

# Laser photothermal spectroscopy of light-induced absorption

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**Abstract.** Basic methods of laser photothermal spectroscopy, which are used to study photoinduced absorption in various media, are briefly considered. Comparative analysis of these methods is performed and the latest results obtained in this field are discussed. Different schemes and examples of their practical implementation are considered.

**Keywords:** photothermal spectroscopy, photothermal methods (techniques), photoinduced absorption, laser-induced absorption, review.

## 1. Introduction

Photoinduced (induced) absorption increases with an increase in the laser intensity. This absorption can be caused by irradiating a material with an intense light source (pump radiation) and be observed by sensing the sample with probe radiation at another wavelength. The spectral dependence of photoinduced absorption yields a large amount of data on the struc-

tural defects of the material studied, which determine to a great extent its characteristics [1].

The investigation of photoinduced absorption spectra appears to be very important to gain information about defect centres in semiconductor materials, for example, in thin films of amorphous and polycrystalline silicon, silicon carbide, etc. [2–4]. In recent years, much attention has been paid to the light-induced absorption and its relationship with the photoelectric properties of films of wide-gap metal oxides (TiO<sub>2</sub>, ZnO, etc.), which are used in solar batteries and in photocatalysis [5–9]. Numerous studies of induced absorption in photorefractive materials have been performed; they were stimulated by wide application of these materials in holographic data storage devices, nonlinear filters, phase-matching devices, and optical switches [10–14]. Photoinduced absorption in crystals used in nonlinear optics and some other effects are actively studied [15–17].

The study of photoinduced absorption is based on modern techniques for measuring low optical absorption in optically transparent materials and coatings. The conventional methods for measuring absorption in both bulk materials and thin films are spectrophotometric techniques (which have a rather large error) [18] and more exact calorimetric methods [19]. Multipass cells with multiple reflection [20, 21] and intracavity techniques, both active and passive [21], with sensitivity on the order of 10<sup>-3</sup>–10<sup>-4</sup>, have been developed to measure

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low absorption. However, this sensitivity is insufficient to detect photoinduced absorption in thin films or (in the case of low exposures) bulk samples.

Laser photothermal spectroscopy is an alternative to conventional absorption spectroscopy techniques. Photothermal methods have the active character; they are nondestructive and, in most cases, contactless. A characteristic sign of all photothermal techniques is that they yield information about the properties and composition of a medium under study based on direct detection of the power absorbed in it from the corresponding changes in the physical and thermodynamic parameters of the material [22–26]. A direct consequence of this is the following set of features: (1) zero-referenced measurements (the output signal is zero in the absence of absorption), (2) an increase in sensitivity with an increase in the radiation power (up to the absorption saturation mode), and (3) fundamental limitation of the limiting sensitivity by thermal fluctuations in the medium under study.

Photothermal techniques can be implemented in two ways. In the first version, a sample is exposed to cw laser radiation periodically modulated in amplitude (the so-called photothermal modulation spectroscopy). The second version is the pulsed photothermal spectroscopy, where periodically repeated laser pulses are used. In both cases, absorption of laser radiation by the object under study leads to excitation of thermal waves in it, as a result of which the temperature and recorded signal become modulated. Having analysed the time dependence of the recorded signal and its phase, one can gain information about various physical properties of the object, including the magnitude and dynamics of photoinduced absorption.

As was mentioned above, photothermal spectroscopy is a modulation measurement technique, which implies periodic perturbation of some parameter of the material under study by modulated (pulsed) laser radiation. The basic advantages of photothermal spectroscopy, as compared with conventional spectroscopy, are due to the possibility of eliminating the background (structureless) component of signal and measuring differential spectra. The reason is that the signal recorded is directly related not to the parameter to be measured but to its change, i.e., to the derivative of this parameter with respect to temperature. Therefore, photothermal spectra have fine features, analysis of which yields data on the properties of material that cannot always be revealed by conventional spectroscopy. In addition, lock-in detection of a signal at a modulation frequency improves significantly the signal-to-noise ratio, thus reducing the measurement error.

Depending on the way of detecting modulated signal, the most widespread methods are photoacoustic spectroscopy techniques, photothermal deflection spectroscopy (mirage-effect), thermal lens technique (thermal lens spectroscopy), photothermal radiometry and photothermal interferometry, and thermorefectance technique. All these methods were described in a number of reviews and monographs [22–32].

In this paper we will not go into details of numerous original studies, as, for example, in [24–26], where an extensive bibliography on different photothermal spectroscopy techniques can be found. We will restrict ourselves to brief consideration of the basic (in our opinion) laser photothermal techniques, which are most widespread and promising for practical analysis of photoinduced absorption in various media. We will refer to the original studies that we believe to be of fundamental importance for the problem under consideration and to a number of new studies that have not been considered in

the aforementioned reviews. Emphasis will be on the specific features of the techniques presented and on the discussion of the latest results obtained generally with the use of new designs.

Because of the limited volume of the paper, the results are described only briefly. Details can be found in the original studies, reviews, and monographs we refer to; they contain extensive data on separate aspects of the problem under consideration.

## 2. Brief review of techniques based on the photothermal effect

### 2.1. Photoacoustic technique

The essence of the photoacoustic technique is as follows [33, 34]. A sample under study is placed in a special cell and exposed to modulated laser radiation, which is completely or partially absorbed in the sample to heat it. The heat released is transferred to the gas medium located in the acoustic cell, as a result of which the pressure in the cell periodically changes. The thus excited acoustic waves are recorded by a highly sensitive microphone, built-in into the cell (Fig. 1). One can also perform contact measurement of the photoacoustic signal when studying, for example, solids with the aid of a piezoelectric sensor, positioned directly on the sample surface. Currently open photoacoustic systems with a sensitive element in the form of a quartz tuning fork have been developed; they are considered to be promising devices for remote detection of chemical compounds on surfaces of solids.

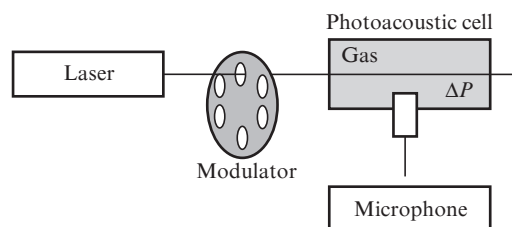
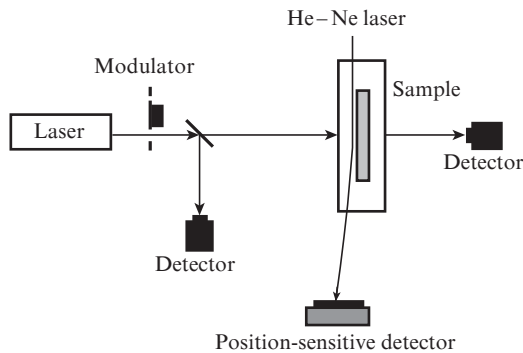


Figure 1. Schematic of the photoacoustic technique [34].

High sensitivity of photoacoustic spectroscopy makes it possible to advance significantly in the study of weakly absorbing media [35, 36]. Highly sensitive photoacoustic multicomponent gas analysers have been developed to solve environmental protection problems [37–40]. The photoacoustic effect was used as a basis for measuring thermodynamic parameters of gaseous, liquid, and condensed media [41–44]. Photoacoustic microscopy and flaw detection are widely used in modern materials science, biology, and medicine [45–48]. Recently much attention has been paid to the photoacoustic spectroscopy as a tool of remote detection of traces of chemical compound [49–51] etc. Many reviews and monographs were devoted to the application of photoacoustic technique for studying matter in different aggregate states [22, 25, 30].

### 2.2. Photothermal deflection (mirage-effect) spectroscopy

In this technique modulated excitation radiation heats the surface of a sample studied. Heat transfer causes periodic



**Figure 2.** Schematic of the deflection technique [52].

heating of the surface layer of the medium contacting the sample. The formation of a temperature gradient in the medium near the surface and the related change in its refractive index are revealed by the deviation of the probe beam from the plane parallel to the sample surface (the mirage effect) and recorded by a position-sensitive photodetector (Fig. 2).

To increase the sensitivity of this technique, the sample is generally placed in a cell containing a transparent liquid, the refractive index of which depends strongly on temperature. Using this scheme, one can measure temperature increments on the sample surface at a level of  $10^{-4}$  K, which correspond to a probe beam deviation angle of  $\sim 10^{-9}$  rad [52]. This sensitivity makes it possible to detect absorption losses in solids at a level of  $\sim 10^{-7}$   $\text{cm}^{-1}$  [53]. This technique is widely applied to measure optical (absorption coefficient [54, 55]), thermal (thermal conductivity [56–58], temperature [59]), and electrical [60] properties of materials. Extensive data on this measurement technique can be found in a number of reviews and monographs [25, 26].

### 2.3. Thermal lens technique

In a simplified form, the essence of this technique is as follows. Irradiation of an absorbing medium by a laser beam with a Gaussian intensity distribution in the transverse cross section induces a temperature gradient in it due to nonuniform heating. In turn, a change in temperature causes local changes in the refractive index of the medium, in correspondence with the laser beam intensity distribution. The occurrence of the refractive index gradient in the medium leads to the formation of an optical element, which acts as a scattering/collecting lens; this element was referred to as a thermal lens. Since the refractive index of most materials in the transparency range decreases with an increase in the temperature, the thermal lens is generally scattering; i.e., the transverse laser-beam size increases when the medium is heated.

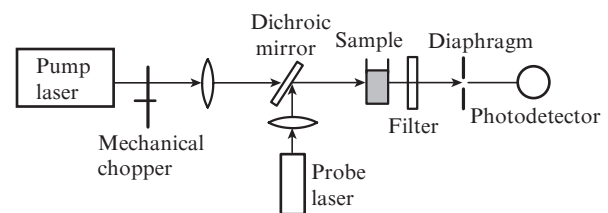
In the more general case variations in the refractive index of the medium can be caused by changes in both the temperature  $T$  and density  $\rho$  of the medium:

$$\Delta n = \left( \frac{\partial n}{\partial T} \right)_p \Delta T + \left( \frac{\partial n}{\partial \rho} \right)_T \Delta \rho.$$

The thermal lens technique can be implemented using both single- and double-beam measurement schemes. In the single-beam scheme radiation of one laser is simultaneously used for excitation (generation of a thermal lens) and probing. Being absorbed, laser radiation heats the sample, and the

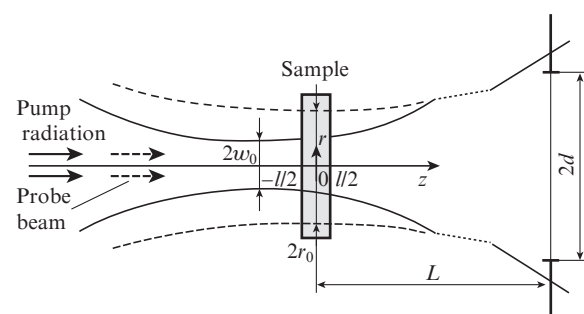
change in its intensity yields information about absorption in the medium. The measurement technique generally implies recording the temporal shape of photothermal signal from a photodetector with a diaphragm, located in the far-field zone.

The double-beam scheme is more universal. Here, a thermal lens induced by excitation (pump) radiation is recorded by measuring defocusing of an additional probe beam. Its main advantage is that it allows one to study the spectral dependence of the absorption of materials; this cannot be done within the single-beam scheme. One of configurations of the classical double-beam measurement scheme is shown in Fig. 3.



**Figure 3.** Thermal lens technique (longitudinal version): double-beam measurement scheme; the pump and probe beams propagate coaxially [22].

The double-beam scheme is implemented in either longitudinal (Fig. 3) or transverse [22, 61] configurations; in the latter case, the excitation beam is focused into the sample perpendicularly to the probe beam. In most cases the longitudinal (collinear) version is used. In this case, applying, for example, a dichroic mirror, one makes both beams propagate coaxially in the sample, due to which the maximum interaction length is provided. Here, the so-called mode-matched and mode-mismatched configurations are distinguished. In the former case the waists of both beams coincide in the measurement cell (sample), whereas in the latter version they are spatially separated (Fig. 4).



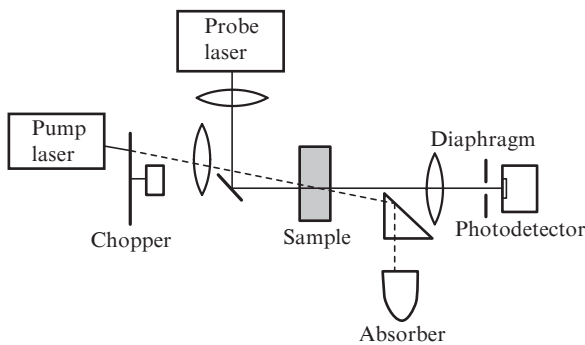
**Figure 4.** Mode-mismatched configuration (measurement scheme with shifted waists) [61].

The measurement scheme based on the mode-mismatched configuration provides higher sensitivity. In this case, the absorption coefficient of the sample at the pump wavelength, which is related to the thermally induced phase shift, is determined from the experimentally observed (recorded by a photodetector) time dependence of the intensity of the central part of the probe beam transmitted through a round diaphragm by ‘fitting’ it to the theoretical dependence or by cali-

brating with the aid of a standard (reference) sample with known absorption.

The pump laser can operate in both pulsed and cw modes, while the probe radiation intensity is generally chosen to be constant; thus, its change on the diaphragm can only be caused by induced modulation from the pump laser. In practice, the threshold sensitivity of this technique is mainly limited by laser power fluctuations. At a fluctuation level not more than 0.5%–1%, the measured absorption threshold is  $10^{-6}$ – $10^{-7}$   $\text{cm}^{-1}$ . This corresponds to the detection threshold of  $\sim 10^{-8}$  for refractive index variations and a temperature variation threshold in the range of  $10^{-6}$ – $10^{-7}$  K [22]. Later it was shown that one can measure the absorption coefficient at a level of  $\sim 10^{-8}$   $\text{cm}^{-1}$  using Z scanning (scanning in the longitudinal direction), which is a kind of thermal lens technique [62].

Recently photothermal common-path interferometry (PCI) has become very popular in measuring weak absorption in transparent media; this technique is based on the thermo-optical effect and is in essence a modified thermal lens technique [16, 63–67]. To provide high spatial resolution of the PCI technique, the probe and pump beams are intersected in the sample at a small angle. This configuration also makes it possible to eliminate the effect of spurious signals from the surfaces of optical elements and the sample. The radical difference of this method from the classical far-field thermal lens technique is in the use of near-field signal detection scheme. In this case, perturbed and unperturbed parts of the same collimated probe beam interfere. Specifically this circumstance makes the PCI sensitivity be close to that of interferometric techniques for measuring absorption. In other words, PCI is a thermal lens technique in which the probe signal is detected in the near-field zone. A schematic of PCI measurements is shown in Fig. 5.



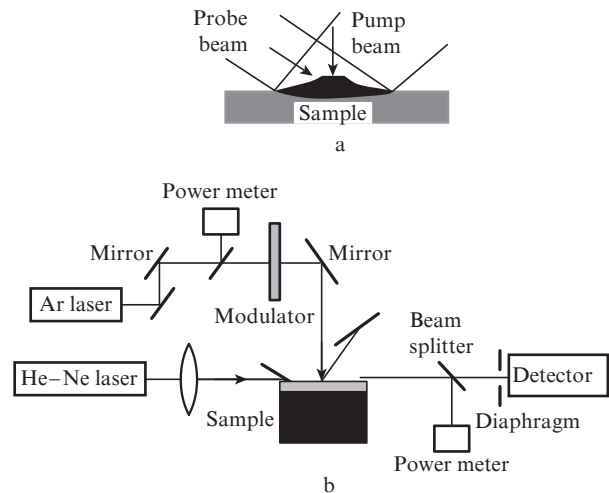
**Figure 5.** Schematic for measuring absorption loss in optical materials by the PCI technique [16].

To date, the thermal lens technique and its modifications (mode-mismatched configuration, PCI, Z scanning) are widely used to measure weak absorption in solids and liquids [68–74], to analyse trace amounts of materials [75] and kinetics of chemical processes [76–78], in nonlinear spectroscopy [79–81], etc. Details of the thermal lens technique and its modifications can be found in [82–85].

#### 2.4. Surface thermal lensing

This technique is an alternative to the deflection photothermal spectroscopy [86, 87]. Being highly sensitive, it has addi-

tionally at least two important advantages over the conventional deflection technique; they are related to the ratio of probe-beam and pump-beam diameters (Fig. 6). If the size of the region irradiated with a probe laser beam exceeds the size of the region heated by pump radiation, there are no stringent requirements on tuning (aligning) the measurement scheme. Moreover, when detecting a diffraction pattern with a CCD camera, one can obtain much more complete information about the character of surface deformation. This is an important advantage over the conventional deflection technique, where the probe beam is focused into a small surface region subjected to deformation. A consequence is a much shorter time necessary for mapping a surface under study, for example, when measuring absorption in thin-film coatings, where the surface thermal lensing is widely used [87, 88].



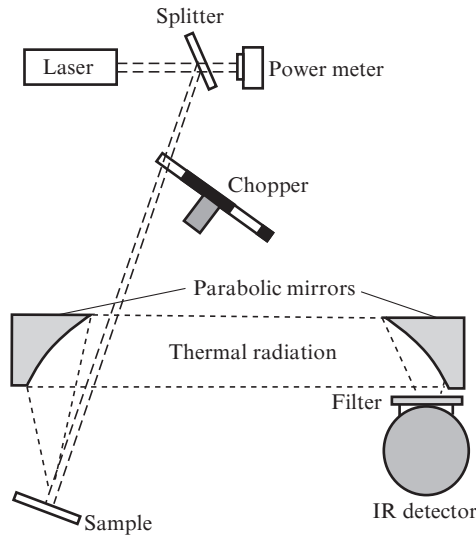
**Figure 6.** (a) Schematic diagram of measurements by the surface thermal lensing and (b) a schematic of the experimental setup [87].

#### 2.5. Photothermal radiometry

For a long time the temperature of a heated body was determined by measuring the radiation flux from this body. This technique has certain advantages over others (for example, those based on the use of a thermocouple), because it does not require direct physical contact with the object studied. However, it has some drawbacks; the main ones are the influence of reflected radiation fluxes from other bodies and that one must have data on the emissive power of the body analysed.

Photothermal radiometry (PTR) is an active method, which eliminates the influence of background radiation from foreign objects surrounding the body studied. The essence of this technique is rather simple (Fig. 7). During measurements a sample is exposed to cw laser radiation with an intensity modulated according to a harmonic law or is irradiated by periodic laser pulses. Partial absorption of laser radiation and the corresponding heat release lead to modulation of the sample surface temperature and the recorded heat flux at the pulse repetition (modulation) frequency. Having measured the time dependence of the dynamic component of recorded thermal signal and its phase, one can obtain data on different physical properties of the object under study.

A modification of photothermal radiometry is the so-called photo-carrier radiometry (PCR), which is used to mea-



**Figure 7.** Schematic of the experimental setup for measurements by laser PTR [103].

sure electrical characteristics of semiconductors, for example, carrier lifetime, concentration, and mobility [89, 90]. There is no established term that would adequately reveal the essence of this phenomenon in the Russian scientific literature. We will refer to it as the radiometry of nonequilibrium IR radiation from photoexcited carriers; in our opinion, this definition reflects most exactly the essence of this technique, in which a sample is exposed to radiation with a photon energy exceeding the band gap of the sample material. Here, a signal recorded contains both a thermal component and a nonequilibrium plasma component, which is due to the relaxation of photoexcited charges in the conduction band. Obviously, to measure photoinduced absorption, it is necessary to consider only the thermal component. At low frequencies the plasma component is small, and the signal recorded is proportional to the heating temperature and, therefore, to the absorption coefficient. It was reported in [91] that modification of the PCR technique due to the use of the second laser with photon energy lower than the band gap improves the detecting ability for subsurface defects.

Concerning PTR, it is used to measure low absorption not only in bulk materials but also in thin films and surface layers [33, 92–96]. This method is used for remote measurement of the temperature of bodies and their thermophysical parameters (thermal conductivity and thermal diffusivity) [97–105], to investigate electronic properties of semiconductor materials and monitor their defect structure [103–105], for remote spectral analysis in different technological problems when studying surfaces of materials and coatings [7–9, 106], and in thermal-wave microscopy and thermography [107].

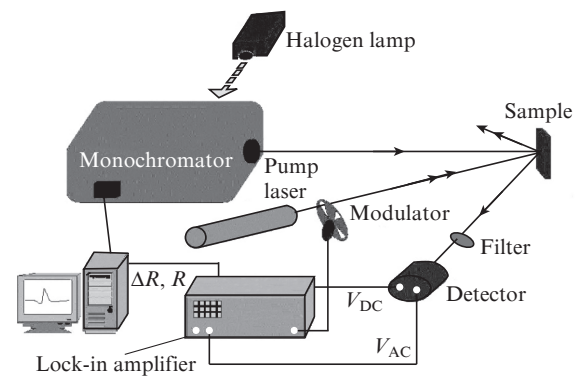
## 2.6. Photothermal reflectance technique

Photothermal reflectance technique (photomodulation reflectance spectroscopy), being one of the most widespread methods of modulation spectroscopy [108], is intensively used to study the energy structure of semiconductor materials, including quantum-size structures [109–119]. This method is very sensitive to the energy structure; it allows one to determine the level energies with an error of few millielectronvolts and record changes in reflection  $[\Delta R(\lambda)/R(\lambda)]$  or transmission

$[\Delta T(\lambda)/T(\lambda)]$  spectra of this probe radiation that are due to photomodulation: change in the optical structural parameters under additional irradiation by light with a wavelength lying in the range of intrinsic absorption of semiconductor (pump radiation). The relative change in the reflection coefficient is defined as

$$\frac{\Delta R}{R} = \frac{R_{\text{off}} - R_{\text{on}}}{R_{\text{off}}},$$

where  $R_{\text{off}}$  and  $R_{\text{on}}$  are the reflection coefficients of probe radiation in the absence and in the presence of pump radiation, respectively. Application of phase-sensitive detection makes it possible to record relative changes in the reflection coefficient at a level of  $10^{-6}$ – $10^{-7}$  [25]. One of possible schemes of the photothermal reflectance technique is shown in Fig. 8.

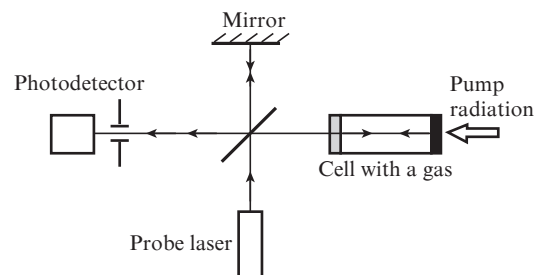


**Figure 8.** One of possible schemes of measurements by photothermal reflectance technique [118].

Along with the aforementioned original papers, more details on this technique and fields of its application can be found in [25, 26, 118, 120].

## 2.7. Photothermal interferometry

As was noted above, variations in the refractive index of irradiated medium change the phase of a radiation wave passing through it. The most sensitive method of phase change detection is the interferometric (phase) technique, where a medium under study is placed in one of interferometer arms (Fig. 9). A variation in the refractive index by  $\Delta n$  leads to a change in the wave phase in this arm by



**Figure 9.** Michelson interferometer with a medium studied in a cell (the rear cell wall is transparent for the pump radiation and mirror-reflective for the probe laser radiation) [22].

$$\Delta\varphi = (2\pi L/\lambda_p)\Delta n,$$

where  $L$  is the length of the spatial alignment region in the sample for the excitation (pump) radiation and probe wave and  $\lambda_p$  is the probe wavelength.

A change in the probe wave phase shifts the interference pattern in the detection plane; this shift is detected by measuring the change in the radiation power with the aid of a photodetector with a diaphragm. Depending on the measurement conditions, one can determine variations  $\Delta n$  using many known interferometric schemes with insignificant modification (for example, Mach–Zehnder, Fabry–Perot, Michelson, and Jamin interferometers) [121, 122]. In comparison with the deflection and thermal lens techniques, the phase method provides higher sensitivity [22, 61]. For example, the sensitivity of the interference measurements in gases was  $\sim 10$  ppt [123]. Nevertheless, the phase method is relatively complex in both design and operation; in addition, it requires reliable vibroacoustic isolation. Apparently, it has not become very popular for these reasons.

### 3. Measurement of light-induced absorption by photothermal techniques (case of low intensities)

#### 3.1. Necessity of modified photothermal techniques to measure light-induced absorption

The mechanism of induced absorption is generally related to the occupation of traps by electrons excited by light to the conduction band from deep donor levels or from the valence band. With allowance for this phenomenon, measurement of induced absorption calls for modifying photothermal techniques in the following way.

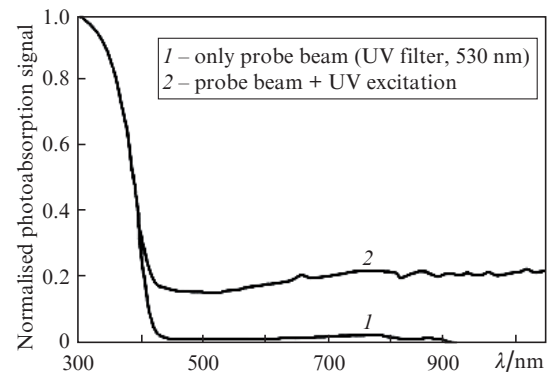
When electrons are excited from the valence band to the conduction band, the sample under study must be exposed simultaneously to at least two light beams. One of them, with a wavelength falling in the range of intrinsic absorption of the material (pump wave), generates electron–hole pairs both in the bulk of the sample and on its surface. A cw laser is generally used as a source of this short-wavelength radiation. The free electrons formed in the conduction band can be captured by traps before recombination. The second radiation flux, with photon energy below the band gap (probe wave), leads to trap depletion, heat release through relaxation electrons in the conduction band, and their further recombination. Thus, having measured (at the long-wavelength pulse repetition frequency) the variable (dynamic) component of the signal induced by periodic variation in temperature (or some related parameter, for example, the refractive index of material), one can measure the induced absorption at this wavelength. The spectral dependence of photoinduced absorption is studied using such radiation sources as, for example, xenon lamps (whose light is transmitted through a monochromator) or wavelength-tunable lasers. The latter have a higher spectral brightness and thus provide higher measurement sensitivity. Note that in the case under consideration the modified photothermal techniques are designed for studying thin films and surface layers of materials. This is due to the fact that pump radiation is absorbed at a depth  $l_a \approx \alpha_f^{-1}$ , where  $\alpha_f \approx 10^5\text{--}10^6\text{ cm}^{-1}$  is the absorption coefficient related to fundamental absorption.

At the same time, depletion of deep donor levels by pump radiation also leads to occupation of electronic traps. In this case, the pump photon energy may be much lower than the band gap; this situation occurs, for example, when studying the photoinduced absorption in the bulk of photorefractive crystals and other optically transparent materials.

Thus, in both cases the above-considered conventional schemes used to measure photoinduced absorption should contain an additional pump channel in order to form excited centres, whose absorption is to be measured. The choice of the pump wavelength is determined to a great extent by not only the nature of materials but also by the specific conditions of their application.

#### 3.2. Modified photoacoustic technique

As far as we know, the modified photoacoustic technique was applied for the first time in [5], where the spectral dependence of photoinduced absorption in powder samples of titanium dioxide (a material promising for photocatalysis) was investigated. This study revealed a strong photochromic effect in the samples: reversible change in absorption under irradiation by UV light. After switching off pumping, the photoacoustic signal relaxed to its ‘dark’ value for several minutes. Based on the analysis of the measured spectral dependences of photoinduced absorption in the range 350–1000 nm (Fig. 10), the nature of the defects responsible for this effect ( $\text{Ti}^{3+}$  ions) was revealed and their concentration was estimated in [5].



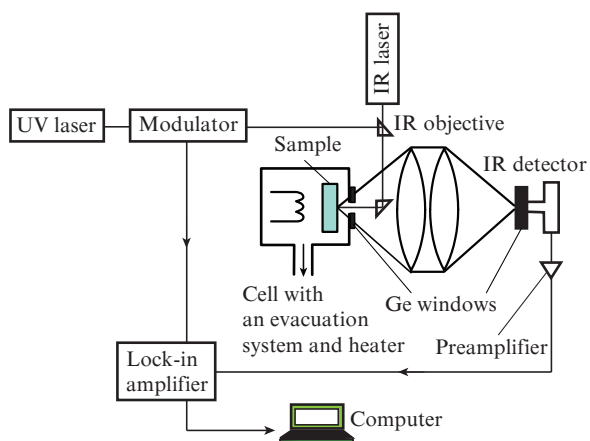
**Figure 10.** Spectral dependence of photoinduced absorption in  $\text{TiO}_2$  films [5].

These investigations were developed in [6], where a new method for determining quantitatively the concentration of defects ( $\text{Ti}^{3+}$  ions) in powder titanium dioxide was elaborated based on modified photoacoustic spectroscopy. It was stated in [6] that this method is a real alternative to the photochemical and electron spin resonance (ESR) methods, which are traditionally used for these purposes.

#### 3.3. Modified photothermal radiometry

The fruitfulness of photothermal techniques in the study of the photochromic effect in thin films and surface layers of various materials was also demonstrated by the example of modified photothermal radiometry [7–9]. A schematic of the experimental setup for measuring photoinduced absorption by modified photothermal radiometry is shown in Fig. 11. The objects of study in the aforementioned works were single-

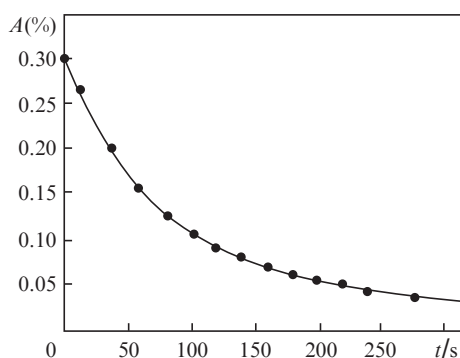
layer titanium dioxide coatings  $\sim 100$  nm thick, deposited on fused silica substrates by electron-beam evaporation. The source of modulated probe 1064-nm radiation was a cw YAG:Nd<sup>3+</sup> laser with an average power of 20 W. Simultaneously the sample was exposed to short-wavelength nitrogen laser radiation with a wavelength of 337 nm (pump wave). The maximum average pump power was 3 mW. Measurements were performed both in air and in vacuum. A heater was used to vary the substrate temperature in the range from 290 to 500 K.



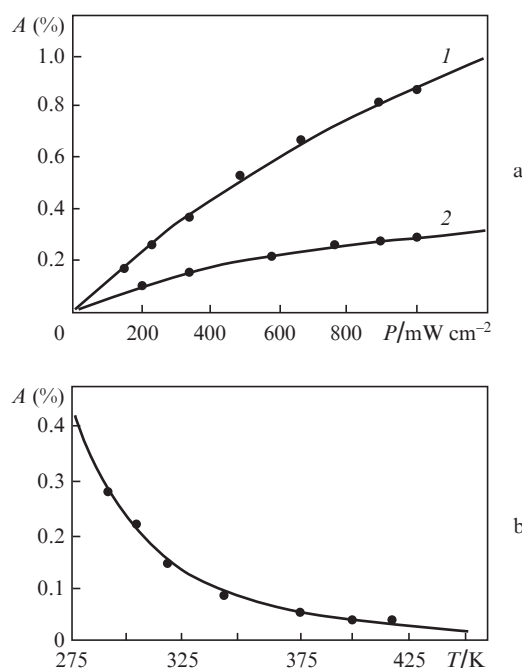
**Figure 11.** Schematic of the experimental setup for measuring photoinduced absorption in thin films and surface layers of materials by modified photothermal radiometry [9].

Note the following main features of photoinduced absorption in the near-IR spectral range for the objects studied. First, the occurrence of photoinduced absorption is a reversible process. After switching off UV light, the absorption in the near-IR range relaxes to its initial ‘dark’ value (Fig. 12). Note that the characteristic relaxation time in vacuum exceeds that in air by a factor of 5.

Second, photoinduced absorption depends on the short-wavelength radiation intensity and the environment pressure, reaching saturation at high pump powers (Fig. 13a). Finally, the temperature dependence of induced absorption is of special interest (Fig. 13b). Upon sample heating to  $\sim 150^\circ\text{C}$  the



**Figure 12.** Time dependence of photoinduced absorption in titanium dioxide films after switching off the pump radiation (air atmosphere, room temperature) [9].



**Figure 13.** (a) Dependences of the induced absorption on the UV radiation intensity for a substrate placed in (1) air and (2) vacuum and (b) the temperature dependence of photoinduced absorption [9].

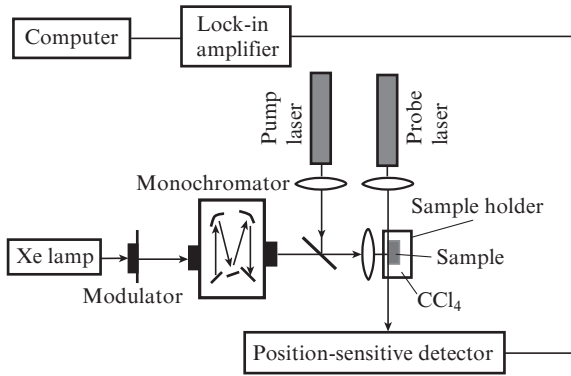
absorption decreases to the ‘dark’ value, which is constant in the entire temperature range.

A possible mechanism of the occurrence of photoinduced absorption in polycrystalline titanium dioxide films in the near-IR spectral range ( $\lambda = 1064$  nm) was proposed in [9]. The decisive role of the energy levels associated with Ti<sup>3+</sup> ions was indicated. The process was considered within the monomolecular recombination approximation; this model was found to be in good agreement with the experimental data. It was shown in [8] that modified photothermal radiometry makes it possible to reveal nonstoichiometric defects with a concentration  $N_{\min} \geq 10^{15} \text{ cm}^{-3}$  in thin layers.

### 3.4. Modified deflection technique

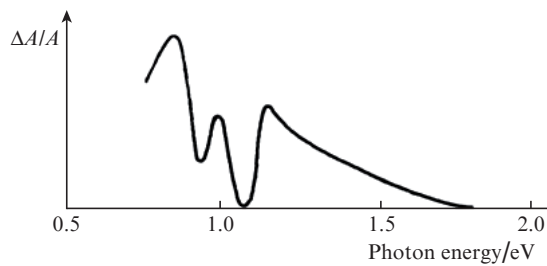
Deflection spectroscopy was also used to study photoinduced absorption [2]. It was modified in the following way. Frequency-tunable radiation was obtained using a 1000-W xenon lamp, whose light was focused on the input slit of the monochromator. The width of the spectral line at the output was 20 nm. The radiation was modulated in amplitude using a mechanical chopper and focused on the surface of a sample placed in a cell filled with liquid carbon tetrachloride. To record photoinduced absorption, the measurement scheme [124] was supplemented with a pump radiation source; the pump photon energy exceeded the band gap of the material under study (Fig. 14).

The objects studied in [2] were samples of thin hydrogenated amorphous silicon (a-Si:H) films deposited on glass substrates. Films were obtained by decomposition of pure silane in a high-frequency glow discharge. The film thickness was 10  $\mu\text{m}$ , the band gap of the film material was 1.75 eV, and the volume hydrogen content was 5–10 at %. Figure 15 shows a room-temperature dependence of the relative value of photoinduced absorption in undoped a-Si:H samples on the probe photon energy. Analysis of this dependence made it



**Figure 14.** Schematic for measuring the spectral dependence of photoinduced absorption by deflection spectroscopy [2, 124].

possible to determine the energy levels of the defects corresponding to the neutral and negatively charged states. It was noted in [2] that the sensitivity of the proposed technique exceeds that of conventional absorption spectroscopy methods by at least four orders of magnitude.



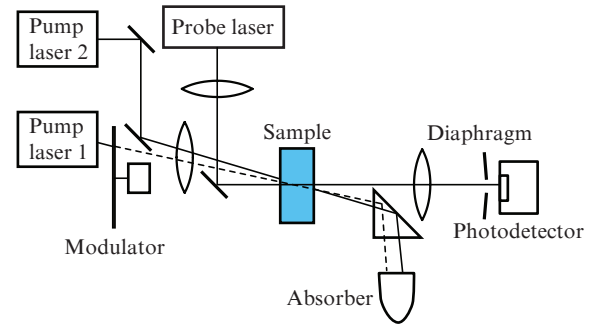
**Figure 15.** Dependence of the relative absorption induced in thin hydrogenated amorphous silicon films on the probe photon energy [2].

### 3.5. Modified thermal lens technique

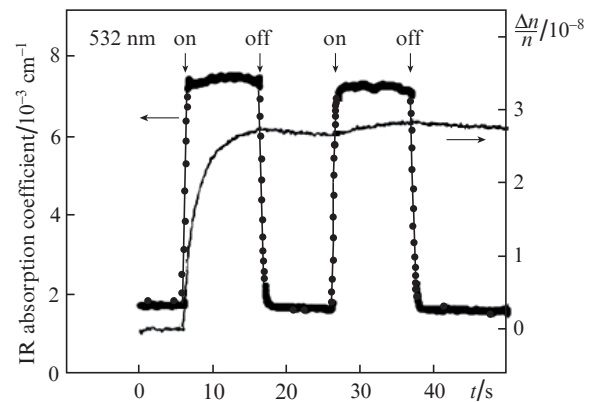
Thermal lens technique in a modified form (specifically, modified PCI) is most widely used to study the mechanisms and nature of photoinduced absorption in transparent optical materials and coatings. We will restrict ourselves to the consideration of only few (most characteristic in our opinion) examples of application of this technique for the aforementioned purposes.

In particular, this method was used to study the photoinduced absorption in magnesium-doped lithium niobate ( $\text{LiNbO}_3$ ) crystals, as well as in lithium tantalate ( $\text{LiTaO}_3$ ) and potassium–titanyl phosphate ( $\text{KTiOPO}_4$ , KTP) crystals, which are widely used in laser technique [15–17]. Green-light-induced infrared absorption (GLIIRA) in these materials was investigated. Later, the effect of blue-light-induced infrared absorption (BLIIRA) was revealed in most of ferroelectrics [14]. A scheme for measuring photoinduced absorption by modified PCI is presented in Fig. 16.

It can be seen that this version is based on the use of two pump beams. In particular, in the case of lithium niobate crystal, the dynamics of absorption of IR pump radiation (1064 nm) was studied in the presence of a weaker pump beam at the second-harmonic wavelength (532 nm) of a Nd:YAG laser. Periodic interruption of the green light beam was per-



**Figure 16.** Schematic for measuring photoinduced absorption using modified PCI technique [16].



**Figure 17.** GLIIRA in a  $\text{LiNbO}_3$  crystal with a close-to-stoichiometric composition [16] for pump intensities of  $3.6 \text{ kW cm}^{-2}$  ( $\lambda = 532 \text{ nm}$ ) and  $21.0 \text{ kW cm}^{-2}$  ( $\lambda = 1064 \text{ nm}$ ).

formed manually. A He–Ne laser served as a probe one. The GLIIRA dynamics for lithium niobate crystals is shown in Fig. 17. The signal rise (falloff) time was less than 30 ms.

We should note successful application of the thermal lens technique in the study of GLIIRA in KTP crystals [17]. In this case, measurements were also performed using a common-path interferometer. However, the configuration of the measurement scheme was such that all three beams (two pump beams and one probe beam) propagated collinearly in the crystals. As was stated in [17], this technique can be used to measure induced absorption at a level of  $\sim 10^{-5} \text{ cm}^{-1}$ .

Along with PCI, there are other techniques based on the thermal lens effect. For example, the photoinduced absorption in photorefractive  $\text{BaTiO}_3$  crystals exposed to laser radiation at different wavelengths was investigated in [12] by a technique in which two waves propagating in a crystal at a small angle with respect to each other are mixed. The measurements were performed according to a somewhat modified scheme, similar to that described in [71]. It was stated in [12] that photoinduced absorption may significantly affect the recording of holographic gratings in photorefractive crystals.

### 3.6. Measurement of light-induced absorption by the photothermal reflectance technique

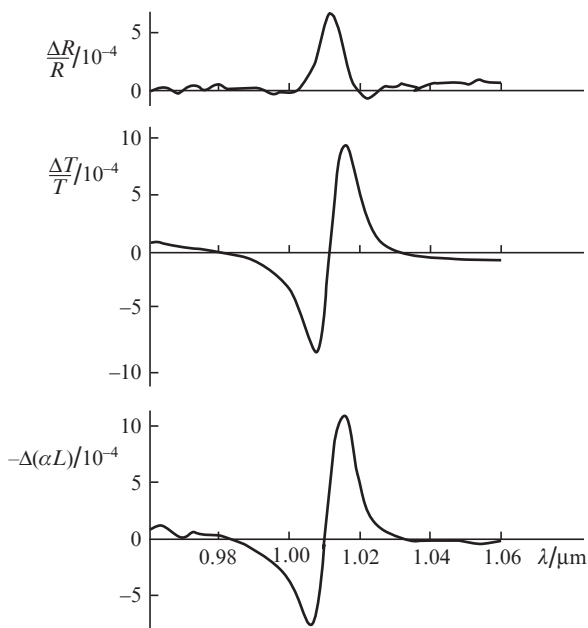
The relative change in the reflection coefficient of probe radiation, measured by this technique,  $\Delta R(\lambda)/R$ , is directly related to the permittivity perturbation:



$$\Delta R/R = \alpha(\varepsilon_1, \varepsilon_2) \Delta\varepsilon_1 + \beta(\varepsilon_1, \varepsilon_2) \Delta\varepsilon_2,$$

where  $\alpha$  and  $\beta$  are the Seraphin coefficients [125], which depend on the permittivity  $\varepsilon(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda)$ ;  $\Delta\varepsilon_1$  and  $\Delta\varepsilon_2$  are, respectively, the changes in the real and imaginary parts of the permittivity, which are linked by the Kramers–Kronig relation.

Figure 18 shows as an example the photomodulation reflection spectra  $\Delta R/R$ ; the transmission spectra  $\Delta T/T$ ; and the spectral dependence of the variation in absorption,  $-\Delta(\alpha L)$  (calculated in correspondence with the results of [111]) [112]. These spectra are typical of the InGaAs/GaAs quantum well. Analysis of the reflection spectrum makes it possible to obtain the photomodulation absorption spectrum of the structure under study:  $\Delta\alpha = \Delta\alpha(\lambda)/\alpha$ ; it is nothing but the relative change in the pump-induced absorption. Therefore, it is not necessary to modify this technique to measure photoinduced absorption. Moreover, according to [112], the intensity of the photorefectance peak and its spectral position can be used to determine the inhomogeneity of quantum well width and composition.



**Figure 18.** Typical photomodulation reflection ( $\Delta R/R$ ) and transmission ( $\Delta T/T$ ) spectra and the calculated (according to [111]) spectral dependence of the change in absorption  $[-D(\alpha L)]$  for an InGaAs/GaAs quantum well [112].

## 4. Measurement of light-induced absorption by photothermal techniques (case of high intensities)

### 4.1. Induced absorption under multiphoton effect

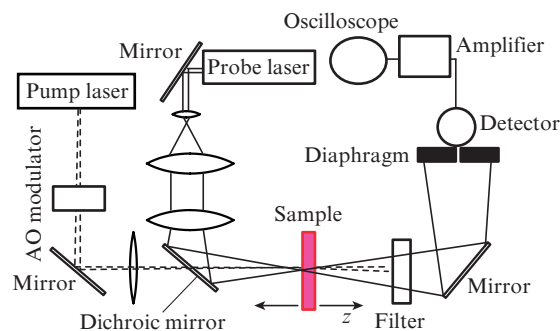
In some materials photoinduced absorption arises as a result of multiphoton (in particular, two-photon) absorption of light [126–128]. These materials are widely used as optical limiters [129], in laser microlithography at two-photon recording [130], in two-photon fluorescent microscopy [131],

in two-photon photodynamic therapy [132], etc. Two-photon absorption can be measured using several conventional methods, for example, two-photon excitation fluorescence or nonlinear transmission technique.

Induced multiphoton absorption spectroscopy, which is based on application of photothermal techniques, is an alternative to the conventional techniques. The theory of multiphoton thermal lens spectroscopy was developed in [133] and in the later study [134]. In turn, the theory of two-photon deflection spectroscopy was considered for the first time in [135]. The high sensitivity of the thermal lens and deflection techniques makes them promising for measuring weak two-photon absorption in optically transparent materials [136–144]. The measurement of two-photon absorption in materials is generally hindered due to the absence of nonlinear ‘references’ and complexity in determining the light intensity in the sample region studied. A number of measurement schemes based on different versions of the thermal lens technique were developed to overcome these difficulties [145–148].

### 4.2. Measurement of induced absorption under two-photon excitation using the thermal lens technique

To increase the sensitivity of measuring nonlinear absorption, a new flexible scheme based on the double-beam thermal lens technique was proposed in [148]. In comparison with the previous Z-scanning schemes [145], the probe beam in it is strongly focused into the sample, whereas the pump beam remains collimated (Fig. 19).



**Figure 19.** Schematic of the experimental setup for measuring nonlinear absorption by the thermal lens technique [148].

Nonlinear absorption plays an important role in the optical breakdown of transparent materials. The thermal lens technique was used in [126] to measure the coefficients of two-photon absorption for a number of borosilicate glasses, which are generally applied as optical components of lasers operating in the visible spectral range.

The measurements in [126] were performed using the same technique as in [136], where two-photon absorption in benzene was studied. The coefficients of two-photon absorption were determined from the slope of the dependences of photothermal signal on the squared light intensity. The observed linear dependence indicates two-photon character of absorption. The two-photon absorption coefficient  $\beta$  of BK-7 glass, measured at a wavelength of 532 nm, was found to be  $7 \times 10^{-11} \text{ cm W}^{-1}$ .

As an example Fig. 20 shows the absorption spectrum of BK-7 glass, induced by two-photon irradiation. It can be seen

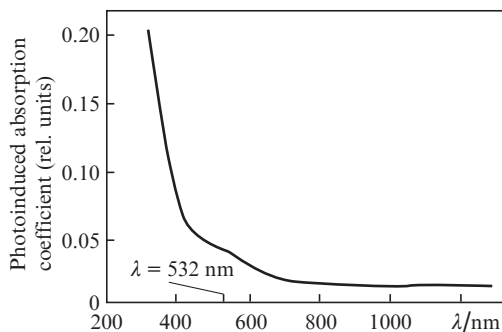


Figure 20. Photoinduced absorption spectrum of BK-7 glass [126].

that induced absorption manifests itself in a wide spectral range and has a long tail, extending to the near-IR range. It was suggested in [126] that two-photon absorption at a wavelength of 532 nm induces some types of optical-absorption (colour) centres in the samples studied.

#### 4.3. Measurement of induced absorption under two-photon excitation using the deflection technique

In some ionic crystals nonlinear absorption was measured by pulsed deflection spectroscopy [127]. The measurements were performed using excimer XeCl laser radiation with a wavelength of 308 nm and power density close to the laser damage threshold of the crystal in the transverse measurement scheme: the probe He-Ne laser beam propagated parallel to the surface of the sample under study (perpendicularly to the pump beam) at a distance of several micrometers from it. The dependences of the photodeflection signal on the laser intensity for a number of materials are shown in Fig. 21.

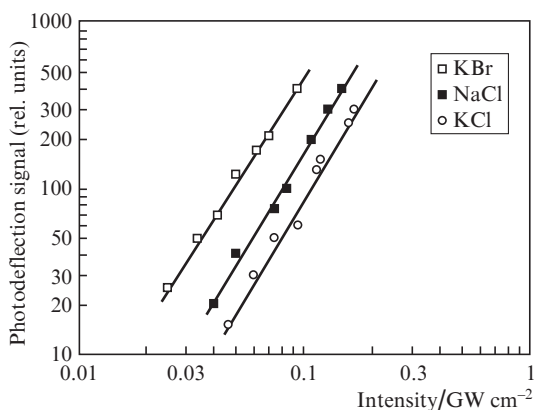


Figure 21. Dependences of the signals recorded by deflection spectroscopy on the radiation intensity for a number of ionic crystals [127].

It can be seen that the experimental data obtained are approximated well by a straight line. The corresponding dependence for  $\text{CaF}_2$  crystals (is omitted) exhibits a kink, which was explained in [127] by the dominant influence of three-photon absorption at radiation intensities above  $50 \text{ MW cm}^{-2}$ . In addition, colour centres were induced in the crystals under study, which were assigned to defects and impurities. It was noted in [127] that photothermal techniques are a unique tool, allowing one to measure multiphoton

absorption coefficients for wide-gap crystals with a high accuracy.

## 5. Conclusions

The above examples of the use of photothermal techniques to analyse the spectral dependence of photoinduced absorption indicate their efficiency for studying the defect structure of thin films, surface layers, and bulk materials, which is extremely important for improving technologies of manufacturing materials and monitoring their quality during manufacture.

However, the photothermal techniques considered above have a number of drawbacks. In our opinion, the main ones are as follows. In photoacoustic spectroscopy, a hermetic acoustic cell must be used and contact measurements must be performed to obtain high sensitivity. In photothermal radiometry, one must use photodetectors cooled to liquid nitrogen temperature and higher power radiation sources. As compared with the other photothermal techniques considered above, photothermal radiometry has the least sensitivity at room temperature. In the deflection technique, samples must be placed in a cell with a liquid having extremely low absorption and high thermo-optical coefficient in order to reach high sensitivity. The photothermal interferometry is not only difficult in operation but also calls for careful vibroacoustic protection. Concerning the thermal lens technique, when it is applied to study photoinduced absorption, one has to use (as in the case of GLIRA) three radiation sources, which leads to obvious complication of the measurement scheme.

Nevertheless, as follows from this review, much attention is currently paid to the development of photothermal techniques of nondestructive diagnostics of materials and the equipment necessary for their realisation. Advances in this field are related to a certain extent to the successful application of photothermal technologies in the semiconductor industry [an example is the Thermo-Probe<sup>TM</sup> metrology tools (KLA-Tencov Corporation)] and to the production of PCI-based photothermal measurement systems by the SPTS (Stanford Photo-Thermal Solutions) corporation.

Table 1 contains a list of the most widespread photothermal techniques, the main (in our opinion) fields of their application, and manufacturers of equipment for the technologies based on these techniques and designed to measure photoinduced absorption. Unfortunately, we have to admit that, despite a large number of laboratory studies, photothermal technologies and the corresponding commercial equipment are not so widespread in the market of control-measuring equipment as expected to be. A likely reason is the complexity of these precise techniques, despite the seeming simplicity of designs proposed.

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**Table 1.** Photothermal techniques, main fields of their application, and the existence of commercial equipment.

Basic photothermal techniques	Main fields of application	Existence of publications on measuring photoinduced absorption	Existence of commercial equipment for basic methods	Existence of commercial equipment for measuring photoinduced absorption	Manufacturer
Photoacoustic technique	Analysis of weakly absorbing media	Yes	Yes	No data	–
Deflection technique	Analysis of weakly absorbing media	Yes	No	No data	–
Thermal lens technique	Analysis of weakly absorbing media	Yes (PCI)	Yes (PCI)	Yes (PCI)	Statford Photo-Thermal Solution
Surface thermal lensing	Surface absorption mapping	No data	No	No data	–
Photothermal radiometry	Remote analysis of absorbing media, measurement and monitoring of semiconductor parameters	Yes	Yes	No data	–
Photothermal reflectance technique	Study of semiconductor materials	Yes	Yes	No data	–
Interferometric technique	Visualisation of thermal and acoustic fields	No data	No	No data	–

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