บทความวิชาการ

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บทคัดย่อ

เทคนิคโฟโตเทอร์มัลได้รับการใช้ในวงกว้างทั้งงานทางด้านวิจัยและด้านอุตสาหกรรม เนื่องจากเป็นเทคนิคที่ไม่สัมผัสและไม่ทำลายชิ้นตัวอย่าง หลักการทำงานของเทคนิคนี้คือ ชิ้นตัวอย่างจะดูดกลืนพลังงานแสงบางส่วนและเปลี่ยนเป็นพลังงานความร้อนโดยทันที ความร้อนที่ได้ส่งผลให้เกิดปรากฏการณ์รองต่อมา เช่น การแผ่รังสีอินฟราเรด การขยายตัวของพื้นผิว เป็นต้น ปรากฏการณ์เหล่านี้จะถูกวัดเพื่อใช้เป็นค่าตอบสนองทางโฟโตเทอร์มัล ซึ่งแสดงสมบัติทางกายภาพเชิงความร้อนของชิ้นตัวอย่าง เทคนิคโฟโตเทอร์มัลที่นิยมใช้กันอยู่ให้ความละเอียดของการวัดสูงถึง 1 ไมโครเมตร และสามารถรองรับการใช้งานในย่านความถี่ 0.01 เฮิร์ตซ์ ถึง 5 เมกะเฮิร์ตซ์

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Photothermal Techniques

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ABSTRACT

Photothermal techniques encompass a wide range of applications in research and industry since they are non-destructive and non-contact methods. These techniques rely on a fraction of the optical energy being absorbed by the sample and being converted rapidly to heat. This heating generates additionally the secondary effects such as infrared emission, surface expansion, etc. All these effects have been used to probe the photothermal response of a medium depending on its thermophysical properties. By far the conventional photothermal techniques give the detected resolution down to 1 μm and serve the frequency range from 0.01 Hz to 5 MHz.

Keywords: photothermal techniques, non-destructive technique, non-contact technique

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Introduction

Thermal waves are temperature distributions which are oscillatory in time and space, $\delta T(\vec{r},t)$. They are well known phenomena in nature. Periodic heating by the sun generates the thermal oscillations of the surface of the earth. In basic and applied research, thermal waves have been a field of scientific investigation for more than a century. Angström was the first to publish, in 1861, an experimental and theoretical study of diffusion waves. In this work, he measured the periodically heating of a long copper bar and calculated the thermal diffusivity of this solid [1]. In 1880, the great discovery of *Photoacoustic Effect* on solid materials was reported by Bell and his coworker [2]. They observed that intermittently chopped sunlight incident on a strongly absorbing substance causes audible sound to emanate from the substance. It was almost a century later when Rosencwaig and Gersho gave the comprehensive theoretical interpretation of the photoacoustic effect of solid on the basis of thermal wave [3]. Rosencwaig also established photoacoustic spectroscopy as a tool for optical studies of solids [4]. Since then, the invention of numerous other detection schemes used in research and industry are rapidly widespread.

By far the most common way of generating thermal waves is to heat a sample with a modulated laser beam. Therefore, thermal wave methods are usually denoted as *photothermal techniques* with an appendix specifying the detection technique. These methods rely on a fraction of the optical energy being absorbed by the sample and being converted rapidly to heat. This heating results in a number of physical changes in and around the sample. In addition to a change in the temperature of the sample, the secondary effects are generated such as infrared emission, acoustic waves, surface expansion, etc. All these effects have been used to probe the photothermal response of a medium depending on its thermophysical properties. Since photothermal method is a fairly rapid non-destructive and non-contact technique that has significant industrial potential. It now encompass a wide range of applications in research and industry in areas such as basic studies of the physics and chemistry of materials, spectroscopy, evaluation of semiconductors, non-destructive testing, pollution monitoring, medical and biological material analysis, etc. In the conventional photothermal methods, most of them are generally applicable to bulk samples and the detected resolution is restricted to some microns. For examples, Chirtoc, *et al.* applied these techniques to evaluate the thickness in the range between 1 and 75 micrometer of transparent coatings on polymer, paper or metallic substrates used as packaging materials [5]. These methods have also been increasingly employed in biomedical studies such as the investigation of the penetration of topically applied drugs into the horny layer of the human skin [6].

The most reported thermal wave techniques in literature are based on modulated techniques, where the amplitude and more often the phase of a periodic temperature variation on the sample surface induced by a modulated source are monitored. The main advantage of modulated techniques is the fact that by a variation of the modulation frequency, the penetration depth of the heat wave can easily be controlled and the measured harmonic part of the heat flow can be restricted to the areas of interest.

For optical based photothermal techniques, the modulated heating is provided e.g. by the absorbed light of a pump laser beam and the temperature is detected either directly by radiation or via secondary effects probed by a second laser beam. Figure 1 is a schematic illustration of the phenomena resulting from the exposure of a sample surface to a localized periodically modulated light source.

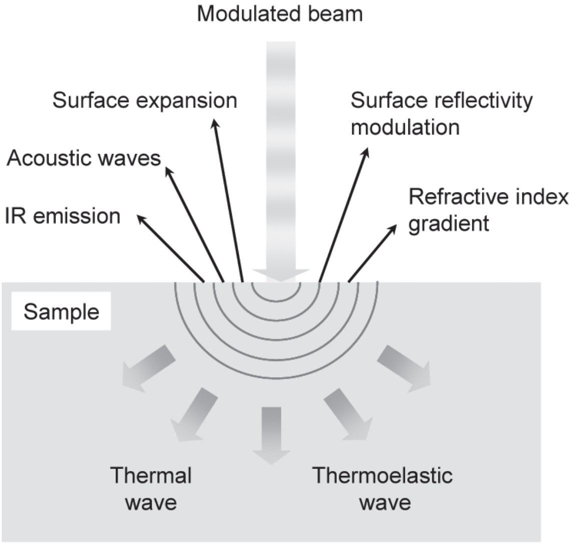
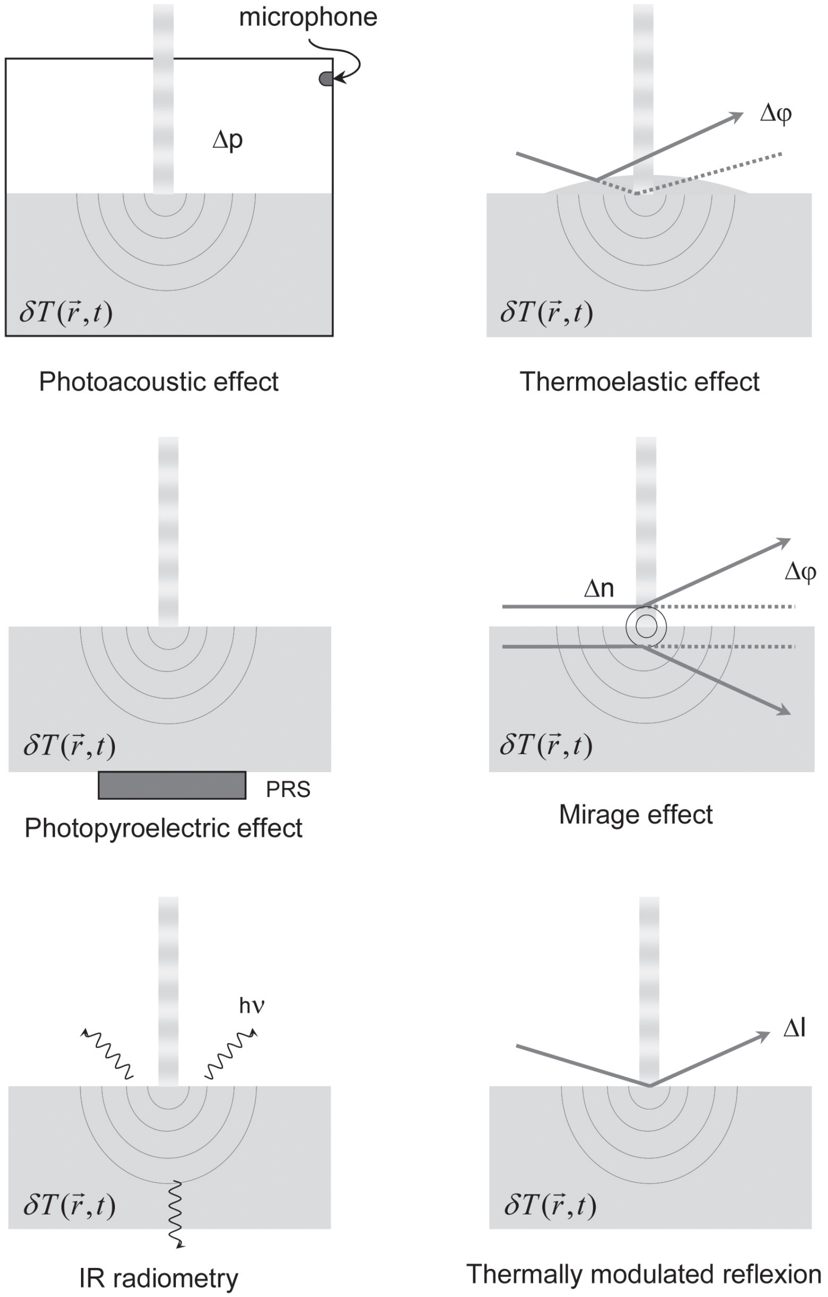


Figure 1 hotothermal phenomena caused by illumination of a surface by a modulated beam of light.

A review of some techniques is described next including the schematic representation of the different configurations in Figure 2.



Photoacoustic effect

Thermoelastic effect

Photopyroelectric effect

Mirage effect

IR radiometry

Thermally modulated reflexion

Figure 2 The schematic representation of the different configurations in photothermal techniques [7].

Photoacoustic Spectroscopy (PAS): In the photoacoustic sensing technique, the periodic thermal response of the sample surface generated by modulated light source is transferred to the surrounding gas in a gas-tight cell. The *pressure fluctuations* induced in the gas volume by the heat flux across the solid/gas interface are detected and converted to an electrical signal by a microphone mounted inside the cell [8]. The photoacoustic signal is proportional to the average of the local modulated temperature rise resulting from optical heating. Photoacoustic spectroscopy requires minimal sample preparation and is used on a broad range of materials such as solids, gases, powders, etc. A serious limitation of this detection is the requirement that the sample being studied must be enclosed in a cell.

Photopyroelectric (PPE) Detection: The use of pyroelectric detectors for the detection of infrared radiation was suggested by Yeou and Chynoweth [9, 10] before practical pyroelectric detectors have been firstly developed [11]. In this technique, the increasing temperature of a sample due to the absorption of radiation is measured by placing a pyroelectric sensor in direct thermal contact with the sample. The pyroelectric material produces a *displacement current* proportional to the temperature change. A theory describing it was soon developed for the case of periodic excitation [12]. This detection is rather simple to design and usually the specimen needs no preparation. By this technique, the materials with the wide range thermal absorption can be investigated [13].

Photothermal Radiometry (PTR): Photothermal radiometry or infrared (IR) radiometry relies on the observation of changes in the *infrared radiation* as a result of the excitation of thermal waves [14]. The conventional experimental arrangements use liquid nitrogen cooled semiconductor detectors to measure the local IR emission at the front or rear surface of a sample [15]. IR radiometry is becoming the most popular photothermal technique. The principal reasons are that it is simple, remote temperature monitoring, robust, non-contacting, and compatible with many industrial requirements [16]. By far it has been used for the investigation of coatings, semi-conductors, composites, biological material, etc. Additionally, this technique can be used to study the samples at high temperatures in vacuum and in inaccessible environments.

Thermoelastic (ThE) Response: This technique is based on the detection of strains or stresses associated with locally and temporally varying temperature fields in solids. The modulated *vertical displacement* of material surface is detected by using a pyroelectric detector or a probe beam [17]. The change in reflection signal of this probe beam sensing on position sensitive diode gives the indirect information of the temperature distribution.

Optical Beam Deflection (OBD): Photothermal Beam Deflection or Mirage Effect was first introduced by Boccara et al. in 1980 [18]. In the typical mirage effect experiment, the solid sample is periodic heated by an intensity-modulated pump laser beam. The thermal waves propagate in the liquid medium, where space-and time-dependent variations of the refractive index are produced. A second laser beam is used to probe the *gradient of the refractive index* either perpendicular or parallel to the sample [19]. The deflection angle of this probe beam is determined by position sensitive detectors such as quadrant or lateral diodes.

Modulated Optical Reflectance (MOR): Thermally modulated reflection monitors the local change in the *optical reflectivity* of the sample. In the typical configuration, the modulated pump beam is focused onto the sample surface while the change of the optical reflectance induced by an intensity modulated pump laser beam is measured by the reflected probe laser [20]. The measured signal provides a relationship between the temperature dependence of optical reflectivity [21] and electrical properties [22]. This technique provides many attractive features, the most important of which are that it is rapid, non-contact, and non-destructive. Especially, it can also offer thermal image with high-spatial resolution.

Table 1 Photothermal techniques in comparison between their detected resolutions and frequency ranges. [23]

Photothermal methods	**Resolution**		**Modulated frequency**
	Excitation	**Detection**	
PAS	≥ 1 μm	-	0.01 Hz-20 kHz
PPE		-	1-20 Hz
PTR		≥ 100 μm	0.01 Hz-100 kHz
OBD		≥ 100 μm	0.01 Hz-20 kHz
ThE		≥ 1 μm	100 Hz-100 kHz
MOR		≥ 1 μm	100 Hz-5 MHz

Table 1 presents the characteristics of photothermal techniques described formerly in comparison between their detected resolutions and the ranges of their measured frequencies. Besides PAS and PPE, one can see that photothermal techniques can provide local thermal properties of the structure. In particrlar, the resolutions of detected signal are improved by applying pump-probe beam techniques which is limited in its spatial resolution to ~ 1 μm. From the modulated frequency to be used in each technique which refers to the restricted areas of interest, the conventional photothermal techniques are generally applicable mostly to bulk samples.

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