Influence of the triethanolamine concentration on the optical properties of tin sulphide thin films by the Photothermal Deflection Spectroscopy

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Abstract. The optical properties of Tin sulphide thin films grown on a glass substrate by chemical bath deposition were investigated by the Photothermal Deflection Spectroscopy. The experimental normalised amplitude curves of the photothermal signal versus wavelength are compared to the corresponding theoretical ones versus optical absorption coefficient in order to determine the optical absorption spectrum. Then using the Tauc law, one can deduce the energy gap. The influence of the triethanolamine concentration (TEA) in the solution bath on the optical properties was successfully studied.

1. Introduction
Tin sulphide material is a IV-VI semiconductor with a direct band gap. Within the last five years SnS films have been attracting considerable attention due to their interesting properties and potential application; it could be used for fabrication of optoelectronic devices such as electro-optical modulator and absorber layers in hetero-junction photovoltaic structures of the type: CdS (n)/ SnS (p) \cite{1}. In this study, tin sulphide thin films have been grown by chemical bath deposition (CBD) which is a very attractive method due to the possibility of large area deposition at low cost. The aim of this work is to determine the optical absorption spectrum and the energy gap of tin sulphide thin films deposited on glass substrate as a function of Triethanolamine (TEA) concentration in the solution bath. Several methods for optical properties measurement have been developed such as spectroscopic ellipsometry \cite{2}, transmission and Photoluminescence spectroscopy \cite{3}, etc. The knowledge of the optical absorption spectrum and/or the gap energy is more and more required in many industrial fields; these are among the most important parameters when heat transfer processes are involved especially in the PDS method \cite{4-6} (Photothermal Deflection Spectroscopy) used in this work. The advantage of this method compared to other spectroscopic methods is that it allows determining directly the optical absorption coefficient in a narrow energy band near the energy gap.

2. Theoretical model
The theoretical model is built on the resolution of the one dimension heat equation in the different media, fluid and sample and backing and by assuming the continuity of the temperature and the heat flow at the different interfaces $z = 0$ and $z = -l$, (Figure 1). The sample fixed on a backing material and
surrounded by a fluid is illuminated perpendicularly by a modulated light pump beam coming from a halogen lamp (uniform heating case). We assume that both fluid and backing are optically non-absorbing media for the incident light. The obtained expression of the periodic elevation temperature at the sample surface $T_0$ [7] given by Eq (1) will permit the calculation of the probe beam deflection $\psi$ [7] given by Eq (2).

$$T_0 = -E \left[ (1 - r)(1 + b) \exp (\sigma_s l_s) - (1 + r)(1 - b) \exp (-\sigma_s l_s) + 2(r - b) \exp (-\alpha l_s) \right] / [(1 + g)(1 + b) \exp (\sigma_f l_f) - (1 - g)(1 - b) \exp (-\sigma_f l_f)]$$

(1)

Where $E = A / (\alpha^2 - \sigma_s^2)$, $b = K_s \sigma_s / K_f \sigma_f$, $g = K_f \sigma_f / K_s \sigma_s$ and $r = \alpha / \sigma_s$.

$\sigma_i = (1 + j) / \mu_i$, $\mu_i = (D_i / \pi \nu)^{1/2}$

$\alpha$ is the optical absorption coefficient of the sample and $\nu$ is the modulation frequency. $K_i$, $D_i$, and $\mu_i$ are respectively the thermal conductivity, the thermal diffusivity and the thermal diffusion length of the $i$ medium.

Here the index $i$ take the subscripts $s, f$ and $b$, respectively, for the sample, fluid and backing.

$$\Psi(z,t) = -L / n_0 \frac{dn}{dT_f} \sqrt{\frac{\pi}{\mu_f}} \left| T_0 \right| \exp \left( -z_0 / \mu_f \right) \exp \left[ j \left( \theta + \frac{\pi}{4} \frac{z_0}{\mu_f} \right) \right] \exp (j \omega t)$$

(2)

Where $z_0$ is the distance between the probe beam axis and the sample surface, $\left| T_0 \right|$ and $\theta$ are respectively the amplitude and phase of the sample’s surface periodic temperature elevation.

3. Experimental set-up

The experimental set-up is described in Figure 2. The sample of SnS sulphide thin films (0.8µm thick) used in this study was grown on a glass substrate by chemical bath deposition (CBD). The sample absorbs the monochromatic light coming from a halogen lamp of power 250W after its passage through a monochromator of type Jobin Yvon HR250. The pump light beam is modulated thanks to a mechanical chopper of type SR540 and then focused on the sample surface. An He–Ne Laser probe beam of wavelength 632.8 nm skimming the sample surface at a distance $z_0$ of average 60µm is deflected. A photodetector of four quadrants (QD50T) connected to a lock-in amplifier (EG&G5210) measures the deflection of the probe beam. Via the intermediary of IEEE bus, a PC microcomputer sets the monochromatic light wavelength and reads the amplitude and phase of the signal from the lock-in and finally draws their variation according to wavelength at a fixed modulation frequency. We note that in our case the fluid and the backing media are respectively paraffin oil and glass whose thermal conductivity and thermal diffusivity are, respectively, $K_f = 0.16 \ W.m^{-1}.K^{-1}$, $D_f = 7 \times 10^{-8} \ m^2.s^{-1}$ and $K_b = 1.5 \ W.m^{-1}.K^{-1}$, $D_b = 6 \times 10^{-7} \ m^2.S^{-1}$.

4. Experimental results

In this section we plot the amplitude and phase variation of the photothermal signal versus wavelength in experimental way and versus absorption coefficient in theoretical one at a fixed modulation frequency value equal to 8 Hz in order to relate in second time these two parameters and determine the gap energy of SnS thin films.
4.1. Determination of the optical absorption spectrum

From Figure 3 we remark that the theoretical amplitude variation according to the optical absorption coefficient saturates respectively for high \((\alpha > 10^6 \text{ m}^{-1})\) and low \((\alpha < 10^2 \text{ m}^{-1})\) optical absorption coefficient values which explains the insensitivity of the “Mirage Effect” in this two regions. The region where the amplitude vary with the optical absorption coefficient will permit us to deduce the optical absorption spectrum by comparing point by point the normalised experimental and corresponding theoretical amplitude variation as shown on figure 3.

So we determine for each wavelength value the corresponding absorption coefficient one. The obtained spectrum is shown on figure 4. On figure 5-a are represented experimental curves giving the variations of the normalized amplitude according to wavelength of SnS thin films at different TEA values. The difference between the two curves reflects the difference between the optical properties of the samples. We note that the phase variation is practically zero because of the low thickness \((0.8 \mu \text{m})\) of SnS layer. So only the amplitude variation was exploited.

4.2. Determination of the band gap shift

The gap energy is obtained from the absorption spectrum by using the Tauc law for energies above the gap: 
\[(\alpha E)^n = \beta(E - E_g),\]
where \(\beta\) is a constant, \(E_g\) is the optical gap energy between bottom of the conduction band and top of the valence band, \(E = h\nu\) is the photon energy, \(n = 2\) for direct transition and \(n=1/2\) for indirect transition.
Figure 3. Experimental (a) curves giving the variations of the amplitude according to wavelength and corresponding theoretical one (b) according to absorption coefficient of SnS thin films at TEA= 13 M.

Figure 4. Optical absorption spectrum versus photon energy E of SnS thin films at different TEA values.

Figure 5. Experimental curves giving the variations of the normalized amplitude according to wavelength of SnS thin films at different TEA values (a) and $(\alpha E)^2$ versus photon energy E near the band gap of SnS thin films at different TEA values (b).
The variation of \((\alpha E)^n\) versus photon energy \(E\) is shown on Figure 5-b. The extrapolation of the straight line to zero absorption coefficient \((\alpha=0)\) led to an estimate of the band gap energy \((E_g)\) value. The two samples gap energy values so deduced are reported in Table 1.

| TEA concentrations | Gap energy (ev) |
|--------------------|-----------------|
| 12.5 M             | 2.16            |
| 13 M               | 1.93            |

5. Conclusion

In this work, we have determined with good precision, the optical absorption coefficient spectrum and the gap energy of SnS thin films at different TEA values using the Photothermal Deflection Spectroscopy (PDS).

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