Addendum: "Frequency-domain probe beam deflection method for measurement of thermal conductivity of materials on micron length scale" [Rev. Sci. Instrum. 94, 014903 (2023)]

Jinchi Sun,[1] Guangxin Lv,[1] and David G. Cahill[1, a)]

[1]*Department of Materials Science and Engineering and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, USA*

[a)]Author to whom correspondence should be addressed: d-cahill@illinois.edu.

(Presented XXXXX; received XXXXX; accepted XXXXX; published online XXXXX)

I. INTRODUCTION

This addendum provides a review of photothermal deflection techniques that are used to measure optical and thermophysical properties of materials. Our purpose is to provide greater context for our work on frequency-domain probe-beam deflection. Photothermal deflection techniques combine an intensity modulated pump beam that heats the sample, and a probe beam that measures the oscillating temperature field via the deflection of the probe beam. In what follows, we categorize variations of photothermal deflection techniques by the mechanisms that produce the probe beam deflection and the properties that are measured.

II. MIRAGE TECHNIQUE

We use the term mirage technique to refer to techniques in which the probe beam is deflected mainly by a gradient of refractive index due to the temperature dependence of the refractive index.

A. Measurement of optical absorption

Photothermal deflection spectroscopy was developed for measurement of optical absorption coefficient via the amplitude of probe beam deflection[1], typically as a function of the wavelength of the pump. In this technique, the sample of interest absorbs the intensity-modulated pump beam, inducing an oscillating temperature field that is proportional to optical absorption coefficient of the sample. The geometry of the probe beam path depends on the optical opacity of the sample at the wavelength of the probe beam. For optically opaque samples, typically a solid sample with a flat surface, transverse photothermal deflection is suitable. In this geometry, the probe beam propagates parallel to and near the sample surface and is deflected by the gradient of refractive index in the layer of gas adjacent to the sample surface[2,3]. For optically thin samples, for example gas[4], liquid[5] and thin solid films[5], collinear photothermal deflection can be used, in which the probe beam traverses the sample with an offset from the pump beam and measures the temperature via deflection by the gradient of refractive index within the sample.

B. Measurement of thermal diffusivity

The photothermal deflection method, also known as the photodeflection method or the mirage method, was developed for measuring the thermal diffusivity of solid samples[6]. The deflection of the probe beam occurs in the layer of gas adjacent to the sample surface. The intensity-modulated pump beam is focused to a small diameter spot on the sample surface. The probe beam propagates parallel to the sample surface in the gas above with a small normal offset z from the surface. As an alternative to this skimming geometry, a bouncing geometry can be used, i.e., the probe beam is bounced from the sample surface at a small glancing angle. The normal component Φ_N and the transverse component Φ_T of the deflection of the probe beam measures the normal and transverse gradient of temperature near the sample surface, respectively. By transverse scanning of the probe beam, i.e., changing the transverse offset y from the center of the pump spot, the deflection signals as a function of transverse offset y can be analyzed to extract the thermal diffusivity of the sample.

There are two simple methods of signal analysis: the zero-crossing method and the phase method. The zero-crossing method is based on the first noncentral zero-crossing point of the in-phase signal of transverse deflection component $\mathrm{Re}[\Phi_T]$, which is linearly dependent on the inverse root of the modulation frequency. The slope of this linear relation m gives the thermal diffusivity of the solid D_s through the relation $m = (\gamma\pi D_s)^{1/2}$, where γ is a known parameter depending on relative magnitude of the optical-absorption length, thermal diffusion length and sample thickness[7]. This method has yielded accurate values of thermal diffusivity of various pure elements and compound semiconductor[8], but is problematic if the thermal diffusivity is below 2 mm^2/s, because either the zero-crossing point disappears or the signal level at the zero-crossing point is small compared to the noise[6]. Typically, to get reliable results from this method, the normal offset z needs to be kept small (z <25 μm), which requires the bouncing geometry[9]. Using the bouncing geometry,

corrections need to be made to account for the curvature of the sample caused by the thermal expansion[10].

The phase method is based on the linear relationship between the phase signal of the transverse component of the deflection $\mathrm{Arg}[\Phi_T]$ and the transverse offset y. The slope of this relationship is given by the reciprocal of thermal diffusion length of the sample. However, the slope deviates from the thermal diffusion length for low-diffusivity materials. An empirical relation for this deviation has been found, based on which the thermal diffusivity can be extracted from the phase signal at two different modulation frequencies[11]. This method allows for measurement of thermal diffusivity to values that are smaller than what are accessible to the zero-crossing method.

To tackle the challenges of low-diffusivity solid samples, such as ceramics and polymers, it is suggested to perform multiparameter fitting of both normal deflection Φ_N and transverse deflection Φ_T signals as a function of transverse offset y[12]. When combined with the use of high-pressure CO_2 gas to improve the sensitivity and signal-to-noise ratio, the lower limit of thermal diffusivity was extended to 0.05 mm^2/s.

The same experimental setup can measure the thermal diffusivity of gases when the absorbing solid has known thermal and optical properties[3]. At zero transverse offset y, the phase of the normal component of the deflection $\mathrm{Arg}[\Phi_N]$ is linearly dependent on the normal offset z, with the slope given by the reciprocal of the thermal diffusion length of the gas[9].

For liquid and solid samples which are semitransparent to the probe beam, collinear photothermal deflection can be used, whereas the phase of the deflection is linearly dependent on the pump-probe radial offset, with the slope given by the reciprocal of the thermal diffusion length of the sample[9].

Frequency-domain probe beam deflection (FD-PBD) was recently developed by our group for measurement of thermal diffusivity of transparent polymers attached to an Al-coated silica substrate[13,14]. We now refer to this approach as "back-side" FD-PBD. The sample geometry is like that for measurement of thermal diffusivity of gases, with the Al-coated silica substrate serving as the absorbing solid. The distinct feature of this implementation of FD-PBD is that the probe beam is incident normal to the surface. and thus the deflection signal is the integration of the transverse temperature gradient over the entire thermal diffusion length of the polymer. An advantage of the FD-PBD geometry is that the pump and probe beams are nearly co-aligned and focused by the same objective lens, making the experiment easier to implement and providing much higher spatial resolution. Another distinction from prior work is that the thermal diffusivity is extracted from the dependence of the deflection signal on the modulation frequency at fixed position of the probe rather than the dependence of the deflection signal on the position of the probe beam at fixed frequency.

III. PHOTOTHERMAL DISPLACEMENT TECHNIQUE

We use the term photothermal deflection technique to refer to techniques in which the probe beam deflection is induced by a gradient of the displacement of a solid surface that that is generated by the thermal expansion of the solid.

Photothermal displacement spectroscopy was developed to measure the optical absorption coefficient and thermal diffusivity of solid samples[15]. In this technique, the pump and probe beams are incident on the sample with an offset. Absorption of the modulated pump beam by the sample gives rise to an oscillating temperature field that is proportional to the absorption coefficient. Thermal expansion of the sample results in a gradient of the displacement of the sample surface, which deflects the reflected probe beam. The amplitude and phase of the deflection of the probe beam as a function of the offset from the pump beam is measured and fitted by an analytical model, which calculates the deflection for a single-layer slab with isotropic thermal and elastic properties. Both the optical absorption coefficient and thermal diffusivity of the sample can be determined from the fitting if the coefficient of thermal expansion of the sample is known. In principle, the coefficient of thermal expansion can be determined if the optical absorption coefficient is known.

A similar technique termed time-domain probe beam deflection (TD-PBD) was developed by our group to measure the coefficient of thermal expansion[16,17]. This technique shares many common features with photothermal displacement spectroscopy: 1) both the pump beam and probe beam impinge on the sample with an offset; and 2) deflection of the reflected probe beam is measured, which is mostly induced by the gradient of the displacement of the sample surface. The novel features of TD-PBD are: 1) the pump and probe laser are ultrafast pulsed lasers, enabling time-domain measurement by measuring the signal at varied delay time between probe laser and pump laser; 2) the two beams are nearly co-aligned and focused by the same lens, making the experiment easier to implement and providing much higher spatial resolution; 3) the probe beam size is similar to that of the pump beam, instead of being much smaller, providing higher spatial resolution and higher signal-to-noise for the same total power; 4) the sample of interest is coated with an approximately 100 nm-thick metal film, making the method applicable to non-absorbing samples.

The technique reported in this paper, termed frequency-domain probe beam deflection (FD-PBD), is developed to measure the thermal diffusivity of solid samples. This technique shares features in common with the two techniques above and share many of the advantageous features of TD-PBD including 2) to 4). What sets FD-PBD apart from TD-PBD is the capability of FD-PBD to simultaneously determine the thermal diffusivity from the frequency dependence of the deflection signal and the coefficient of thermal expansion from the overall magnitude of the signal. Furthermore, we have achieved advances in modeling of the probe beam deflection. Unlike the

conventional approach of treating a single-layer slab with isotropic thermal and elastic properties, our model applies to multi-layer structures with arbitrary anisotropic coefficients of thermal expansion and elastic constants, which significantly broadens the range of samples amenable to quantitative measurements.

REFERENCES

[1] W.B. Jackson, N.M. Amer, A.C. Boccara, and D. Fournier, "Photothermal deflection spectroscopy and detection," Appl Opt **20**(8), 1333–1344 (1981).

[2] A.C. Boccara, D. Fournier, and J. Badoz, "Thermo-optical spectroscopy: Detection by the''mirage effect'','' Appl Phys Lett **36**(2), 130–132 (1980).

[3] J.C. Murphy, and L.C. Aamodt, "Photothermal spectroscopy using optical beam probing: mirage effect," J Appl Phys **51**(9), 4580–4588 (1980).

[4] D. Fournier, A.C. Boccara, N.M. Amer, and R. Gerlach, "Sensitive in situ trace-gas detection by photothermal deflection spectroscopy," Appl Phys Lett **37**(6), 519–521 (1980).

[5] A.C. Boccara, D. Fournier, W. Jackson, and N.M. Amer, "Sensitive photothermal deflection technique for measuring absorption in optically thin media," Opt Lett **5**(9), 377–379 (1980).

[6] A. Salazar, A. Sánchez-Lavega, and J. Fernandez, "Thermal diffusivity measurements in solids by the '"mirage"'technique: Experimental results," J Appl Phys **69**(3), 1216–1223 (1991).

[7] A. Salazar, A. Sánchez-Lavega, and J. Fernandez, "Theory of thermal diffusivity determination by the '"mirage"'technique in solids," J Appl Phys **65**(11), 4150–4156 (1989).

[8] P.K. Kuo, M.-J. Lin, C.B. Reyes, L.D. Favro, R.L. Thomas, D.S. Kim, S. Zhang, L.J. Inglehart, D. Fournier, and A.C. Boccara, "Mirage-effect measurement of thermal diffusivity. Part I: experiment," Can J Phys **64**(9), 1165–1167 (1986).

[9] A. Salazar, and A. Sánchez-Lavega, "Thermal diffusivity measurements using linear relations from photothermal wave experiments," Review of Scientific Instruments **65**(9), 2896–2900 (1994).

[10] 1_TR Anthony, W.F. Banholzer, J.F. Fleischer, L. Wei, P.K. Kuo, R.L. Thomas, and R.W. Pryor, "Thermal diffusivity of isotopically enriched C 12 diamond," Phys Rev B **42**(2), 1104 (1990).

[11] M. Bertolotti, R. Li Voti, G. Liakhou, and C. Sibilia, "On the photodeflection method applied to low thermal diffusivity measurements," Review of Scientific Instruments **64**(6), 1576–1583 (1993).

[12] J. Rantala, L. Wei, P.K. Kuo, J. Jaarinen, M. Luukkala, and R.L. Thomas, "Determination of thermal diffusivity of low-diffusivity materials using the mirage method with multiparameter fitting," J Appl Phys **73**(6), 2714–2723 (1993).

[13] G. Lv, E. Jensen, C. Shen, K. Yang, C.M. Evans, and D.G. Cahill, "Effect of amine hardener molecular structure on the thermal conductivity of epoxy resins," ACS Appl Polym Mater **3**(1), 259–267 (2020).

[14] J. Shin, J. Sung, M. Kang, X. Xie, B. Lee, K.M. Lee, T.J. White, C. Leal, N.R. Sottos, and P. V Braun, "Light-triggered thermal conductivity switching in azobenzene polymers," Proceedings of the National Academy of Sciences **116**(13), 5973–5978 (2019).

[15] M.A. Olmstead, N.M. Amer, S. Kohn, D. Fournier, and A.C. Boccara, "Photothermal displacement spectroscopy: an optical probe for solids and surfaces," Applied Physics A **32**, 141–154 (1983).

[16] X. Zheng, D.G. Cahill, R. Weaver, and J.-C. Zhao, "Micron-scale measurements of the coefficient of thermal expansion by time-domain probe beam deflection," J Appl Phys **104**(7), (2008).

[17] X. Xie, X. Zheng, R. Weaver, J.-C. Zhao, and D.G. Cahill, "Erratum:'Micron-scale measurements of the coefficient of thermal expansion by time-domain probe beam deflection'[J. Appl. Phys. 104, 073509 (2008)]," J Appl Phys **122**(21), (2017).