# INVESTIGATION OF THERMAL PROPERTIES OF SULFOSALT $SnSb_2S_4$ THIN FILMS BY THE PHOTOTHERMAL DEFLECTION TECHNIQUE

I. Gaied [1], A. Gassoumi [2], M. Kanzari [2] and N. Yacoubi [1]*
[1] *Institut Préparatoire Aux Etudes d'Ingénieur de Nabeul IPEIN Merazka 8000 Nabeul-Tunisie*
[2] *ENIT BP 37, le belvédère 1002 Tunis-Tunisia*
imen.gaied@ipein.rnu.tn
yacoubi20042003@yahoo.fr

## ABSTRACT
The thermo-physical properties of sulfosalt $SnSb_2S_4$ thin films deposed at two different glass substrate temperatures by Thermal Evaporation were investigated using the Photothermal Deflection method in its uniform heating case instead of traditionally a non uniform heating one. The advantage of applying this method in this way lies in its simplicity and its sensitivity to both thermal conductivity and thermal diffusivity. These films undergo abrupt changes in thermal properties on both sides of the transition temperature of 140°C which may be show the influence of the substrate temperature on thermal properties of the material.

## NOMENCLATURE

| | | | | | |
|---|---|---|---|---|---|
| $\nu$ | Modulation frequency | (Hz) | $K_i$ | Thermal conductivity of i media | ($Wm^{-1}K^{-1}$) |
| $n_0$ | Refractive index of the fluid | | $D_i$ | Thermal diffusivity of i media | ($m^2S^{-1}$) |
| $\phi$ | Phase of the photothermal deflection | (rad) | $\alpha$ | Sample's optical absorption coefficient | ($m^{-1}$) |
| $z_0$ | Distance between the probe beam axis and the sample surface | (m) | | | |

## 1. INTRODUCTION
The knowledge of the thermal conductivity and / or the thermal diffusivity is more and more required in many industrial fields; these are the most important parameters when heat transfer processes are involved.
Several methods for thermo-physical properties measurement have been studied such as Photoacoustic [1] and Photothermal techniques [2-4], etc
Since its discovery [2], the Photothermal Deflection method (e.g. the so-called "Mirage Effect") has been widely used to measure thermal properties of materials especially thermal diffusivity whether by using the PTD [5, 6] or the PDS technique [7, 8].
Many authors [8, 9] have used the spectroscopic method to determine thermal diffusivity for bulk samples. In fact in this case the phase variation of the photothermal signal depends sensibly on the thermal diffusivity. However for thin coating sample the phase variation is practically zero, so it couldn't be exploited to determine thermal diffusivity. This show the limits of the spectroscopic study for thin layer sample.
In a previous work, we have exposed one simple and cheap method applied to bulk semi-conductor using the PTD way [10] and we have shown its great sensitivity to thermal diffusivity although its insensitivity to thermal conductivity.
Here we will apply the same method for thin coating semiconductor and we will show its ability for being sensitive to both thermal conductivity and thermal diffusivity.
The samples studied in this paper are the sulfosalt $SnSb_2S_4$ thin films deposed at two different glass substrate temperatures by thermal evaporation.

## 2. PRINCIPLE OF THE PHOTOTHERMAL DEFLECTION TECHNIQUE
Briefly, the "Mirage Effect" technique consists in heating a sample with a modulated light pump beam. The thermal wave generated by the optical absorption of the sample will propagate in the sample and in the surrounding fluid (air in our case) inducing a temperature gradient then a

refractive index gradient. A Laser probe beam skimming the sample surface and crossing the inhomogeneous refractive index region undergo a deflection. This deflection may be related to the thermal properties of the sample.

## 3. THEORETICAL MODEL

The theoretical model is built on the resolution of the one dimension heat equation in the different media, fluid, sample and backing by assuming the continuity of the temperature and the heat flow at the different interfaces z = 0 and z = $-l_s$ (Figure 1).
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 $T_0$ [11] given by Eq. (1) will permit the calculation of the probe beam deflection $\psi$ [11] given by Eq. (2).

$$T_0 = -E\,[(1-r)(1+b)\exp(\sigma_s l_s) - (1+r)(1-b)\exp(-\sigma_s l_s) + 2(r-b)\exp(-\alpha l_s)]\,/\,[(1+g)(1+b)\exp(\sigma_s l_s) - (1-g)(1-b)\exp(-\sigma_s l_s)] \quad (1)$$

Where $E = A/(\alpha^2 - \sigma_S{}^2)$ , $b = K_b\sigma_b/K_s\sigma_s$ , $g = K_f\sigma_f/K_s\sigma_s$ *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.

$$\Psi(z,t) = \frac{-L}{n_0}\,\frac{dn}{dT_f}\,\frac{\sqrt{2}}{\mu_f}\,|T_0|\,\exp(-z_0/\mu_f)\,\exp[j(\theta + \frac{\pi}{4} - \frac{z_0}{\mu_f})]\,\exp(j\omega t) \quad (2)$$

where $z_0$ is the distance between the probe beam axis and the sample surface.
As $T_0$ and $\psi$ are complex numbers, their may be written as:

$$T_0 = |T_0|\exp(j\theta) \quad \text{and} \quad \Psi = |\Psi(z_0)|\exp(j\Phi)$$

Where $|\Psi(z_0)| = -\frac{L}{n_0}\,\frac{dn}{dT_f}\,\frac{\sqrt{2}}{\mu_f}\,|T_0|\,\exp(-z_0/\mu_f)$ and $\Phi = \frac{-z_0}{\mu_f} + \theta + \frac{\pi}{4}$

are the amplitude and phase of the Photothermal deflection signal whereas $|T_0|$ and $\theta$ are respectively the amplitude and phase of the sample's surface temperature.

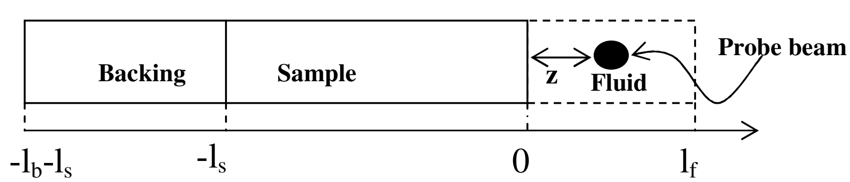


**Figure 1 :** Schematic representation for different media browsed by the heat.

## 4. EXPERIMENTAL SET-UP

The experimental set-up is described in [11]. The samples of sulfosalt $SnSb_2S_4$ thin layer ($1\mu m$ thick) used in this study were deposed at ambient (20°C) and 250°C glass substrate temperature by Thermal Evaporation. The sample absorbs the light coming from a halogen lamp of power *100W*. In our case the fluid and the backing media are respectively air and glass whose thermal conductivity and thermal diffusivity are, respectively, $K_f$ = 0.026 $W.m^{-1}.K^{-1}$, $D_f$ = $2\times10^{-5} m^2.s^{-1}$ and $K_b$=1.5$Wm^{-1}K^{-1}$, $D_b$=$6\times10^{-7}$ $m^2S^{-1}$.

## 5. EXPERIMENTAL RESULTS

The thermal conductivity and the thermal diffusivity of $SnSb_2S_4$ thin coating are obtained by fitting the experimental normalized amplitude and phase variation of the photothermal signal versus square root modulation frequency. So while varying this two parameters ($K_s$ and $D_s$) we seek the best theoretical curves which coincide best with the experimental ones.

To determine the sensitivity of our experimental set-up towards the thermal properties we
have plotted in figures 2-a and 2-b respectively the theoretical normalized amplitude and phase variations for different couples ($K_s$, $D_s$) of $SnSb_2S_4$ thin layer deposed at 250°C substrate temperature.

We notice from these curves that both the normalized amplitude and the phase variation are sensitive to $K_s$ and $D_s$, however they are more sensitive to $D_s$ than to $K_s$.

Then, while the slope of the normalized amplitude and phase variation increases with the thermal conductivity, it decreases with the thermal diffusivity.

The best theoretical fitting of the experimental curves is obtained for the couple ($k_s$=80 $W.m^{-1}.K^{-1}$ , $D_s$ = $9\times10^{-6} m^2.s^{-1}$)

Now in order to verify that the couple ($K_s$ , $D_s$) which we have founded is unique, we have plotted respectively in figure 3-a and 3-b the normalized amplitude and the phase variation versus square root modulation frequency for three fixed values of $Z_0$ of the $SnSb_2S_4$ thin films deposed at 250°C substrate temperature.

The coincidence between the theoretical curves and the experimental ones is obtained for the same couple ($K_s$ , $D_s$) which prove its uniqueness.

In Figs 4-a and 4-b the normalized amplitude and the phase variation versus square root modulation frequency are plotted for different values of $K_s$ and for any thermal diffusivity value of $SnSb_2S_4$ thin layer deposed at an ambient ( 20°C ) substrate temperature; In fact the PTD signal in this situation is independent with the thermal diffusivity variation.

We notice from these curves that both the normalized amplitude and the phase variation are very sensitive to $K_s$. The theoretical curves which fit best the experimental ones are obtained for $k_s$=0.095 $W.m^{-1}.K^{-1}$.

In figures 5-a and 5-b are represented the experimental and the corresponding theoretical curves of the normalized amplitude and the phase variation versus square root modulation frequency of $SnSb_2S_4$ thin layer deposed at respectively an ambient ( 20°C ) and 250°C substrate temperature at a same distance $Z_0$=170µm. We note from these figures the good agreement between the experimental and the theoretical curves for both the normalized amplitude and the phase variation and we can clearly see the big difference between the two curves which reflects the great difference between the two samples thermal conductivity.

The two samples thermal properties values so deduced are reported in Table 1.

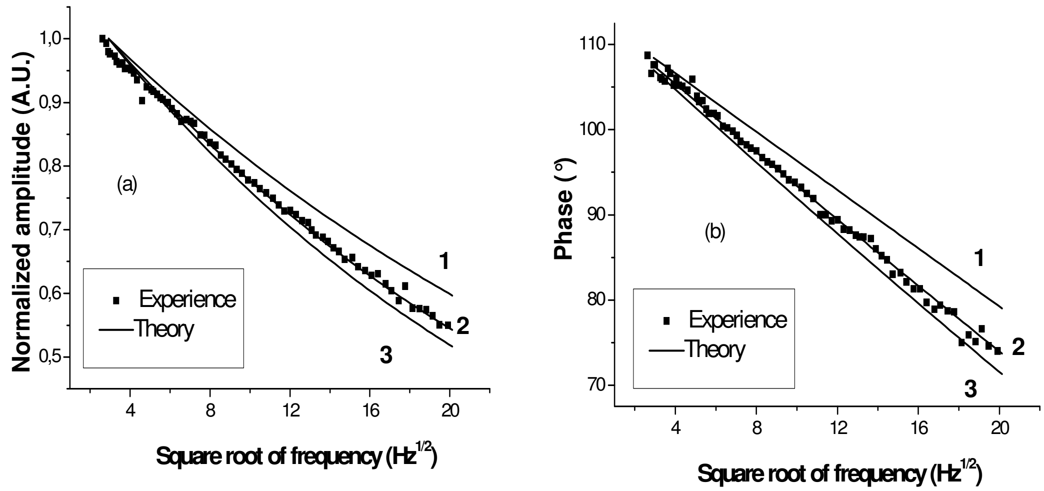


**Figure 2**: Experimental and theoretical curves giving the variations of the normalized amplitude (a) and phase (b) according to the square root modulation frequency at a distance $Z_0$=73µm of $SnSb_2S_4$ thin layer deposed at 250°C substrate temperature for 1: ($k_s$=80 $W.m^{-1}.K^{-1}$ , $D_s = 3\times10^{-5} m^2.s^{-1}$), 2: ($k_s$=80 $W.m^{-1}.K^{-1}$ , $D_s = 9\times10^{-6} m^2.s^{-1}$) and 3: ($k_s$=110 $W.m^{-1}.K^{-1}$ , $D_s = 9\times10^{-6} m^2.s^{-1}$).

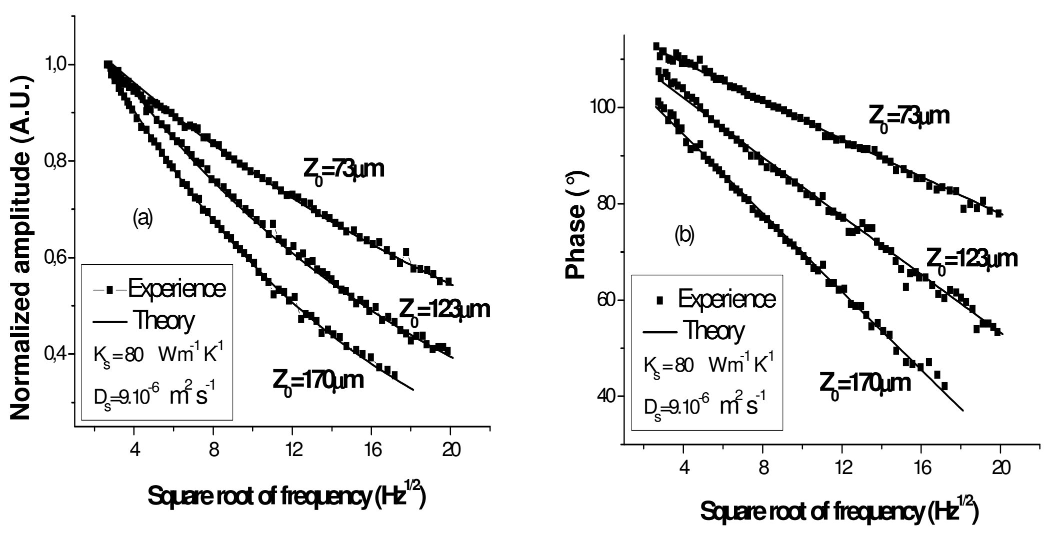


**Figure 3**: Experimental and corresponding theoretical curves giving the variations of the normalized amplitude (a) and phase (b) according to the square root modulation frequency for three values of $Z_0$ of $SnSb_2S_4$ thin layer deposed at 250°C substrate temperature for the same couple ($k_s$=80 $W.m^{-1}.K^{-1}$ , $D_s = 9\times10^{-6} m^2.s^{-1}$).

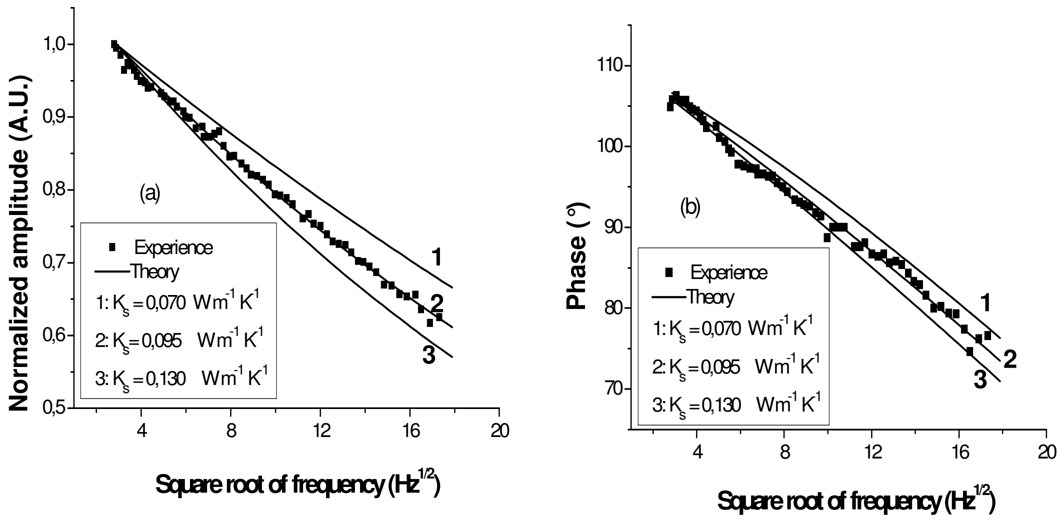


**Figure 4**: Experimental and theoretical curves giving the variations of the normalized amplitude (a) and phase (b) according to the square root modulation frequency for different values of $K_s$ at a distance $Z_0$=135µm of $SnSb_2S_4$ thin layer deposed at an ambient ( 20°C ) substrate temperature.

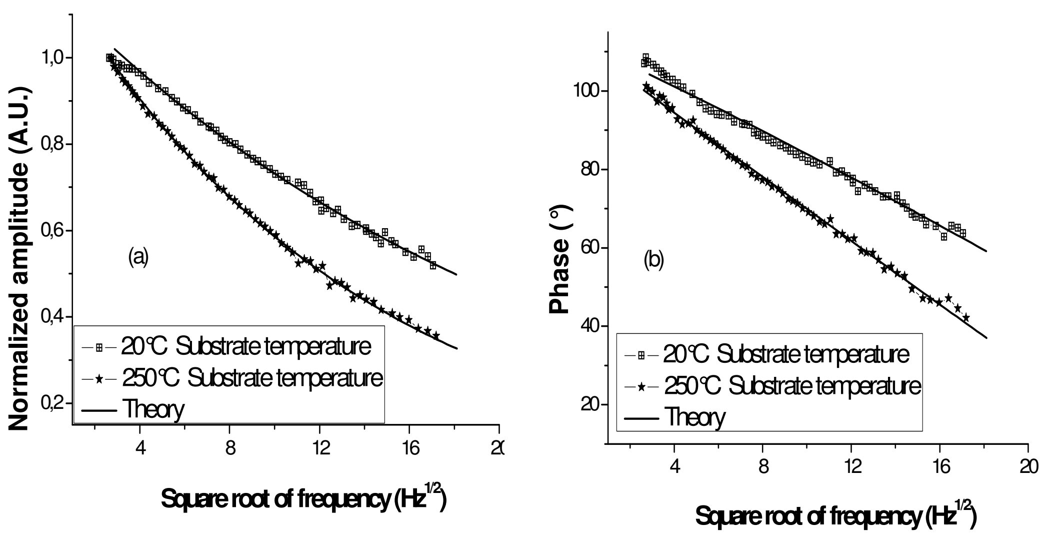


**Figure 5**: Experimental and corresponding theoretical curves giving the variations of the normalized amplitude (a) and phase (b) according to the square root modulation frequency at a same distance $Z_0$=170µm of $SnSb_2S_4$ thin layer deposed at an ambient ( 20°C ) and 250°C substrate temperature respectively.

Table 1: Experimental thermal diffusivities and thermal conductivities values of the two $SnSb_2S_4$ samples

| Samples | *Ds* ($10^{-6}$ x $m^2$. $S^{-1}$) | *Ks* (W $m^{-1}$ $K^{-1}$) |
|---|---|---|
| $SnSb_2S_4$ (deposed at ambient temperature) | --- | $0.095 \pm 0.002$ |
| $SnSb_2S_4$ (deposed at 250°C) | $9.0 \pm 0.5$ | $80 \pm 5$ |

## 6. CONCLUSION

In this work, we have shown that the Photothermal Deflection Technique (PTD) may be used to investigate simultaneously thermal diffusivity and thermal conductivity of a sulfosalt $SnSb_2S_4$ thin films deposed at two different glass substrate temperatures.
At the ambient temperature the films show law thermal conductivity (insulating behaviour), but above the transition temperature the films exhibit semiconductor behaviour and show relatively high thermal conductivity.

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