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Absolute Measurement of Thermophysical and Optical Thin-Film Properties by Photothermal Methods for the Investigation of Laser Damage[1]

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Perspectives and limits of the application of the photothermal technique are given for the measurement of absorption, thermal, and thermoelastic properties in thin films. The peculiarities of this technique in the frequency and time domains are discussed in some detail, and selected important results with respect to laser damage studies in optical coatings are pointed out. Emphasis is placed on the absolute measurement of both optical and thermophysical properties in dielectric materials in thin-film form and, also, on the influence of both absorption and changed thermal properties in thin films on their thermally induced laser damage resistance.

KEY WORDS: absorption measurements; laser damage; optical properties; photothermal measurements; thermal conductivity; thermophysical properties; thin-film properties.

1. INTRODUCTION

The development of laser systems for research and technical applications is often governed by the quality of the system's optical components. In particular, optical coatings act as limiting factors, i.e., both intrinsic optical and thermophysical thin-film properties, as well as randomly distributed defects and inhomogeneities, can cause reduced values of reflectance, transmittance, stability, and laser-induced damage threshold. Any optical coating

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optimization depends on the correlation between optical losses, thermal and thermoelastic properties, thin-film microstructure, coating design, deposition technique, and a better understanding of the fundamental laser damage mechanisms. The absorptive losses and thin-film thermal conductivity play important roles in thermally induced damage.

Thin-film absorption in the range of 10^{-4} to 10^{-7} for high-reflecting mirrors at 633 nm can currently be achieved for typical dielectric materials, due to the development of deposition techniques and the selection of materials. The ultimate value is close to the related bulk data, indicating the limiting case of residual intrinsic absorption. These extremely low losses are measurable exclusively by the photothermal technique, a nondestructive material inspection method that measures optical, thermal, and thermoelastic material properties with high sensitivity [1, 2]. On the other hand, the thermal conductivity of most oxide thin-film materials is usually small, in the range of 10^{-1} to $10^{-2}\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and it is some orders of magnitude lower than that of the respective bulk data. Although thermal conductivities of thin films can be measured by classical contact methods [3], the advantages of the photothermal technique are its excellent high sensitivity, spatial resolution, and noncontact measuring procedure [4, 5].

To outline the aim of this paper, let us mention that, in principle, with respect to thermally induced laser damage in optical coatings, it is not important whether the photothermal response is dominated by an absorptive or by a thermoelastic origin. For instance, the laterally or depth-resolved photothermal mapping of optical thin-film structures would give the first insight into their laser resistance quality [6–9]. Because the peculiarities of the photothermal signal depend on both optical and thermophysical properties, the photothermal sample response in the sense of damage resistance quality shows "constructive" acting of the ensemble of the above-mentioned properties, hence providing an ideal tool for the investigation of thermally induced laser damage.

A brief description of the photothermal principle with respect to this topic is sketched in Section 2, showing that it is possible to measure inherently optical as well as thermophysical parameters simultaneously, similarly to the measurement of the complex index of refraction. Hence, at a first glance, any measurement of absorption must also take into consideration the thermal conductivity, and vice versa.

A review of papers concerning this topic and the progress in this field is presented in comprehensive treatises [1, 2, 10]. Thus, after the brief description of the principal peculiarities in the recent applied photothermal technique, given in Section 2, we present in Section 3 a discussion of some selected results based on original ideas and absolute measurements of optical absorption and thermal conductivity in optical thin-film coatings.

2. PHOTOTHERMAL PRINCIPLE

The basic process of a photothermal measurement, the so-called photothermal effect, is caused by the heating of a sample after absorption of optical energy. The material photothermal probing or characterization technique generally relies on the application of high-sensitivity detection methods to monitor this effect. The photothermal technique requires modulation of the excitation light, which can be carried out in the form of a short laser pulse, in the time domain, or in the form of a periodic intensity modulation of continuous laser light, the frequency domain.

As a consequence of the absorption of the modulated excitation light, thermal waves are produced within the sample which can be measured by different detection channels. The crucial point is that the photothermal signal represents the characteristic material response related to the specially chosen domain, the optical and thermophysical sample properties, and the geometric parameters of the illuminating laser light as well as the special detector configuration.

The principle is illustrated is Fig. 1. Whenever absorption takes place, both thermal and acoustic waves lead to a response of the sample under

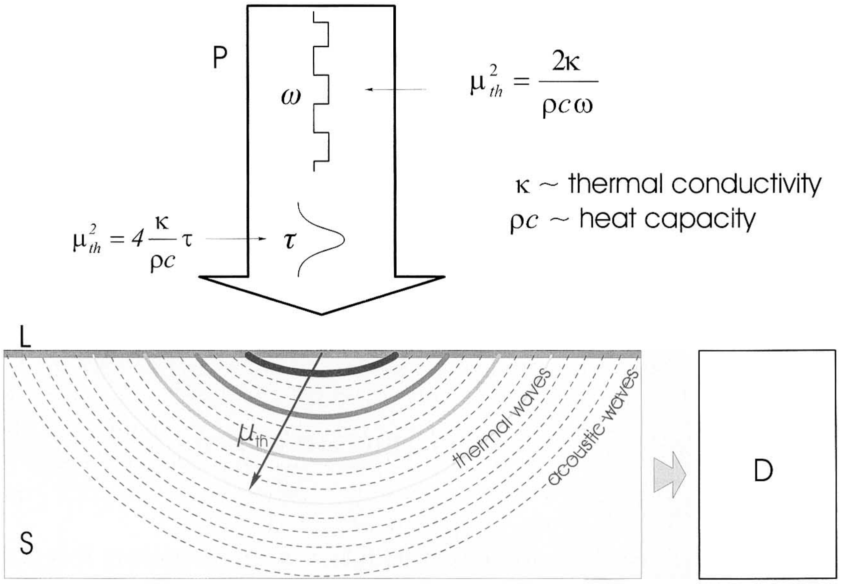

Fig. 1. Principle of a photothermal measurement: pulsed (τ) or modulated (ω) laser irradiation (P) will be absorbed in a thin surface layer (L), creating heavily damped thermal (full lines) waves as well as acoustic (dashed lines) waves within the sample. Their detection (D) is performed in different ways. The heat penetrates the sample only up to the distance μ_{th}, which is called the thermal diffusion length.

investigation. While thermal waves are heavily damped within a characteristic distance near the sample surface, where their generation is assumed to take place, acoustic waves, in general, penetrate the sample without being damped. Thermal waves are very dispersive, i.e., their propagation velocity depends strongly on the laser modulation frequency or on the respective pulse duration. Assuming a thin absorbing layer, situated in the depth l within a transparent sample irradiated with a modulated light, a proper detector mounted at the sample surface will detect the increase in temperature after the characteristic travel time. In the case of harmonic intensity modulation, this increase in temperature will be measured by the amplitude A of the signal, while the delay of the response is detected by the phase φ of the signal. (For pulsed laser light, the analogy to φ is the time delay between the laser pulse and the detected temperature maximum.)

Hence, A is a function of the surface temperature, while φ can be considered as a function of the travel time of thermal waves. From this, it follows that A depends on both optical and thermophysical sample properties, in contrast to φ, which is dependent only on thermal sample properties. Note that, in this simple model, the depth l should be small and the focus diameter of the laser beam large compared to the thermal diffusion length [11]. This simple consideration gives more insight into the question: How can optical and thermophysical properties of thin films be measured properly?

Taking into account the fundamentals of a photothermal experiment, the basic question with respect to the measurement of optical and thermophysical properties, especially absorption and thermal conductivity, is, What are the conditions to exploit properly amplitude as well as phase information in order to yield these thin-film properties? It means that there is no preferred photothermal technique, but cleverly devised conditions to measure A and φ.

In the next section selected experimental measurements are considered in light of the above viewpoint.

3. MEASUREMENTS ON DIELECTRIC THIN-FILM COATINGS

3.1. Thermal Conductivity

The thermal conductivity of thin films is a critical factor for the realization of optical components with improved performance and durability and a high laser-induced damage threshold [1, 12, and references therein]. Also, the precise measurement of thermal conductivity provides information with respect to finite size effects, defects and impurities, structural anisotropies, and thermal barriers at interfaces [2, 12–14]. According to the aim of our paper, we restrict our interest to the consideration of an effective isotropic thermal conductivity which incorporates any thermal impedance acting at the thin-film interfaces similar to the measurement of an effective thin-film absorption including the potential contribution of interface absorption. The first reported photothermal method applied to thermal conductivity measurement of optical coatings was given by Ristau et al. [4, 15, 16], using an infrared scanning laser calorimeter based on the principle of the photothermal radiometry technique. This remote sensing detection of the temperature profile on the sample surface is generated by the absorbed energy of an intensive cw laser beam impinging on single layers. The recorded temperature, by scanning the infrared radiation at the heated surface area, has been compared with the surface temperature calculated theoretically.

From the scope of Section 2, this technique consists of an absolute dc amplitude measurement (the surface temperature) of at least two comparable samples with different film thicknesses. (Note that the phase information vanishes for a dc measurement.) Hence, performing this measurement, the thin-film thermal conductivity as well as the absorption coefficient could be determined simultaneously from the experimental data. The authors measured e-beam-deposited oxide single layers such as Al_2O_3, TiO_2, HfO_2, and Ta_2O_5 on fused silica substrates with an ultimate sensitivity of about $0.6\,cm^{-1}$ for the absorption per unit length and, also, for the first time, their thermal conductivity, confirming by photothermics that thin dielectric films exhibit remarkable lower values than the corresponding bulk materials [3–17, 18, 19].

In 1994 another new idea, to measure the thermal conductivity of thin films by a thermal pulse method [5], was reported. The operation principle of this technique, which was improved later [20], is based on a propagation time measurement. From the basic viewpoint of the photothermal effect, this technique consists of a noncontact, nondestructive phase (time delay) measurement, hence, not utilizing any amplitude information. Therefore, neither must optical constants be available nor are complex calibration procedures or exact temperature recordings necessary.

The method is based on the measurement of the time delay between the pump laser pulse and the thermal wave induced by the absorption of the laser pulse in the sample; see Fig. 2. A pumped laser beam is directed onto a sample consisting of a thin transparent test layer and a totally absorbing substrate at the laser wavelength. As a consequence of absorption of the laser pulse, a temperature profile builds up at the substrate–film interface. A thermal pulse starts to diffuse from the substrate–film interface to the surface of the layer. Therefore, the temperature rise at the surface of the test layer starts with a time delay Δt with respect to the laser pulse.

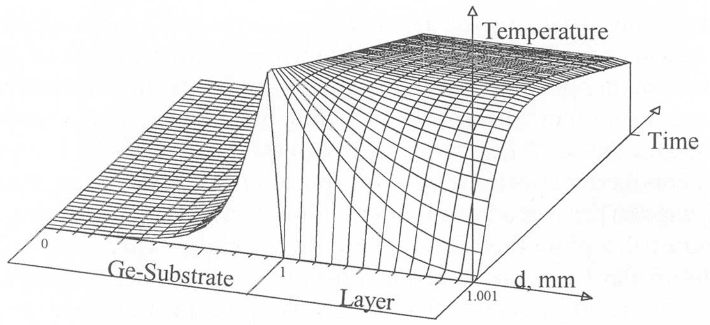

Fig. 2. Temporal behavior of the laser-induced temperature profile in the center of a sample consisting of an absorbing substrate and a thin transparent test layer. The laser intensity penetrates the transparent layer without losses and strikes the absorbing film substrate interface. Thus, a heat pulse propagates from the film–substrate interface through the layer, from the rear to the front surface. The travel time of the heat from the substrate to the film surface is related to the thermal conductivity and the thickness of the film.

Δt depends on the propagation velocity v of the thermal wave through the layer with $v^2 = (4/\Delta t)\,\kappa/\rho c$ and is related to the thermal conductivity κ, the heat capacity ρc, and, according to $l = v\,\Delta t$, to the thickness l of the film layer

$$\Delta t = \frac{1}{4}\frac{\rho c}{\kappa} l^2 \tag{1}$$

Substrates, ideally suited to the thermal pulse method, should be highly absorbing at the laser wavelength and transparent to far-infrared radiation. In contrast, ideal testing films should be transparent at the laser wavelength and highly absorbing for far-infrared radiation. With such characteristics of the film and substrate materials, the time delay Δt of the thermal wave on the surface of the test sample is directly related to the thermal conductivity κ and the thickness l of the layer; see Eq. (1). For a more comprehensive description of experimental details and procedure, see Refs. 5 and 20, respectively.

Single layers of Al_2O_3, SiO_2, Ta_2O_5, and HfO_2 on Ge substrates were investigated. Layers of different thicknesses were deposited on identical polished germanium. Samples of the same material have been grown in the same run, and the different thicknesses were achieved by depositing all the layers on the polished germanium substrates in subsequent steps. In this way approximately the same film–substrate thermal resistance is achieved for different thicknesses, and the variations associated with the processing conditions are minimized. Time delays Δt were calculated using the hypothesis of an ideal substrate–film interface. To rule out the contribution of interfacial properties, Δt values measured from samples with $l = 500$-nm layer thickness were substracted from all time delays measured from the layer of the same material. In order to determine κ for a certain layer material, measured and calculated relative time delays were plotted in the same diagram for different l. The value of κ for a certain film thickness was determined from the calculated curve containing the experimental point as shown for the measurement on SiO_2 films onto Ge substrates in Fig. 3.

In Table I thermal conductivity values measured by the above-described pulse method are [5, 11] compared to the results of other photothermal approaches. As expected, κ values of the analyzed dielectric thin films are shown to be significantly lower than those of the corresponding materials in bulk form.

Finally, let us briefly sketch the approach of Reichling et al. [13, 21], which described the measurement of thin-film conductivity utilizing phase measurements by the photothermal surface displacement technique (PTD) (see Fig. 4) in the frequency domain. Because of the excellent lateral resolution as well as sensitivity (see Section 3.2), some efforts have been made to calculate and check the photothermal signal of dielectric thin films [6, 11, 13, 22]. It could be shown that the phase of the PTD signal versus

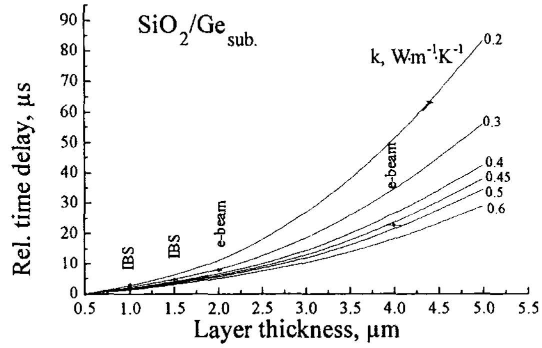

Fig. 3. Calculated relative time delays versus film thickness for SiO_2 films, with respect to a layer thickness of 0.5 μm. The curves correspond to different thermal conductivities and are obtained by a program based on the finite-difference method. Measured values are also reported for films of different thicknesses. The thermal conductivity for a certain film thickness can be determined with respect to the calculated relative time delay curve that contains the experimental point.

Table I. Thermal Conductivity Data for SiO_2, Al_2O_3, Ta_2O_5, and HfO_2 Films Measured by Different Groups[a]

	Thermal conductivity κ ($W \cdot m^{-1} \cdot K^{-1}$)					
Material	Bulk	Ref. 4	Ref. 13	Ref. 14	Ref. 5	Ref. 20
SiO_2						
e-beam	1.4	0.1	0.25	0.25	0.37–0.73	0.2–0.5
IBS	—	—	—	—	—	0.2–0.3
Al_2O_3	27.0	33.0	150	—	5.2–12.3	0.7–1.1
Ta_2O_5	—	0.026	0.2	—	2.8–15	0.3–0.6
HfO_2	17.0	8×10^{-4}	—	0.08	—	0.07–0.2

[a] Data measured by several photothermal methods: radiometry [4], surface displacement [13], probe beam refraction (Mirage) [14], and thermal pulse delay [5, 20]. The range of values in the last two columns was caused by an additional dependence on layer thickness.

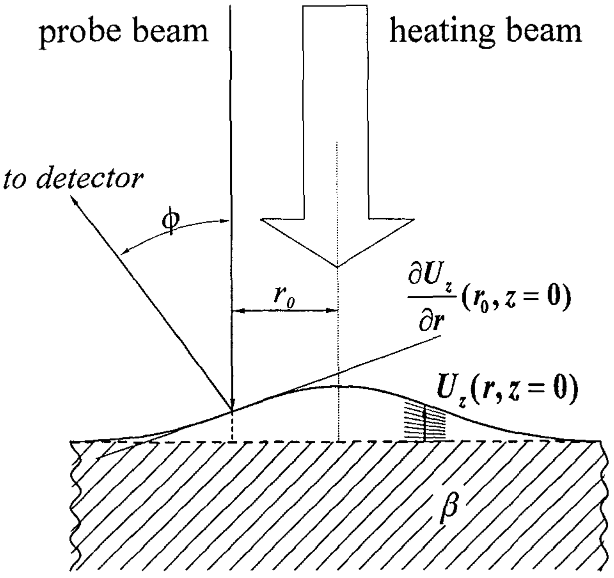

Fig. 4. Deflection angle ϕ of the probe beam (PB) due to surface displacement U_z caused by bulk absorption per unit length β of the irradiated heating beam (HB). The distance r_0 is the offset between HB and PB for the maximum derivative.

modulation frequency exhibits a local extreme value at a frequency ω which corresponds to the value of the thermal diffusion length equal to the physical film thickness, i.e.,

$$2\frac{\kappa}{\rho c\omega}=l^2 \tag{2}$$

see Section 2 and Fig. 1. From this equation, for the measured resonant ω, κ values have been calculated for selected single-layer coatings; see Table I and Ref. 13. This behavior may be understood by the fact that, because of the strongly dispersive thermal propagation velocity, a thermal resonant thin-film layer leads to an extreme amount of related phase delay.

It should be noted that, in contrast to the above-described range $\mu_{\text{th}} \geqslant l$, both the PTD amplitude A and the phase φ in the case of $\mu_{\text{th}} \ll l$, i.e., for modulation frequencies of the order of megahertz, are shown to be nearly independent of the thin-film conductivity κ [1, 6, 13]. This would give the potential of using the PTD technique to determine the absorption of optical coatings by measuring the photothermal amplitude because of the partial absence of this important thin-film parameter in the amplitude response itself; see Section 3.2.

3.2. Absorption

As explained in Section 2, only the photothermal amplitude is dependent on both optical and thermophysical properties of the sample under investigation. Hence, only amplitude measurements can provide information covering optical absorption in thin films. In the light of the investigation of thermally induced damage in optical coatings, the potential of the photothermal surface displacement technique for a spatially high-resolved defect mapping should be mentioned. Figure 4 shows a typical sketch [11]: a probe beam, incident perpendicular to the sample surface and parallel to the heating beam, is directed at the flank of the thermoelastically induced sample deformation bulge. The measured deflection angle of the reflected probe beam at the sample surface is proportional to the local slope of the surface displacement perpendicular to the sample surface, and therefore, both amplitude and phase detection provide insight into optical as well as thermophysical inhomogeneities. Hence, thermally induced damage events like melting and cracking [1, 11] can be mapped. Weak "photothermal defects," of the order of microns, which are not visible by optical microscopy, have been detected.

Recently, the potential of micrometer resolved PTD scans on UV multilayer coatings was demonstrated [8]. It could be shown that the *lateral* *position* of photothermal inhomogeneities is related to the onset of optical breakdown. Moreover, laterally distributed coating defects have been investigated *prior* to laser radiation by illuminating with low fluences and correlated with damage events *after* irradiation with laser fluences in the damage onset range. It should be emphasized again that such a PTD measurement, i.e., spatially resolved amplitude and phase mapping in this modification, acts as photothermal microscopy rather than absolute measurement of thin-film absorption.

When a determination of the portion of absorbed laser power has to be performed, these thin-film thermophysical properties, which in general are modified in thin-film form, must be eliminated in the photothermal amplitude. This is in contrast to the situation where photothermal coating characterization yields a potential damage failure mapping as considered above. This is valid especially for the changed amount of thin-film thermal conductivity. To overcome this uncertainity, the photothermal amplitude must be calibrated electrically by calculating the thermal load induced temperature rise within the sample [23, 24]. To do this, thin gold films on quartz were prepared which are comparable to the dielectric coating samples.

4. CONCLUSION

The photothermal technique is a versatile tool for the characterization of high-performance optical components. During the past decade, it has stimulated progress in optical thin-film technology because of its outstanding sensitivity and high efficiency.

There is strong evidence that highly sensitive two-dimensional sample surface mappings are important, whenever the origin of the radiation breakdown has to be investigated. Any correlation between the spatial distribution of the "photothermal inhomogeneities" and the damage statistics would be an indication of the thermal origin of the considerably different laser damage resistivity over the sample surface.

Here, the intention was to demonstrate the importance of a unique exploitation of photothermal amplitude and phase information, rather than to use a supposedly favorable technique. In principle, the optical absorption can be precisely measured photothermally only by the response amplitude, strictly avoiding the influence of serious thermophysical thin-film properties, or by rigorous calorimetry, while the thermal conductivity can be determined by the phase of the response. In the case of very low values of absorptivity and thermal conductivity, additional optical and thermal interface properties, respectively, have to be taken into account.

Improved future measurements that include both theoretical calculations and simultaneous detection of photothermal amplitude as well as phase are possible. Using such an approach, absolute measurements of both optical absorption and thermal conductivity could be obtained, after the calibration of the experimental setup.

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