Journal of Thermal Analysis, Vol. 44 (1995) 795-802

MEASUREMENT OF THERMAL DIFFUSIVITY BY THE PHOTOACOUSTIC METHOD

A computer simulation

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(Received January 5, 1994)

Abstract

Analysis of the photoacoustic signal *vs.* the modulation frequency allows the determination of thermal diffusivity. Computer simulations have been carried out to determine the optimal conditions, in the case of rear surface illumination, for which the thermal diffusivity is accurately measured. In accordance with these conditions, measurements were performed on a reference sample (silicon).

Keywords: photoacoustic method, thermal diffusivity

Introduction

Photothermal techniques have been widely applied to the study of the optical properties and thermal parameters of liquids and solids [1, 2]. Several methods have been developed for the determination of thermal diffusivity [3]. The photoacoustic method we have used allows measurements of the thermal diffusivity through a sample. In this technique, the sample is enclosed in an air-tight cell and is excited by a chopped light beam. Light modulated at a frequency $f=\omega/2\pi$ is absorbed and totally or partially converted into heat. As a result of the of periodic heating of the sample, the pressure in the cell oscillates at the chopping frequency; this is detected by a sensitive microphone coupled to the cell.

Frequency analysis of the photoacoustic signal in the case of the rear configuration leads to determination of the thermal diffusivity of the sample [4]. In such a configuration, the sample is heated by the modulated light source on one side and the temperature oscillations introduced are detected on the opposite side of the sample. The theoretical model of Rosencwaig and Gersho [5] shows that two conditions are necessary to measure the thermal diffusivity with precision: (i) the sample must be optically thick, and (ii) the sample must be thermally thick.

0368–4466/95/ $ 4.00

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In the present study, we specify the relations between the sample thickness, the optical absorption length and the thermal diffusion length which satisfy the two above-mentioned requirements and therefore allow an accurate measurement of the thermal diffusivity.

Theoretical

In the theoretical model of Rosencwaig and Gersho [5], it is assumed that the amplitude and the phase angle of the pressure variation in the gas are determined by the temporal variation of the temperature distribution in the sample and gas, while the effect of thermal expansion of the sample is negligible, and the length of the gas column is much greater than the thermal diffusion length. Figure 1 schematically shows an idealized configuration of a photoacoustic cell. The sample of thickness l_s is mounted so that its rear surface is illuminated and the photoacoustic signal is detected by means of front microphonic detection. According to the one-dimensional model applied to the case of rear-surface illumination, the periodic pressure variation in the cell is given [5] by

$$\Delta P = \frac{\gamma P_o}{\sqrt{2}\, l_g a_g T_o} \theta e^{j(\omega t - \pi/4)} \qquad (1)$$

where γ is the ratio of the specific heats of the gas, P_o and T_o are the ambient pressure and the ambient temperature respectively, l_g is the thickness of the gas, and a_g is the inverse of the thermal diffusion length of the gas.

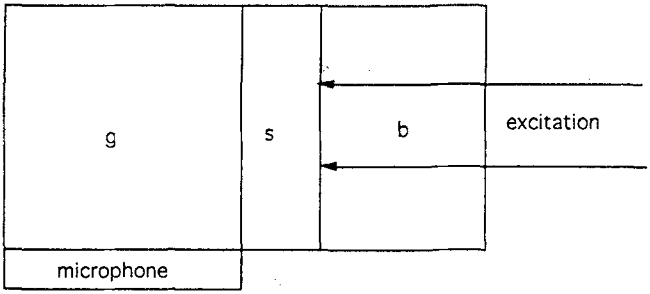

Fig. 1 Schematic representation of the photoacoustic cell for the rear surface excitation. b: backing; s: sample; g: gas

The term θ is related to the optical, thermal and geometrical properties of the sample and to the backing and the gas media as follows:

$$\theta = \frac{\beta I_o}{2k_s(\beta^2 - \sigma_s^2)} \frac{2(r+g) - [(r+1)(g+1)e^{\sigma_s l_s} + (r-1)(g-1)e^{-\sigma_s l_s}]e^{-\beta l_s}}{(b+1)(g+1)e^{\sigma_s l_s} - (b-1)(g-1)e^{-\sigma_s l_s}} \qquad (2)$$

Here we define the following parameters: β is the optical absorption coefficient; I_o is the incident radiation intensity; $\sigma_i=(1+j)/\mu_i$ where $\mu_i=(\alpha_i/\pi f)^{1/2}$ denotes the thermal diffusion length in the material i; $r=\beta/\sigma_s$;

$b=\frac{k_b\sigma_b}{k_s\sigma_s}=\frac{\sqrt{k_b\rho_b c_b}}{\sqrt{k_s\rho_s c_s}}$ is the backing-effusivity-to-sample-effusivity ratio;

$g=\frac{k_g\sigma_g}{k_s\sigma_s}=\frac{\sqrt{k_g\rho_g c_g}}{\sqrt{k_s\rho_s c_s}}$ is the gas-effusivity-to-sample-effusivity ratio; c_i is the

specific heat capacity at constant pressure of material i; k_i is the thermal conductivity of material i; ρ_i is the density of material i; and $\alpha_i=k_i/\rho_i c_i$ is the thermal diffusivity of material i. The subscript i denotes s (sample), g (gas), and b (backing), respectively.

Principle of measurement

To determine the thermal diffusivity of the sample, the photoacoustic signal is analysed *vs.* the modulation frequency. For an optically opaque sample (i.e. $l_s\beta>>1$, $r>>1$), we can make the following approximations:

$$e^{-\beta l_s}\approx 0;\quad r+g\approx r;\quad \frac{\beta}{\beta^2-\sigma_s^2}\approx\frac{1}{\beta}$$

Equation (2) reduces to

$$\theta=\frac{1}{k_s\sigma_s}\frac{2I_o}{(b+1)(g+1)e^{\sigma_s l_s}-(b-1)(g-1)e^{-\sigma_s l_s}} \tag{3}$$

When the sample is also thermally thick (i.e. $l_s>>\mu_s$), $e^{-\sigma_s l_s}\approx 0$, and we obtain

$$\theta=\frac{1}{k_s\sigma_s}\frac{2I_o e^{-\sigma_s l_s}}{(b+1)(g+1)} \tag{4}$$

On substituting this expression into Eq. (1), we obtain

$$\Delta P=Ae^{j(\omega t+\Phi)} \tag{5}$$

where A, the modulus of ΔP, and φ, the phase angle, depend on the modulation frequency f as follows:

$$A = \frac{K}{f}\exp(-\,l_s(\pi f/\alpha_s)^{1/2})$$
$$\varphi = -\,l_s(\pi f/\alpha_s)^{1/2} - \pi/2 \tag{6}$$

$$K = \frac{\gamma P_o I_o \alpha_g^{1/2}\alpha_s^{1/2}}{\pi l_g T_o k_s(b+1)(g+1)} \tag{7}$$

where K is a term independent of frequency. Thus, the thermal diffusivity can be evaluated from modulation frequency analysis of either the signal amplitude or its phase.

Discussion

In the method presented here, we have shown that the thermal diffusivity can be determined under two conditions:

$$\mu_\beta << l_s \quad \text{(optically opaque sample)} \tag{8}$$

$$\mu_s << l_s \quad \text{(thermally thick sample)} \tag{9}$$

Here, $\mu_\beta = 1/\beta$ is the optical absorption length.

In order to obtain a sufficient photoacoustic signal, since we use rear-surface illumination, the sample thickness l_s must in any case be less than the sample thermal wavelength $\lambda_s = 2\pi\mu_s$. In the following, we determine the ratio μ_s to l_s and the ratio μ_β to l_s so that the inequalities [8] and [9] are satisfied and, therefore, the simplifications of Eq. (2) are valid. To this end, we use simulations of photoacoustic data for samples with known thermal diffusivity.

a. Comparison between l_s and μ_s

Using Eq. (2) (i.e. the expression not simplified with ΔP), we have calculated the amplitude A of the photoacoustic signal for a silicon sample. Calculations were made with the known thermal diffusivity of silicon, $\alpha_s = 0.91\cdot10^{-4}$ m2/s. The reference value for the sample thickness is $l_s = 2$ mm; the backing and the gas in the cell are air ($\alpha_g = \alpha_b = 2.15\cdot10^5$ m^2/s, $k_g = k_b = 0.026$ W m^{-1}K^{-1}). The value of the optical absorption coefficient β is chosen to be equal to 10^7 m^{-1} ($\mu_\beta = 1/\beta = 0.1$ μm) so that the first condition, $\mu_\beta << l_s$, is satisfied and, therefore, the first simplification of Eq. (2) is valid.

For different modulation frequency ranges (i.e. for different values of μ_s), we plotted $\ln(Af)$ as a function of $(f)^{1/2}$ (Fig. 2) and deduced the sample thermal diffusivity from the slope of the curve. Table 1 lists values of thermal diffusivity obtained from simulated data for three frequency ranges corresponding to different ratios l_s to μ_s.

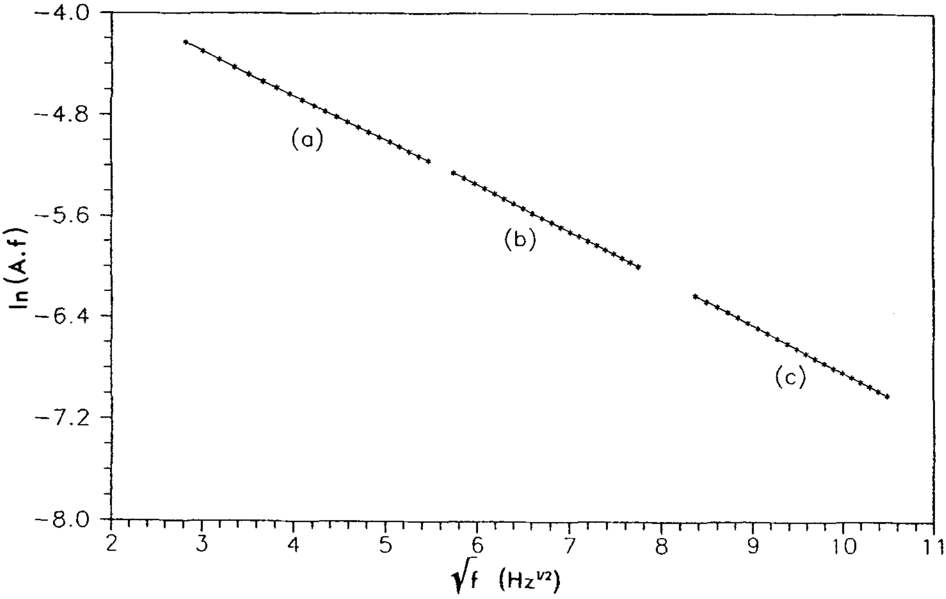

Fig. 2 Theoretical plots of $\ln(Af)$ *vs.* $f^{1/2}$ for different frequency ranges with $l_s=2$ mm, $\alpha_s=0.91\cdot10^{-4}$ m^2/s and $\beta=10^7$ m^{-1}

As this ratio increases, the relative error $\Delta\alpha_s/\alpha_s$ as concerns the expected value of α_s decreases. A correct value of thermal diffusivity ($\Delta\alpha_s/\alpha_s<3\%$) is reached when the frequency range is such that $l_s>2\mu_s$. This means that the condition $l_s>>\mu_s$ (thermally thick sample) reduces in fact to $l_s>2\mu_s$.

Table 1 Thermal diffusivity α_s of the sample obtained for different modulation frequency ranges

f / Hz	l_s / mm	α_s / m^2·s^{-1}	$\Delta\alpha_s\cdot\alpha_s^{-1}$ / %
$8<f<27$	$\mu_s<l_s<2\mu_s$	1.040×10^{-4}	14.50
$32<f<60$	$2\mu_s<l_s<3\mu_s$	0.930×10^{-4}	2.13
$70<f<110$	$3\mu_s<l_s<4\mu_s$	0.905×10^{-7}	0.47

b. Comparison between l_s and μ_β

For a given value of l_s (2 mm), we calculated $\ln(Af)$ as a function of $(f)^{1/2}$ in the frequency range so that $l_s>2\mu_s$ (i.e. the condition required for Eq. (4) is satisfied). This is plotted in Fig. 3. Table 2 lists the values of thermal diffusivity obtained for different values of μ_β. It can be observed that for $\beta=2\cdot10^3$ m^{-1} the curve is not linear. This means that the condition $\mu_\beta<<l_s$ required in arriving at

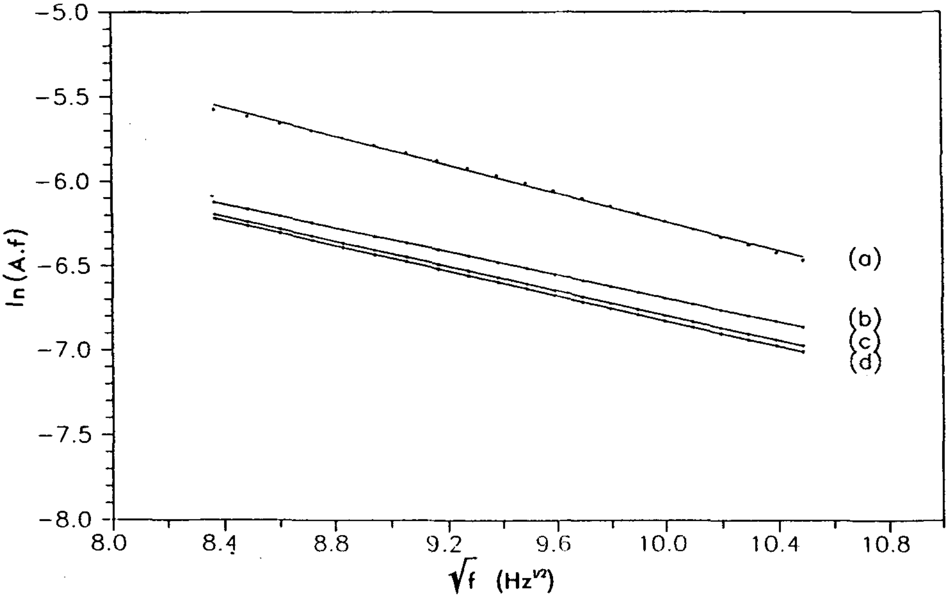

Fig. 3 Theoretical plots of ln(Af) *vs.* $f^{1/2}$ in a frequency range so that l_s>3 μ_s. The sample thickness is l_s=2 mm, its diffusivity α_s=0.91 $\cdot 10^{-4}$ m^2/s and its optical absorption coefficients are: (a) $\beta=2\cdot 10^3$ m^{-1}, (b) $\beta=5\cdot 10^3$ m^{-1}, (c) $\beta=10^4$ m^{-1}, (d) $\beta=5\cdot 10^4$ m^{-1}

Table 2 Thermal diffusivity α_s obtained for different values of the optical absorption coefficient β

β / m^{-1}	μ_β / mm	α_s / $m^2 \cdot s^{-1}$	$\Delta\alpha_s \cdot \alpha_s^{-1}$ / %
2×10^3	0.2	1.04×10^{-4}	14.4
10^4	0.1	0.93×10^{-4}	3.1
5×10^4	0.02	0.90×10^{-4}	0.4

Eq. (3) is not satisfied. For the other values of β, the curve is linear and the thermal diffusivity is obtained with higher precision when β increases. The precise value of α_s is reached when $l_s \geq 100$ μ_β. Then, the sample can be assumed to be optically thick.

Experimental and discussion

We used a modulated beam from a 514.3 nm argon laser of 100 mW power to heat the sample. The sample was placed in a photoacoustic cell 30 mm in diameter and 8 mm in length. We used disk-shaped silicon samples 30 mm in diameter and 1.5–3 mm thick. The sample was attached to a sample holder and

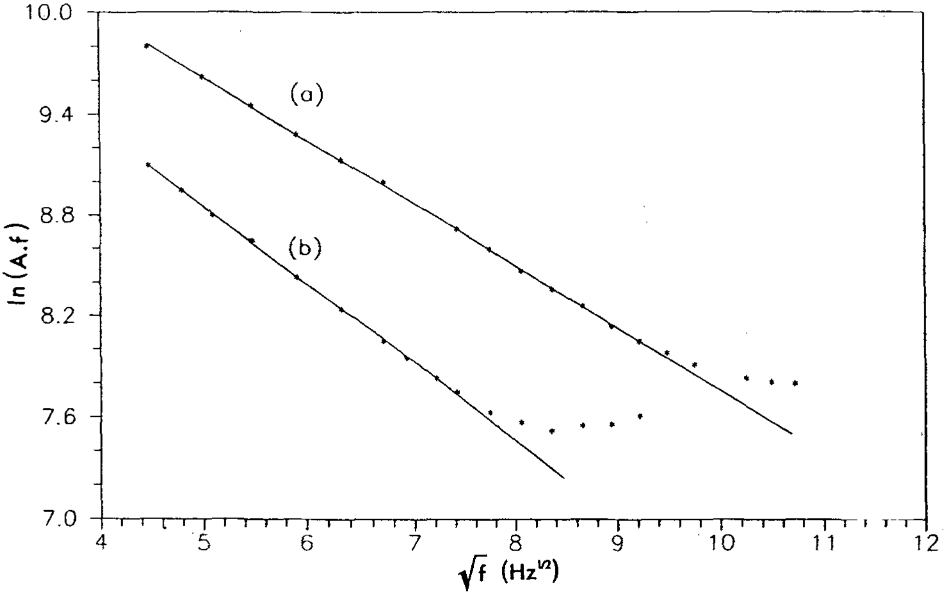

Fig. 4 Experimental plots of ln(*Af*) *vs.* $f^{1/2}$ for (a) the 2 mm-thick silicon sample and (b) 2.5 mm-thick silicon sample

its backing material was air. The amplitude of the photoacoustic signal obtained with a two-phase locking amplifier was recorded as a function of modulation frequency *f*. Finally, the experimental curves were fitted by means of a least-square program.

The optical absorption coefficient of silicon for the incident radiation is $\beta=7.3\cdot10^5$ m^{-1}; the corresponding length of optical absorption is $\mu_\beta=1.37$ µm, and therefore the conditions $l_s>100$ μ_β is satisfied for the samples used. The experiments were carried out in a modulation frequency range such that the conditions $l_s>2\mu_s$ was satisfied for each sample.

In the case of the 2 mm-thick sample, as an example, this condition is satisfied for $f>30$ Hz. Figure 4(a) shows the variation in ln(*Af*) as a function of $(f)^{1/2}$ for the 2 mm-thick sample. The graph exhibits two different parts: linear behaviour for $f<85$ Hz, and non-linear behaviour for $f>85$ Hz. The thermal diffusivity of the silicon sample was determined from the slope of the linear part of the curve: we found $\alpha_s=0.89\cdot10^{-4}$ m^2/s. This value agrees very well with literature data [6]. Different experiments performed under the same conditions reveal the good reproductibility of the slope measurements. The incertitude in α_s determination is mainly due to the sample thickness measurements. It is estimated to be 20 µm, which leads to a precision of about 1%.

The non-linear behaviour of the curve for the higher frequency is explained [4] by the contribution to the photoacoustic signal from the thermoelastic bending of the embedded sample. This effect is related to the temperature gradient set within the sample along the thickness direction. The vibrating sample acts as a mechanical piston, thereby contributing to the pressure variation. To minimize this mechanical contribution, the sample must lean against a solid transparent backing.

From Eq. (7), it can be seen that analysis of the signal phase *vs.* the modulation frequency also allows determination of the thermal diffusivity. However, no measurements of α_s have been performed with signal phase Φ analysis. This is mainly due to the fact that the signal to noise ratio becomes relatively important in the frequency range where the condition $l_s > 2\ \mu_s$ is satisfied.

Through analysis of the signal amplitude A *vs.* modulation frequency f, the photoacoustic technique allows determination of the thermal diffusivity of optically and thermally thick samples. It has been shown that these conditions are expressed through two well-defined relationships between the sample thickness and the optical absorption length on one hand and between the sample thickness and the thermal diffusion length on the other hand.

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Zusammenfassung — Die Analyse des fotoakustischen Signales in Abhängigkeit von der Modulierungsfrequenz erlaubt die Feststellung des thermischen Diffusionsvermögens. Für den Fall einer Oberflächenbestrahlung, für die das thermische Diffusionsvermögen präzise vermessen wurde, ergaben Computersimulationen die optimalen Bedingungen. In Übereinstimmung mit diesen Bedingungen wurden Messungen an einer Referenzprobe (Silikon) durchgeführt.