Structural analysis of indium sulphide thin films elaborated by chemical bath deposition

B. Yahmadi a, N. Kamoun a,*, R. Bennaceur a, M. Mnari b, M. Dachraoui b, K. Abdelkrim c

a Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis (2092) El Manar, Tunisia
b Laboratoire de Chimie Analytique et Electrochimie, Faculté des Sciences de Tunis (2092) El Manar, Tunisia
c Laboratoire de Photovoltaïque et des Matériaux Semiconducteurs, Ecole Nationale d’Ingénieurs de Tunis, Tunis El Manar, Tunisia

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Abstract

X-ray diffraction and scanning electron microscopy show that the crystalline state of indium sulphide thin films, elaborated by chemical bath deposition technique on various substrates, is strongly affected by deposition parameters (deposition time $t_D$, pH solution and thioacetamide concentration), as well as by annealing treatment. We show that $\beta$-In$_2$S$_3$ thin films grown on glass substrate during $t_D = 60$ min, and annealed under nitrogen at 400 °C during 1 h are well crystallized according to the cubic structure with the preferential orientation (610). They have a good homogeneity and crystallinity. © 2004 Elsevier B.V. All rights reserved.

Keywords: Chemical bath deposition; Indium sulphide; Structural analysis; Heat treatment

1. Introduction

Recently, attention has been paid to $\beta$-In$_2$S$_3$ thin films. It is an important material for opto-electronic and photovoltaic applications [1], and a promising candidate for many technological applications due to its stability, its interesting structural characteristics [2], as well as its optical [3], acoustical [4] and electronic [5] properties. In addition, efforts are also concentrated on replacing CdS buffer layers for environmental reasons by using a material with a wider bandgap compared to CdS. Among others, indium sulphide has been recognized as a satisfactory alternative material [6], whose electrical properties have not yet been widely studied [7,8].

Preparation of the indium sulphide thin films has been carried out by different methods such as chemical vapour deposition [9], atomic layer epitaxy [10], spray pyrolysis [11], and chemical bath deposition (CBD) [12]. CBD is a relatively inexpensive, simple, and convenient method for large area deposition at low temperatures. CBD is emerging as an excellent technique for elaboration of several chalcogenide semiconductors [13].

In the present work, we depose by CBD indium sulphide thin films on glass and on SnO$_2$/glass substrates. Using X-ray diffraction (XRD) and scanning electron microscopy (SEM), we study the effects of: (i) deposition time $t_D$, (ii) pH of the precursor solution, (iii) concentration of one of the precursor, and (iv) heat treatment, on the crystal structure and morphology of the films.

2. Experimental details

Indium sulphide thin films are elaborated by CBD, both on ordinary glass slides ($2.5 \times 2.5 \times 2$ mm) and on SnO$_2$/glass substrates. The bath contains indium chloride with constant concentration (0.025 M) and thioacetamide (TA) as sulphur precursor (its concentration ranges between 0.10 and 0.65 M). Bath temperature is 70 °C. The pH of the solution is controlled to 2.35 and 2.45 by adding acetic acid into the reaction mixture.

Substrate preparation ensures the success of the process. Glass substrates are prepared in the following way: First,
they are dipped during 5 min (min) into hydrochloric acid and nitric acid solution (in the proportion: 1/3 HCl and 2/3 HNO₃). Then, they are rinsed thoroughly with distilled water, immersed into methanol solution (purity: 99.8%), rinsed again with distilled water and chemically cleaned with fluorydric acid solution (HF 7%). Finally, they are rinsed and put in a dried box during 10–15 min. SnO₂/glass substrates are prepared by spray pyrolysis (V_{SnCl₄} = 23 cm³, m_{NH₄F} = 5 g; V_{H₂O} = 7 cm³; V_{CH₃OH} = 970 cm³, substrate temperature: T_S = 440 °C and spray time: t_S = 10 min) [14]. Substrates are finally introduced vertically into the hermetic closed deposition cell.

The deposition cell is mounted on a heating magnetic agitator, which controls both temperature and homogeneity of the solution. Deposition time varies from 45 to 90 min.

After deposition, film thickness is estimated by the double weight method (i.e. by weighting sample before and after film deposition). It results in film thickness ranging between 0.30 ± 0.01 and 0.68 ± 0.01 μm. Some films are also annealed under nitrogen during 1 h at 400 °C.

Indium sulphide thin films are characterized by X-ray diffraction (Philips 1050-37 and λ = 1.5418 Å) and by scanning electron microscopy (SEM, EDAX XL 30 (S.E)). Preliminary experiment procedures allow to determine the deposition conditions range.
3. Results and discussions

3.1. X-ray diffraction analysis

3.1.1. Effect of the deposition time

In the following study, the pH of the solution is 2.35 and the TA concentration is 0.10 M. Experiments correspond to deposition time of 45, 60 and 90 min.

Fig. 1 presents the XRD spectra of indium sulphide thin films deposited by CBD on glass before (1) and after (2) annealing during 1 h at $T = 400 \, ^\circ C$ in nitrogen atmosphere. After deposition, all the layers contain the $\beta$-$\text{In}_2\text{S}_3$ (440) phase, for $t_D = 45$ min, it is the only phase, but for $t_D = 60$ min and $t_D = 90$ min, respectively, $\text{In}_6\text{S}_7$ (214) and $\beta$-$\text{In}_2\text{S}_3$ (400) appear. Annealing induces a number of other phases: $\beta$-$\text{In}_2\text{S}_3$ (311) appears for the three values of $t_D$, $\text{In}_6\text{S}_7$ (504) appears for $t_D = 90$ min (Fig. 1-2c). The best crystallinity is obtained for $t_D = 60$ min (Fig. 1-2b). In that last condition, the spectrum shows a high and well-defined peak corresponding to an important proportion of $\beta$-$\text{In}_2\text{S}_3$ (610).

We notice that the pH of the solution changes during deposition: the initial value is 2.35 and it decreases to 1.35 after 1 h of growth. We also noticed the existence of an additional $\text{In}_6\text{S}_7$ phase in films grown at $t_D = 60$ min without annealing and at $t_D = 90$ min after annealing (Fig. 1-1b and 1-2c). We conclude that thin film crystallinity is affected not only by the initial deposition parameters, but also by the evolution of the process conditions during deposition and by the annealing. Therefore we propose to study the effect of these deposition parameters on the thin films quality for a fixed growth time of $t_D = 60$ min.

3.1.2. Effect of the pH of the solution

In the following paragraph, TA concentration is 0.20 M and deposition time is 60 min. Experiments are realized for...
two values of pH: 2.35 and 2.45. The pH is varied through the addition of acetic acid (as complexing agent) to the reaction mixture. Explored pH range is very limited and determined by deposition conditions leading film growth. On the other hand, indium (III) ion is very acid and leads in aqueous solution to undesirable hydrolysed species. Therefore, acetic acid is added to the reaction mixture in order to reduce the pH, and to favour the TA hydrolysis instead of the formation of uncontrolled hydrolysed species, as well as to complex the In$_3^+$ ions.

Fig. 2 presents the XRD patterns of films deposited on glass substrates, before (1) and after (2) annealing treatment.

At pH = 2.35, the deposited films present the β-In$_2$S$_3$ phase only (Fig. 2-1a). At pH = 2.45, the films are formed by a mixture of different phases (Fig. 2-1b).

As previously mentioned, annealing improves the layer crystallinity. For pH = 2.35, the film crystallography is preferentially oriented in the (440) direction (Fig. 2-2a). For pH = 2.45, films are essentially formed by the In$_6$S$_7$ compound, preferentially oriented towards (106). From these results, we conclude that the best-tested pH value is 2.35.

### 3.1.3. Effect of the thioacetamide concentration

The effect of the thioacetamide concentration was made with glass and SnO$_2$/glass substrates. Experiments were carried out at 70 °C, and films were deposited from an acidic bath (pH = 2.35) with $t_D = 60$ min.

<table>
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<th>[TA] (M)</th>
<th>0.10</th>
<th>0.15</th>
<th>0.20</th>
<th>0.25</th>
<th>0.35</th>
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<tr>
<td>β-In$_2$S$_3$ (a)</td>
<td>(440)</td>
<td>(440)</td>
<td>(440)</td>
<td>(440)</td>
<td>(311)</td>
<td>(440)</td>
</tr>
<tr>
<td>β-In$_2$S$_3$ (b)</td>
<td>(610)</td>
<td>(440)</td>
<td>(440)</td>
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<td>(440)</td>
</tr>
<tr>
<td>In$_6$S$_7$ (a)</td>
<td>(214)</td>
<td>– – – – –</td>
<td>(410)</td>
<td>(304)</td>
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<tr>
<td>In$_6$S$_7$ (b)</td>
<td>– – – – –</td>
<td>(200), (110), (301)</td>
<td>SnO$_2$; and (211) to In$_2$S$_2$ phase.</td>
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Table 1

| Preferential orientations of layers CBD-deposited on glass for different values of TA concentrations: (a) before, (b) after annealing under nitrogen at 400 °C during 1 h, and (–) absent phases, $t_D = 60$ min, pH = 2.35. |

Fig. 4. XRD spectra of films, CBD-prepared on SnO$_2$/glass with pH = 2.35, $t_D = 60$ min and for various TA concentrations: (1) 0.15 M, (2) 0.30 M, (3) 0.50 M and (4) 0.65 M. (a) Before and (b) after annealing at 400 °C under nitrogen; the lines labelled (610), (440), (551), (111) corresponds to β-In$_2$S$_3$ phase; (214), (313), (014), (106), (410), (120) to In$_6$S$_7$; (200), (110), (301) to SnO$_2$; and (211) to In$_2$S$_2$ phase.
3.1.3.1. Case of glass substrates. In this study, TA concentration is varied from 0.10 to 0.45 M and indium (III) concentration is kept constant. XRD pattern of the layers is reported in Fig. 3.

The XRD pattern of the films is shown in Fig. 3, which exhibited a crystallinity improvement after heat treatment. However, for TA concentration ranging between 0.10 and 0.25 M, films are formed only by the $\beta$-In$_2$S$_3$ compound, and their preferential orientation depends on the TA concentration value. The film crystal structure corresponds to the cubic structure preferentially oriented towards: (610) at [TA] = 0.10 M (Fig. 1-2b), (440) at [TA] = 0.15 M (Fig. 3-1b), [TA] = 0.20 M (Fig. 2-2a) and 0.25 M (Fig. 3-2b). At higher thioacetamide concentration, films are not well crystallized, after annealing, they contain the unwanted In$_6$S$_7$ phase (Fig. 3, patterns 3–4). Analysis results are summarized in Table 1.

3.1.3.2. Case of SnO$_2$/glass substrates. The TA concentration is varied from 0.15 to 0.65 M. The XRD spectra of the obtained films are presented in Fig. 4. Even though samples showed better crystallinity, the presence of the unwanted phases such as In$_6$S$_7$ and In$_2$S$_2$ materials should be noted. For [TA] = 0.15 M, after annealing, samples are essentially formed by the $\beta$-In$_2$S$_3$ phase, preferentially oriented according to the (610) direction, as well as the presence of In$_6$S$_7$ (214) and In$_2$S$_2$ (211) as a secondary phase (Fig. 4-1b). However, the In$_6$S$_7$ peak intensity increases to the detriment of the $\beta$-In$_2$S$_3$ phase if the TA concentration value increases. In fact, for [TA] = 0.65 M, after heat treatment, layers are essentially formed by the In$_6$S$_7$ phase with (214) as preferential orientation (Fig. 4-4b).

From the TA concentration effect study, we conclude that the structure state of the indium sulphide thin films CBD-prepared depends on the TA concentration as well as on the substrate nature.
3.2. SEM analysis

SEM gives microscopic information of the surface topography. In this work, we have used this technique to study the influence of growth parameters on film homogeneity and surface roughness.

Fig. 5 shows surface topography of films deposited on glass for various deposition times and for TA concentration equal to 0.10 M. Relatively well distributed fibrous structures are present at the films surface prepared at \( t_D = 45 \) min and \( t_D = 90 \) min before annealing (Fig. 5a and c). Films grown on SnO\(_2\)/glass substrate with \([TA] = 0.15\) M (Fig. 6a) present large lumps. There is a similarity in the surface topography between films deposited with \([TA] = 0.15\) and \(0.30\) M (Fig. 6a and b), whereas films deposited with \([TA] = 0.65\) M (Fig. 6c) present some fibrous structure. These different structures are attributed to the different phases as shown by XRD analysis. Fibrous structure corresponds to the \(\beta\)-In\(_2\)S\(_3\) phase and the large “lumps” to the In\(_6\)S\(_7\) phase.

Figs. 7 and 8 for layers prepared by CBD and grown on glass and on SnO\(_2\)/glass substrates, respectively. Annealing improves surface roughness of the films (Figs. 7b and 8b). However, Fig. 8b shows large, angular crystals, which can be explained by the effect of the substrate nature. In fact, the SnO\(_2\) substrate was used to achieve the ohmic contact in the CuInS\(_2\)/\(\beta\)-In\(_2\)S\(_3\) solar cells where CuInS\(_2\) is the absorber material and \(\beta\)-In\(_2\)S\(_3\) the optical window.

Film surface homogeneity and roughness is correlated to crystal structure analysis. The surface morphology we observed is consistent with results reported in Ref. [13].

4. Conclusion

We have investigated structural and morphological properties of indium sulphide thin layers with the scope of photovoltaic structure growth such as CuInS\(_2\) (p)/\(\beta\)-In\(_2\)S\(_3\) (n).

Indium sulfide thin films were elaborated in acidic medium by CBD, using thioacetamide as sulfur precursor.

In this work, we have studied the influence of the deposition time, the pH of the precursor solution and the precursor concentration, on the films properties.

Films grown on glass slides using \([TA] = 0.10\) M, pH = 2.35 and \( t_D = 60\) min as deposition conditions and annealed were well crystallized, with good surface homogeneity and roughness. Whatever the deposition conditions, all samples elaborated on SnO\(_2\)/glass substrate contain the unwanted In\(_6\)S\(_7\) phase even after annealing treatment. Nevertheless, all annealed thin films show an improvement of their structural and morphological state.

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References