LASER INDUCED PHOTOTHERMAL INVESTIGATIONS ON THERMAL AND TRANSPORT PROPERTIES OF CERTAIN SELECTED PHOTONIC MATERIALS

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Front cover: *"Mirage in a desert"* Painting in the digital art medium.
Back cover: *A typical experimental setup to observe PTD phenomenon.*

Dedicated to

My loving parents
and
Dearest Brother

CERTIFICATE

Certified that the work presented in this thesis entitled **"LASER INDUCED PHOTOTHERMAL INVESTIGATIONS ON THERMAL AND TRANSPORT PROPERTIES OF CERTAIN SELECTED PHOTONIC MATERIALS"** is an authentic record of the bonafide research work done by Mr. Sajan D George, under my guidance and supervision in the International School of Photonics, Cochin University of Science and Technology, India – 682 022 and it has not been included in any other thesis submitted previously for the award of any degree.

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DECLARATION

I hereby declare that the work presented in this thesis entitled **"LASER INDUCED PHOTOTHERMAL INVESTIGATIONS ON THERMAL AND TRANSPORT PROPERTIES OF CERTAIN SELECTED PHOTONIC MATERIALS"** is based on the original research work done by me under the guidance of Dr. C. P. Girijavallabhan, Emeritus Professor in International School of Photonics, and the co-guidance of Prof. V. P. N. Nampoori, Professor, International School of Photonics, Cochin University of Science and Technology, and it has not been included in any other thesis submitted previously for the award of any degree.

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PREFACE

The last twenty five years have witnessed the emergence of nondestructive photothermal technique as an effective research and analytical tool for the characterization of matter in all its different states. Most of these photothermal methods depend upon the detection, by one means or other, of thermal waves generated in the specimen on illumination with a chopped or pulsed optical radiation. As the photothermal technique monitors the nonradiative path, it can throw light into several properties of the materials which are hard to measure using conventional spectroscopic techniques. The advancement in the detecting and measuring systems have made the photothermal techniques an effective tool for the in situ and in vivo studies on the thermal, transport and optical properties of materials, especially those of condensed matter. Among the variety of photothermal techniques employed, the laser induced nondestructive photoacoustic (PA) and photothermal deflection (PTD) techniques are the two popular techniques employed for the evaluation of material parameters due to its simplicity and versatility. The noncontact and nondestructive PTD technique allows point by point scanning on the sample surface as well as the characterization of anisotropy in thermophysical properties of specimen under investigation. Even though, the PA technique is an indirect technique, it allows the evaluation of material parameters with accuracy using a simple and elegant experimental setup.

In the present technological era emerging in the modern world, photonics replaces electronics due to several advantages of optical signal as compared to electronic signal. However, the progress in this field demands better understanding of the fundamental properties of the materials used in this industry. The class of materials used here are the compound semiconductors, nanometal dispersed ceramics, composites of conducting polymer and liquid crystal mixtures. Compound semiconductors are widely used for the generation and detection of optical radiation whereas ceramics are considered to be the ideal material for many of the electronic and optoelectronic devices. In recent times, the fourth generation of polymers, viz., conducting polymers is widely used for the fabrication of plastic LED and many other optoelectronic sources. Liquid crystals are extensively used in the optical data storage devices. The performance and reliability of the device depends greatly on the thermal and transport properties of these materials. The work done here is focused on the evaluation of transport properties of some of these photonic materials using laser induced PTD and PA technique. The present thesis contains the details of the work done and it is organized into six separate chapters.

In chapter 1, an overview of various photothermal techniques are presented. The detailed account of the PA signal generation in condensed matter is given. A review of the work done by various researchers on the class of photonic materials using the experimental techniques employed in the present thesis is presented. Motivation of the present work is also well explained.

Chapter 2 is subdivided into two parts. In the first part, evaluation of the thermal diffusivity of intrinsic InP and InP doped with Sn, S and Fe using PTD technique is presented. The influence of doping as well as the nature of dopant on the thermal diffusivity value is investigated. The influence of plane of cleavage on the thermal diffusivity value of the semiconductor samples is also discussed. In the second part of the chapter, results related to the heat transport through double GaAs epitaxial layer grown on GaAs substrate with varying concentration of Si and a particular concentration of Be are included. Analysis of the results shows that samples exhibit singnificant anisotropy in heat transport and hence show anisotropy in thermal diffusivity values along in-plane and cross plane direction.

Chapter 3 deals with the simultaneous measurement of thermal and transport properties viz. thermal diffusivity, diffusion coefficient, surface recombination velocity and nonradiative recombination time of some direct and indirect bandgap semiconductors. These thermal and transport properties of semiconductors are evaluated by fitting the experimentally obtained phase spectrum of the PA signal under heat transmission configuration to that of theoretical phase spectrum based on the thermal piston model of Rosencwaig and Gersho. This chapter is contains three sections. In the first section, evaluation of thermal and transport properties of some direct bandgap semiconductors namely InP, GaAs and InSb are presented. The second section deals with the measurement of the same in the case of intrinsic Si and Si doped with B and P. The latter section of this chapter discusses the measurement of thermal and transport properties of GaAs epitaxial layers. All these measurements are carried out using a home made Open Photoacoustic Cell.

In chapter 4, focus is made on the measurement of thermal diffusivity of nano Ag metal dispersed ceramic Alumina matrix and composites of conducting polymers, namely Camphor Sulphonic Acid doped Polyaniline with Cobalt Phthalocyanine. For the measurement of thermal diffusivity of ceramics, PA technique under Reflection Detection Configuration (RDC) is employed due to the finite thickness of the specimen under investigation. The thermal diffusivity values are evaluated by knowing the transition frequency, at which sample changes from thermally thin to thermally thick region, from the amplitude spectrum of the PA signal. However, the thermal diffusivity values of the composites are measured using PA technique under heat transmission configuration. The thermoelastic bending of the specimen due to the finite temperature gradient existing within the specimen is also incorporated in the evaluation of thermal diffusivity. In this case the phase data of the PA signal as a function of modulation frequency is utilized for the evaluation of thermal diffusivity of the specimen.

Complete thermal characterization of liquid crystal mixtures namely, Cholesterol and 1 hexadecanol using PA technique is presented in chapter 5. The thermal diffusivity value of the specimen, by including the contribution from thermoelastic bending, is done using PA technique under heat transmission configuration. The phase data of the PA signal is used for the evaluation of thermal diffusivity of the specimen. The thermal effusivity values of the same are investigated using PA technique in RDC. In this case, the amplitude of the PA spectrum is utilized. By knowing these parameters, the thermal conductivity and thermal capacity of the samples as a function of the relative mass fraction of the constitutes is studied.

Conclusions based on the present work are presented in the Chapter 6. The future prospectus and possibility of the continuation of the present work are also included in this chapter.

LIST OF PUBLICATIONS

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14. **Sajan D George,** A. K. George, P. Radhakrishnan, V. P. N. Nampoori and C. P. G. Vallabhan *Thermal characterisation of liquid crystal mixtures using photoacoustic technique* (communicated)
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SAJAN D GEORGE

Contents

Imagination is more important than knowledge

– Albert Einstein

Chapter 1

Photothermal methods and their applications to photonic materials

Abstract

This chapter which is of an introductory nature, presents a short description of various phenomena arising due to light matter interaction with special emphasis on the nonradiative processes and that lead to photothermal phenomena. An overview of various photothermal methods and their applicability for the characterisation of photonic materials are explained in detail. A comprehensive account of the various techniques used for the detection of photothermal signal is also given here. The experimental techniques employed in the present thesis and their significance and uniqueness are well addressed. A review of the work done by various researchers on the applicability of photothermal deflection and photoacoustic technique for the characterisation of photonic materials is also included. The motivation behind the present work is highlighted in this chapter.

1.1. Light Matter Interaction

Interaction of light with matter gives a better understanding of microscopic as well as macroscopic properties of matter in all its different states. The advent of coherent, monochromatic and highly directional light source, namely, laser has lead to a major renaissance in this field. Depending on the strength of the interacting electric field of the electromagnetic radiation, materials exhibit several linear and nonlinear phenomena [1-2]. When the strength of interacting electric field is of the order of atomic field, materials show different nonlinear optical properties such as harmonic generation, hyper polarisability, higher order susceptibility, etc. [3]. The interactions of matter with intense short optical pulses give rise to more interesting phenomena such as laser ablation, plasma generation, etc [4-5]. However, the light-matter interaction at low levels of optical power results in various thermo-optical and photo chemical reactions [6]. Irradiation of a specimen with an optical radiation results in the excitation of the atoms in the sample to higher energy levels from which they release their energy either in the form of light or heat so as to return to the ground state energy level. These processes can takes place either in a radiative way or through nonradiative way. The emission of light by a substance due to any processes other than due to temperature rise is called luminescence [7]. If the deexcitation is taking place from a metastable state, it is called phosphorescence so that the luminescence persists significantly even after the exciting source is removed. However, in the case of fluorescence, the emission of radiation occurs instantaneously [8-9]. The excitation of specimen can also results in the transfer of energy through chemical reaction [6]. During the last two decades, many researchers has explored the nonradiative path of deexcitation of specimen after excitation with a chopped optical radiation to investigate the thermal, optical, transport and structural properties of material in all its different states [10-21]. Various experimental techniques such as 3ω method, Laser calorimetry and Photothermal methods are used for studying these thermal waves generated due to nonradiative deexcitation of samples [15-20]. The present thesis deals with the use of two photothermal methods, namely, photoacoustic and photothermal deflection technique to investigate the thermal and transport properties of certain selected photonic materials.

1.2. Photothermal methods

In recent years, thermal wave physics has emerged as an effective research and analytical tool for the characterisation of materials [22-25]. The nondestructive and nonintrusive photothermal methods are based on the detection by one means or the other, of a transient temperature change that characterizes the thermal waves generated in the sample after illumination with a pulsed or chopped optical radiation [26-40]. The detected photothermal signal depends on the optical absorption coefficient at the incident wavelength as well on how heat diffuses through the sample [41-45]. Dependence of photothermal signal on how heat diffuses through the specimen allows the investigation of transport and structural properties such as thermal diffusivity, thermal effusivity, thermal conductivity, voids, etc [46-55]. Photothermal methods can be effectively used for the optical characterisation of the sample due to its dependence on optical absorption coefficient [56-60]. The unique feature of photothermal methods is that the detected photothermal signal depends only on the absorbed light and it is independent of transmitted or scattered light. The two features that make photothermal methods superior to conventional methods is that it can directly monitor the nonradiative path of deexcitation in addition to being sensitive to very small optical absorption coefficient [59-60]. Apart from this, photothermal effects can amplify the measured optical signal which is referred to as enhancement factor and it is the ratio of the signal obtained using photothermal spectroscopy to that obtained using conventional transmission spectroscopy. Enhancement factors depend on thermal and optical properties of the sample, the power or energy of the light source used to excite the sample and the optical geometry used to excite the sample [61]. As these parameters can vary externally, photothermal methods can be used even for specimens having relatively poor thermal and optical properties. The merit of these methods also lies in the extremely sensitive detection technique used here in comparison to conventional transmission methods. The various photothermal methods are depicted in figure 1. The magnitude of photothermal signal depends on the specific method used to detect the photothermal effect and on the type of the sample analyzed.

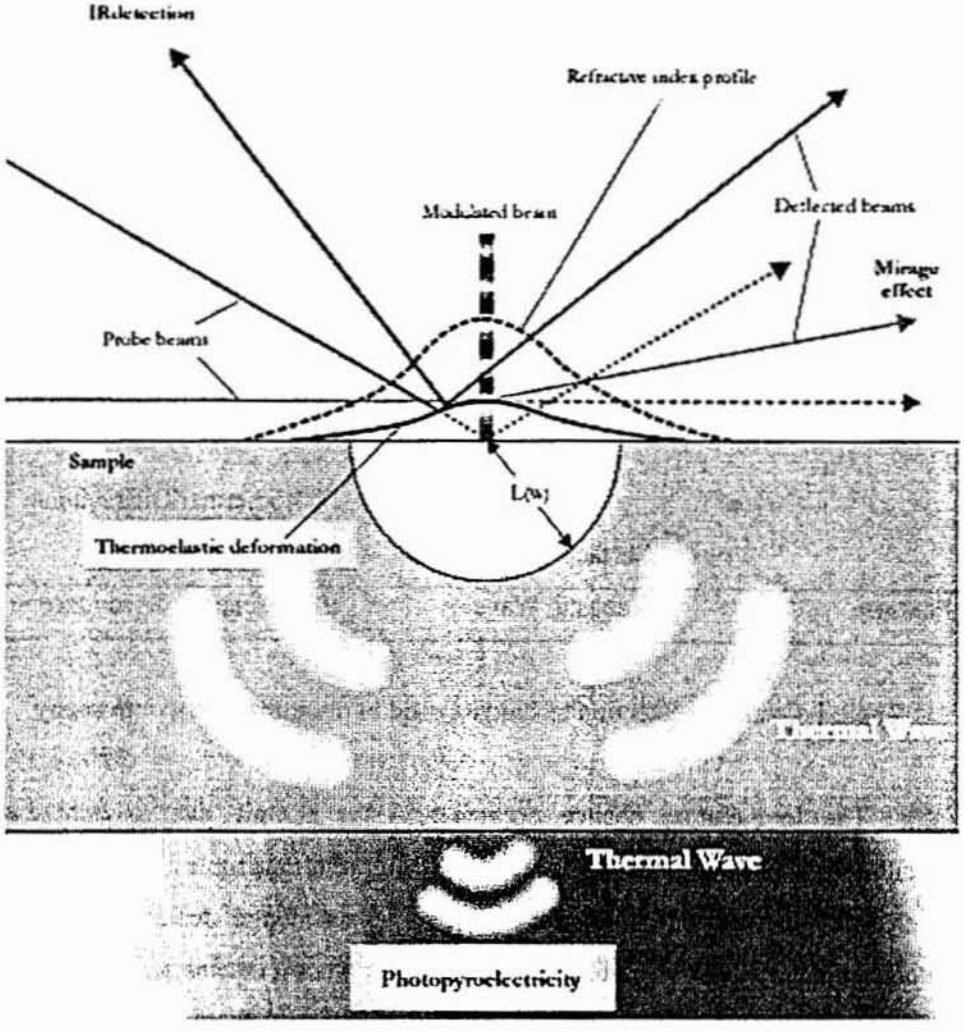

Figure 1. Different types of photothermal signal generation

1.3. A brief account of the different photothermal methods

The common techniques that are employed in photothermal methods are shown in the table I. Eventhough all these techniques are based on the same principle, the detecting parameter changes from one technique to other.

Thermodynamic Parameter	**Measured Property**	**Detection Technique**
Temperature	Temperature	Calorimetry
	Infrared Radiation	Photothermal Radiometry
Density	Refractive Index	Photothermal Lens Photothermal Interferometry Photothermal Deflection Photothermal Refraction Photothermal Diffraction
	Surface Deformation	Surface Deflection
Pressure	Acoustic Wave	Photoacoustic Spectroscopy

Table I. Common detection techniques used in photothermal spectroscopy

The temperature change occurring in the sample due to nonradiative deexcitation can be directly measured using thermocouples, thermistors or pyroelectric devices and the corresponding experimental technique is called *photothermal calorimetry* [62-65]. In the *photopyroelectric technique* [66-68], which can be used for the simultaneous measurement of different thermal parameters such as thermal diffusivity, effusivity etc., a thermally thick pyroelectric film (thickness of the film is greater than thermal diffusion length of the film) is attached to one side of the thermally thick sample and the combination is mounted on a thermally thick backing medium. The other side of the specimen is illuminated by an intensity