Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

To be presented at the Third International Conference on Infrared Physics, Zurich, Switzerland, July 23-27, 1984

NEW APPROACHES TO PHOTOTHERMAL SPECTROSCOPY

N.M. Amer

February 1984

APPLIED SCIENCE DIVISION

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

Nabil M. Amer

New Approaches to Photothermal Spectroscopy

Lawrence Berkeley Laboratory, University of California,
Berkeley, California, 94720, USA

I. Introduction

In recent years, the small rise in temperature associated with the absorption of light has provided the basis for a new 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 suitable transducer. Although this approach has proven to be useful, the ultimate sensitivity of 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 cannot be employed. To overcome these limitations the optical heating has to be exploited in different ways.

II. Photothermal Deflection Spectroscopy and Detection

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), 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 (see Fig. 1). This type of spectroscopy is known as photothermal deflection spectroscopy.[1] 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.

We have achieved sensitivities of $\alpha l \sim 10^{-8}$ 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.

The superiority of photothermal deflection in terms of sensitivity and flexibility has been demonstrated in a recent investigation of the properties of defect states in amorphous silicon.[2] 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 physics of amorphous semiconductors, as well as to technological factors governing the efficiency of solar cells.

The advantages of photothermal deflection detection extend beyond condensed matter. We have demonstrated that an ultratrace detection of part per billion in gas-phase samples 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.[3] 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.

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 surfaces and interfaces. 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 new manner. Optical heating 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.[4] 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.

The simplest and most versatile method of detecting the displacement is the beam deflection scheme shown in Fig. (2). The probe beam, which is reflected from the sample surface, is deflected by the slope of the surface displacement. The deflection is measured with a position-sensitive detector. In addition to optical information, thermal information is obtained by measuring the shape and phase of the

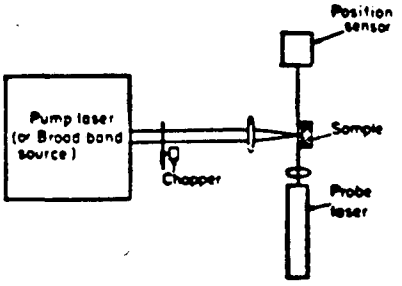

Fig. 1.a

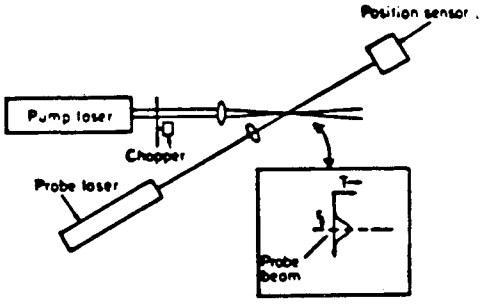

Fig. 1.b

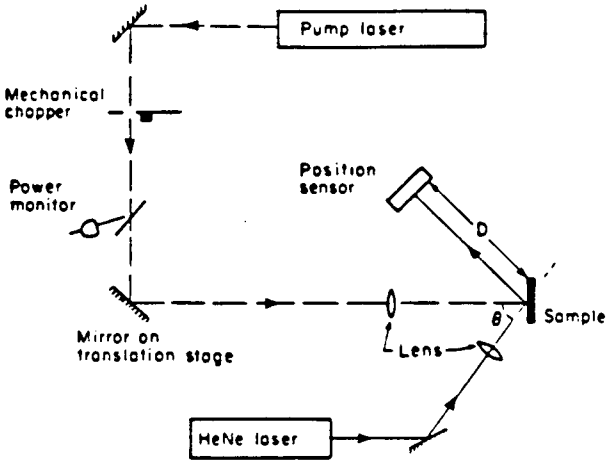

Fig. 2

displacement as a function of the modulation frequency.

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

In summary, an overview of recent developments in photothermal spectroscopy was given, and the potential of this family of techniques was demonstrated.

References

(1) W.B. Jackson, N.M. Amer, A.C. Boccara, and D. Fournier, Appl. Opt. 20, 1333 (1981); A.C. Boccara, D. Fournier, W. Jackson, and N.M. Amer, Opt Lett. 5, 377 (1980); A.C. Boccara, D. Fournier, and J. Badoz, Appl. Phys. Lett. 36, 130 (1980).

(2) W.B. Jackson, and N.M. Amer, Phys. Rev. B 25, 5559 (1982).

(3) D. Fournier, A.C. Boccara, N.M. Amer, and R. Gerlach, Appl. Phys. Lett. 37, 519 (1980).

(4) N.M. Amer and M.A. Olmstead, Surf. Sci. 132, 68 (1983); M.A. Olmstead, N.M. Amer, S. Kohn, D. Fournier, and A.C. Boccara, Appl. Phys. A 32, 141 (1983); M.A. Olmstead, S.E. Kohn, and N.M. Amer, Bull. Amer. Phys. Soc. 27, 227 (1982).

This work was supported by the Office of Energy Research, Physical and Technological Research of the US Department of Energy under contract No. DE-AC03-76SF00098 and by DARPA Contract No.3343.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720