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Spray pyrolysis deposition of indium sulphide thin films

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ABSTRACT

In_2S_3 thin films were grown by the chemical spray pyrolysis (CSP) method using the pneumatic spray set-up and compressed air as a carrier gas. Aqueous solutions containing $InCl_3$ and $SC(NH_2)_2$ at a molar ratio of In/S = 1/3 and 1/6 were deposited onto preheated glass sheets at substrate temperatures T_s = 205–410 °C. The obtained films were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM,) optical transmission spectra, X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS). According to XRD, thin films deposited at T_s = 205–365 °C were composed of the (0 0 12) orientated tetragonal β-In_2S_3 phase independent of the In/S ratio in the spray solution. Depositions performed at T_s = 410 °C led to the formation of the In_2O_3 phase, preferably when the 1/3 solution was sprayed. Post-deposition annealing in air indicated that oxidation of the sulphide phase has a minor role in the formation of In_2O_3 at temperatures up to 450 °C. In_2S_3 films grown at T_s below 365 °C exhibited transparency over 70% in the visible spectral region and E_g of 2.90–2.96 eV for direct and 2.15–2.30 eV for indirect transitions, respectively. Film thickness and chlorine content decreased with increasing deposition temperatures. The XPS study revealed that the In/S ratio in the spray solution had a significant influence on the content of oxygen (Me–O, BE = 530.0 eV) in the In_2S_3 films deposited in the temperature range of 205–365 °C. Both XPS and EDS studies confirmed that oxygen content in the films deposited using the solution with the In/S ratio of 1/6 was substantially lower than in the films deposited with the In/S ratio of 1/3.

1. Introduction

Indium sulphide (In_2S_3) thin films have attracted research interest due to their potential use in the manufacturing of optoelectronic devices. These films have wide band gap of 2.0 eV to 3.7 eV depending on the preparation method [1], and a high transmittance in the visible spectrum [2,3]. Therefore, they have been used as buffer layer in photovoltaic structures [4–6]. They also have been used as an absorber layer in nanostructured solar cells [7,8]. Indium sulphide films are relatively non-toxic and can be prepared by numerous dry and wet methods, such as thermal evaporation (PVD) [9,10], chemical bath deposition (CBD) [11,12], atomic layer deposition (ALD) [13], spray ion layer gas reaction (Spray-ILGAR) [14], spin coating [15], successive ionic layer adsorption and reaction (SILAR) [16], and chemical spray pyrolysis (CSP) [2,3,17]. However, films prepared by different methods also have different crystalline, electrical and optical properties [1].

The CSP method has been chosen in this work because the method is economical, requires short processing time, can be performed in atmospheric conditions and can prepare thin films using both pneumatic and ultrasonic spray modes [18,19]. The effect of growth temperature, solution composition and annealing temperature on the crystal structure, chemical composition and optical properties of In_2S_3 thin films prepared by CSP has been studied in previous works [2,3,17–20]. It has been demonstrated by several studies that the main parameters influencing the properties of In_2S_3 films are the molar ratio of In and S sources (In/S) in the precursor solutions and the deposition temperature [2,17,19]. It has also been found that the In/S ratio in the spray solution has an effect on the crystal structure, the crystallite size [3,18], and the optical band gap of the In_2S_3 films [2,17,19]. For example, John et al. [2] have reported that the use of a sulphur-rich solution (In/S = 2/8 instead of In/S = 2/1) can decrease the optical band gap from 2.81 to 2.64 eV. The growth temperature has been found to control the crystallite size and the crystal structure of In_2S_3 [2,3,17,18]. According to XPS, oxygen bonded to In has been found to be present in the films deposited at 340 °C with the In/S ratio of 1/2 in the spray solution [20]. When In_2S_3 films were deposited at temperatures below 300 °C using the In/S ratio of 2/8 [2], oxygen was present only on the film surface. Chlorine residues have been observed throughout the In_2S_3 films when they were grown at low temperatures using $InCl_3$ as In-source [2]. To avoid chlorine contamination, the $InCl_3$ precursor has been replaced by $In(CH_3COO)_3$. [3] or $In(NO_3)_3$ [19], but amorphous films were obtained with a growth temperature of approximately 300 °C.

In addition to the technological parameters listed above, solvents such as water [2,19,20] or alcohols [3,17,18] and the CSP equipment may also have an effect on the properties of CSP-deposited In_2S_3 films.

In our previous study, a nanostructured solar cell that included In_2S_3 as a buffer layer was made by the CSP method [5]. In order to

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prepare an effective solar cell, it is important to know the properties of each layer in the solar cell structure. However, few studies have been done on the deposition of In_2S_3 films by pneumatic spray of aqueous $InCl_3$ and thiourea solutions [2,20], as we are using for the In_2S_3 buffer layer in the solar cell [5].

Therefore, the aim of this paper was to study the effect of the deposition temperature and the molar ratio of precursors (In/S) in the spray solution on the phase and elemental composition, as well as on the structural and optical properties of In_2S_3 films deposited by pneumatic CSP using aqueous spray solutions containing $InCl_3$ and $SC(NH_2)_2$ as precursor materials.

2. Experimental details

2.1. Film preparation

In_2S_3 thin films were deposited by the CSP technique from aqueous solutions containing indium chloride ($InCl_3$) and thiourea ($CS(NH_2)_2$) with the molar ratio (In/S) of 1/3 and 1/6 (at an $InCl_3$ concentration of 2×10^{-3} mol/l), using a pneumatic spray set-up and compressed air as a carrier gas. Glass sheets with a size of $20\times20\times1.1$ mm^3 were used as substrates placed on a molten tin bath. Deposition temperatures were varied from 205 to 410 °C, and kept within an accuracy of ±5 °C using a feedback control system for the heater supply. The film deposition temperature was measured from the glass surface when deionised water was sprayed. Total volume of the solution sprayed was 50 ml and the rate of spray was 2.5 ml/min in all cases. The scheme of the spray pyrolysis set-up used in this study is presented in Fig. 1.

2.2. Film characterisation

The deposited thin films were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmission spectra, X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) measurements. XRD measurements were performed on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5406 Å, 40 kV at 40 mA) using the silicon strip detector D/teX Ultra. Crystallite size and lattice constants were calculated using the software on the Rigaku's system (PDXL Version 1.4.0.3). LaB_6 (from NIST) was used as an external standard to determine the instrumental peak broadening. The crystallite size was calculated using the Debye-Scherrer method and a Scherrer's constant of 0.94. Surface morphology of In_2S_3 films was examined using a high-resolution SEM (Zeiss HR FESEM Ultra 55) at an operating voltage of 10 kV. Film thicknesses were measured from the SEM cross-sectional images taken on a Zeiss EVO-MA15 at an operating voltage of 10 kV. The elemental composition of films was evaluated by an energy dispersive X-ray (EDS) analysis using Röntec EDX XFlash 3001 detector and the Oxford Instruments INCA Energy system. The accelerating voltages used were 6.5 and 7 kV, respectively. The optical total transmittance spectra of the films were measured in the wavelength range of 300–2500 nm on a Jasco V-670 UV–VIS–NIR spectrophotometer equipped with an integrating sphere. XPS measurements were performed using a Kratos AXIS Ultra DLD X-ray Photoelectron Spectrometer with monochromatic Al Kα X-rays (1486.6 eV) in conjunction with a 165 mm hemispherical electron energy analyzer and a delay-line detector. XPS spectra were recorded using an aperture slot of 300 μm × 700 μm and pass energy of 20 eV. Spectra were recorded from the un-cleaned surface and from the surface after 11 Ar^+ ion sputtering cycles (about 30–40 nm below the top surface). Energy calibration was performed using the C1s line at 285.0 eV as a reference. The atomic concentrations were determined from $In3d_{5/2}$, O1s, S2p, Cl2p and Si2p core level peak areas using the sensitivity factors provided by the Vision 2.2.6 analysis software.

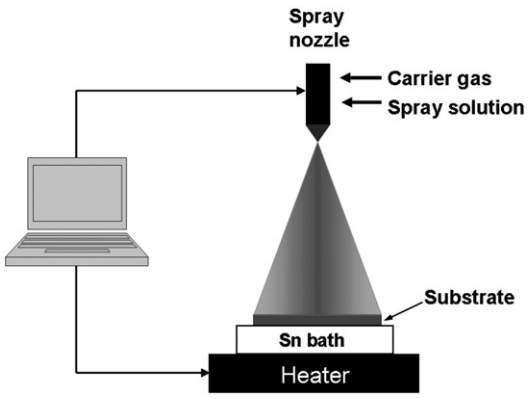

Fig. 1. The scheme of the spray pyrolysis set-up.

3. Results and discussion

3.1. XRD analysis

The XRD patterns in Fig. 2 show that thin films deposited at temperatures (T_s) of 205–365 °C exhibited diffraction peaks belonging to the tetragonal β-In_2S_3 phase (JCPDS 01-074-7284) [21] irrespective of the In/S ratio in the spray solution. No other crystalline phases were detected. The films deposited at T_s = 205–320 °C showed preferential growth along the (0 0 12) plane. According to the XRD pattern of the film deposited at 365 °C, the (1 0 3) and (2 0 6) reflections became more apparent and the relative intensity of the (0 0 12) peak decreased compared to the films deposited at lower temperatures. This indicates weakening of the (0 0 12) orientation in the films grown at higher temperatures.

Lattice constants a, b and c of the films calculated from the XRD patterns are presented in Table 1. It shows that by increasing the deposition temperature (from 205 °C to 320 °C), the lattice parameters increased slightly and approached the values characteristic of the powder reference β-In_2S_3 (a = b = 7.617 Å, c = 32.331 Å). Interestingly, the lattice parameters of the In_2S_3 film grown using a precursor solution with the In/S ratio of 1/6 were higher than those obtained from the In/S = 1/3 solution. According to the XPS study, the oxygen content was higher in the In_2S_3 films grown with the In/S ratio of 1/3 (see Section 3.4). Thus, the smaller lattice parameters of the films grown using solutions with the In/S ratio of 1/3 are likely due to higher oxygen content in the film compared to the films grown from solutions with the In/S ratio of 1/6.

The crystallite sizes in the films calculated from the full width at half maximum (FWHM) of the (0 0 12) XRD peak are presented in Table 1. With increasing deposition temperature (T_s = 205 to 320 °C),

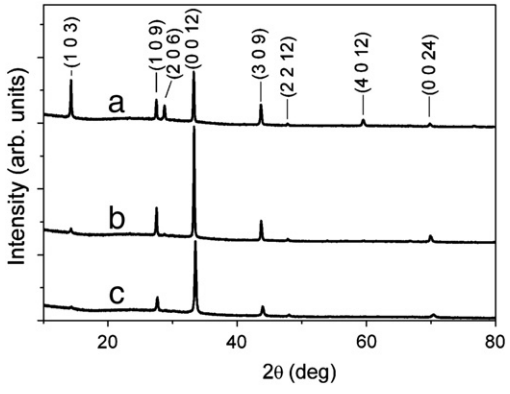

Fig. 2. XRD patterns of In_2S_3 films sprayed at different deposition temperatures (T_s) of 365 °C (a), 320 °C (b) and 205 °C (c) using the precursors molar ratio of In/S = 1/6 in the spray solution.