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CHARACTERIZATION OF THE OPTICAL AND THERMAL PROPERTIES OF MATTER BY
PHOTOTHERMAL TECHNIQUES

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N.M. Amer

April 1985

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**CHARACTERIZATION OF THE OPTICAL
AND THERMAL PROPERTIES OF MATTER
BY PHOTOTHERMAL TECHNIQUES**

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April 1985

Characterization of the Optical and Thermal Properties of Matter by Photothermal Techniques

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When an intensity-modulated beam of electromagnetic radiation is incident upon an absorbing medium, heating will occur. Typical temperature rise associated with this process is on the order of 10^{-5} - 10^{-4} °C. In recent years we have exploited such a small temperature rise to develop a novel and powerful class of spectroscopy called photothermal spectroscopy. As I shall show below, this experimental tool provides a highly sensitive and non-invasive probe of the optical and thermal properties of matter.

There are two primary ways of implementing photothermal spectroscopy: photothermal deflection, and photothermal displacement. I shall first describe the experimental details of both approaches, and give brief examples of their application. Next, I shall describe the applicability of the technique to the investigation of thermal properties of solids.

I. PHOTOTHERMAL DEFLECTION SPECTROSCOPY AND DETECTION:⁽¹⁻⁴⁾

Concomitant with the optical heating described above is a change of the index of refraction of the illuminated material. The heat will also flow out into the surrounding medium inducing a corresponding change of its refractive index. To achieve maximum sensitivity, the intensity of the optically-exciting beam (pump beam) is modulated, and phase sensitive techniques are employed. The experimental arrangement is shown in

Fig. (1):

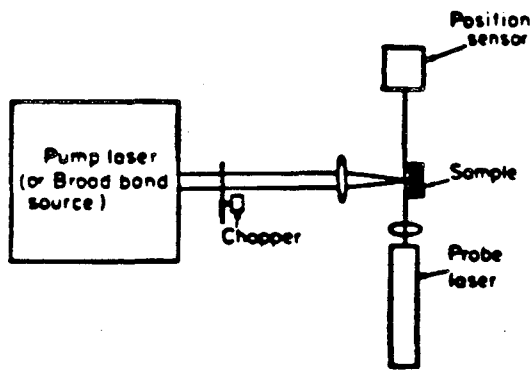


Fig. 1.a

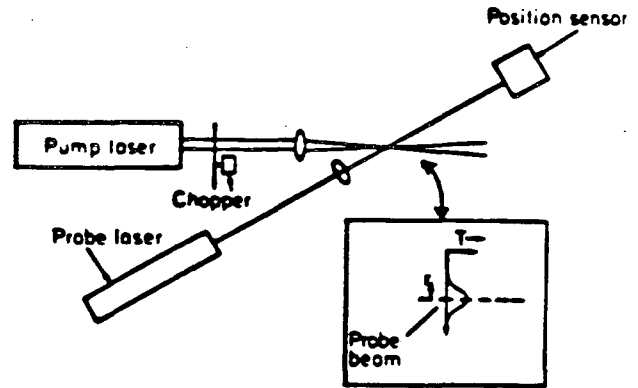


Fig. 1.b

Thus, the time-dependent change in the medium temperature, and the corresponding modulated index of refraction gradient are employed to deflect a probe beam intersecting the pump beam *within* the sample or the medium in which it resides (e.g., air). The deflection can be as small as 10^{-9} - 10^{-10} radians, which is well within the detectivity levels of available position sensitive detectors.

To quantitatively relate the deflection signal to the optical absorption, the theory⁽¹⁾ consists of four steps:

- (1) The spatial distribution of the optical field is determined within the sample and in the surrounding media.
- (2) The optically-generated heat/unit volume is then determined. The heat energy is the source term for the temperature equations which are solved for the sample and the surrounding media.
- (3) The deflection of the probe beam (caused by the temperature rise, which in turn induces a gradient in the index of refraction) is calculated.
- (4) The deflection is related to the voltage output of the position sensor.

Following these steps, and considering the case where thermal diffusion length of the medium is much smaller than the Gaussian pump beam radius (the case of high frequency modulation and/or low thermal conducting medium), the deflection angle ϕ is given by:

$$\phi = (dn/dT)(P/\omega\rho c\pi^2a^2)[1 - \exp(-\alpha l)][(-2x/a^2)\exp(-x^2/a^2)] \quad (1)$$

where dn/dT is the temperature coefficient of the index of refraction of the medium, P is the incident laser power, ω is the angular modulation frequency of the pump beam, ρc is the heat capacity per unit volume, a is the radius of the pump beam at $1/e$ intensity, x is the separation between the intensity maxima of the pump and probe beams, α is the optical absorption coefficient, and l is the optical path length in the absorbing medium. For small αl ($\lesssim 2$) the deflection amplitude is proportional to the optical absorption and to the power, while inversely proportional to the modulation frequency. Furthermore, ϕ exhibits a maximum near $x/a \sim 1$ defining the optimum optical separation between the pump and probe beams.

On the other hand, in the case where the thermal diffusion length is much larger than the pump beam radius, ϕ is given by:⁽¹⁾

$$\phi = (dn/dT)(P/\kappa\pi^2x)[1 - \exp(-\alpha l)][1 - \exp(-x^2/a^2)] \quad (2)$$

where κ is the thermal conductivity of the medium. Note that in this regime, ϕ is independent of ω . The experimental arrangement is shown in Fig. (1). An intensity modulated beam, from either a laser or a broad-band source, is focussed on the sample. The associated index of refraction gradient deflects a tightly focused ($<$ pump beam spot size) probe beam intersecting the pump beam at the *maximum gradient* of the index of refraction. The amplitude of the deflection is measured with a position sensitive detector. The output of the position sensor is connected to the differential input of a lock-in amplifier to discriminate against fluctuations in the intensity of the probe beam. Under these conditions, maximum deflection and good transverse resolution across the heated region were achieved. To optimize the sensitivity:

- (1) Care should be taken to insure that the probe beam is probing the maximum gradient of the index of refraction change.
- (2) The probe beam should be tightly focussed, with the focal spot of the latter being smaller than that of the pump beam.
- (3) Whenever feasible, the deflecting medium should have as large a dn/dT as possible (e.g., immerse solid samples in CCl_4).
- (4) The pointing stability of the probe beam can be the factor limiting the sensitivity of the technique.

We achieved sensitivities of $\alpha l \sim 10^{-8}$ for liquids and 10^{-7} for gasses and solids. In terms of temperature rise, for 1 cm interaction length, a change of 10^{-5} °C in air and 10^{-7} °C in liquids can be readily detected.

The superiority of photothermal deflection in terms of sensitivity and flexibility has been demonstrated in a recent study of the properties of defect states in amorphous silicon.⁽⁵⁾ These weakly absorbing states were not accessible for study by conventional absorption or photoacoustic techniques, since the typical films of this material are $\lesssim 1 \mu$ thick. The defect nature was identified and its energy level and density were measured. These results have both fundamental implications to the density-of-states of amorphous semiconductors, as well as to technological applications such as factors governing the efficiency of solar cells.

The advantages of photothermal deflection detection extend beyond condensed matter. It has been demonstrated that an ultratrace detection of part per billion in gases⁽³⁾ can be readily achieved in an experimental configuration which obviates the need for sampling (see Fig. 1b). By intersecting the probe and pump beams in space, *in situ*, real-time measurements can be performed. An interesting possibility using this scheme is to do spatial and temporal remote sensing of the atmosphere. A limiting factor, in this case, can be atmospheric turbulence and scintillation. However, preliminary results in our laboratory show that by modulating probe beam at 1 kHz - 1 MHz, the effects of turbulence are practically eliminated.

II. Photothermal Displacement Spectroscopy

There exists a class of experimental conditions for which photothermal deflection would be unsuitable for studying optical and thermal properties of matter. Examples of such experiments are those which require ultrahigh vacuum and/or cryogenic temperatures. Such are the conditions encountered in the study of adsorbates and of surface and interface states of solids. Similar requirements exist for the task of *in situ* and in real-time characterization of thin films. A major problem associated with the use of conventional reflection and transmission measurements is the uncertainty associated with separating the large background due to bulk (substrate) absorption from that due to the surface (thin film). In principle, the modulation frequency dependence of photothermal techniques provides a unique tool of "depth profiling" the source of the photothermal signal. This ability, combined with the high sensitivity of photothermal spectroscopy, motivated the exploitation of optical heating in a manner which overcomes the limitations of photothermal deflection and photoacoustics. Optical heating of solids should result in the buckling and displacement of the illuminated surface. A measure of the displacement is a means for determining the optical and thermal properties of the sample.^(6,7) To determine the optimum method of detecting this displacement, its magnitude and shape have been calculated.⁽⁷⁾ The steps of the calculation are:

- (1) Solve the three-dimensional heat equation for a source of exponentially decaying Gaussian beam.
- (2) Solve the Navier-Stokes equation, with the condition of no normal component to the stress at the boundary of the slab.

An approximate solution for the height of the displacement h is given by:

$$h \sim \alpha_{th} \beta P / (2A f \rho C) \quad (3)$$

where α_{th} is the thermal expansion coefficient of the solid, β is the fraction of absorbed light, P is the incident power, f is the modulation frequency, A is the optically heated area, ρ the density, and C the heat capacity.

An important characteristic parameter in photothermal spectroscopy is the thermal diffusion length L_{th} which defines the depth within the solid from which the photothermal signal is generated. L_{th} is given by:

$$L_{th} = (K_{th} / \pi f \rho C)^{1/2} \quad (4)$$

where K_{th} is the thermal conductivity of the material. It can be seen from Eq. (4) that by increasing the modulation frequency of the pump beam, one is able to enhance the ratio of the surface to bulk contribution to the signal.

A numerical estimate of the displacement height is in order: Consider a 1 mW laser beam, focussed to 75 μ radius and modulated at 300 Hz, being fully absorbed by a 0.3 cm thick silicon crystal. The calculated h is $\sim 10^{-2}$ \AA and the corresponding slope is $\sim 10^{-8}$.

This small displacement can be detected in a variety of ways:

- (1) The most obvious is to use interferometric techniques. As shown in Fig. (2), the sample serves as one arm of a conventional Michelson interferometer. The mirror on the other arm is mounted on a piezoelectric transducer for signal stabilization. Detection limits of $10^{-4} \text{\AA} / \sqrt{\text{Hz}}$ are readily achieved.
- (2) As shown in Fig. (3), the displacement can be measured in an attenuated total reflection scheme. A transparent prism is placed in proximity to the sample surface. Since the evanescent field of an internally totally reflected beam decays exponentially in the gap d as $\exp(-d)$, small changes in the gap result in large changes in the intensity of the reflected probe beam.
- (3) The simplest and most versatile method of detecting the displacement is the beam deflection scheme shown in Fig. (4). The probe beam, which is reflected from the sample surface, is deflected by the slope of the surface displacement.

The deflection is measured by a position sensor whose output is amplified by a phase-sensitive lock-in amplifier. In addition to optical information, thermal information is obtained by measuring the shape and phase of the displacement as a function of the modulation frequency. A slope of $10^{-9}/\sqrt{\text{Hz}}$ is easily measured. The effect of the relative position of the probe and pump beams is shown in Fig. (5).

While the sensitivities of all schemes is comparable ($\alpha l \sim 10^{-6}$; signal saturation does not occur until $\alpha l \sim 7$; minimum absorbed power μW), clearly, the beam deflection method is the most attractive because of its simplicity and ease of implementation.

To optimize the displacement signal, both the pump and probe beams should be tightly focussed, with the probe focal spot being smaller than that of the pump. An increase in the distance between the sample and the detector enhances the sensitivity. In our experience, the pointing stability of the probe beam is a factor limiting the achieved sensitivity.

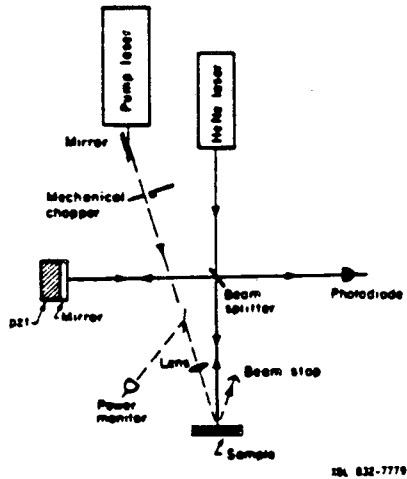


Fig. 2

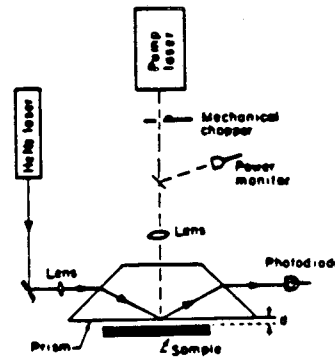


Fig. 3

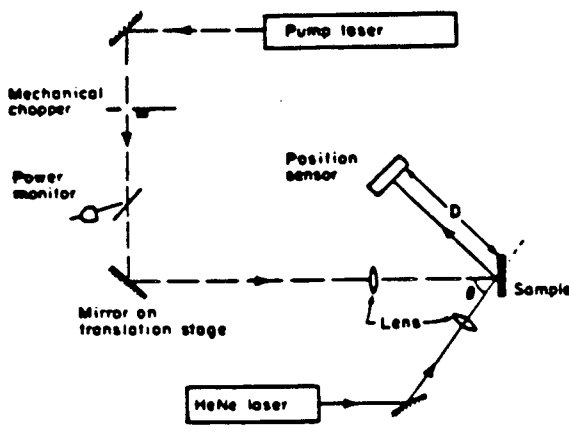


Fig. 4

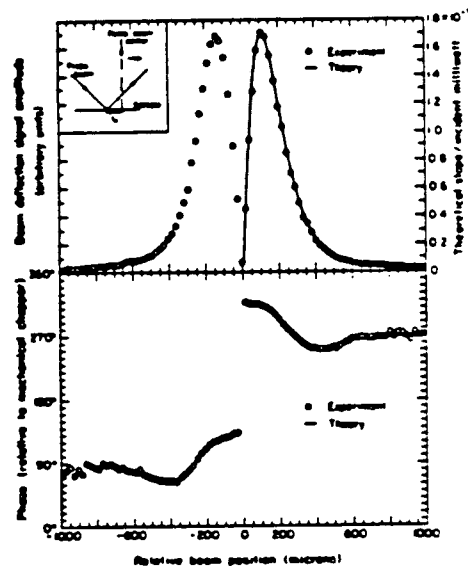


Fig. 5

Given the fact that the deflection scheme relies on the reflection of the probe beam from the sample surface, the question arises as to the required surface quality of the surface. As a good rule of thumb, the ratio of the average variation over the wavefront to the dimension of the surface roughness should be smaller than the position sensor aperture ($\sim 10^{-2}$ radians). In most cases this condition is met without the need to polish the surface. As to any contribution of thermal lensing to the signal, for bulk absorptions, or for samples with high thermal expansion coefficients, this contribution is negligible.

The ability of photothermal detection to differentiate between surface and bulk or substrate absorptions is demonstrated in (Fig. 6a). A 50 Å gold film was evaporated on a 2 mm thick didymium glass. [The absorption spectra of the gold (50 Å film on a transparent substrate), and of pristine didymium (without the gold film) are shown in Fig. (6b)].

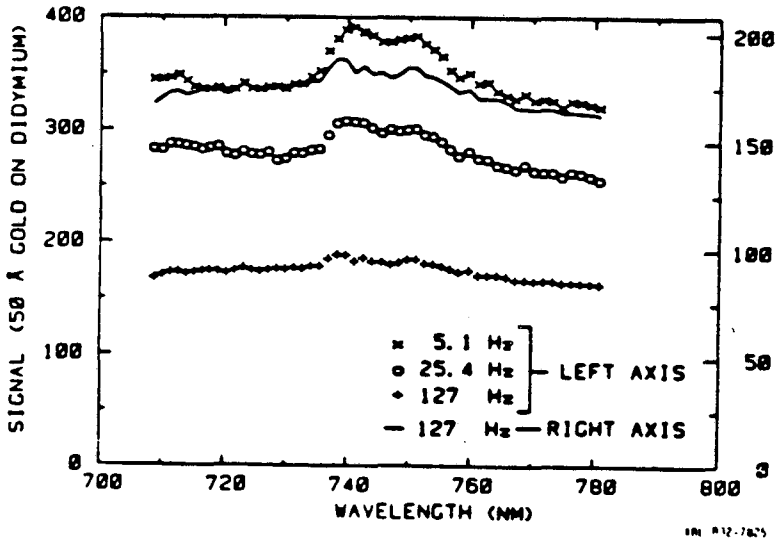


Fig. (6.a)

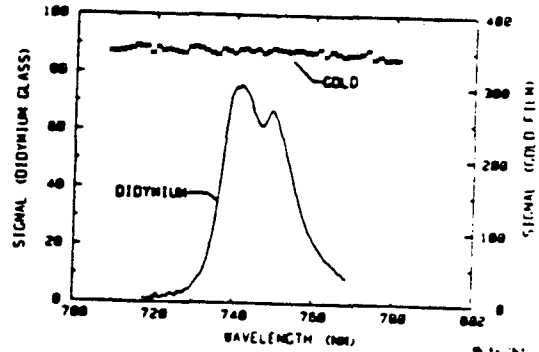


Fig. (6.b)

In the region of 700-800 nm, approximately 25% of the incident light is absorbed by the gold film; with the didymium having a strong absorption coefficient of $\sim 6.5 \text{ cm}^{-1}$ around 740 nm. As shown in Fig. (6a), at a modulation frequency of 5 Hz, the photothermal signal of the gold-coated didymium is the sum of the featureless gold absorption plus the peaks of the didymium absorption band. As the modulation frequency is increased to 127 Hz, the gold signal is decreased only by a factor of 2, while the didymium peaks are decreased by an *additional* factor of 2-3. Clearly, higher modulation frequencies will result in a further reduction of the substrate (or the bulk) contribution to the photothermal signal.

Recently, we have employed this technique to directly measure, in UHV, the polarization dependence of the Si and Ge(111)2x1 surface state absorption. This measurement provides a crucial test for the various models of the surface reconstruction of tetrahedrally-bonded semiconductor surfaces. Our results support the "chain model" and rule out the possibility of a buckled surface. (8,9)

III. DETERMINATION OF THE THERMAL PROPERTIES OF MATTER:

An interesting property of photothermal spectroscopy is its ability to measure, directly, the thermal parameters of matter. This is a natural outcome of the very nature of this family of techniques: the conversion of the energy of the exciting beam (typically, but not solely, electromagnetic radiation) into heat via non-radiative processes. This can be accomplished in a non-invasive manner and without the use of contacts.

There are two possible manners in which the measurement can be carried out: one which employs an intensity-modulated cw pump beam, and another where a pulsed laser pump beam is used.

1. Periodically-Modulated cw Pump Beam:

The basic concept is rather straightforward: by measuring the amplitude and phase of the photothermal signal as a function of the separation between the pump and probe beams one can determine the thermal diffusivity.

To illustrate this approach, let us consider the photothermal deflection case. The deflection can be written as:

$$\phi = (e/n)(\partial n/\partial T)(\partial T/\partial x) \quad (5)$$

where e is the pump and probe beam interaction length, n is the refractive index, T is the temperature, and x is the separation between the pump and probe beam intensity maxima.

The term $(\partial T/\partial x)$ contains the material's thermal parameters. When written explicitly, the deflection has the following form:

$$\phi = (e/n)(\partial n/\partial T)(2T_0/\mu) \exp(-x/\mu) \cos(\omega t - x/\mu + \pi/4) \quad (6)$$

where T_0 is the sample temperature at $t = 0$, $\omega = 2\pi f$, $\mu = (\kappa/\rho C\omega)^{1/2}$, κ is the thermal conductivity, ρ is the mass density, and C is the heat capacity.

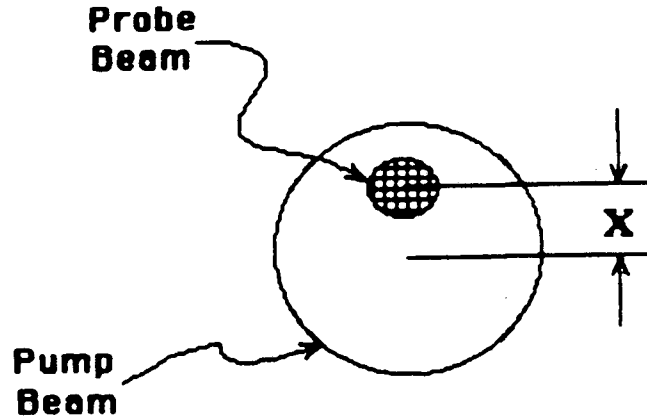


Fig. (7)

2. Pulsed Pump Beam:

In this case, the thermal information of interest is contained in the time dependence of the deflection signal. To perform the measurement, the evolution of the deflection in the time domain is captured with an oscilloscope, or digitized with a transient digitizer.

For a Gaussian pump beam, the time dependence of the temperature gradient is given by:

$$\partial T(t)/\partial x = (4E\alpha/\pi\rho C)(x/[a^2 + 8Dt]^2) \exp(-2x^2/a^2 + 8Dt) \quad (7)$$

where α is the optical absorption coefficient, E is the laser pulse energy, a is the Gaussian width at $1/e$, D is the thermal diffusivity ($\kappa/\rho C$), t is the time, and x is the distance between the pump and probe beam intensity maxima.

It can be readily shown that the time dependence of the deflection is given by:

$$\phi(t) \approx (\alpha E/n\rho C \sin\theta)(\partial n/\partial T)(2x/[a^2 + 4Dt]^{3/2}) \exp(-x^2/[a^2 + 4Dt]) \quad (8)$$

where θ is the intersection angle between the pump and probe beams.

In the following, Table I gives thermal diffusivity values for a variety of materials which were measured using photothermal spectroscopy. Also given are published values obtained from conventional techniques.

Table I

Material	Photothermal Diffusivity Values (cm²/sec)	Literature Values (cm²/sec)
SiC	0.51	0.43
Si ₃ N ₄	0.21	0.16
Al	0.98	0.98
In	0.54	0.56
GaP	0.50	0.51

While the values for Al, In, and GaP agree well, those for SiC and Si₃N₄ showed significant discrepancy. This is not surprising given the well known unreliability of conventional methods when used to measure materials such as SiC and Si₃N₄. Thus, I believe that the photothermal values provide the first accurate values of thermal diffusivity for these materials.

In summary, photothermal spectroscopic techniques provide a highly sensitive experimental probe which enables the measurement of optical and thermal properties of matter. In addition to being quantitative, they are relatively easy to implement and provide unique experimental flexibility.

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