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NEW APPROACHES TO PHOTOTHERMAL SPECTROSCOPY

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NEW APPROACHES TO PHOTOTHERMAL SPECTROSCOPY

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Résumé -

Abstract - Recent developments in photothermal spectroscopy and detection are reviewed.

I - Introduction

In recent years, the small rise in temperature, associated with the absorption of electromagnetic radiation, has provided the basis for a class of spectroscopy which can be loosely called photothermal spectroscopy. Until recently, the more familiar member of this family has been photoacoustic spectroscopy where the optical heating is converted into sound and is detected with a microphone. Using this relatively simple technique, ultratrace gas detection achieved impressive sensitivity levels /1-6/. In the case of condensed matter samples, the poor coupling between the sample and the microphone has led to the use of piezoelectric transducers in order to overcome this limitation /7,8/. Although this approach has proven to be useful /8,9/, the ultimate sensitivity of piezoelectric photoacoustics can be limited by the scattering of light on the transducer. Furthermore, in the case of experiments requiring a wide range of temperatures and pressures, or involving hostile environment, both microphone and piezoelectric photoacoustic detections can not be employed.

II. Photothermal Deflection Spectroscopy and Detection

To overcome these limitations, the optical heating was exploited in different ways. It is well known that heating causes a corresponding change in the index of refraction of the heated medium. Hence, when an intensity-modulated beam of light (pump beam) is absorbed, part or all of the absorbed energy will be converted to thermal energy. The heat flows into the surrounding medium causing a corresponding modulation of the index of refraction. A second weak beam (probe beam), probing the gradient of the time-dependent change in the index of refraction, will experience a periodic deflection synchronous with the intensity modulation. The amplitude and phase of the periodic deflection can be measured with a position sensor and a differential ac synchronous detection scheme (see Fig. 1). Thus, by varying the wavelength of the pump beam, the deflection of the probe beam is a measure of the optical absorption of the material of interest. This type of spectroscopy is known as photothermal deflection spectroscopy /10-13/.

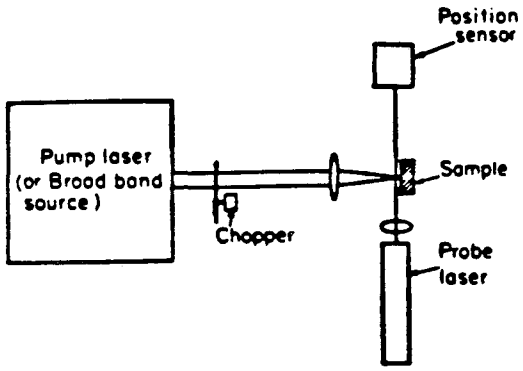

Fig. 1.a

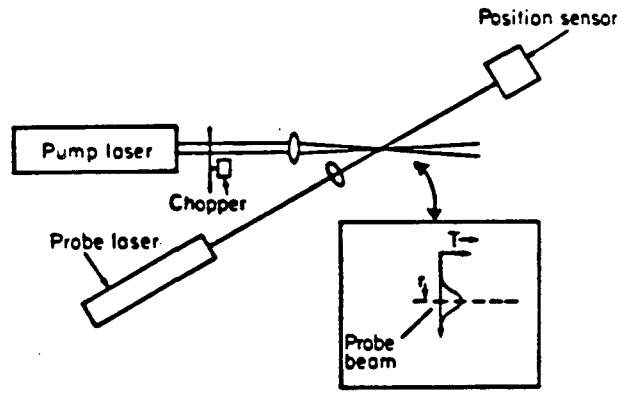

Fig. 1.b

To quantitatively relate the deflection signal to the optical absorption, the theory /13/ 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, the deflection signal S is given by:

$$S \sim F(1/n_o)\ (dn/dT)L\ dT(z_o)/dz \qquad (1)$$

where F is the position sensor transduction factor (typically $\sim 10^3$V/radian), $(1/n_o)$ (dn/dT) is the relative index of refraction change with temperature of the deflecting medium, L is the interaction length between the optically heated region and the probe beam, T is the amplitude of the ac temperature rise above the average temperature.

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 $\alpha\ell \sim 10^{-8}$ for liquids and 10^{-7} for gases 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.

It is instructive to write the photothermal deflection signal for a solid, in terms of temperature rise $\tau(0)$, integrated over the heated area. This would provide a basis for comparing the sensitivities of photothermal deflection and photoacoustics. Eq. (1) can be evaluated to give $S \sim 10$ V cm^{-2} C $\tau(0)$. In the case of

photoacoustic detection, the corresponding factor is ~ 0.1 V cm^{-2} C τ (0). Thus, photothermal deflection is about 100 times more sensitive than photoacoustics.

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 /14/. 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 can be readily achieved in an experimental configuration which obviates the need for sampling (see Fig. 1.b). 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 1kHz-1MHz, the effects of turbulence are practically eliminated.

III. Photothermal Displacement Spectroscopy

There exists a class of experimental conditions for which both photoacoustic and 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 /15-19/. To determine the optimum method of detecting this displacement, its magnitude and shape are calculated. The steps of the calculation are /19/:

(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

$$h \sim \alpha_{th} \beta P/(2Af\rho C) \qquad (2)$$

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

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 ~ 10^{-2} Å and the corresponding slope is ~ 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 peizoelectric transducer for signal stabilization. Detection limits of 10^{-3} Å/$\sqrt{Hz}$ 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. Again displacements on the order of 10^{-3} Å/ Hz can be detected.

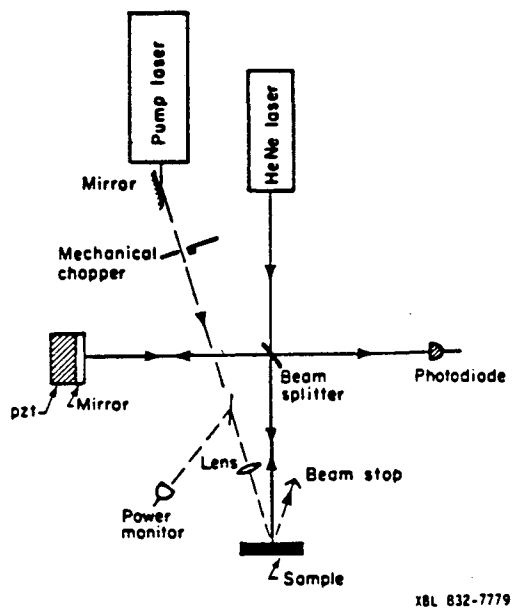

Fig. 2

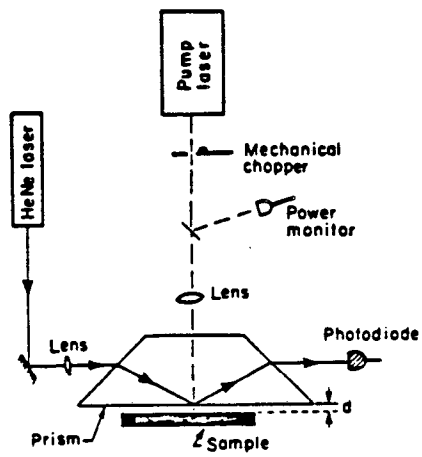

Fig. 3

(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 $10^{-9}/\sqrt{Hz}$ 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 three schemes is comparable ($\alpha\ell \sim 10^{-6}$; signal saturation does not occur until $\alpha\ell \sim 7$; minimum absorbed power μ W), 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.

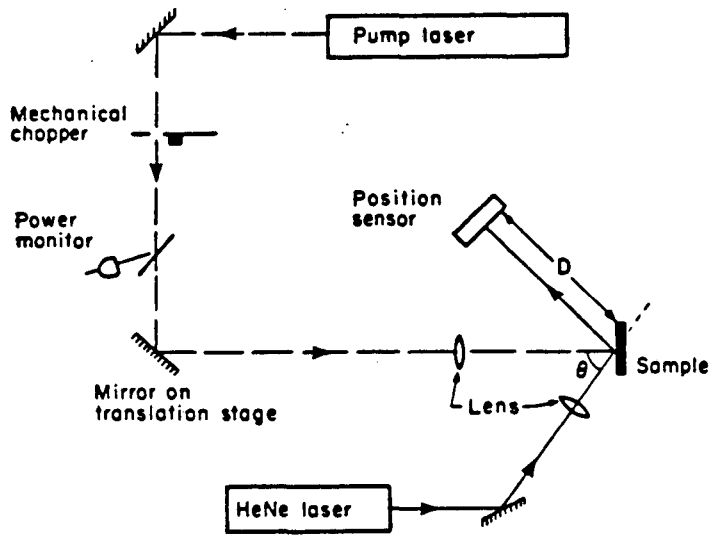

Fig. 4

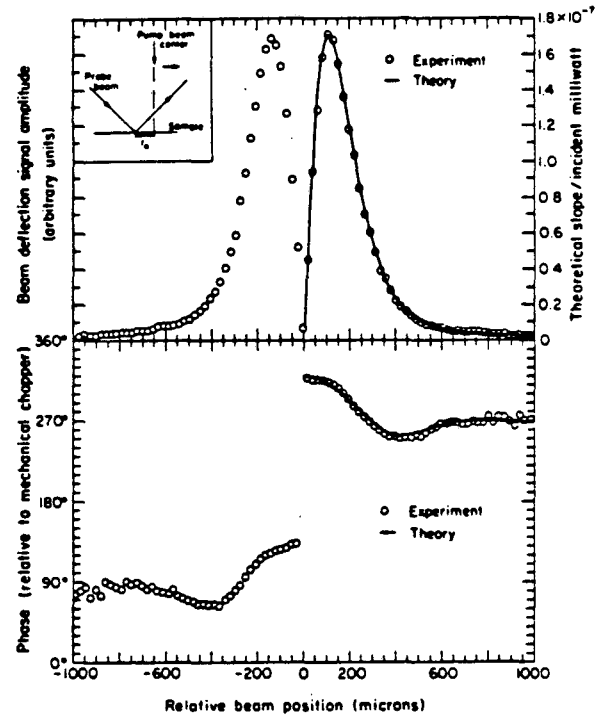

Fig. 5

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 (~ 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 completely negligible. Otherwise, a small correction might be necessary.

The spectroscopic applications of the displacement technique, its suitability for investigations requiring vacuum, and its ability to distinguish between surface (thin films) and bulk (substrate) are reported elsewhere in this colloque.

IV. Concluding Remarks

The ultimate significance of any new technique lies in its ability to provide the tools necessary for unraveling new science. Given the auspicious and productive beginning of the deflection and displacement techniques, it appears that they will satisfy this criterion.

V. Acknowledgements

It gives me great pleasure to acknowledge the fruitful collaboration with Daniele Fournier and Claude Boccara which, over the past few summers, resulted in most of the work presented here.

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