Investigation of optical properties of the sulfosalt new absorber Sn$_2$Sb$_2$S$_5$ thin films using Photothermal Deflection Spectroscopy

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Abstract. The thin Sn$_2$Sb$_2$S$_5$ films which are new absorber material useful for photovoltaic cells are studied in this paper by the photothermal deflection spectroscopic method. Our study consists to draw the experimental normalized amplitude and phase of the photothermal signal versus wavelength at a fixed modulated monochromatic light pump beam frequency. The phase curves are independent of wavelength which is predicted theoretically. However the amplitude ones show saturated regions for high and low absorption coefficient and great variations in the vicinity of the energy gap. These curves show two energy gaps which may be explained by the coexistence of two phases. By comparison of the experimental and theoretical normalized amplitude of the PDS signal one can deduce the optical absorption coefficient and then the energy gaps. The obtained values of the energy gaps are in good agreement with those obtained by reflectivity and transmission measurements.

1. Introduction
Thin semiconductors films have been extensively studied in recent year, owing to their novel physical properties as well as their wide range of potential applications especially in photovoltaic solar cells. The Sn$_2$Sb$_2$S$_5$ thin semiconductor film which is a new absorber material appears to be serious candidate in this field [1]. In this work, we have studied its optical properties (the optical absorption spectrum and the energy gap) using the Photothermal Deflection Spectroscopy (PDS) [2-4] which has proved to be a useful technique to investigate the optical properties of semiconductor samples either in form of bulk components [5] or coatings [6]. The films of Sn$_2$Sb$_2$S$_5$ studied here are deposited on unheated glass substrate (at the room temperature) by thermal vacuum evaporation. The pressure during the evaporation was maintained at $10^{-5}$ Torr.

2. Experimental set-up
The experimental set-up is described in Figure 1. The films of Sn$_2$Sb$_2$S$_5$ (0.4 µm thick, the length and the width are respectively 10 mm and 8 mm) absorb 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. A He–Ne Laser probe beam of wavelength 632.8 nm skimming the sample surface at a
distance \( z_0 \) of average 60\( \mu \)m 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 \( K_b = 1.5 \) \( W.m^{-1}.K^{-1} \), \( D_b = 6 \times 10^{-7} \) \( m^2.S^{-1} \).

3. Experimental results

In this section we plot the amplitude variation of the photothermal signal versus wavelength in experimental way and versus optical absorption coefficient in theoretical one at a fixed modulation frequency value equal to 8 Hz in order to relate these two parameters and determine the energy gaps of the \( \text{Sn}_2\text{Sb}_2\text{S}_3 \) thin films. On figure 2 is represented the experimental curve giving the variations of the normalized amplitude according to wavelength of \( \text{Sn}_2\text{Sb}_2\text{S}_3 \) thin films. From this curve one can clearly remark the existence of three saturated zones which may be attributed to the coexistence of two phases which are the amorphous and crystalline one [1], so two optical transitions gap for the material. This observation was confirmed by another spectroscopic technique based on the study of optical transmittance and reflectance [1].

3.1. Determination of the optical absorption spectrum

On figure 3-a is represented the experimental normalized amplitude of the photothermal deflection signal versus wavelength at a fixed modulation frequency equal to 8 Hz for \( \text{Sn}_2\text{Sb}_2\text{S}_3 \) thin semiconductor films in the vicinity of the first phase energy gap. One can notice from this curve that the normalized amplitude is only sensitive to wavelength in the vicinity of the energy gap and saturates elsewhere.
From figure 3-b we remark that the theoretical amplitude variation \([5, 6]\) according to the optical absorption coefficient saturates respectively for high \((\alpha > 10^6 \text{ m}^{-1})\) and low \((\alpha < 10^4 \text{ m}^{-1})\) optical absorption coefficient values which explains the insensitivity of the “Mirage Effect” in these 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 amplitude and the corresponding theoretical one as shown on figure 3; so we determine for each wavelength value the corresponding optical absorption coefficient. Make the same way as above (figure 4); we can determine the optical absorption spectrum for the second phase of Sn\(_2\)Sb\(_2\)S\(_5\) thin films. The deduced optical absorption spectra are shown on figure 5-a. The experimental phase of the photothermal signal as was expected is independent of wavelength because the thickness of the layer which is 0.4 \(\mu\text{m}\) is much smaller than the thermal diffusion length.
Experience phase 2

Figure 4. Experimental (a) curves giving the variations of the normalized amplitude according to wavelength and corresponding theoretical one (b) according to absorption coefficient of Sn$_2$Sb$_2$S$_5$ thin films in the vicinity of the second phase energy gap.

3.2. 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. The variations of $(\alpha E)^n$ versus photon energy $E$ for Sn$_2$Sb$_2$S$_5$ thin films are 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. Given the dispersion of the experimental points we can draw two limit straight lines whose intersections with the axis of energies will permit to deduce the uncertainty on the energy gap $E_g$. The two phases gap energy values so deduced are reported in Table 1.

Figure 5. (a) Optical absorption spectrum versus photon energy $E$ of Sn$_2$Sb$_2$S$_5$ thin films and (b) $(\alpha E)^2$ versus photon energy $E$ near the band gap of Sn$_2$Sb$_2$S$_5$ thin films
Table 1. Experimental Gap energy values of Sn$_2$Sb$_2$S$_5$ thin films.

| Samples                  | Gap energy (eV) | Gap energy (eV)  |
|--------------------------|-----------------|------------------|
| Sn$_2$Sb$_2$S$_5$ (phase 1) | 1.77 ± 0.05  | 1.775            |
| Sn$_2$Sb$_2$S$_5$ (phase 2) | 2.18 ± 0.02  | 2.18             |

4. Conclusion
In this work, we have determined with good precision, the optical absorption coefficient spectrum and the gap energy of two phases Sn$_2$Sb$_2$S$_5$ thin films using the PDS technique. The deduced energy gaps values are in good agreement with those obtained by transmission and reflectivity methods.

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