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Thermal diffusivity measurement using the photopyroelectric effect

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A novel and simple method using the photopyroelectric effect is described for the measurement of the thermal diffusivity of solids. The method is used in the case of metals, semiconductors, and insulators, covering several orders of magnitude in thermal diffusivity. It has advantages over conventional thermal wave spectroscopic methods.

In the last few years a great deal of effort has been devoted to the development of thermal wave spectroscopies, such as photoacoustic spectroscopy (PAS),[1,2] photothermal radiometry,[3,4] and photothermal deflection spectroscopy (PDS).[5–7] The common basic principle of these thermal spectroscopies consists of measuring the temperature fluctuation in a sample as a result of the nonradiative deexcitation processes that take place following the absorption of radiation. Apart from providing us with optical absorption spectra these techniques exhibit the unique feature of allowing us to measure the depth profile[8–11] (microscopy) of samples as well as their thermal properties.[12–16] More recently, Coufal,[17] Mendelis,[18] and Ghizoni and Miranda[19] have opened the way to a new technique using pyroelectric thin films to detect optical absorption and nonradiative energy conversion processes in solids. This new technique consists of using a thin pyroelectric [polyvinylidene difluoride (PVF_2)] film in intimate contact with a solid sample on which a monochromatic light beam whose intensity is sinusoidally modulated at a frequency ω is incident. Following the absorption of the incident light, the nonradiative deexcitation processes within the solid cause the sample temperature to fluctuate and, through heat diffusion to the surrounding pyroelectric film, the temperature of the sample-pyroelectric-film interface fluctuates, thereby creating a temperature gradient in the pyroelectric film. As a result of this temperature gradient, the pyroelectric film changes its polarization, thus producing a net dipole moment which results in a pyroelectric voltage V given by[20]

$$V=\frac{pl_d}{\epsilon}\Delta T \ , \tag{1}$$

where p is the pyroelectric coefficient of the film, l_d is the film thickness, ϵ is the film dielectric constant, and ΔT is the spatially averaged temperature fluctuation in the pyroelectric film, namely,

$$\Delta T=\frac{1}{l_d}\int T_d(x,t)dx \ . \tag{2}$$

In the experiments by Coufal[17] the pyroelectric character of 9-μm thin PVF_2 films was used to obtain the absorption characteristics of Nd_2O_3-doped polymethyl methaacrylate films. In the work by Mandelis the potentiality of this new photopyroelectric technique was demonstrated by using this technique for obtaining the optical spectrum of Ho_2O_3 hydrated powders as well as to monitor the kinetics of the chemical reduction of CuO into metallic copper by HCl. Ghizoni and Miranda[19] have used the method to measure thermal diffusivity of silicon crystal using a lateral heating source.

In this paper we describe the application and potential of the photopyroelectric effect as a new, simple, and sensitive method for measuring the thermal properties of solids, covering the range from conductors, through semiconductors, to insulators. This approach is schematically shown in Fig. 1. A monochromatic light beam whose intensity is modulated at a frequency $\omega=2\pi f$ is incident on a solid sample of thickness l_s. The sample is in intimate contact with the thin PVF_2 film of thickness l_d, by means of a thin coupling fluid layer of thickness l_c, and the sample-transducer system is supported by an optically transparent backing material of thickness l_b, large compared with l_s, l_c, and l_d. The temperature fluctuation in material i ($i=g,c,d,b$) of our system resulting from the periodic optical heating of the sample denoted by $T_i(x,t)$ can be obtained by solving the coupled set of thermal diffusion equations,

$$\frac{\partial^2 T_i}{\partial x^2}-\frac{1}{\alpha_i}\frac{\partial T_i}{\partial T}=\begin{cases} S(x,t), & i=s, \\ 0, & i=g,c,d,b, \end{cases} \tag{3}$$

where the heat density $S(x,t)$ produced in the sample by the absorption of light is given by

$$S(x,t)=\frac{\beta' I_0}{2}\delta(x-l_s)e^{j\omega t} \ . \tag{4}$$

In Eqs. (3) and (4), k_i is the thermal conductivity of material i; $\alpha_i=k_i/\rho_i c_i$ is the thermal diffusivity of material i, where ρ_i is the density of material i; c_i is the specific heat

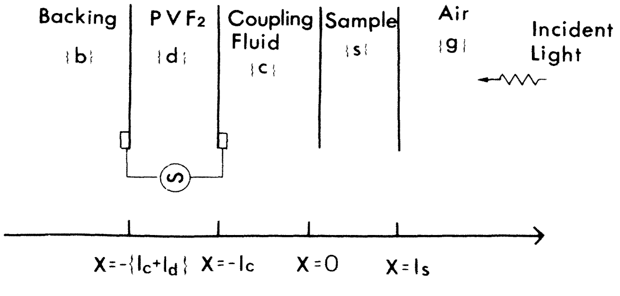

FIG. 1. Configuration of a photopyroelectric system.

of material i, I_0 is the intensity of the incident light, and β' is the surface absorption coefficient of the sample. The quantity of interest is $T_d(x,t)$ and the actual temperature fluctuation in the pyroelectric film as a function of position and time is given by the real part of $T_d(x,t)$. Solving Eq. (3) together with the boundary conditions of heat-flux and temperature continuity at the interfaces one finds the periodic temperature fluctuation in the pyroelectric film. Knowing $T_d(x,t)$ and performing the spatial average indicated in Eq. (2), one gets

$$\Delta T=\left(\frac{2c\beta' I_0}{k_s\sigma_s l_d\sigma_d}\right)\left(\frac{(1-e^{-l_d\sigma_d})-\gamma(1-e^{l_d\sigma_d})}{[(1+c)e^{l_s\sigma_s}-(1-c)e^{-l_s\sigma_s}]\xi_1 e^{l_c\sigma_c}+[(1-c)e^{l_s\sigma_s}-(1+c)e^{-l_s\sigma_s}]\xi_2 e^{-l_c\sigma_c}}\right), \tag{5}$$

where $\sigma_i=(1+j)a_i$, $i=b,c,d,g,s$, $a_i=(\omega/2\alpha_i)^{1/2}=\mu_i^{-1}$ is the thermal diffusion coefficient, μ_i is the thermal diffusion length, $\xi_1=c(1+\gamma)+d(1-\gamma)$ and $\xi_2=c(1+\gamma)-d(1-\gamma)$. Here $b=k_b a_b/k_s a_s$, $c=k_c a_c/k_s a_s$, $d=k_d a_d/k_s a_s$, and $\gamma=[(d-b)/(d+b)]\exp(-2l_d\sigma_d)$.

The above expression for the average temperature fluctuation in the pyroelectric film is quite complicated to interpret in the general case. It, however, reduces to simpler expressions in some limiting cases depending on the thermal thickness (i.e., the product $l_s\sigma_s$) of our sample. For the purpose of measuring the thermal diffusivity, the case of interest is that of thermally thick sample, namely, when $l_s\sigma_s \gg 1$. We note that both the pyroelectric film and the coupling fluid may be considered thermally thin. Thus, setting in Eq. (5) $\exp(-l_s\sigma_s)=0$, $\exp(\pm l_c\sigma_c)\simeq 1\pm l_c\sigma_c$, and $\exp(\pm l_d\sigma_d)\simeq 1\pm l_d\sigma_d$ the temperature fluctuation in the pyroelectric film should then decay exponentially for $l_s\sigma_s \gg 1$, i.e.,

$$\Delta T=e^{-\sqrt{f/f_s}}, \text{ where } f_s=\alpha_s/\pi l_s^2 . \tag{6}$$

This exponential decay of the signal with the modulation frequency depends only on the thermal diffusion time in the sample f_s^{-1} and, consequently, allows us to measure the thermal diffusivity, provided the sample thickness is known.

To demonstrate the versatility of the above method for measuring thermal diffusivity we have carried out the measurements on copper, on silicon crystal wafer, and on glass (microscope cover plate). The experimental setup is shown in Fig. 2. The beam from a 1-mW He-Ne laser modulated by a variable frequency chopper is focused on the sample which is in thermal contact with a 9-μm-thick PVF$_2$ film (Pennwalt Corp.) supported by a Plexiglass backing. To optimize the sample-PVF$_2$ thermal contact a thin (50–100-μm thick) layer of thermally conducting grease (thermal compound No. 120-8, Wakefield, England) was used as the coupling fluid. The output from the PVF$_2$ detector after preamplification was fed to a lock-in amplifier. In Figs. 3 and 4 we show the variation of the pyroelectric signals as a function of $\sqrt{f}$ for the Si (l_s=0.37-mm) and Cu (l_s=0.50-mm) samples, respectively. Figure 5 shows the corresponding changes in signal for a thin microscope cover glass plate ($l_s=60$ μm). The front surface of the glass plate was coated with a thin carbon-black layer to ensure the optically thick condition for the He-Ne laser light. The semilog plots of Figs. 3 and 4 clearly show two distinct straight-line regions as a function of $\sqrt{f}$. These features can be understood from Eq. (5) as follows. For the materials used in our work in the frequency range where the samples are thermally thick one has $d/b=0.97$, $\gamma\cong 0$, $\xi_1=c+d$, and $\xi_2=c-d$. Making these substitutions in Eq. (5), and neglecting $\exp(-l_d\sigma_d)$ as compared to one, we get for a thermally thick sample,

$$\Delta T=\frac{c\beta' I_0}{k_s\sigma_s l_d\sigma_d}\,\frac{e^{-l_s\sigma_s}}{[c\cosh(l_c\sigma_c)+d\sinh(l_c\sigma_c)]} . \tag{7}$$

Equation (7) shows that as long as the coupling fluid is not thermally thick (i.e., as long as $l_c\sigma_c<1$) the exponential decay of the pyroelectric signal, as a function of $\sqrt{f}$, is entirely due to the sample and varies as $\exp(-\sqrt{f/f_s})$

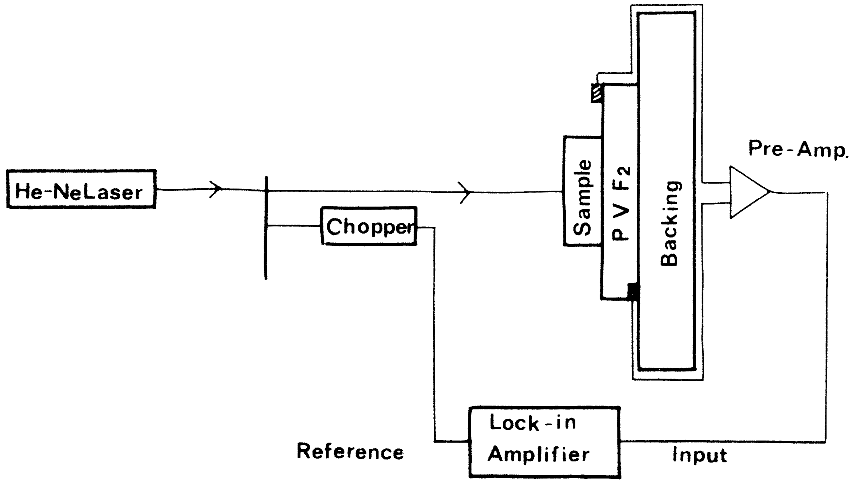

FIG. 2. Schematic of the experimental setup used for measuring the thermal diffusivity.

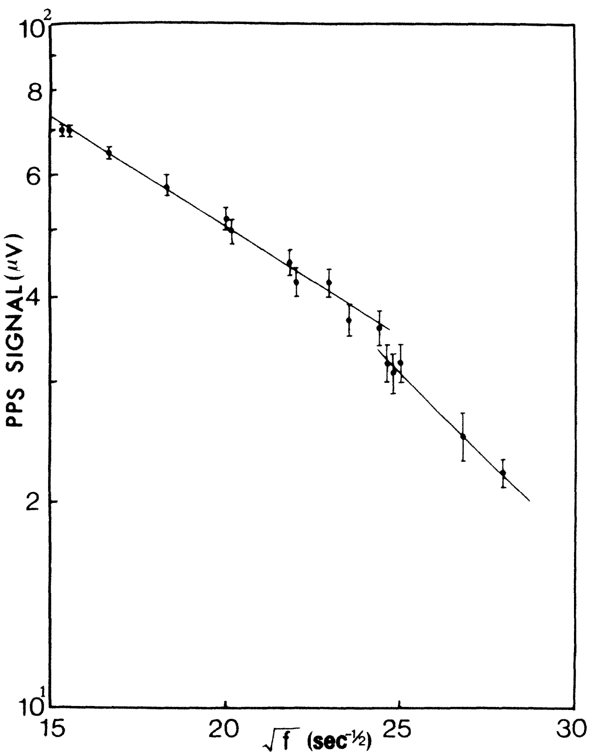

FIG. 3. Semilog plot of the phyotpyroelectric signal (PPS) of a Silicon wafer, 370 μm thick, as a function of the square root of the modulation frequency. The solid lines represent the least-squares linear fitting of the experimental data.

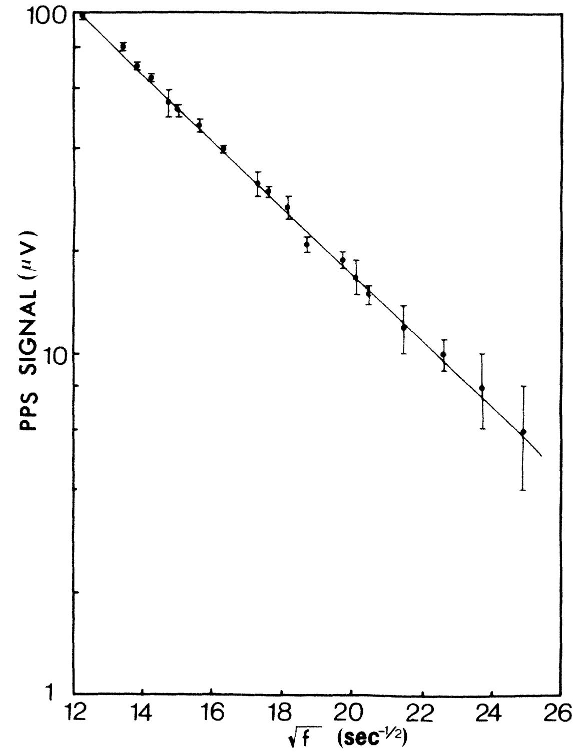

FIG. 5. Semilog plot of the photoelectric signal of a cover glass plate, 60 μm thick, as a function of the square root of the modulation frequency. The solid line represents the least-squares linear fitting of the experimental data.

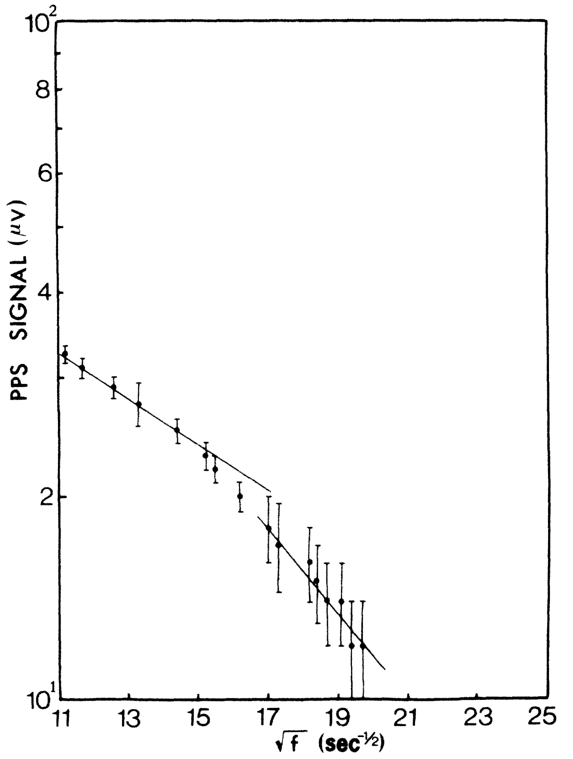

FIG. 4. Semilog plot of the photopyroelectric signal of a Cu plate, 500 μm thick, as a function of the square root of the modulation frequency. The solid lines represent the least-squares linear fitting of the experimental data.

where $f_s = \alpha_s/\pi l_s^2$. As one increases the modulation frequency one eventually reaches a situation where the coupling fluid becomes thermally thick (i.e., $l_c\sigma_c > 1$). At this point the exponential decay is due to both the sample and the coupling fluid and the pyroelectric signal varies as $\exp[-(f_s^{-1/2}+f_c^{-1/2})\sqrt{f}\,]$, where $f_c = \alpha_c/\pi l_c^2$. This means that by performing a least-squares fitting of the straight-line regions of the logarithm of the pyroelectric signal as a function of $\sqrt{f}$, one is able to calculate the thermal diffusivity of both the sample and the coupling fluid. In the case of Si (Fig. 3), the fitting in the region between 200 and 600 Hz yielded $f_s = 182.6$ Hz from which $\alpha_s = \pi l_s^2 f_s$ can be calculated, which gives $\alpha_s = 0.8$ cm^2/s. This value of α_s in in very good agreement with the published values of Si as given in Table I. From the fitting in the region between 600 and 800 Hz we obtained $f_c = 567$ Hz. Using the measured value of the thermal compound thickness, $l_c \simeq 25$ μm, the value of $\alpha_c = \pi l_c^2 f_c$ was then calculated to be $\alpha_c = 0.012$ cm^2/s. Similarly in the case of Cu (Fig. 4), the least-squares fittings in the two linear regions yielded $f_s = 151.6$ Hz and $f_c = 244$ Hz. Using the thickness of the thermal compound layer in this case $l_c \sim 50$ μm and of the copper foil $l_s = 500$ μm, the calculated values of α_s and α_c were $\alpha_s = 1.2$ cm^2/s and $\alpha_c = 0.019$ cm^2/s. Similar to the measurements of Si, the agreement between our measured value for the thermal diffusivity of Cu and the value of $\alpha_s = 1.15$ cm^2/s quoted in the literature (see Table I) is very good. As for the values of α_c of the thermal compound obtained from the two experiments, the agreement

TABLE I. Thermal diffusivity (α) for the materials used in our experiment.

Material	Si	Cu	Glass
Measured value (cm^2/s)	0.9	1.15	0.002
Standard value (cm^2/s)	0.9 (Ref. 22)	1.2 (Ref. 23)	0.004 (Ref. 24)

is within the error limits[21] at high frequencies. In the case of the glass plate the semilog plot of the pyroelectric signal as a function of $\sqrt{f}$ exhibited just one straight line as shown in Fig. 5. The reason for this is that for glasses the thermal diffusivity ($\alpha \sim 10^{-3}$ cm^2/s) is much smaller than that of metals and semiconductors. This means that for the case of glasses, on increasing the modulation frequency, the pyroelectric signal would die out before the coupling fluid becomes thermally thick. The least-squares linear fitting of the logarithm of the pyroelectric signal as a function $\sqrt{f}$ yielded $f_s = 17.3$ Hz from which we get $\alpha_s = 0.002$ cm^2/s.

In conclusion, we have demonstrated in this paper the potential use of the photopyroelectric effect for measuring the thermal diffusivity of solids over a very wide range. The specific examples we have considered varied from the high thermal diffusivity (metals) to the low thermal diffusivity (glasses) materials covering a range of more than 4 orders of magnitude in thermal diffusivity. The extreme simplicity, sensitivity, as well as its adaptability to practical restrictions imposed by experimental systems requirements suggest that photopyroelectric method is a potentially powerful technique, especially when *in situ* nondestructive testing of samples with minimal preparation is required.

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