Photothermal properties of Al doped In$_2$S$_3$

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ABSTRACT

Photothermal deflection is carried out in order to investigate thermal and optical properties of Al doped In$_2$S$_3$. The influence of thermal annealing on its gap energy as well as its thermal properties is revealed. In this way, we notice that thermal properties are enhanced and the gap energy is reduced. These features are probably due to the improvement of the crystalline structure of the sample.

Index terms— photothermal deflection, thermal conductivity, diffusivity, gap energy,

1. INTRODUCTION

In$_2$S$_3$ is one of the most important materials in solar cells, optical detectors and optoelectronic devices, due to its high stability [1], wide band gap (~ 2.5 eV) and high absorption coefficient [2].

Growth of thin layer indium sulphide has been carried out by different methods such as MOCVD, spay pyrolisis and chemical bath deposition (CBD) [3-5]. The characteristics of the obtained film depends closely to the fabrication method and can be changed by introducing of doping impurities such as Aluminium which is used to improve electrical conductivity and to adjust the band gap of the film.

Structural, optical and electrical techniques have been used for characterization of In$_2$S$_3$ films. Among all the techniques used for thin layer characterization, photothermal deflection [6-9] is one of the mostly used.

In this work, photothermal deflection is used to investigate the influence of Al doping on thin layer β-In$_2$S$_3$ grown by CBD on glass substrate. Modifications in optical absorption, band gap energy and thermal properties are revealed.

2. EXPERIMENTAL DETAILS

The experimental device [6] is shown in Fig. 1; monochromatic light beam out coming of a monochromator illuminated with 250 W halogen lamp, and modulated with a mechanical chopper at a frequency $F$ is focused on the sample surface. The absorption of the pump beam by the sample generates a thermal wave that propagates in the sample and in the deflecting fluid (CCl$_4$ or air), leading to the deflection of a probe laser beam (He-Ne) skimming the sample surface. This deflection is detected with a position photodetector linked to a lock in amplifier giving us the amplitude and phase of the measured PDS signal. Then, the normalized amplitude is obtained from the ratio of the amplitude measured for a given semiconductor sample to the reference amplitude obtained with a carbon black sample.

![Figure 1. Experimental setup](image)

3. RESULTS AND DISCUSSION:

3.1. Determination of thermal properties:

Three films of In$_2$S$_3$ grown by CBD on glass substrate have been investigated. The first (S1) is undoped and the two others (S2 and S3) are Al doped (20%). One of the doped layers (S3) is annealed at 500°C.

Samples are irradiated with monochromatic radiation while varying the modulation frequency $F$. The obtained experimental phase and amplitude of the photothermal signal versus square roots of frequency are shown on figures 2 and 3. These curves should be compared to the correspondent theoretical ones obtained from a known one-dimension model obtained by resolving heat equation in the sample and the surrounding fluid, this model is described elsewhere [7, 8].

For high modulation frequency, the amplitude and the phase decrease following linear variations. This drop is closely related to thermal properties of the deflecting medium (air) and the distance $x_0$ between
probe beam and sample surface. The comparison between the slopes of experimental curves to theoretical ones leads to $x_0 = 115 \, \mu m$.

In the other hand, the phase presents a maximum at a frequency $F \approx 31$ Hz for the undoped layer. This maximum shifts toward lower frequencies for the doped samples. From the comparison between experimental maximum and theoretical one, we have determined the thermal diffusivity of each layer (Table 1). We notice that thermal diffusivity is reduced by Al doping, this is probably due to phonon scattering on the Al atoms and the doping-induced defects. However it is enhanced by annealing at 500°C, as the crystalline structure is improved.

Furthermore, thermal conductivity is also determined while fitting the experimental curves to theoretical ones as shown in figure 2 and 3, the obtained values are shown on Table 1. We notice that conductivity increases after Al doping because the electronic contribution to thermal conduction is improved by the doping-induced free carriers. For annealed sample, conductivity is improved by the same way as diffusivity.

3.2. Determination of the optical spectra

Here the modulation frequency is fixed at 11 Hz, and the wavelength of the pump beam is varied, from visible to near infra-red range. The experimental phase is almost constant in the whole spectral range, however the amplitude (figure 4) shows, after a saturation zone, an important drop of nearly two decades. The saturation corresponds to high absorption for energies above the band-gap. The amplitude decreases while the sample becomes transparent. In the sub-band gap region, the amplitude saturates at different minimum values for each sample.

![Figure 2](image2.png)

**Figure 2.** Phase of the experimental photothermal signal versus $F^{1/2}$ for the three In$_2$S$_3$ samples S1 (squares), S2 (circles) and S3 (triangles), fitted with theoretical curves (lines).

![Figure 3](image3.png)

**Figure 3.** Amplitude of the experimental photothermal signal versus $F^{1/2}$ for the three In$_2$S$_3$ samples S1 (squares), S2 (circles) and S3 (triangles), fitted with theoretical curves (line).

![Figure 4](image4.png)

**Figure 4.** Amplitude of the experimental photothermal signal versus wavelength for the three In$_2$S$_3$ samples.

The comparison of experimental curves of amplitude versus wavelength to theoretical amplitude versus absorption coefficient permits to obtain the optical absorption spectrum for the three samples shown on figure 5. We notice that doped sample (before annealing) has a relative higher absorption in the transparency region, which can be due to the great amount of defects and free carriers. In this region, the annealed sample has almost is more transparent than doped and not annealed sample. Indeed, annealing improves the crystalline structure and reduces the amount of doping-induced defects. However, the absorption edge near the gap is slightly shifted toward lower energies with the same quantity as for not annealed sample. This is certainly due to the band gap shrinkage by the donor level induced by Al doping.
In the other hand, we have used the absorption spectra in order to determine band gap energy $E_g$ for each sample. For this purpose, we use the Tauc method \[10\] which suppose that the curve $(\alpha E)^2$ versus energy $E$ should have linear behaviour above the gap. In figure 6, we have drawn this curve for undoped In$_2$S$_3$ and we have obtained $E_g = 2.47$ eV. For the other samples, we have obtained a shift of the gap energy to 2.35 eV for the doped one then a weak increase to 2.41 eV after annealing. This lowering of $E_g$ is easily explained by the band gap shrinkage due to doping.

![Figure 6. Determination of the gap energy of undoped In$_2$S$_3$ from the curve $(\alpha E)^2$ versus pump beam energy $E$.](image)

**Table 1.** thermal properties and gap energy of three samples of In$_2$S$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness ($\mu$m)</th>
<th>Thermal diffusivity ($m^2s^{-1}$)</th>
<th>Thermal conductivity ($Wm^{-1}K^{-1}$)</th>
<th>Gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1.5</td>
<td>$4\times10^{-6}$</td>
<td>4</td>
<td>2.47</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>$2.3\times10^{-6}$</td>
<td>9</td>
<td>2.37</td>
</tr>
</tbody>
</table>

4. CONCLUSION:

Doped and undoped In$_2$S$_3$ are investigated with two configuration of photothermal deflection. Thermal properties are obtained while varying the modulation frequency, however optical spectrum is obtained while changing the pump beam wavelength at a fixed frequency. The results show that thermal conductivity is clearly improved by doping, but this is not the case for diffusivity where small reduction is obtained. These two parameters are enhanced after annealing. Furthermore, a bandgap shift is induced by doping then reduced after annealing.

5. REFERENCES: