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Absolute measurement of thermophysical and optical thin-film properties by photothermal methods

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Abstract

An overview of the current state of the art as well as perspectives and limits of the application of the photothermal technique for the measurement of both absorption and thermal as well as thermoelastic properties in thin films is given. The peculiarities of this technique in the frequency as well as time domain are discussed in some detail, and selected important results are pointed out.

Emphasis is placed on the absolute measurement of both optical and thermophysical properties in dielectric material in thin -film form, and also on the influence of residual absorption and changed thermal properties in thin films on their laser damage resistance and predamage behaviour.

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 cause reduced values of reflectance, transmittance, stability, and laser induced damage threshold. Any optical coating optimization is shown to be dependent 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.

With respect to the thermally induced damage especially two material properties are of outstanding interest: absorptive losses and thin-film thermal conductivity.

Caused by the refinement of deposition technique and selection of materials, currently, thin film absorption for high-reflecting mirrors at 633nm in the order of 10^{-4} to 10^{-7} can be achieved for typical dielectric materials. The ultimate value is in the vicinity of the related bulk data, indicating the limiting case of residual intrinsic absorption.

These extremly low losses are measurable exclusively by photothermal technique, a nondestructive material inspection which covers the highly sensitive measurement of optical, thermal and thermoelastic material properties [1 - 7]

Contrarily, there are some indications that the thermal conductivity of most of the oxide thin-film materials is in the range of 10^{-1} - 10^{-2} W/mK , and hence of 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 [8 - 10], also the photothermal technique is capable because of its excellent sensitivity,

spatial resolution- and noncontact measuring procedure [11 - 15].

To obtain an appropriate approach to the aim of this review, let us mention that, in principle, with respect to the thermally induced laser damage in optical coatings, it is not of importance whether the photothermal response is dominated by absorptive or by thermoelastic origin.

For instance, the laterally or depth-resolved photothermal mapping of optical thin-film structures would give a first insight over their the laser resistance quality [16 - 19].

Because of the peculiarities of the photothermal signal depending on both optical and themophysical properties, the photothermal sample response in the sense of damage resistance quality shows the "constructive" acting of the ensemble of the above mentioned properties, hence giving an ideal tool for the investigation of thermally induced laser damage.

A brief description of the photothermal principle with respect to this topic will be sketched in Chapter 2 showing that photothermics measures, in general, inherently optical as well as thermophysical parameters simultaneously, considered similarily to the measurement of the complex index of refraction. Hence, at first glance, any measurement of absorption have to take into consideration also the amount of thermal conductivity and vice versa. Only in this way the complexity is understandable which arises in the case of these quantities are to be determined absolutely.

A review of papers concerning this topic and the progress in this field is presented in comprehensive treatises [5 - 7, 19, 22]. Thus, after the brief sketch a description of the principal peculiarities in the recent applied photothermal technique, given in Chapter 2, we would like to focus our interest in Chapter 3 on a discussion of some selected results based on original ideas and suggestion which measure optical absorption and thermal conductivity

in optical thin-film coatings, absolutely.

2. Photothermal principle and basic potentiality

The basic process of a photothermal measure, the so-called photothermal effect, is caused by the heating of a sample after absorption of optical energy. The photothermal material probing or characterization technique generally rely on the application of high-sensitivity detection methods to monitor this effect.

Photothermal technique requires a modulation of the excitation light which can be carried out in the form of a short laser pulse, the time domain, or a periodic intensity-modulation of continuous laser light, the frequency domain.

In consequence, thermal waves are preduced within the sample which can be measured by - different detection channels. The crucial point is that the photothermal signal represents the characteristic material response depending on 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 by Fig. 1. Whenever absorption takes place, both thermal and acoustic waves lead to a response of the sample under 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. For the following a second distinction must be mentioned. Thermal waves are very dispersive, i.e. their propagation velocity depends strongly on the thermal diffusivity as well as the laser modulation frequency respective pulse duration.

Assuming an absorbing layer, situated in the deph ℓ within a transparent sample, a proper

detector mounted at the sample surface will detect the increase in temperature after the characteristic travelling 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 analogous to φ is the delay between laser pulse and detected temperature maximum.)

Hence, A is a function of the surface temperature, while φ can be considered as a function of the travelling time respective the travelling velocity of the thermal wave. From this follows that A depends on both, optical and thermophysical sample properties in contrast to φ which is only dependent on thermal 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, see [23].

This simple consideration gives more insight in the question: <u>How optical and thermophysical properties of thin films can be measured properly ?</u>

Taking into account these essentials of a photothermal experiment, the basic question with respect to the measure of optical and thermophysical properties, especially absorption and thermal conductivity, is: <u>What are the conditions to exploit properly amplitude as well as phase information in order to yield these thin-film properties ?</u> That means, there exists ad hoc no favoured photothermal techniques, but cleverly devised conditions to measure A and φ, respectively.

In the next following paragraph selected experimental verifications are considered in the light of the above scetched view point.

3. Selected examples of measurement on dielectric thin-film coatings

3.1 Thermal conductivity

Thermal conductivity of thin films is a critical factor for the realization of optical components with improved performance, long servic life and high laser induced damage threshold [6, 7, 24 and references therein].

Beyond, the precise measurement of thermal conductivity provides information with respect to finite size effects, defects and impurities, structural anisotropies and thermal barriers at interfaces [5, 24, 29]. According to the aim of our paper we restrict our interest on the consideration of an effective, isotropic thermal conductivity which incorporates any thermal impendance 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 is given by Ristau et al. [11 - 13], using an infrared scanning laser calorimeter based on the principle of photothermal radiometry technique [16]. 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 Chapter 2 this suggestion consists of an absolute dc amplitude measurement (the surface temperature!) of at least two comparable samples exhibiting different film thicknesses. (Note that the phase information vanishes for a dc-measurement.) Hence, performing this, the thin-film thermal conductivity as well as the absorption coefficient could be determined simultaneously from the experimental data. The authors measured in 1984 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, [8 - 10; 25].

The authors offered in 1994 another original idea to measure the thermal conductivity of thin films by a thermal pulse method [14]. The operation principle of this technique which could be refined later on [30], is based on a propagation time measurement. From the basic view point of photothermics this technique consists of a noncontact, nondestructive phase (time delay) measurement, hence, not utilizing any amplitude information. Therefore, neither optical constants must be available nor complex calibration procedures or exact temperature recordings are 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 pump laser beam is directed onto a sample consisting of a thin transparent test layer and a totaly absorbing substrate for the laser wavelength. As a consequence 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. Δt depends on the propagation to velocity v of the thermal wave through the layer with $v^2 = 4/\Delta t \cdot \varkappa/\varrho c$ and is related to the thermal conductivity $\varkappa$, the heat capacity ϱc and, according to $\ell = v \cdot \Delta t$, to the thickness ℓ of the film layer

$$\Delta t = \frac{1}{4}\frac{\rho c}{\varkappa}\ell^2. \qquad \textbf{(1)}$$

Substrates, ideally suited to thermal pulse method, should be highly absorbing for the laser

wavelength and transparent to the far infrared radiation. In contrast, ideal testing films should be transparent to the laser wavelength and highly absorbing for the 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 $\varkappa$ and the thickness ℓ of the layer, see Equ.(1). For a more comprehensive description of further experimental details and procedure see Refs. 14 and 30, respectively. Single layers of Al_2O_3, SiO_2, Ta_2O_5 and HfO_2 on Ge substrates have been 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 for different thicknesses is achieved and the variations associated with the processing conditions, are minimized. Time delays Δt have been calculated using the hypothesis of 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 $\varkappa$ for a certain layer material, measured and calculated relative time delays have been plotted in the same diagram for different ℓ. The value of $\varkappa$ for a certain film thickness has been determined from the calculated curve containing the experimental point as it is shown for the measurement on SiO_2 films onto Ge-substrates in Fig.3.

In Table 1 thermal conductivity values measured by the above described pulse method are compared to the results of other photothermal approaches. As espected, $\varkappa$ of the analyzed dielectric thin films are shown to be significantly lower than those of the corresponding materials in bulk form.

Finally, let us finally briefly sketch the approach of Reichling et al. [15, 26] 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 has been performed to calculate and check the photothermal signal of dielectric thin-films. [15, 16, 23, 31]. It could be shown that the phase of the PTD signal versus modulation frequency exhibits a local extreme value at that frequency ω which corresponds to the value of the thermal diffusion length equal to the physical film thickness, i.e.

$$2 \frac{\varkappa}{\varrho c \omega} = \ell^2 \qquad \textbf{(2)}$$

see Chapter 2 and Fig. 1 again. From this Equation (2), for the measured resonant ω, $\varkappa$ values has been calculated for selected single layer coatings, see Table 1, Ref. 15.

This behavior may be understood by the fact that, caused by the strongly dispersive thermal propagation velocity a thermal resonant thin-film layer leads to an extreme amount of the related phase delay.

It should be noted that in contrast to the above described range $\mu_{th} \geq \ell$, both the PTD amplitude A and phase φ in the case of $\mu_{th} << \ell$, i.e. for modulation frequencies in the order of some MHz is shown to be nearly independent of the thin-film conductivity $\varkappa$. [6, 15, 16] This would give the potentially of PTD-technique to determine the absorption of optical coatings by measuring the photothermal amplitude because of the partial absence of this serious thin-film parameter in the amplitude response itself, see Section 3.2.

3.2. Absorption

As explained in Chapter 2, only the photothermal amplitude is depending on both optical and thermophysical properties of the sample under investigation. Hence, exclusively amplitude measurements can provide information covering optical absorption in thin films. In the light of the investigation of thermally induced damage in optical coatings and the related remarks given in Chapter 1, first, the potentiality of the photothermal surface displacement technique for a spatially high-resolved defect mapping should be mentioned, see again Fig. 4 as a typical sketch: A probe beam incident perpendicularly 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 provides an insight of optical as well as thermophysical inhomogeneities. Hence, the diminished quality with respect to thermally induced damage events like melting or cracking [6, 7, 16 - 18 , 20] can be mapped. Weak "photothermal" defects in the order of microns which are not visible by optical microscopy, has been detected. This is due to the proportionality of the lateral resolution to the quadratic inverse of the heating beam diameter [23] and a tightly focused probe beam.

Recently, the potentiality of micrometer resolved PTD scans on UV multilayer coatings was demonstrated [18, 20, 32]. It could be shown that the lateral position of photothermal inhomogeneities is related to the onset of optical breakdown. Moreover, laterally distributed coating defects has been investigated *prior* to laser radiation by illuminating with low fluences, and correlated to damage events *after* an irradiation with laser fluences

in the damage onset range. It should be emphasized once more that such a PTD measurement, i.e. spatially resolved amplitude and phase mapping, in this modification acts as photothermal microscopy rather than absolute measure of thin-film absorption.

When a determination of the portion of absorbed laser power has to be performed, those thermophysical properties, which 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.

From this scope the well known laser calorimetry (LCA) measures the initial slope of the photothermal dc amplitude which can be assumed in a good appoximation as being completely independent on thin-film thermophysical properties and heat losses, but only depending on the heat capacity $C=\varrho c$ of the substrate material [33]. In this measuring range, the heat accumulated by the sample is equal to the radiation power converted in unit time by optical absorption. This heating is measured directly by the monitoring of the rise in temperature, see Fig.5 Utilizing the known heat capacity of the substrate, the ratio of the absorbed power to the incident power P_0,i.e. the thin-film absorption can be determined absolutely from the measured time derivative of the initial increase in temperature. The rate calorimetry is capable of measuring the absorption of thin films with a sufficient accuracy as described elsewhere [6, 34]. For absorption measurements in the UV-range, a modified LCA-technique utilizing pulsed irradiation has been developed [35]. Recently, a draft international standard for the measurement of optical absorption in laser compounds (FDIS 11551) which is based on laser calorimetry was circulated by the working group [6] of ISO/TC 172/SC for the final voting procedure [36,37]. Currently, sensitivity limits in the range of 1ppm which is sufficient for most high quality coatings can be achieved [34]. Note

that a combination of LCA and spatially resolving photothermal technique can be of usefulness, whenever an absorption average over the inspected thin-film area is of interest [31, 38]. Otherwise the calibration might be performed by the use of a thin-film sample of known absorptivity [22, 5], but from the view point of the discussed photothermal essentials, this proceeding seems to be more then difficult.

Finally, the rigorous calibration of a photothermal amplitude measurements which is carried out by calculating the electrically induced thermal load within the sample, should be mentioned [20, 39]. This Joule heating of a comparable sample requires the same time resolution as performed during the photothermal experimental procedure and is not simple to realize. The authors made an attempt to determine the increase in absorption in UV optical coatings when irradiated with an increasing number of laser shots in close vinicity to their damage onset laser fluence. Performing such measurements, more insight can be achieved about the physical process immediately before the onset of optical breakdown. Also, accumulation phenomena after laser irradiation in the predamage range would be investigable. This is of basic physical interest because of the different damage mechanisms depending on exciting laser intensity as well as pulse duration [6, 24, 32, 35, 42].

In detail, the single and multishot experiments were performed by a two-probe-beam, a one-heating-beam technique using Mirage as well as PTD configuration simultaneously, see Fig.6 [40,41]. (The Mirage configuration of the probe beam technique probes the surface temperature-induced change in refractive index normal to the sample surface.). Therefore, both the thermally and the thermoelastically induced thin-films amplitude response can be detected. The transient calorimetry has been performed as follows: The linear sub-damage mirage response which is proportional to the absorbed laser fluence and, hence, to the surface temperature, must be calibrated in portions of thin-film melting or cracking

temperature. This procedure is checked by the electrically heating of thin gold films on quartz. Carrying out this calibration, the accumulated laser energy per volume and laser shot is determined absolutely. According to Fig. 7 [20], an accumulation- induced change in absorption coefficient per laser shot $\Delta\beta \simeq 80\ cm^{-1}$ was measured for UV high-reflecting LaF_3/MgF_2 multilayers at a laser fluence of 11,3 Joule/cm^2 within a range of 5 to 7 shots. After visible damage the mirage signal reaches a constant value, but the displacement increases following the proceeding rupture. The authors believe that the latter experiment is an impressive example for the potentiality of photothermal technique to give also quantitative insight and, hence, indications with respect to fundamental mechanisms.

4. Conclusion and Outlook

Photothermal technique has been shown to be a versatile tool for the characterization of high-performance optics. During the post decade, they have stimulated progress in optical thin-film technology because of their outstanding sensitivity and high efficiency.

There is strong evidence that highly sensitive two dimensional sample surface mappings are of importance, 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 considerally different laser damage resistivity over the sample surface.

The authors intention was to demonstrate the importance of a clever exploitation of photothermal amplitude and phase information, respectively, rather than a supposed

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 a rigerous dc or transient calorimetry, while the thermal conductivity can by yield by the phase of the response. In the case of very low values of absorptivity and thermal conductivity respectivily additionally optical and thermal interface properties have to be taken into account.

Refined future measurements which cover both theoretical calculation and simultaneous detection of photothermal amplitude as well as phase would be imaginable. From such an approach both optical absorption and thermal conductivity could be obtained absolutely, when the apparatus function has been measured additionally with sufficient accuracy. The measurement has to be carried out with a single chosen photothermal technique as well as thin-film sample.

References

1 Fournier,D. and Roger,J.P. (Eds.),*8th International Topical Meeting on Photoacoustic and Photothermal Phenomena*, J.de Phys.,C7,Vol.4 (1994)

2 Zhang,S.Y.(Ed.),*9th International Conference on Photoacoustic and Photothermal Phenomena*, Progress in Natural Science (PRC), Suppl. to Vol.6 (1996)

3 Tam, A.C., " Overview of Photothermal Spectroscopy," in *Photothermal Investigation of Solids and Fluids*, ed. by J.A. Sell, Academic Press , Boston, pp. 1-33, (1989)

4 Bein, B.K., Pelzl, J., " Analysis of Surfaces Exposed to Plasmas by Nondestructive Photoacoustic and Photothermal Techniques," in *Plasma Diagnostics Surface Analysis and Interactions*, ed. by O. Auciello and D.L. Flamm, Academic, New York, pp. 211-325, (1989)

5 Wu, Z.L., "Overview of photothermal characterization of optical thin-film coatings," in Laser-Induced Damage in Optical Materials: 1995, H.E.Bennett, A.H.Guenther, M.R.Kozlowski, B.E.Newnam, M.J.Soileau (Eds.), Proc. SPIE 2714, pp.465-481, (1996) Wu, Z.L.,Thomsen,M.,Kuo,P.K.,Lu,Y.,Stolz,C. and Kozlowski,M., *Photothermal characterization of optical thin film*, Opt.Eng. Vol. 36(1), pp. 251-262, (1997)

6 Hummel,R.E. and Guenther,K.H.(Eds.), *Optical Properties*, Vol.1, Chap.9, Thin Films for Optical Coatings,CRC Press, Boca Raton,FL.(1995)

7 Welsch,E. and Ristau,D., *Photothermal Measurements on optical thin films*, Appl.Opt. 34:7239-7253

8 Lambropoulos, J.C., Jolly, M.R., Amsden, C.A., Gilman, S.E., Sinicropi, M.J., Diakomihalis, D., Jacobs, S.D.1989. Thermal conductivity of dielectric thin films. *J. Appl. Phys.* 66:4230-4242 and ref. therein

9 Decker, D.L., Koshigoe, L.G. and Ashley ,E.J., *Thermal properties of optical thin film material*, NBS Spec. Publ., Vol. 727 ,pp.291-297, (1986)

10 Jacobs,S.D.,*Thermal conductivity in dielectric thin films*, Lab. Laser Eng. Rev.,Vol.29,pp. 30-38, (1986)

11 Ristau, D., Dang, X.C., Ebert, J.," Interface and bulk absorption of oxide layers and correlation to damage threshold at 1.064 µm," *Natl.Bur.Stand.(U.S.) Spec. Publ.* No. 727(1984)298-312

12 Akhtar, S.M.J., Ristau, D., Ebert, J. 1988. Thermal Conductivity of Dielectric Films and Correlation to Damage threshold at 1064 nm. *NIST Spec. Pub.* 752:345-351 in *Laser Induced Damage in Optical Materials* 1986

13 Ristau, D., Ebert, J. 1986. Development of a thermographic laser calorimeter. *Appl. Opt.* 25:4571-4578

14 Dieckmann, M., Ristau, D., Willamowski, U. Schnmidt, H. 1994 Measurement of Thermal Conductivity in Dielectric Films by the Thermal Pulse Method. *SPIE proceedings* 2253,712-719 ,Optical Interference Coatings

15 Reichling, M., *Photothermische Charakterisierung von Dünnschichtsystemen*, Dissertation FU Berlin, (1992)

16 Welsch, E., Reichling, M., " Micrometer resolved photothermal displacement inspection of optical coatings," *J.Mod.Opt.* 40(1993)1455-1475

17 Reichling, M., Welsch, E., Duparré, A., Matthias E.," Photothermal Microscopy Defects in ZrO_2 and MgF_2 Single-Layer Films, Opt. Eng., Vol. 33, 1334-1342, (1994)

18 Bodemann, A., Reichling, M., Kaiser, N., "The role of thin film defects for laser damage in HR multilayer coatings for 248nm," to be published in Thin Solid Films

19 Commandre',M.,Roche,P.,"Characterization of absorption by Photothermal deflection,"in Flory,F.,(Ed.)Thin films for optical systems,Vol.49 of Optical Engineering Series ,Marcel Decker Inc.,USA,pp.329-365, (1995)

20 Welsch,E.,Ettrich,K.,Blaschke,H.,Thomsen-Schmidt,P.,Schäfer,D., and Kaiser,N., *Investigation of the absorption induced damage in ultraviolet dielectric thin films,* Opt.Eng., Vol. 36 (2), pp.504-514 ,(1997)

21 Welsch,E., *Photothermal Absorption Measurement on Optical Thin Films*, Laser und Optoelektronik, Vol. 29(1), pp.63-70, (1997)

22 Commandre',M.,Roche,P.,"Characterization of optical coatings by photothermal deflection," Appl.Opt. 35(1996) 5021-5034

23 Welsch, E.,"Photothermal surface deformation technique-a goal for the nondestructive evaluation in thin-film optics," *J. Mod. Opt.* 38(1991)2159-2176

24 Guenther, A. H., McIver, J.1988. The role of thermal conductivity in the pulsed laser damage sensitivity of the optical thin films. *Thin Solid Film* 163:203-214 and Ref. therein

25 Swartz, E.T., Pohl, R.O., 1987. Thermal resistance at interfaces. *App. Phys.Lett.* 51:2200-2202

26 Reichling, M., Groenbeck, H. 1994. Harmonic Heat Flow in Isotropic Layered Systems and its Use for Thin Film Thermal Conductivity Measurements. *J. Appl. Phys.* 75:1914-1922 and Ref. therein

27 Groenbeck,H. and Reichling,M., *Harmonic heat flow in anisotropc thin films*, J.Appl.Phys., Vol. 78(11), pp. 6408-6413, (1995)

28 Hartmann,J., Voigt,P.,Reichling,M. and Matthias,E., *Photothermal measurement of thermal anisotropy in pyrolytic graphite*, Appl.Phys. B, Vol. 62,pp.493-497,(1996)

29 Wu,Z.L.,Kuo,P.K.,Wei,L. and Thomas,R.L., *Photothermal characterization of optical thin films*, Thin Solid Films, Vol. 236,pp. 191-198,(1993)

30 Grilli,M.L., Aumann,T.,Ristau,D.,Dieckmann,M., v.Alvensleben,F. and Masetti,E., Thermal Conductivity of E-Beam and IBS Coatings, SPIE 2775, (1996)

31 Zimmermann, P., Ristau, D., Welsch, E., "Potentiality of Photothermal Surface-Displacement Technique for the Precisly Performed Absorption Measurement of Optical Coatings," *Appl.Phys.A* 58(1994)377-383

32 Kaiser,N., *High damage threshold Al_2O_3/SiO_2 dielectric coatings for excimer lasers*,Thin Solid Films Vol. 260, pp. 86-92, (1995)

33 Pinnow, D.A., Rich, T.C., "Development of a calorimetric method for making prescision optical absorption measurements," *Appl. Opt.* 12 (1973)984-988

34 Willamowski,U.,Gross,T.,Ristau,D.,Welling,H.,"calorimetric measurement of optical absorption and transmission with sub ppm sensitivity," in Proc. Int. Symp. Opt.Syst.Des. and Prod.2, SPIE 2775 (1996)

35 Eva,E. ,Mann,K., "Calorimetric measurement of two-photon absorption and color -center formation in ultraviolet-window materials,"Appl.Phys.A62(1996)143-149

36 "Test method for absorptance of optical laser components", ISO/FDIS 11551,1996

37 Ristau,D.,"Round robin test on absorption at 10.6 m" in Laser-Induced Damage in Optical

Materials:1995 H.E.Bennett, A.H.Guenther, M.R.Kozlowski, B.E.Newnam, M.J.Soileau(Eds.)Proc. SPIE 2714 (1996) 120-136

38 Welsch, E., Walther, H.G., Schaefer, D., Wolf, R., Müller, H. 1988 Correlation between Morphology, Optical Losses and Laser Damage of MgF_2-SiO_2 Multilayers. *Thin Solid Films* 156:1-10

39 Reichling, M., Welsch, E., Matthias, E.,"Thin Film Characterization and photothermal absolute calibration measurements using high frequency electric currents," *SPIE Vol.* 1781 (1992) *Specification and Measurements of Optical Systems*,L.R.Baker (Ed.) pp.205-213

40 Welsch,E.,Ettrich,K.,Blaschke,H.,Kaiser,N.,"Excimer laser interaction with dielectric thin films,"Appl.Surf.Sc.96-98(1996)393-398

41 Welsch,E., Ettrich,K.,Peters,M.,Ziegler,W. and Blaschke,H., *Application of photothermal probe beam deflection technique for ablation and damage measurements by using short UV laser pulses*, J.de Phys.,C7,749-752, (1994)

42 Kautek,W.,Krueger,J.,Lenzner,M.,Sartania,S.,Spielmann,C. and Krausz,F. ,*Laser ablation of dielectrics with pulse durations between 20fs and 3ps*, Appl.Phys.Lett. Vol. 69(21), pp.3146-3148, (1996)

Figure and Table Captions

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) 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.

Fig.2: Temporal behaviour of the laser induced temperature profile in the centre of a sample consisting of an absorbing substrate and a thin transparent test layer. A heat pulse propagates from the film-substrate interface through the layer, from rear to the front surface. The travelling time of the heat from the substrate to the film surface is related to the thermal conductivity and the thickness of the film.

Fig.3: Calculated relative time delays vs. film thickness for the SiO_2 films, with respect to a layer thickness of 0.5 µm. The curves correspond to different thermal conductivities and are obtained by the 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.

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_o is the offset between HB and PB for the maximum derivative

$$\frac{\partial U}{\partial r}\,(r_0;\ z=0) \quad .$$

Fig.5: Principle of absorption measurement by laser calorimetry

P ~ laser source of constant power P_0

S ~ sample under investigation

TC ~Thermocouple

A ~ measured optical absorption

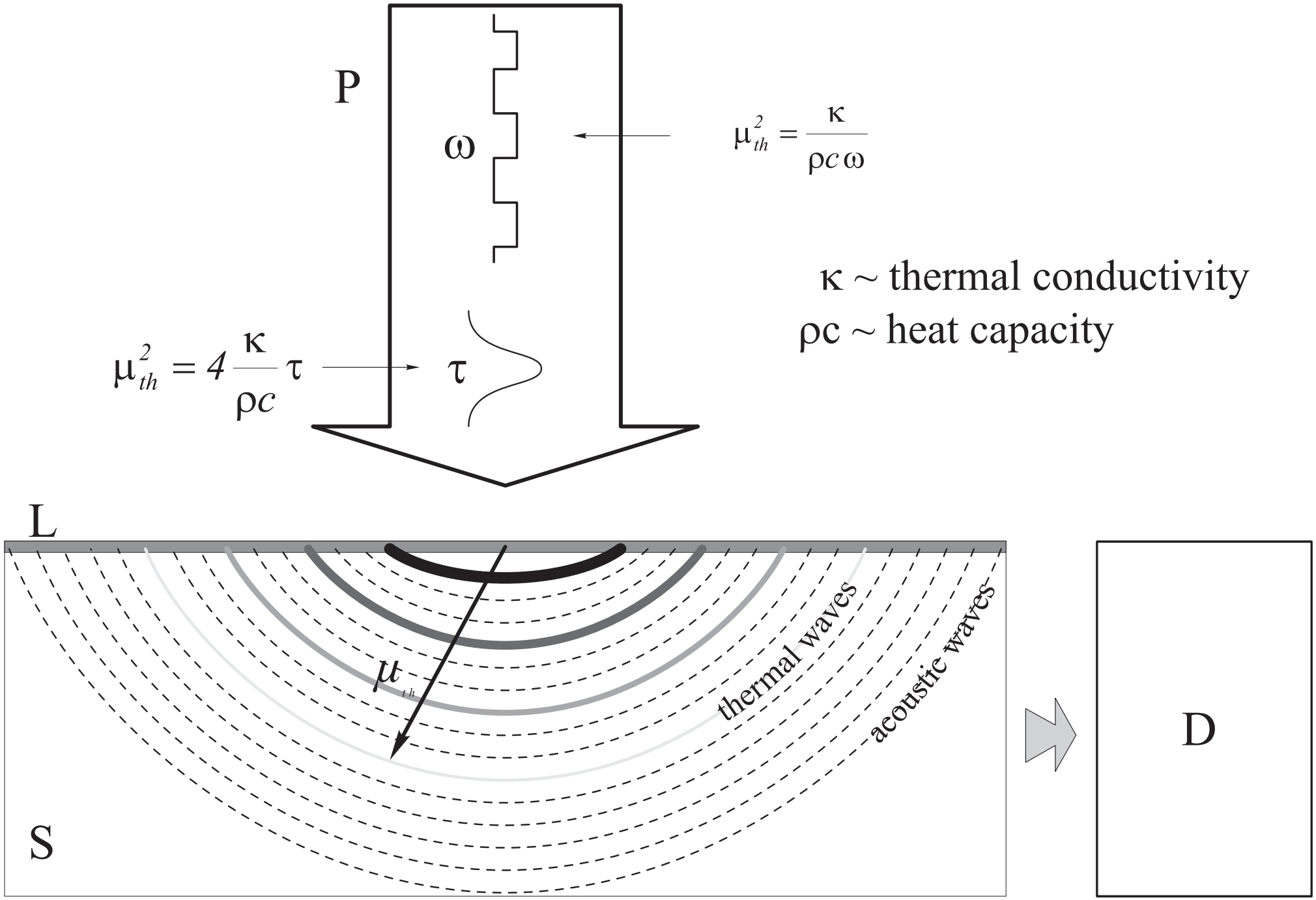
C ~ heat capacity of the sample

$(dT/dt)_{on}$ ~ time derivative of the tmperature increase, when the laser is turned on

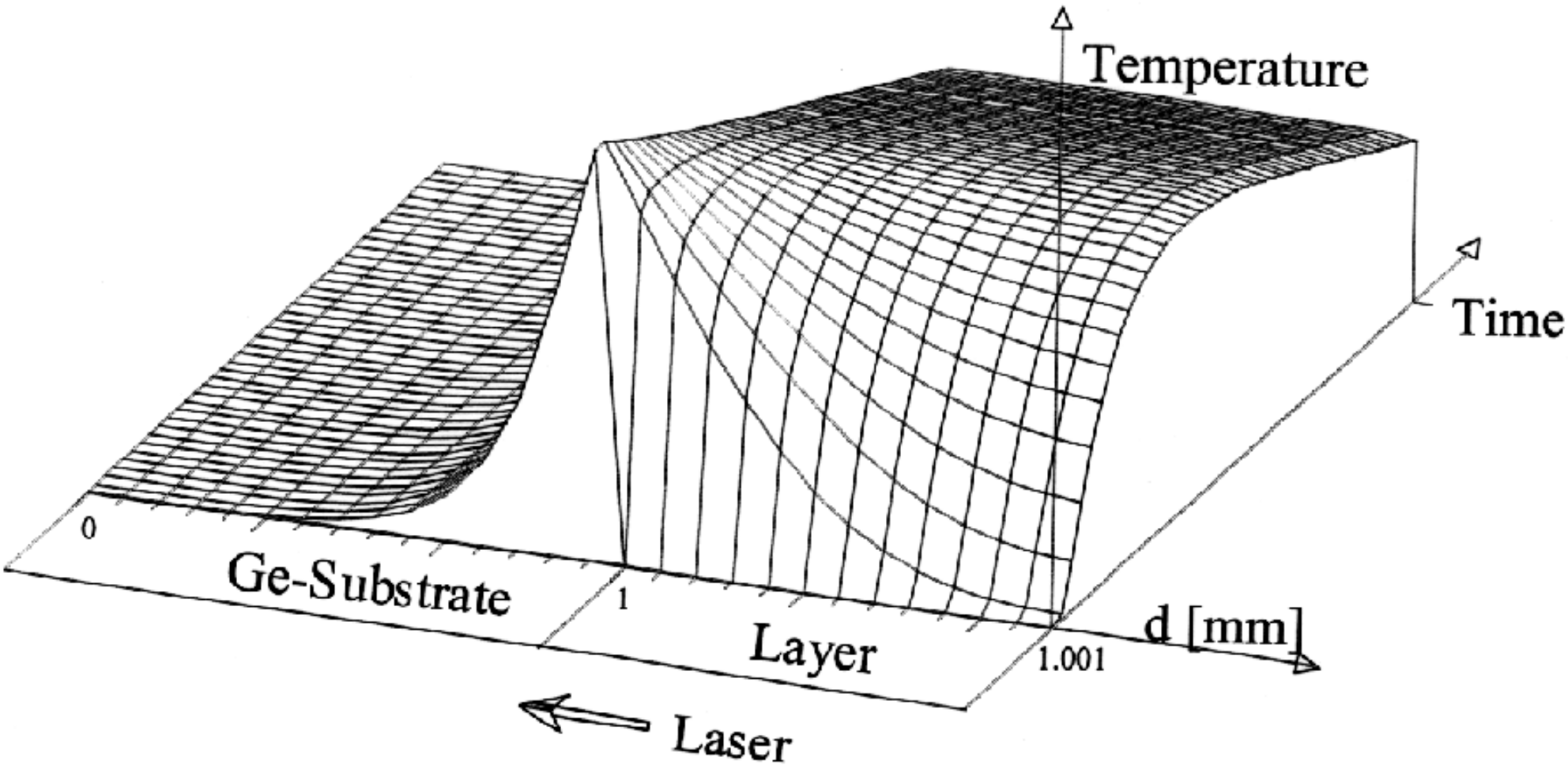
Fig.6: Experimental setup (a) and heating beam profile (b) of the photothermal two-probe beam technique

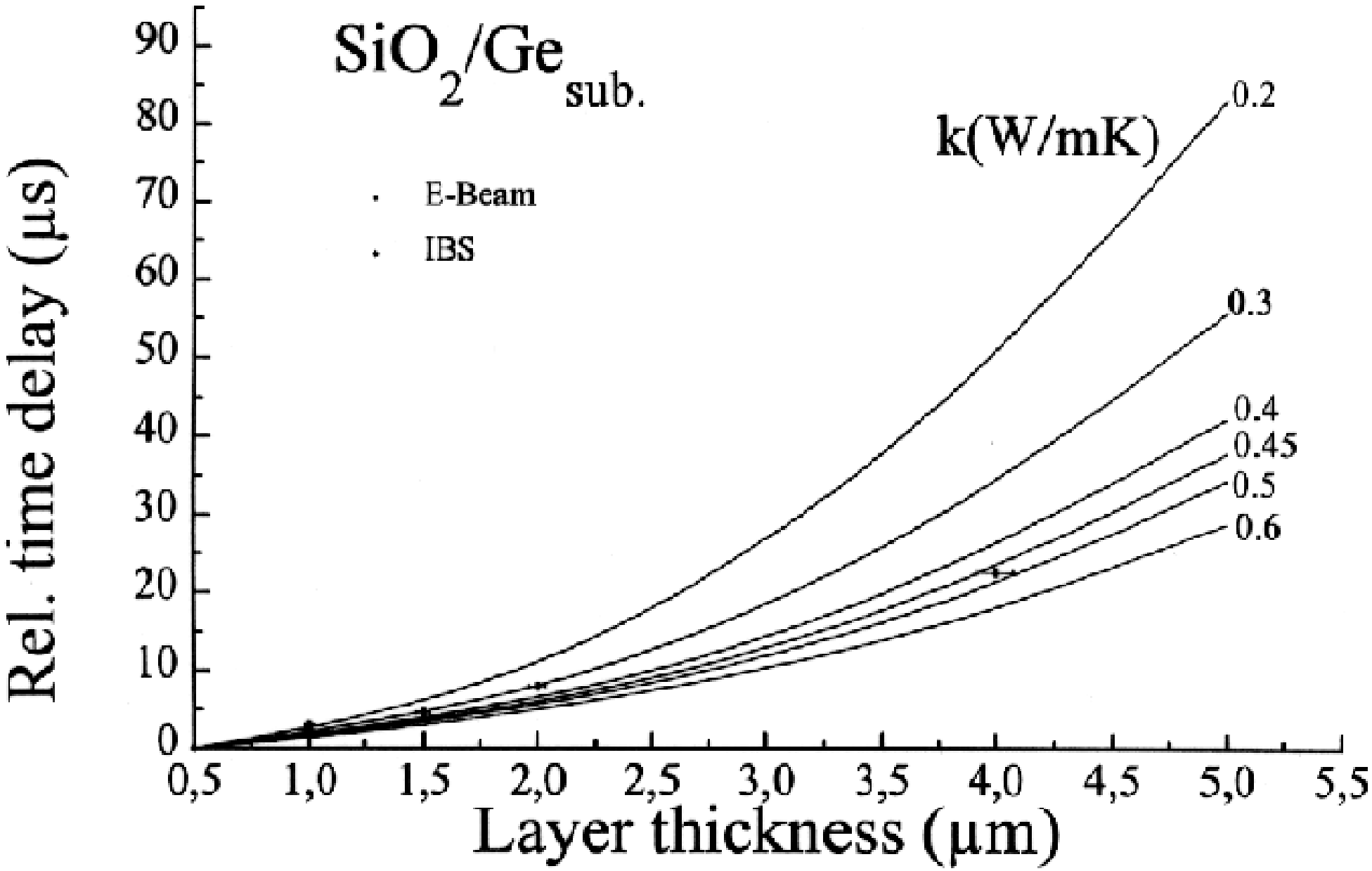
Fig.7: (a) Normalized mirage and displacement signal vs. laser fluence of a LaF_3/SiO_2 laser mirror (LZH); 20 HL pairs; substrate is quartz. The advent of a single shot damage onset is detected by the displacement component. As illustrated, mirage detection shows subdamage sensitivity. The slope represents the calculated thermal load with respect to change in absorptivity per laser shot.(b) Normalized mirage and displacement signals vs. shot number of the same sample as investigated in (a)

Tab.1: Thermal conductivity data for SiO_2, Al_2O_3, Ta_2O_5 and HfO_2 films measured by different working groups. Data measured by several photothermal methods:Ref.12: radiometry, Ref.13: surface displacement, Ref.29: probe beam refraction (Mirage), Ref:14,30: thermal pulse delay. The range of values in the both right columns has been caused by an additional dependence on layer thickness.


P
ω
$\mu_{th}^2 = \frac{\kappa}{\rho c \omega}$
κ ~ thermal conductivity
ρc ~ heat capacity
$\mu_{th}^2 = 4 \frac{\kappa}{\rho c} \tau$
τ
L
μ_{th}
thermal waves
acoustic waves
S
D

Figure


Temperature
Time
0
Ge-Substrate
1
Layer
1.001
d [mm]
Laser


SiO2/Gesub.
E-Beam
IBS
k(W/mK)
0.2
0.3
0.4
0.45
0.5
0.6
Rel. time delay (µs)
Layer thickness (µm)
0
10
20
30
40
50
60
70
80
90
0,5
1,0
1,5
2,0
2,5
3,0
3,5
4,0
4,5
5,0
5,5

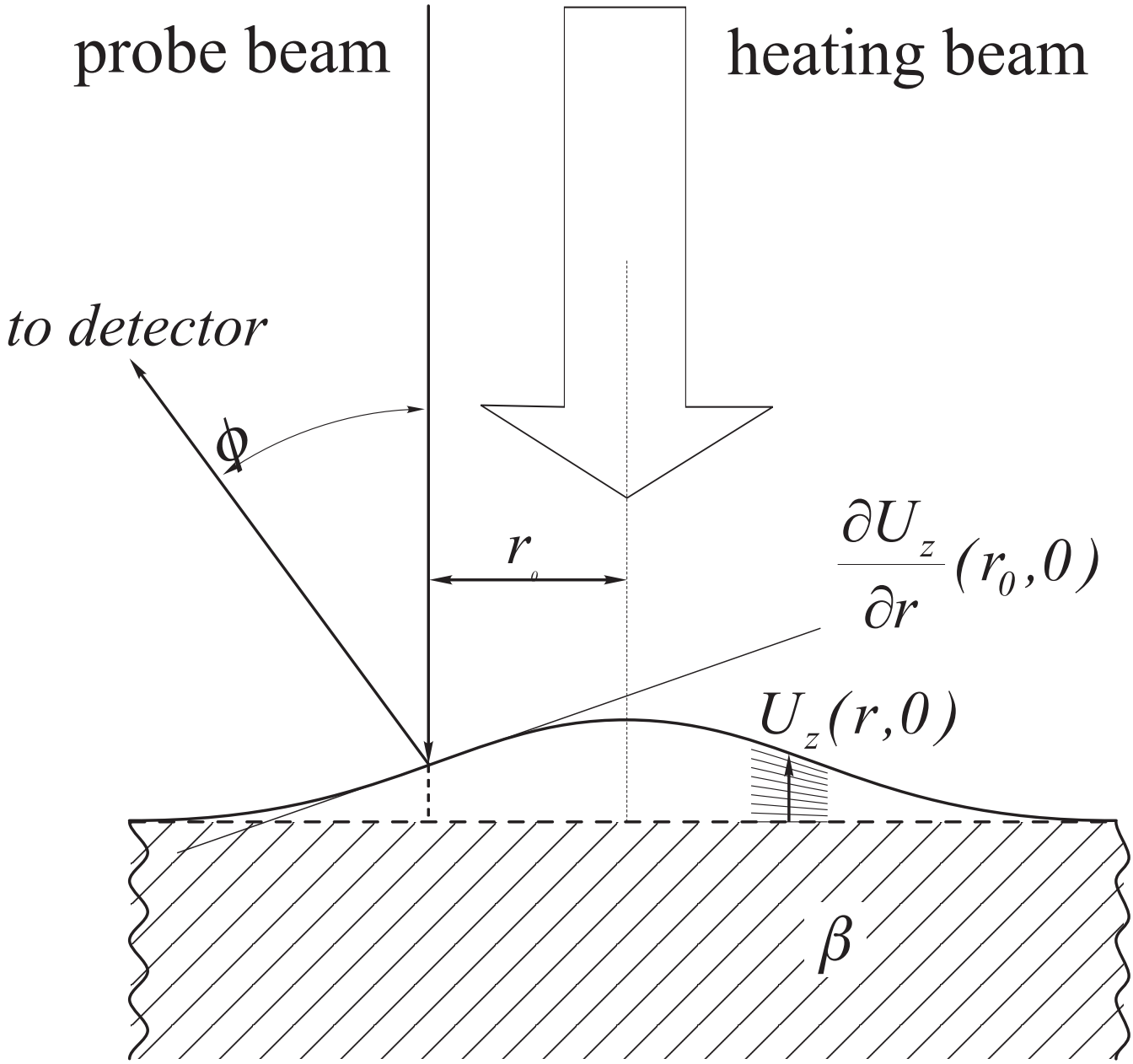
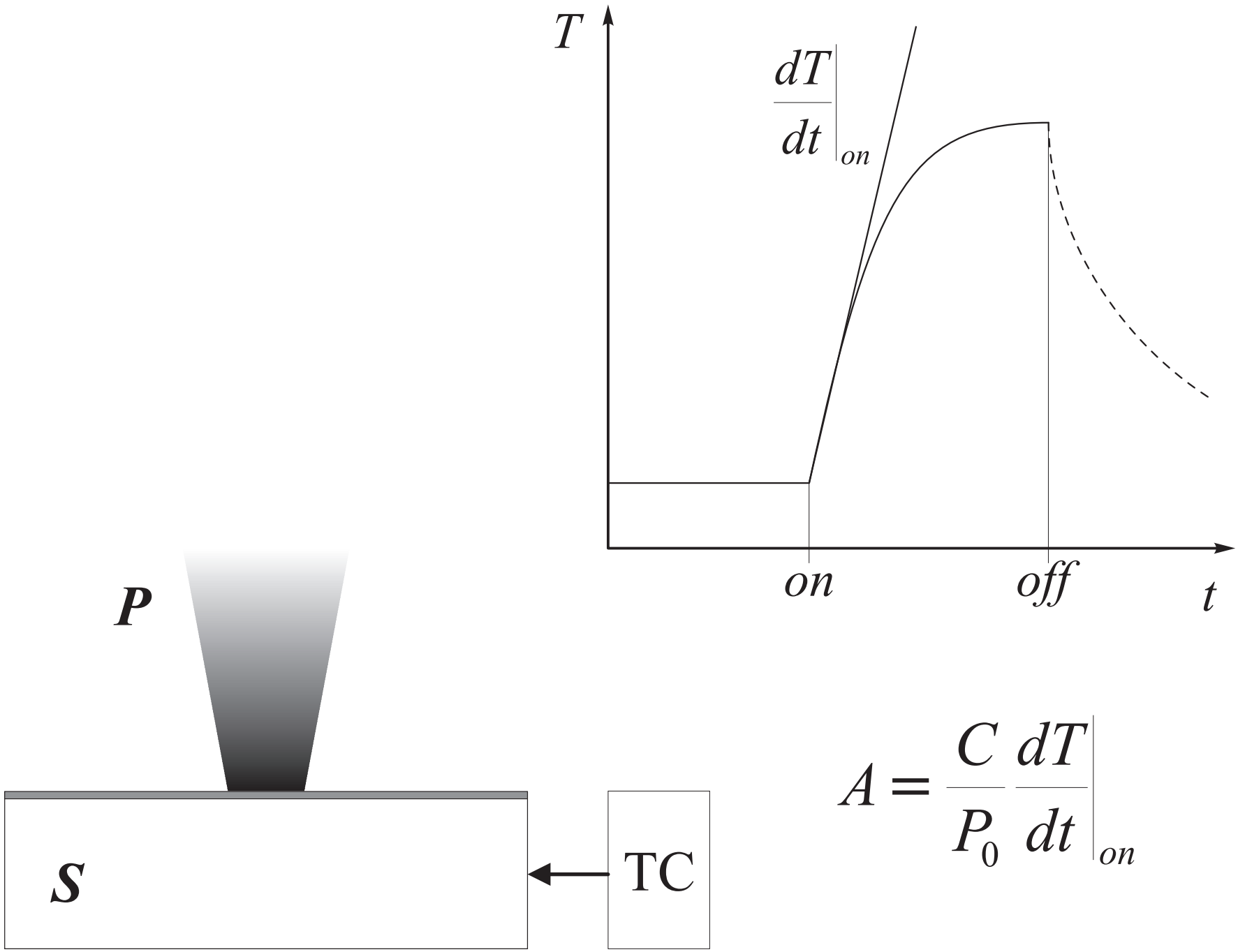

probe beam
heating beam
to detector
ϕ
r_o
$\frac{\partial U_z}{\partial r}(r_0,0)$
$U_z(r,0)$
β

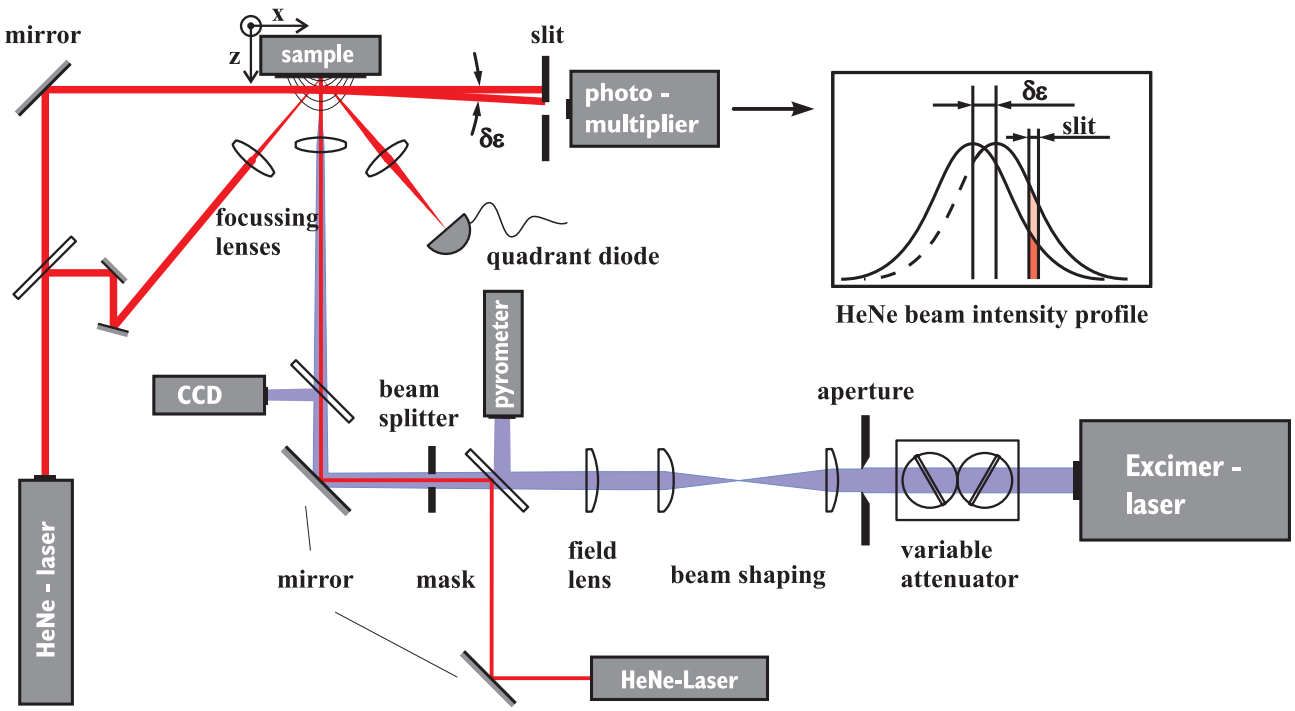
Figure 4



$$A = \frac{C}{P_0} \left.\frac{dT}{dt}\right|_{on}$$

Figure 5

(a)


mirror
x
z
sample
slit
δε
photo - multiplier
δε
slit
HeNe beam intensity profile
focussing lenses
quadrant diode
pyrometer
CCD
beam splitter
aperture
Excimer - laser
HeNe - laser
mirror
mask
field lens
beam shaping
variable attenuator
HeNe-Laser

(b)

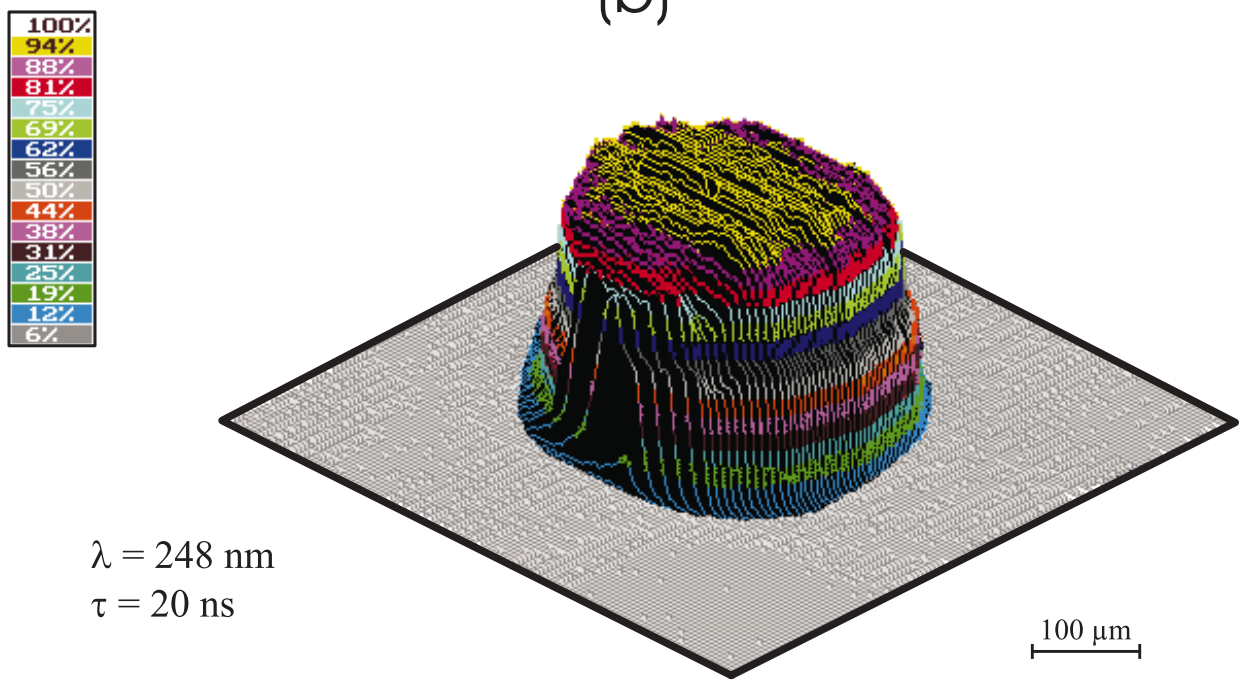
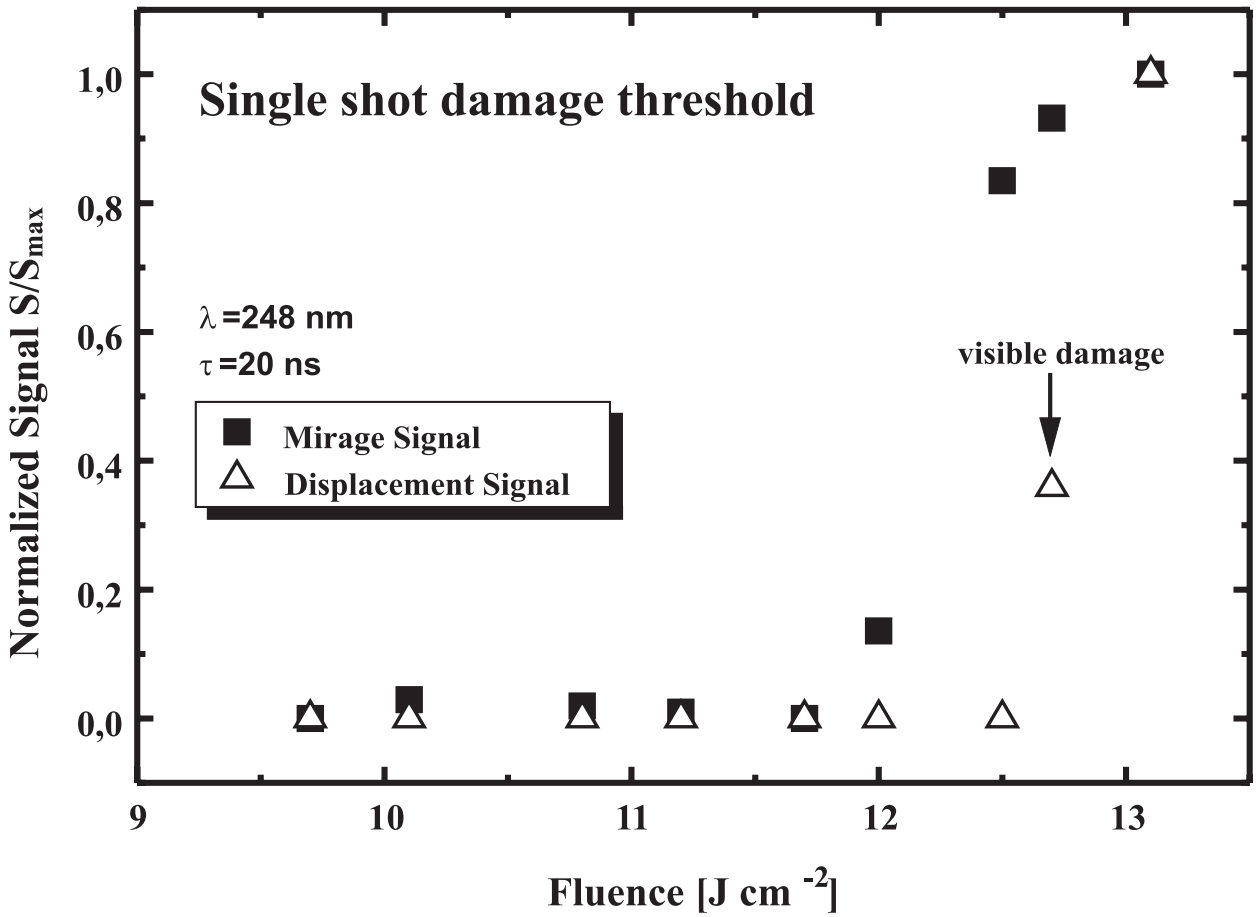

100%
94%
88%
81%
75%
69%
62%
56%
50%
44%
38%
31%
25%
19%
12%
6%
λ = 248 nm
τ = 20 ns
100 µm

Figure 6

(a)


Single shot damage threshold
λ =248 nm
τ =20 ns
Mirage Signal
Displacement Signal
visible damage
Normalized Signal S/S$_{max}$
Fluence [J cm $^{-2}$]
1,0
0,8
0,6
0,4
0,2
0,0
9
10
11
12
13

(b)

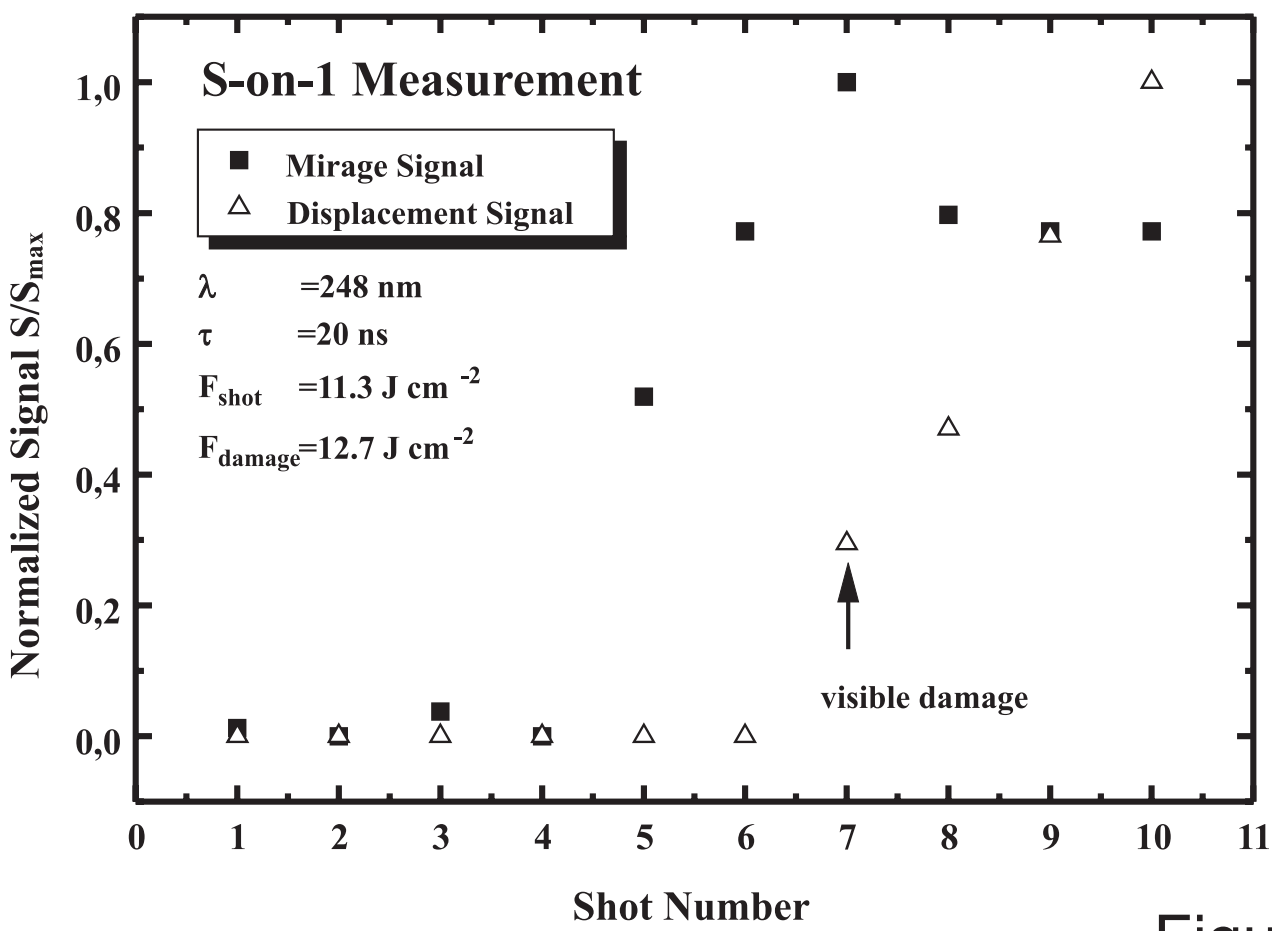

S-on-1 Measurement
Mirage Signal
Displacement Signal
λ =248 nm
τ =20 ns
F$_{shot}$ =11.3 J cm $^{-2}$
F$_{damage}$=12.7 J cm^{-2}
visible damage
Normalized Signal S/S$_{max}$
Shot Number
1,0
0,8
0,6
0,4
0,2
0,0
0
1
2
3
4
5
6
7
8
9
10
11

Figure 7

Material	Thermal Conductivity $\varkappa$ (W/mK)					
	bulk	Ref.12	Ref.15	Ref.24	Ref.14	Ref.30
SiO_2 e-beam	1,4	0,1	0,25	0,25	0,37 - 0,73	0,2 - 0,5
SiO_2 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	$8 \cdot 10^{-4}$	-	0,08	-	0,07 - 0,2