictates the crystalline, electrical and optical properties of  $\text{In}_2\text{S}_3$  thin films [4]. The CSP grown  $\text{In}_2\text{S}_3$  has been used as a buffer layer in thin film solar cells and in extremely thin inorganic absorber (eta) layer solar cells [2,5]; a study on the feasibility of  $\text{In}_2\text{S}_3$  as an electron selective layer in a polymer solar cell has been published [6]. The CSP is an economical, simple and a non-vacuum method available in pneumatic and ultrasonic spray modes [2,7,8].

The crystal structure and the optical properties of the CSP-deposited  $\text{In}_2\text{S}_3$  films at different deposition temperatures and molar ratios of indium and sulfur sources ( $\text{In:S}$ ) in either aqueous or alcoholic spray solutions have been published [2,7–11].

XPS study of  $\text{In}_2\text{S}_3$  films shows that oxygen bounded to indium is present in all sprayed films grown in the temperature range of 205–365 °C, however oxygen

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concentration is always higher in the films prepared from the  $\text{InCl}_3:\text{SC}(\text{NH}_2)_2=1:3$  solution compared to those obtained by spray of the  $\text{InCl}_3:\text{SC}(\text{NH}_2)_2=1:6$  solution [8]. In addition, the use of the  $\text{InCl}_3:\text{SC}(\text{NH}_2)_2=1:6$  solution leads to a slightly larger crystallite size [8]. To understand the relevance of the sulfur source content in the spray solution and the origin of the oxygen content in the films, the formation chemistry of  $\text{In}_2\text{S}_3$  in spray pyrolysis process has been studied. As a result of thermal analysis, we found that the formation of  $\text{In}_2\text{S}_3$  films in the CSP process passes through an intermediate complex compound,  $\text{In}(\text{tu})_3\text{Cl}_3$  that formed in aqueous solutions containing  $\text{InCl}_3$  and  $\text{SC}(\text{NH}_2)_2$  as starting chemicals. The excess of thiourea compared to solution containing  $\text{InCl}_3:\text{SC}(\text{NH}_2)_2$  at a molar ratio of 1:3 (which is needed for formation of  $\text{In}(\text{tu})_3\text{Cl}_3$  complex), minimizes the formation of  $\text{In}_2\text{O}_3$  phase [12,13]. Therefore, in this study, the  $\text{InCl}_3:\text{SC}(\text{NH}_2)_2$  molar ratio of 1:6 instead of 1:3 in the spray solution is used to deposit  $\text{In}_2\text{S}_3$  films.

Raman spectroscopy has been used to characterize  $\text{In}_2\text{S}_3$  films prepared by different methods such as co-evaporation of In and S [14], flash evaporation technique [15], electrochemical deposition [16], chemical spray pyrolysis [11,17], chemical bath deposition [18], atomic layer deposition [19] and photochemical deposition technique [20].

The literature on Raman spectroscopy of the CSP-deposited  $\text{In}_2\text{S}_3$  is yet insufficient. Valdés et. al. presented a Raman spectrum of the sprayed  $\text{TiO}_2/\text{In}_2\text{S}_3$  layers [17]. Spasevska et. al. studied the effect of growth temperature and post-deposition annealing at varied temperatures in air on the properties of  $\text{In}_2\text{S}_3$  films using ultrasonic spray of  $\text{InCl}_3$  and  $\text{SC}(\text{NH}_2)_2$  aqueous solution at a molar ratio of 1:7 [11]. An improvement of  $\text{In}_2\text{S}_3$  film quality was reported when increasing the deposition temperature from 220 to 340 °C or when applying post-deposition annealing in air [11]. The use of alternative solvents in spray solution and the effect of post-deposition annealing in  $\text{H}_2\text{S}$  have not been reported on the Raman spectra of  $\text{In}_2\text{S}_3$  films deposited by CSP.

We focus on Raman study of  $\text{In}_2\text{S}_3$  thin films deposited at different growth temperatures using pneumatically sprayed aqueous or alcoholic solutions; and the effect of post-deposition heat treatment on  $\text{In}_2\text{S}_3$  in  $\text{H}_2\text{S}$  atmosphere. We aim to improve the  $\text{In}_2\text{S}_3$  film grown by spray so that it would be considered attractive as a host material suitable for doping and thus usable as an absorber in the intermediate band solar cell [3].

## 2. Experimental

Aqueous or alcoholic solutions, containing indium chloride ( $\text{InCl}_3$ ) and thiourea ( $\text{SC}(\text{NH}_2)_2$ ) as precursors, have been used to deposit  $\text{In}_2\text{S}_3$  thin films by CSP; respective CSP procedure in more detail can be found in [8,10]. Here we use  $\text{InCl}_3$  to  $\text{SC}(\text{NH}_2)_2$  molar ratio of 1:6 (with the  $[\text{In}^{3+}]$  concentration of  $2 \times 10^{-3}$  mol/L), and deionized water or alcoholic mixture ( $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}=1:1$ , by volume) as solvent in the precursor solution. The solutions were pneumatically sprayed onto a preheated soda-lime or borosilicate glass substrate placed on a tin bath at a temperature of 250, 280, 330 and 380 °C, corresponding to a surface temperature of the substrate

$T_s$  of 205, 230, 275 and 320 °C in case of the aqueous solutions sprayed. The temperature differences are due to an inevitable temperature gradient in the substrate; while the main factor is the cooling effect of the carrier gas. In addition, the use of aqueous solutions resulted in a 10 °C lower  $T_s$  compared to that when alcoholic solutions were deposited at similar tin bath temperatures. After deposition, the films grown from aqueous solutions onto borosilicate glass were heat-treated for 30 min at 500 °C; subjected to flowing gas in proportion of 5%  $\text{H}_2\text{S}$  (99.99% purity) and 95%  $\text{N}_2$  (99.999% purity); followed by cooling to room-temperature at a rate of 25 °C/min.

X-ray diffraction (XRD) patterns were recorded by a Rigaku Ultima IV diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5406$  Å, 40 kV at 40 mA) using the silicon strip detector D/teX Ultra. Crystallite size and lattice constants were calculated using Rigaku PDXL Version 1.4.0.3 software; NIST external standard ( $\text{LaB}_6$ ) was used to determine the instrumental peak broadening. The crystallite size was calculated using the Debye-Scherrer method and a Scherrer constant of 0.94, using the full width at half maximum (FWHM) of the XRD peak with highest intensity. The Raman spectra were measured in a backscattering configuration at room temperature using a confocal micro-Raman spectrometer HORIBA Jobin Yvon Model HR 800. The excitation radiation wavelength was 532 nm while the power density was sufficiently low without excessive heating the sample area of ca 100  $\mu\text{m}^2$ , during 100 s of data acquisition. The Raman peak analysis is based on Lorentzian-fitting performed in the range of 100–450  $\text{cm}^{-1}$ . The elemental composition of the films was evaluated by Energy Dispersive X-ray (EDX) analysis using an Oxford Instruments spectrometer with INCA Energy system, at a Zeiss EVO-MA15 scanning electron microscope operating at an accelerating voltage of 7 kV.

## 3. Results and discussion

### 3.1. Effect of film growth temperature and solvent type on the Raman spectra of the sprayed $\text{In}_2\text{S}_3$

Raman scattering spectroscopy gives knowledge about the vibration modes characteristic of a crystal phase. The modes are affected by local atomic arrangement, including factors like stress, defects and structural disorder. According to Raman spectra, see Fig. 1, the as-deposited films consist of  $\beta\text{-In}_2\text{S}_3$  [21]. In this study, the peaks expected near 244 and 306  $\text{cm}^{-1}$  are of interest. These peaks have been attributed to the vibrations of  $\text{InS}_6$  octahedra and  $\text{InS}_4$  tetrahedra, respectively [22,23]. In the  $\beta\text{-In}_2\text{S}_3$  the cation vacancies are ordered in the tetrahedral sites while most of the indium (75%) is expected to be in the octahedral sites [3]. In particular, the existence of the octahedral sites has been proven to support two-photon absorption process in vanadium-doped  $\text{In}_2\text{S}_3$  for the intermediate solar cell application [3].

An increase of  $T_s$  up to 320 °C resulted in a pronounced 'octahedral peak' at 244  $\text{cm}^{-1}$  for films deposited using aqueous solutions, see Fig. 1a. Yet, the use of alcoholic solutions allows to reach a similar Raman profile already at a lower  $T_s$  of 285 °C (Fig. 1b). It seems that, in case of

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