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Effect of annealing on structural and electrical properties of ZnO and In$_2$S$_3$:Al thin layers

N Jebbari$^a$, M Ajilia, C Guasch$^b$, N Kamoun$^a$ and R Bennaceura$^a$

$^a$Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis 2092, le Belvédère, Tunis, Tunisie.

$^b$Laboratoire d’Analyse des Interfaces et de Nano physique, Université Montpellier II, Sciences et techniques de Languedoc, case courrier 062, Place Eugène bataillon 34095 Montpellier cedex 05 France

E-mail: neila2710@yahoo.fr

Abstract. Thin films of ZnO and In$_2$S$_3$:Al are deposited on Pyrex substrates by spray technique. Structural and electrical properties of ZnO and β-In$_2$S$_3$:Al compounds were studied using X Ray Diffraction (XRD), (MEB) and the Vander Pauw method before and after annealing. The X-rays revealed that, ZnO and In$_2$S$_3$:Al were well crystallized respectively in the hexagonal and cubic structure. The main orientations of ZnO were (101), (100) and (110). The (101) direction is the preferentially one. The annealing favors the preferential peak crystallization with a reduction of the grains size and the thickness layer. The β-In$_2$S$_3$ contain Aluminum inclusion by introducing the ratio x = [Al$^{3+}$]/[In$^{3+}$] in sprayed solution. X-ray diffraction spectra of In$_{2-x}$Al$_x$S$_3$ thin layer, realized for the value of $x$ equal to 0.20, show well-defined peaks of (311), (400), (511), and (440) principal orientations corresponding to cubic structure of β-In$_2$S$_3$. For In$_2$S$_3$:Al, we note that the annealing increase the intensity of all peaks with an increase of the grains size and the thickness layer. Besides, thanks to the determination of the resistance from which we calculated resistivity, we note that the annealing increase conductivity of β-In$_2$S$_3$:Al and decrease it for ZnO.

1. Introduction

Zinc oxide ZnO and β-In$_2$S$_3$ are the most important materials in solar cells, optical sensors and optoelectronic devices due to their high stability [1,2].

β-In$_2$S$_3$ can be classified as mid-band gap semiconductors (2.5 eV [2]) as compared to materials such as ZnO (3.2 eV, wide band gap [1]).

ZnO is a semiconductor n-type, crystallizes following the hexagonal structure. It is characterized by a low reflection and high value transmission (≈ 80%) [1]. On the other hand, doping of ZnO thin films with indium helps to improve conductivity [1].

The β-In$_2$S$_3$ material is a semiconductor type n. It is characterized by a high absorption coefficient [3]. Doping of β-In$_2$S$_3$ thin films with aluminium helps to increase the band gap energy

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1 To whom any correspondence should be addressed.
[4], one can deduce that concentration value of the ratio $z = [\text{Al}^{3+}] / [\text{In}^{3+}] = 0.2$ is the maximum for which the layer is well crystallized.

In this paper thin films of ZnO, ZnO:In and $\beta$-In$_2$S$_3$ are deposited on Pyrex substrates by spray technique. Structural and electrical properties of these compounds were studied using X Ray Diffraction (XRD), (MEB) and the Vander Pauw method before and after annealing to improve their properties.

2. Films elaboration
All compounds of cell are deposited using spray pyrolysis techniques. Optimum parameters fabrication of ZnO:In and $\beta$-In$_2$S$_3$:Al are reported respectively in tables 1, 2. These layers are deposited on Glass substrate.

Table 1: Optimum conditions for the spray deposited ZnO:In [1,5] films.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Value or suitable item</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item Solvent</td>
<td>Propanol-2 and H$_2$O</td>
</tr>
<tr>
<td>Solution concentration</td>
<td>$[\text{In}^{3+}] / [\text{Zn}^{2+}] = 0.03$</td>
</tr>
<tr>
<td>Precursors</td>
<td>(CH$_3$CO)$_2$Zn$_2$H$_2$O</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>470 °C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Compressed air</td>
</tr>
<tr>
<td>Distance sample-Nozzle</td>
<td>25 cm</td>
</tr>
<tr>
<td>Rate of spray</td>
<td>20 ml/min</td>
</tr>
<tr>
<td>Time of spray</td>
<td>30 min</td>
</tr>
</tbody>
</table>

Table 2: Optimum conditions for the spray deposited $\beta$-In$_2$S$_3$:Al [5] films.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Value or suitable item</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item Solvent</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>Solution concentration</td>
<td>$[\text{In}^{3+}] / [\text{S}^{2-}] = 0.50$</td>
</tr>
<tr>
<td>Precursors</td>
<td>InCl$_3$, SC(NH$_2$)$_2$</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>340 °C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Compressed air</td>
</tr>
<tr>
<td>Distance sample-Nozzle</td>
<td>30 cm</td>
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<tr>
<td>Rate of spray</td>
<td>5 ml/min</td>
</tr>
<tr>
<td>Time of spray</td>
<td>30-60 min</td>
</tr>
</tbody>
</table>
3. Annealing effect on structural properties

3.1. Study of ZnO thin layer

The X-ray diffraction of ZnO thin films deposited on Glass and doped with the Indium concentration equal to 3% \(y=\frac{[\text{In}^{3+}]}{[\text{Zn}^{2+}]}=3\%\), show well crystallinity of (100), (002) and (101) directions, indicating an hexagonal structure (Fig. 1.a). Variation of the ratio \(y\) is studied by M. Amlouk and all [2]. They prove that \(y=3\%\) correspond to the maximum of conductivity and the better crystallinity of (101) direction. The annealing of ZnO:In in air, at \(T = 500 \, ^\circ\text{C}\) for 15 minutes (fig1a) increase the intensity of (101) preferential peak (fig1b).

![Figure 1. X-ray spectra of ZnO:In thin films deposited on Glass substrate, (a) before annealing and (b) after annealing.](image)

Fig. 2 shows that the width at half peak height of (101) direction increases after annealing despite the increased intensity. This result means that grain size zinc oxide decrease with annealing in air.

![Figure 2. Annealing effect on structure of ZnO:In (a) before annealing and (b) after annealing.](image)
Visualization in a Scanning Electron Microscope SEM of ZnO:In surface films, shows that these layers are formed by agglomeration of semi-spherical crystallites (fig. 3 a and b) whose size decreases after annealing Fig. 3b.

![Figure 3. S.E.M images of ZnO:In films sprayed on glass substrate ((a) before annealing and (b) after annealing)](image)

Heat treatment also affects the thickness of the ZnO thin layer. In fact it decreases from 1.7μm to 1.3μm (Fig 4.a and b).

![Figure 4. Thickness from S.E.M images of ZnO:In films sprayed on glass substrate ((a) before annealing and (b) after annealing)](image)

3.2. Study of β-In<sub>2</sub>S<sub>3</sub> thin layer

The indium sulfide β-In<sub>2</sub>S<sub>3</sub>:Al crystallizes in the cubic structure. This layer is characterized by the directions (111) (311) (400) (511) and (440) (Fig 5). The principal peak is (311) before annealing it become (400) and the intensity of all directions increase after annealing in air at T = 500° C for 15 minutes (fig 5.b).

After annealing we remark a shift of the peaks (311) and (400) to increasing angles is presented respectively in Fig. 6 and 7. This phenomenon can be explained by the existence of a certain quantity of aluminum in the amorphous way and after annealing it substitute the indium resulting in compression of the lattice and in increasing of intensity. Moreover, the mean width at half height of these peaks decreases so the grain size increases after annealing.
Figure 5. X-ray spectra of $\beta$-In$_{2-x}$Al$_x$S$_3$ thin films deposited on Glass substrate, ((a) before annealing and (b) after annealing).

Figure 6. Annealing effect on structure of In$_{2-x}$Al$_x$S$_3$ ((a) before annealing and (b) after annealing).

Figure 7. Annealing effect on structure of ZnO:In ((a) before annealing and (b) after annealing).
The SEM image shows that the thin films of $\beta$-$\text{In}_{2-x}\text{Al}_x\text{S}_3$ have a relief relatively compact and homogeneous (Fig. 8.a). After annealing the number of rounded small clutters increase.

Annealing affects the thickness of the $\beta$-$\text{In}_{2-x}\text{Al}_x\text{S}_3$ thin layer. It decreases from 1.14µm to 1.83µm (Fig. 9 (a) and (b)).

4. Annealing effect on electrical properties

Thickness ($e$) of thin films is directly related to the square resistance ($R$) of materials by: $R = \rho/e$ [6], where $\rho$ is the resistivity of material. So the increase of thickness decreases resistance $R$. Annealing of ZnO and In$_2$S$_3$ layers decrease the thickness of the ZnO and increase the thickness of In$_2$S$_3$ layer. So the resistance increase for ZnO and decrease for In$_2$S$_3$ after annealing, electrical study result is reported in Table 3 and table 4.

5. Conclusion:
The elaboration by Spray technique is accompanied by air inclusion in the crystalline layer. The annealing eliminates all these air cavities and contribute to the recrystallisation of layer. These two phenomena have opposite effect. So the influence of annealing on thin layers varied from one element to other. For ZnO the thickness is reduced that’s mean the first phenomenon is the most important. For $\beta$-$\text{In}_2\text{S}_3$, the second phenomenon is predominant and annealing improves the crystallinity, increases the thickness and the size of crystallites, the conductivity and introduce compression stress.
References: