Indium sulfide thin films deposited by chemical spray of aqueous and alcoholic solutions

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Abstract

In\textsubscript{2}S\textsubscript{3} films were grown by pneumatic chemical spray method using aqueous and alcoholic solutions containing InCl\textsubscript{3} and SC(NH\textsubscript{2})\textsubscript{2} at molar ratios of [In]/[S]=1/3 and 1/6. Films were deposited onto preheated glass sheets in air at heater (molten Sn bath) temperatures of 250 and 330 °C. Films were characterized by means of XRD, SEM, UV-VIS spectra and XPS. β-In\textsubscript{2}S\textsubscript{3} films were formed independent of the technological variables. The films from aqueous solutions are highly orientated along (0 0 12) plane parallel to the substrate, with E\textsubscript{g} of 2.2-2.3 eV (indirect transitions). Spray of alcoholic solutions results in thinner but more compact films with reduced (0 0 12) orientation, E\textsubscript{g} of ca. 2.0 eV, and no chlorine contamination when deposited at 330 °C. According to XPS, the films have uniform concentration of the elements through the film thickness, spray of sulfur-rich solutions ([In]/[S]=1/6) results in the films with lower oxygen content.

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Keywords: Indium sulfide; chemical spray pyrolysis; solvents; structural properties; morphology; elemental composition; XRD; SEM; XPS

1. Introduction

Indium sulfide (In\textsubscript{2}S\textsubscript{3}) thin films have attracted researchers’ interest due to their potential use for the manufacturing of optoelectronic devices. In\textsubscript{2}S\textsubscript{3} thin films have been successfully used as a buffer layer instead of CdS in chalcopyrite absorber based photovoltaic structures [1 - 4]. In nanostructured solar cells In\textsubscript{2}S\textsubscript{3} has also been used as an absorber layer [5, 6]. In\textsubscript{2}S\textsubscript{3} thin films can be obtained by numerous dry and wet methods, while crystalline, electrical and optical properties of the films depend on the deposition method [4].

Chemical spray pyrolysis (CSP) method has been chosen because it is economical, fast, non-vacuum and simple for both pneumatic and ultrasonic spray (USP) modes to prepare thin films [3, 7, 8]. The efficiency of 12.4 % is obtained with CuInGa(S,Se)\textsubscript{2} absorber layer solar cell using USP-deposited In\textsubscript{2}S\textsubscript{3} as a buffer layer [3]. In our laboratory, a nanostructured solar cell with In\textsubscript{2}S\textsubscript{3} buffer layer was made by the CSP method [2, 9].

There are several studies, where In\textsubscript{2}S\textsubscript{3} thin films by CSP have been investigated depend on different technological parameters, such as type of precursors, molar ratio of the precursors in the spray solution, growth and annealing temperatures [3, 7, 8, 10, 11]. In these studies it has been shown, that the main parameters influencing the In\textsubscript{2}S\textsubscript{3} thin films properties are the molar ratio of In and S sources (In/S) in the precursor solution and the deposition
temperature. Besides these main parameters, also solvents (water, alcohol) may have an effect on the properties of CSP-deposited In$_2$S$_3$ films. Alcohol has been usually used as a solvent for ultrasonic spray [3]. In the case of pneumatic spray, aqueous solutions have been commonly used [2, 7, 9, 11], alcoholic solutions have been infrequently used for deposition of In$_2$S$_3$ films [8, 10].

In this study we investigated the structural and optical properties, also composition and morphology of In$_2$S$_3$ thin films deposited by pneumatic CSP method using aqueous and alcoholic spray solutions.

2. Experimental

In$_2$S$_3$ films were obtained by pneumatic spray of the solutions containing indium chloride (InCl$_3$) and thiourea (CS(NH$_2$)$_2$) at the molar ratio [In]/[S] of 1/3 and 1/6 ([InCl$_3$] = $2 \times 10^{-3}$ mol/l). Three different solvents were used: deionized water, H$_2$O; H$_2$O with ethanol (H$_2$O:C$_2$H$_5$OH =1:1, by volume) and H$_2$O with isopropyl alcohol (H$_2$O:C$_3$H$_8$O =1:1, by volume). Total volume of the solution sprayed was 50 ml and the rate of spray was 2.5 ml/min in all cases. Compressed air served as a carrier gas. Glass sheets with a size of 20 x 20 x 1.1 mm$^3$ were used as substrates and molten tin bath served as a heater. The films were deposited at tin bath temperatures ($T_{Sn}$) of 250 and 330 °C. The bath temperature was kept with accuracy of ± 5 °C with the help of the feedback control system for the heater supply.

The sprayed films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmittance spectra and X-ray photoelectron spectroscopy (XPS) measurements. XRD measurements were performed on a Rigaku Ultima IV diffractometer with Cu K$_\alpha$ radiation ($\lambda$= 1.5406Å, 40 kV, 40 mA) using the silicon strip detector D/teX Ultra. Crystallite size was calculated using the Debye-Scherrer method and the Scherrer’s constant of 0.94. Surface morphology and cross-sectional views of the films were examined by high-resolution SEM on Zeiss HR FESEM Ultra 55. The 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 K$_\alpha$ 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 x 700 μm and pass energy of 20 eV. Energy calibration was performed taking the C1s line at 285.0 eV as a reference. The atomic concentrations of the elements were determined from In3d$_{5/2}$, O1s, S2p, Cl2p and Si2p core level peak areas using the sensitivity factors provided by the Vision 2.2.8 analysis software. Ar$^+$ ion sputtering was used for the depth profiling in order to obtain information of the film bulk composition.

3. Results and discussion

3.1. Film thickness and morphology

SEM micrographs of the films prepared with different solvents at $T_{Sn}$ of 250 and 330 °C are presented in Figure 1. All deposited films show uniform coverage of the substrate with no cracks or pin-holes, also at low magnifications. SEM study shows that film thickness and surface morphology is different for the films obtained from aqueous or alcoholic solutions using solution feeding rate of 2.5 ml/min. Spray of alcohol-based solutions results in thinner films as determined from the SEM cross-sections (Table 1).

The films obtained by spray of aqueous solutions at $T_{Sn}$=250 °C show thickness of ca 500 nm and are composed of grains with a size of ca 150-200 nm. These grains seem to be aggregates of smaller crystallites (Fig. 1a). Deposition at higher temperature results in the film with thickness of ca. 350 nm, the film is composed of grains with a size of ca. 100 nm (Fig.1d). Deposition of alcoholic solutions at $T_{Sn}$=250 °C results in the film with thickness of ca 150-200 nm, at higher temperature the film thickness is ca. 100 nm (Table 1). The films from alcoholic solutions are composed of grains with size below 100 nm and exhibit more compact structure (Fig. 1 b, c, e, f). The [In]/[S] in the solution has insignificant effect on the film thickness and grain size.
Figure 1. SEM micrographs of the films deposited at heater temperatures of 250 °C (a, b, c) and 330 °C (d, e, f) using solvents: H₂O (a, d), ethanol + H₂O (b, e), isopropyl alcohol + H₂O (c, f). The films were deposited from the solutions with [In]/[S]=1/3.

It is well-known that use of alcoholic solutions instead of aqueous ones facilitates the formation of smaller spray droplets because of low surface tension of alcohols [12]. In our study we used mixtures of an alcohol and water in volume ratio of 1:1. For the mixture of ethanol and water (1:1 by volume), the surface tension is ca. 29 mN/m [13]. This value is well below of that characteristic of water (72 mN/m) and relatively close to that of pure ethanol (22 mN/m) [13]. As a result, smaller droplet size of alcoholic solutions leads to more compact and homogeneous films (Fig.1). Significantly lower film thicknesses in the case of spray of alcoholic solutions could be explained by 1) the convection–induced repelling of smaller droplets from the reaction zone; 2) slightly (about 10 degrees) higher growth temperature; 3) smaller amount of the solution per substrate area unit due to wider spray cone when spray nozzle solution gap was set to a new position to maintain the spray rate of 2.5 ml/min also for alcoholic solution.

3.2. Optical properties

The films deposited from aqueous and alcoholic solutions show total optical transmittance above 80 % in visible and near-infrared spectral region (Fig. 2). According to the optical transmittance spectra, the number of interference fringes is independent of the [In]/[S] in the spray solution being lower for the films deposited from alcoholic
solution. It indicates that films from alcoholic solutions have smaller thickness. This observation accords well with the results of the SEM cross-sectional study (Table 1).

The optical band gap ($E_g$) values were determined from the well-known equation for allowed indirect transitions:

$$\alpha h\nu = A(h\nu - E_g)^2,$$

where $\alpha$ is the absorption coefficient, calculated from the optical spectra, $A$ is a constant, $h$ is the Planck constant, $E_g$ is the band gap energy and $h\nu$ is the incident photon energy.

Optical band gap values for the sprayed In$_2$S$_3$ films deposited from aqueous solutions at $T_{Sn} = 250$ and 330 °C were 2.3 and 2.2 eV, respectively, and independent of the [In]/[S] in the spray solution (Table 1). Deposition of alcohol-based solutions results in the films with $E_g$ of 2.0 eV (Table 1). This value is slightly lower than 2.2 eV and 2.2-2.4 eV reported by M. Calixto-Rodriguez et. al. [8] and Kim et. al. [10] for the In$_2$S$_3$ films which also were obtained by spray of alcoholic solutions. However, the $E_g$ value of 2.0 eV is close to that reported for ALD-deposited In$_2$S$_3$ films [14].

### 3.3. Structural properties

XRD patterns of the films obtained by spray of aqueous and ethanolic solutions at similar heater temperatures ($T_{sn}$) are presented in Figures 3 and 4, respectively. According to XRD, the sprayed films are composed of tetragonal $\beta$-In$_2$S$_3$ phase as all diffraction peaks were identified according to JCPDS Card No. 01-074-7284 [15]. The ratio of the intensities of the (0 0 12) and (1 0 9) diffraction peaks ($I_{0012}/I_{109}$) is ca. 5 for the films deposited from aqueous solutions (Fig. 3). For the powder reference, $I_{0012}/I_{109} = 0.4$ [15]. Thus, In$_2$S$_3$ films deposited from aqueous solutions show preferred growth of the crystallites along the (0 0 12) plane parallel to the substrate. The effects of the [In]/[S] in the solution or the growth temperature on the crystallite orientation are inconsiderable. Narrowing of the diffraction peaks is observed at higher growth temperatures (Fig. 3). The films deposited at $T_{Sn} = 250$ °C show crystallite size below 40 nm, while at higher temperature the crystallite size is ca. 50 nm (Table 1). This result is in good accordance with the literature data [7, 8, 11].

![Figure 2. Total optical transmittance spectra of the films deposited at $T_{Sn} = 330$ °C from aqueous and ethanol solutions with precursors ratio [In]/[S]=1/3 and 1/6.](image-url)
For the films obtained by spray of alcoholic solutions, the \( I_{(0012)/I_{(109)} < 2, \text{ while } (103) \text{ and } (206) \text{ diffraction peaks become more pronounced (Fig. 4) compared to the films from aqueous solutions (Fig. 3). The (103) and (206) diffraction peaks were also prominent in XRD patterns of indium sulfide films made by spray of ethanol-based solutions at Sn bath temperatures close to 400 °C [8]. Thus, deposition of alcoholic solutions reduces orientation along (0012) plane. The crystallite sizes in the films prepared from ethanolic solutions at both temperatures are in the order of 50 nm (Table 1), which is twice larger than reported by Calixto et al. [8] for the films with similar thickness of ca 100 nm.

### 3.4. Elemental composition

The sprayed In\(_2\)S\(_3\) films were investigated by XPS using Ar\(^+\) ion sputtering for depth-profiling. The In3d\(_{5/2}\), S2p, O1s core level peaks were detected in the XPS spectra of all studied films (Fig. 5). The positions of the In3d\(_{5/2}\) peak at BE=444.7 eV and S2p peak at BE=161.6 eV are in good agreement with that reported for spray-deposited β-In\(_2\)S\(_3\) [16]. No shift in the In3d\(_{5/2}\) and S2p peak positions has been observed after Ar\(^+\) ion sputtering (Fig. 5). The O1s peak

| Table 1. Film thickness (t) measured from the SEM cross-sectional views, crystallite size (d) determined from the XRD patterns (Scherrer equation), optical band gap (Eg, indirect transitions) calculated from the optical spectra and elemental composition calculated from XPS spectra (after determined number of Ar\(^+\) ion etching cycles) for the films deposited by pneumatic spray of aqueous and alcoholic solutions with \([\text{In}]/[\text{S}]=1/3 \text{ and } 1/6 \text{ at different heater (molten Sn bath) temperatures (T\(_{\text{Sn}}\)).}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T(_{\text{Sn}}), °C</th>
<th>[In]/[S] in sol.</th>
<th>t, nm</th>
<th>d, nm</th>
<th>Eg, eV</th>
<th>Ar(^+) etching cycles</th>
<th>In, at.%</th>
<th>S, at.%</th>
<th>Cl, at.%</th>
<th>O, at.% (Me-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>250 1/3</td>
<td>550</td>
<td>33</td>
<td>2.3</td>
<td>11</td>
<td>43</td>
<td>53</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 1/6</td>
<td>450</td>
<td>38</td>
<td>2.3</td>
<td>11</td>
<td>44</td>
<td>53</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>330 1/3</td>
<td>340</td>
<td>55</td>
<td>2.2</td>
<td>10</td>
<td>43</td>
<td>54</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>330 1/6</td>
<td>350</td>
<td>51</td>
<td>2.2</td>
<td>10</td>
<td>42</td>
<td>56</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>H(_2)O + Ethanol</td>
<td>250 1/3</td>
<td>150</td>
<td>48</td>
<td>2.0</td>
<td>3</td>
<td>42</td>
<td>55</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 1/6</td>
<td>200</td>
<td>58</td>
<td>2.0</td>
<td>2</td>
<td>40</td>
<td>57</td>
<td>2</td>
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</tr>
<tr>
<td></td>
<td>330 1/3</td>
<td>100</td>
<td>53</td>
<td>2.0</td>
<td>3</td>
<td>42</td>
<td>56</td>
<td>0</td>
<td>2</td>
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<tr>
<td></td>
<td>330 1/6</td>
<td>120</td>
<td>55</td>
<td>2.0</td>
<td>3</td>
<td>43</td>
<td>56</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
at BE=532.0 eV was detected on the un-cleaned surface for all samples as a surface contamination. A weak O1s core level peak at BE=530.0 eV, characteristic of oxygen bonded to metal (Me-O) [16], is present in the spectra recorded from the films surface and bulk. The Cl2p peak at BE = 198.5 eV (spectrum is not presented) was detected in the films deposited from aqueous solutions at both temperatures and in the films from alcoholic solutions at lower temperature. Chlorine contamination originated from the InCl3 precursor and decreases increasing the deposition temperature. There is no chlorine in the films deposited from alcoholic solutions at TSn=330 °C.

According to the XPS depth profiling (Fig. 5), all samples show uniform distribution of the elements in the film thickness. The elemental composition (in at.%) according to the XPS study is presented in Table 1.

The [In]/[S] in the spray solution has an effect on the content of oxygen (Me-O, BE=530.0 eV) as earlier reported for the films deposited from aqueous solutions [7, 11]. The spray of the solution with [In]/[S] =1/6 results in lower oxygen content than the deposition of the solutions with [In]/[S] =1/3 independent of the solvent.

XPS study confirms that In2S3 films with uniform elemental composition throughout the film thickness could be deposited by chemical spray. Oxygen contamination could be minimized using [In]/[S] =1/6 in the spray solution. Alcoholic solutions are preferred to obtain the films with lower content of chlorine. Although according to XPS the In/S of 0.7-0.8 refers to the deficiency of sulfur in sprayed films compared to stoichiometric In2S3, the elemental composition should be examined by another method additionally to discuss this problem.

4. Conclusions

In this paper we presented that \(\beta\)-In2S3 films could be successfully deposited by the pneumatic spray pyrolysis method in air using aqueous and alcoholic solutions containing indium chloride and thiourea. The films from aqueous solutions are highly orientated along (0 0 12) plane parallel to the substrate, with \(E_g\) of 2.2-2.3 eV (indirect transitions). Spray of alcohol based solutions results in thinner films composed of smaller grains and as a result, more compact films with lower content of chlorine are formed. \(\beta\)-In2S3 films from alcoholic solutions show reduced orientation along (0 0 12) and \(E_g\) of ca 2.0 eV. XPS study confirms that sprayed films have uniform concentration of elements throughout the film thickness and deposition of solutions with [In]/[S] =1/6 decreases oxidation. In2S3 films with content of oxygen of ca. 1 at. % could be obtained by chemical spray at growth temperatures close to 300 °C in air.
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References


