Investigation of thermal and optical properties of thin $\text{WO}_3$ films by the photothermal Deflection Technique

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Abstract. Owing to its novel physical properties, as well as its technological implication in many fields, the thermal and optical properties of $\text{WO}_3$ thin films are studied here. These thin films are prepared from Ammonium Tungstate and deposited on a glass substrate at 400°C by the Spray Pyrolysis Technique. The thermal properties (Thermal conductivity and thermal diffusivity) were studied by the Photothermal Deflection method in its uniform heating case instead of traditionally a non uniform heating one by comparing the experimental amplitude and phase variations versus square root modulation frequency to the corresponding theoretical ones. The best coincidence between theory and experience is obtained for well-defined values of thermal conductivity and thermal diffusivity. The optical properties (optical absorption spectrum and gap energy) were measured using the Photothermal Deflection Spectroscopy (PDS) by drawing the amplitude and phase variation versus wavelength in experimental way and versus absorption coefficient in theoretical one at a fixed modulation frequency. By comparing point by point the normalised experimental and corresponding theoretical amplitude variation, one can deduce the optical absorption spectrum. Using the Tauc law for energies above the gap we can deduce the gap energy. We notice that these films show low thermal conductivity and high transparency in the visible range.

1. Introduction
Research involving $\text{WO}_3$ thin films has grown in recent years, owing to its novel physical properties, as well as its technological implication in many fields. In the present work, we are interested in its thermal and optical properties which we will determine using the Photothermal Deflection Method (Mirage Effect). This method which was first introduced in the early1980s by Boccara and all [1] has been widely used to determine the thermal [2-6] and optical [7-9] properties of materials. It 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 inducing a temperature gradient then a refractive index gradient. By probing this gradient with a second beam (laser probe beam), one can relate its deflection to the thermal and optical properties of the sample.

2. Experimental set-up
For the thermal study, the experimental set-up (Figure. 1) is described in detail in [10]. The sample studied in this work is the $\text{WO}_3$ thin films (1.3µm thick) which are prepared from Ammonium...
Tungstate and deposited on a glass substrate at 400°C by the Spray Pyrolysis Technique. For the optical study we interpose between the halogen lamp and the mechanical chopper a Monochromator (Jobin Yvon HR250) and we plot the amplitude and phase variation of the photothermal signal versus wave length at a fixed modulation frequency. Note that in the case of the thermal study the fluid is air, however in the spectroscopic study the fluid is paraffin oil.

3. Experimental results

3.1. Thermal study

The thermal conductivity and the thermal diffusivity of WO$_3$ thin films are obtained by fitting the experimental 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 theoretical curves [10] which coincide better with the experimental ones. To show the sensitivity of our experimental set-up towards the thermal properties we have plotted in figures 2 and 3 the theoretical curves for different values of $K_s$ and $D_s$ respectively. In figures 2-a and 2-b the logarithm of the amplitude and phase variations are plotted for different values of $K_s$ at a fixed thermal diffusivity value of a WO$_3$ layer. We notice from these curves that both the logarithm of the amplitude and the phase are sensitive to $K_s$. Then, we remark that the slope of the logarithm of the amplitude and phase variation increase with the thermal conductivity. The theoretical curves which fit best the experimental ones are obtained for $k_s=9$ $W.m^{-1}.K^{-1}$. In figures 3-a and 3-b we plot the logarithm of the amplitude and the phase for different values of $D_s$ at a fixed thermal conductivity value of a WO$_3$ thin films. As in the precedent figures, we can clearly remark the sensitivity of the logarithm of amplitude and phase to the thermal diffusivity variation.
Figure 2. Theoretical and experimental curves giving the variations of the logarithm of the amplitude (a) and phase (b) according to the square root modulation frequency for different values of $K_s$ at a fixed thermal diffusivity $D_s = 3 \times 10^{-6} \text{m}^2 \text{s}^{-1}$ and at a distance $z_0 = 115 \mu\text{m}$.

Figure 3. Theoretical and experimental curves giving the variations of the logarithm of the amplitude (a) and phase (b) according to the square root modulation frequency for different values of $D_s$ at a fixed thermal conductivity $k_s = 9 \text{W.m}^{-1}\text{K}^{-1}$ and at a distance $z_0 = 115 \mu\text{m}$.

We can also see that when the thermal diffusivity increases the slope of the logarithm of amplitude and phase decrease. The best theoretical fitting of the experimental curves is obtained for the thermal diffusivity $D_s = 3 \times 10^{-6} \text{m}^2 \text{s}^{-1}$. To determine the uncertainty on the thermal diffusivity (or thermal conductivity) value we vary slightly the thermal diffusivity (or thermal conductivity) near the value for which we obtain the coincidence between experimental and theoretical curves in order to obtain one curve very close but different from the curve of coincidence.
3.2. Optical study
In this section, contrary to the thermal study in which we have varied the modulation frequency, here we plot the amplitude and phase variation of the photothermal signal at a fixed modulation frequency value versus wavelength in experimental way and versus absorption coefficient in theoretical one in order to relate this two parameters and determine the gap energy of WO$_3$ thin films.

3.2.1 Determination of the optical absorption spectrum.
From Figure. 4 we remark that the theoretical amplitude variation according to the optical absorption coefficient saturates respectively for high ($\alpha>10^6$ m$^{-1}$) and low ($\alpha<10^2$ 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 4 ; so we determine for each wavelength value the corresponding absorption coefficient one. The obtained spectrum is shown in figure 5- a. We note, here, that the phase variation is practically zero because of the low thickness ($1.3\mu m$) of WO$_3$ layer. So only the amplitude variation was exploited.

3.2.2 Determination of the band gap shift.
The gap energy is obtained from the optical 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, $E=\hbar\nu$ is the photon energy, $n = 2$ for direct transition and $n=1/2$ for indirect transition. The variation of $(\alpha E)^n$ versus photon energy $E$ is shown in 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; we obtain $E_g=3.26$ eV. 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 $E_g$.

![Figure 4](image_url)

Figure 4. Experimental curves (a) giving the variations of the normalized amplitude according to wavelength and corresponding theoretical ones (b) according to optical absorption coefficient.
Figure 5. Optical absorption spectrum versus photon energy $E$ (a) and $(\alpha E)^2$ versus photon energy $E$ near the band gap of WO$_3$ thin films (b).

Table 1. Experimental thermo-optical properties values of WO$_3$ thin films.

| Properties       | Values                     |
|------------------|----------------------------|
| Thermal conductivity | $(9.0 \pm 0.5) \text{ W.m}^{-1}.\text{K}^{-1}$ |
| Thermal diffusivity               | $(3.0 \pm 0.5) \times 10^{-6} \text{ m}^2.\text{S}^{-1}$ |
| Gap energy       | $(3.26 \pm 0.02) \text{ ev}$ |

4. Conclusion:

In this work, we have investigated the thermal diffusivity and thermal conductivity of a WO$_3$ thin layer, using the Photothermal Deflection Technique (PTD) by fitting the experimental amplitude and phase of the photothermal signal versus square root modulation frequency and we have determined, with good precision, its optical absorption spectrum and its gap energy using the Photothermal Deflection Spectroscopy (PDS).

References

[1] A.C. Boccara, D. Fournier and J. Badoz, Appl. Phys. Lett. 36, 130-132 (1980).
[2] M. Bertolotti, G. Liakhov, R. Li Voti, F. Michelotti, and C. Sibilia, J. Appl.Phys. 74 (12), 7078-7084 (1993).
[3] P.K. Kuo, M.J. Lin, C.B. Reyes, L.D. Favro, R.L. Thomas, D.S. Kim, S. Zhang, L.J. Inglehart, D. Fournier, A.C. Boccara, N. Yacoubi, Part I. Experiment, Can. J. Phys. 64, 1168 (1986).
[4] F. Saadalah, N. Yacoubi and A. Haffaiedh, 1996, J. Opt. Mater. 6, pp. 35-39.
[5] N. Yacoubi and M. Fathallah, 1987, Springer Series in Optical Sciences, vol 58, p.347
[6] I. Gaied, S. Abroug and N. Yacoubi, 2008, accepted to be published in Physics Procedia (Elseiver)
[7] J. C. Murphy and L. C. Aamodt, J.Appl.Phys.51, 4580-4588 (1980).
[8] W. B. Jackson, N. M. Amer, A. C. Boccara, and D. Fournier, Appl.Opt.20, 1333-1344 (1981).
[9] S. Abroug, F. Saadalah and N. Yacoubi, 2007, Physica B, 400, pp.163-167
[10] Imen Gaied, Aymen Amara, Noureddine Yacoubi and Taher Ghrib, Applied Optics, Vol. 47, Issue 8, pp. 1054-1062 (2008).