Photothermal measurement of thermal conductivity of optical coatings

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ABSTRACT

In this paper we report our recent measurements of thermal conductivities of optical coatings by two photothermal methods, namely photothermal reflectance (PTR) and photothermal deformation technique (PDT). We will first give a brief introduction of the principles and the apparatus for the experiments, and then present the measured thermal conductivities of various coatings including oxide layers (SiO_2, ZrO_2, Ta_2O_5) on BK_7 glass, a MgF_2 film on MgF_2 substrate and metallic films (Au). The results are compared between the two methods as well as with those previously reported by other techniques and those of the related bulk materials.

Key words: thermal conductivity, optical coatings, photothermal reflectance, photothermal deformation, non-contact and nondestructive evaluation.

1. INTRODUCTION

The study of thermal conductivity of thin films is of great importance both theoretically and practically. If we know the thermal conductivity we can draw conclusions about the mechanisms involved in the mean free path of phonons, in the kinetics of nucleation and growth of thin films, as well as in the laser damage and ablation of various coatings. For this reason, growing attention has been paid to the measurement of this quantity in recent years [1,2]. Among the various experiments reported in the literature, those based on optical detection of photothermal effects [3-8] appear to be most promising since these techniques have the advantage of being sensitive, noncontact and nondestructive, and applicable for in-situ investigations [9-12].

In this paper we report on thermal conductivity studies of optical thin films by two photothermal methods, namely the photothermal reflectance (PTR) and the photothermal deformation technique (PDT). Thermal transport studies of thin films based on PTR detection have been reported earlier by different groups [13–15]. The limit of those work, however, exists in that the data analysis was based on one-dimensional heat conduction models. As a result, they either failed to fit their experimental data [13,14], or they used only the amplitude of the PTR signals to analyze their samples [15]. This latter approach would not lead to good results since the amplitude behaviour of PTR is actually more sensitive to optical properties rather than the thermal ones. For PTR measurements of thermal conductivity, model calculations based on three-dimensional heat conduction [16,17] predict that the phase behaviour is most sensitive.

For the measurement of thermal properties by photothermal deformation technique [4,6], several experiments with pulsed pump laser have been published [8,12,18]. In the following we will describe the experimental methods and present the results of intensity modulated PDT and PRT measurements, and compare them with each other as well as those previously reported by other techniques [7,9,10].

2. PRINCIPLE

The PTR technique is based on the fact that the optical reflectance of a sample surface depends to a certain extent on its temperature [21]. This temperature can be modulated by irradiating the sample with a modulated pump laser beam [13–15]. The amplitude and phase of the modulated surface temperature would then be dependent on the modulation frequency. This frequency dependent surface temperature, when in the case that the sample is a film-on-substrate system, will have a transition in its frequency dependent behaviour when the modulation frequency changes from the range where the substrate dominates the thermal behaviour (the thermal diffusion length $Lth >>$ the film thickness l) to the range where the thin film effect is dominant ($Lth < l$). Fig. 1 shows typical results of gold films with different thicknesses, where the frequency dependence of the surface temperature is calculated based on a 3-D heat diffusion model [17]. We observe that the transition occurs at the frequency range where the thermal diffusion length Lth in gold is equal to the film thickness, and that it is more pronounced in the phase behaviour, indicating that the phase is more sensitive for investigating the thin films.

Similar phenomena can be observed also for dielectric coatings. Fig. 2 shows typical results of ZrO_2 thin films on BK_7 glass. In these calculations we keep all the parameters of the system constant but the coating thermal conductivities. We observe again a more pronounced transition in the phase behaviour.

Based on the above description, it is obvious that the thermal conductivity can be derived

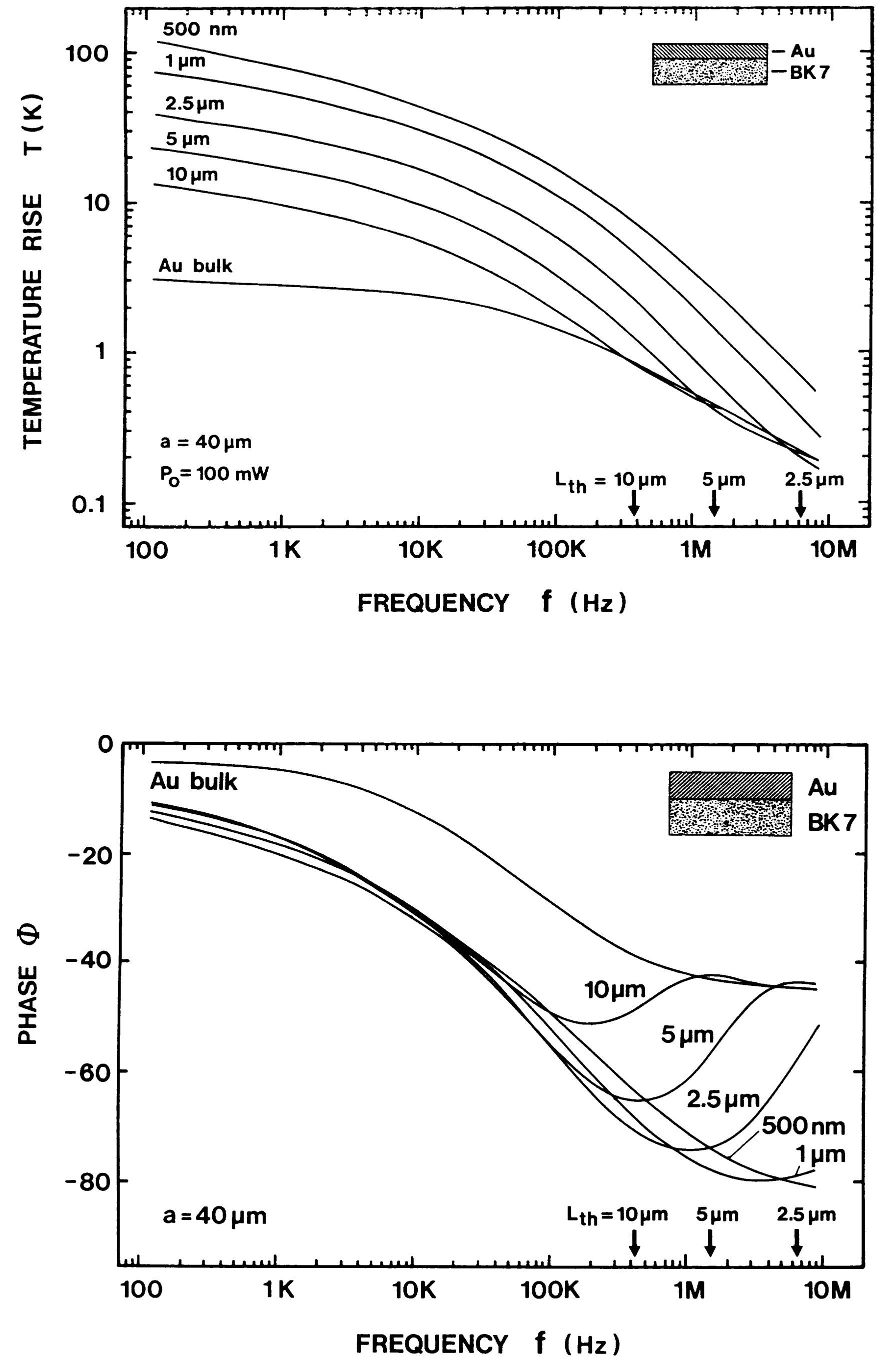

Fig. 1. Frequency dependent amplitude and phase of the surface temperature rise for Au films of different thicknesses on BK_7 substrates. The optical and thermal properties of the gold films and BK_7 are taken from the tabled bulk value [17].

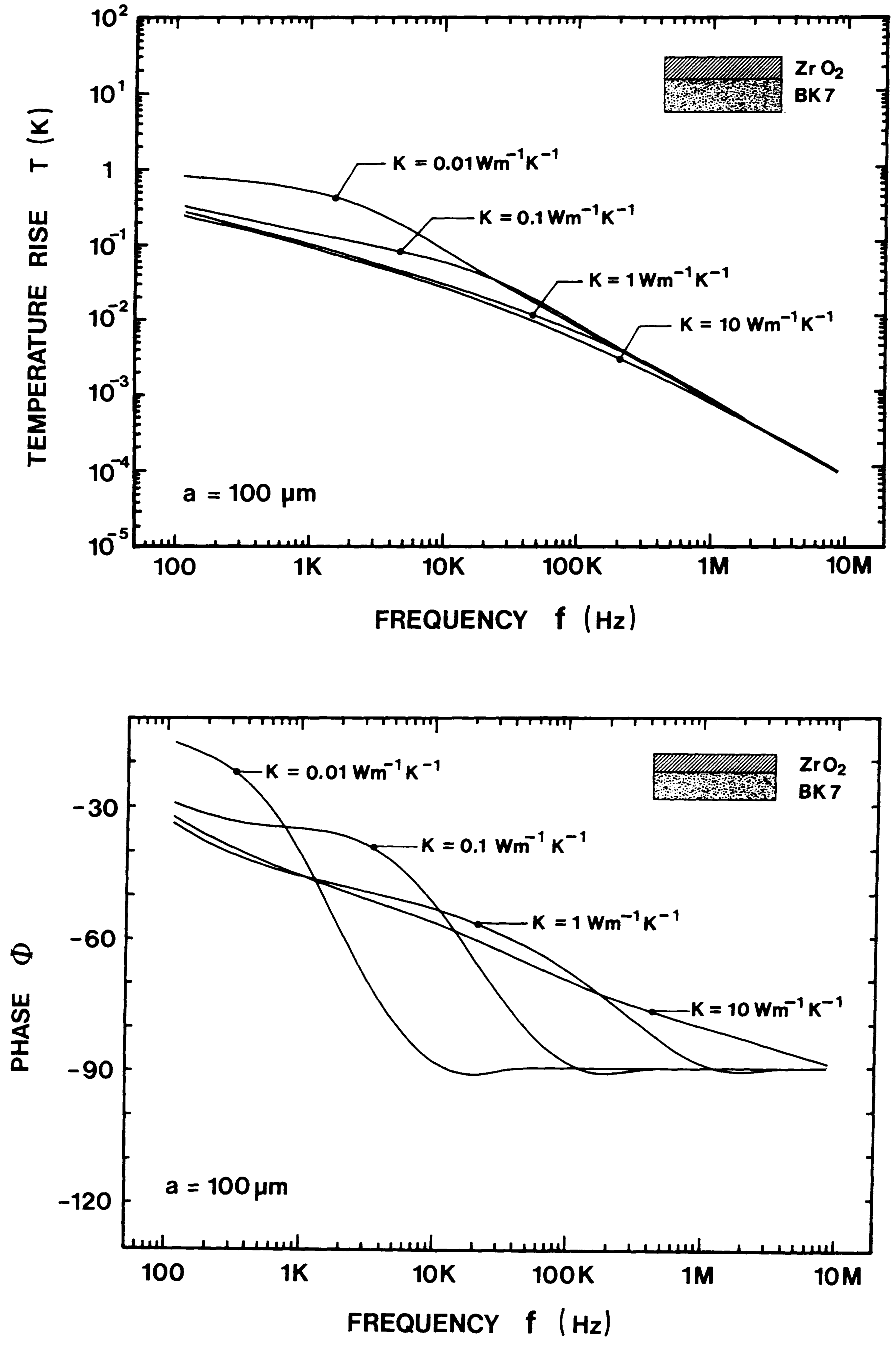

Fig. 2. Frequency dependent amplitude and phase of the surface temperature rise for a 1 μm ZrO_2 film on BK_7 substrate assuming different thermal conductivities of the film. The optical properties of the film and BK_7 glass are taken from typical literature value [17].

from a fit of theoretical curves to experimental data, provided that the thickness of the thin film is known.

The surface temperature rise is accompanied by a thermal deformation at the sample surface which can be monitored by a probe laser beam through the cw photothermal deformation technique [4]. The cw-PDT signal, though a rigorous solution of the Navier-Stockes Equation is not available for thin films at the present time, calculations based on appropriate approximations [16,17] predict also a transition in its frequency dependent phase behaviour. Fig. 3 shows a calculation of the ZrO_2/BK_7 system. The phase behaviour of the photothermal deformation signal has a clear local maximum at the modulation frequency which satisfies

$$Lth = l \tag{1}$$

where l is the thickness of the film, $Lth = (K/\pi f \rho c)^{1/2}$ is the thermal diffusion length in the film, with K being the thermal conductivity, ρ the density and c the specific heat of the film, and f the modulation frequency of the pump laser. Thus, by finding the maximum of the frequency dependent photothermal deformation signal, the thermal conductivity of the film can be directly extracted if the film thickness is known.

3. EXPERIMENTAL

The modulated laser induced surface temperature rise can be monitored by a He-Ne probe beam focused on the heated area, as illustrated in Fig.4. The change in the sum signal from the four-quadrant photodetector represents the change in the intensity of the reflected probe beam. This change in surface reflectivity, when in thermally dominated case, can be expressed as [15]

$$\Delta/R_o = (1/R_o)(dR/dT)\Delta T \tag{2}$$

where R_o is the reflectivity at the equilibrium temperature, $(1/R_o)(dR/dT)$ the thermal coefficient of reflectivity, and ΔT the surface temperature rise.

By using the same He-Ne probe laser, we can also monitor the surface deformation as shown in Fig. 4. In this case we record the difference between the output of two of the four cells of the quadrant detector. This difference, which represents the deflection angle of the reflected He-Ne probe beam, is proportional to the slope of the surface deformation [4].

Fig. 5 shows the overall schematic of our experimental setup, which is designed for PTR

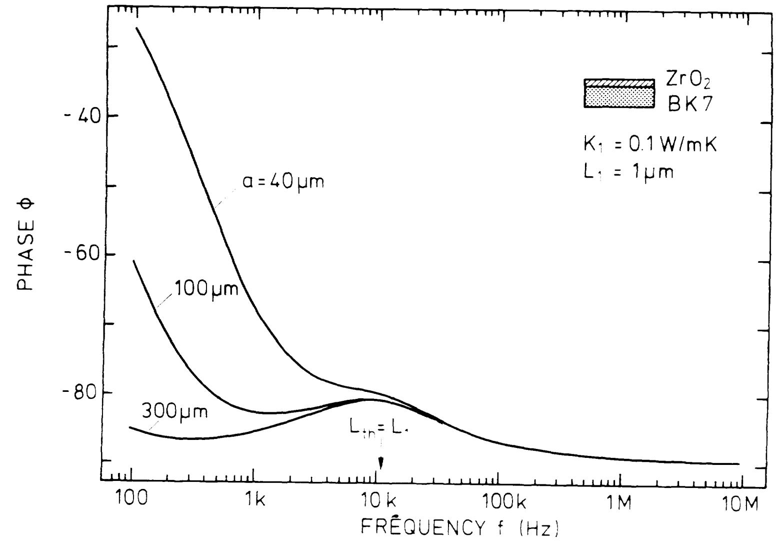

Fig. 3. Frequency dependent phase behaviour of the PDT signal for a 1 μm ZrO_2 film on BK_7 substrate. There exists a local maximum at the frequency where the thermal diffusion length in the film is equal to the film thickness.

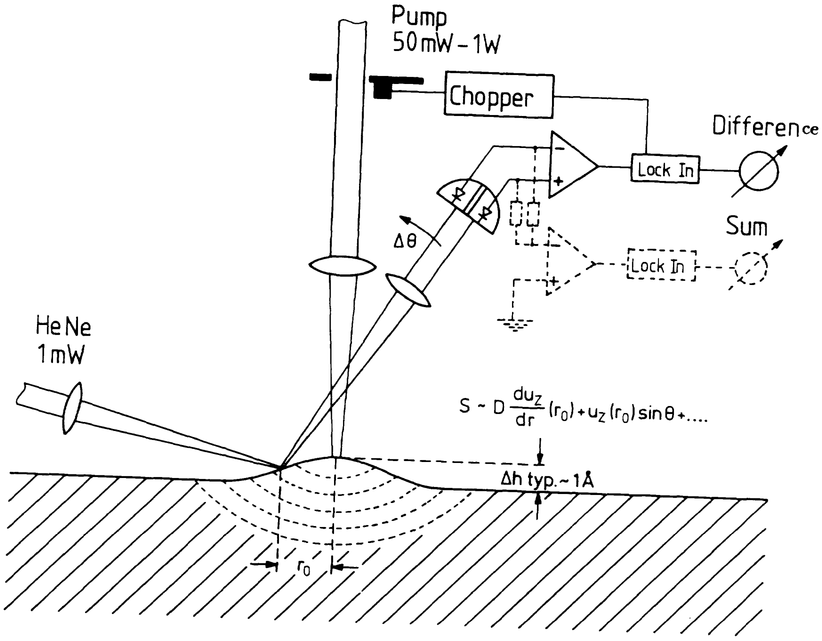

Fig. 4. Optical sketch of the principle of the experiments.

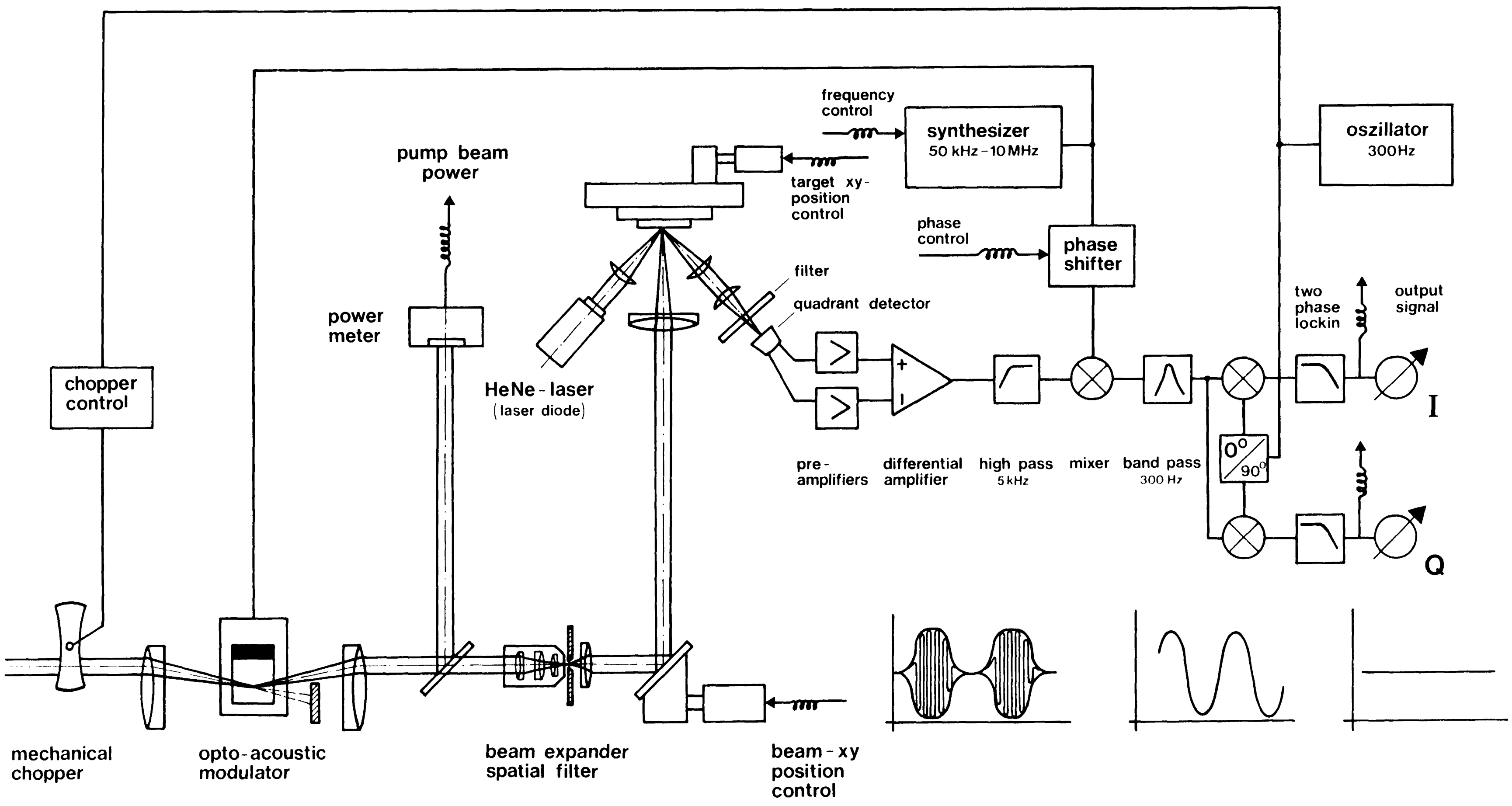

Fig. 5. Experimental setup for PTR and PDT measurements at a large frequency range (10 Hz - 10 MHz).

and PDT measurements at a large frequency range (from 10 Hz to 10 MHz). We use the mechanical chopper to modulate the Ar^+ pump laser at low frequencies (below 10KHz), and the opto-acoustic modulator in the medium frequency range (500Hz-100KHz). For high frequencies (50KHz-10MHz) we use a double modulation technique by applying both of the modulators and using a high frequency lock-in mixer in addition to the conventional lock-in amplifier (Fig. 6). By this double modulation technique we not only achieve a better signal/noise ratio but also avoid spurious signals due to electronic stray fields at high frequencies. The usable dynamic range of the system is about 140 dB.

For detecting the average thermal property of the sample, we use a relative large pump beam size, ranging typically from 40 μm to 300 μm. In case of local analysis [22], however, the optical system allows a pump beam diameter as small as 5 μm, which could be further improved till about the diffraction limit of the Ar^+ laser beam [23,24].

4. RESULTS AND DISCUSSION

We first apply the PTR technique on absorbing gold films of different thicknesses, typical results of which are demonstrated in Fig. 6. In these results, as well as all the other PTR measurements, the data have been normalized by a same bulk gold sample so as to avoid any systematic errors introduced by the apparatus. The thermal conductivities of the gold films are obtained through a numerical fitting procedure, and the results reproduce the bulk gold value only for the 2.5 μm Au films. The uncertainties of the measurements, as indicated by the error bars, are better than ±20% for these gold films.

For the measurements on dielectric optical coatings, an additional thin metallic overcoat is introduced so as to enhance the PTR signal. This enhancement comes from the fact that the metallic layer has a stronger absorption and a larger coefficient of thermal reflectance compared with the dielectric coatings. Fig. 7 shows the result of a 100 nm Ag overcoated 1 μm SiO_2 film on BK_7 substrate, a typical example for the oxide thin films that has been investigated. The fitting yields a thermal conductivity of 0.25 $Wm^{-1}K^{-1}$, much lower than the corresponding bulk data [1,20] yet comparable to the literature film values [7,19,20].

For fluoride thin films, previous damage experiments [1,25,26] showed that their behaviour differed from that of oxides, which was later supported by thermal transport studies on MgF_2 films deposited on both MgF_2 and Al_2O_3 substrates [1,27], where the thermal conductivities of the MgF_2 films reproduced the bulk value, in a sharp contrast to the case of oxide layers [1,7,19,20]. In our PTR experiments, we have also studied a electron beam evaporated MgF_2 film on a MgF_2 substrate. The result is shown in Fig. 8, where the PTR signals of the Au overcoated MgF_2 film

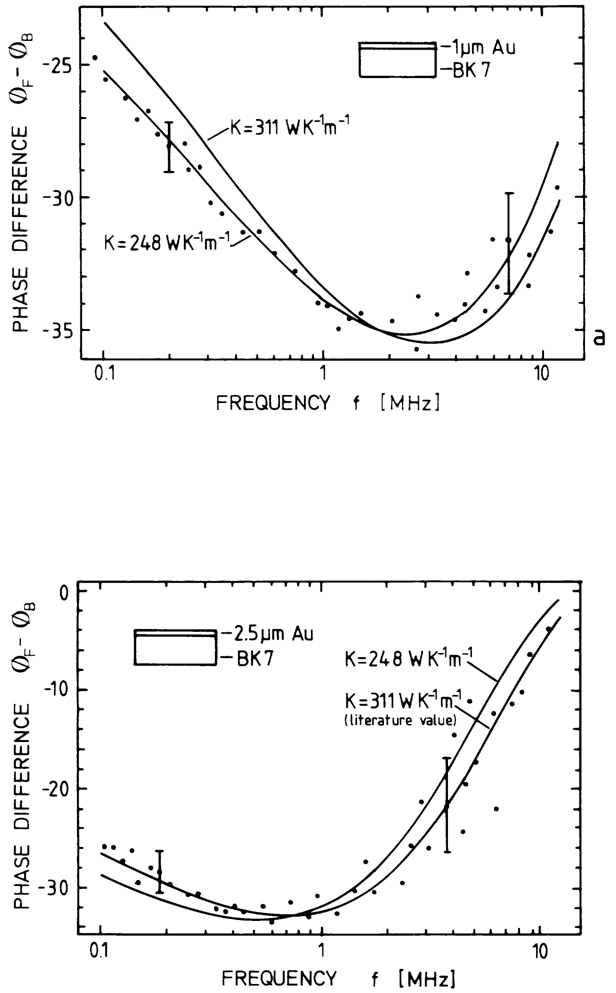

Fig. 6. Measured phase behaviour of the PTR signals of the 1 and 2.5 μm gold films on BK$_7$ glass. The solid lines are theoretical calculations without any parameter adjusting but the thermal conductivities of the gold films.

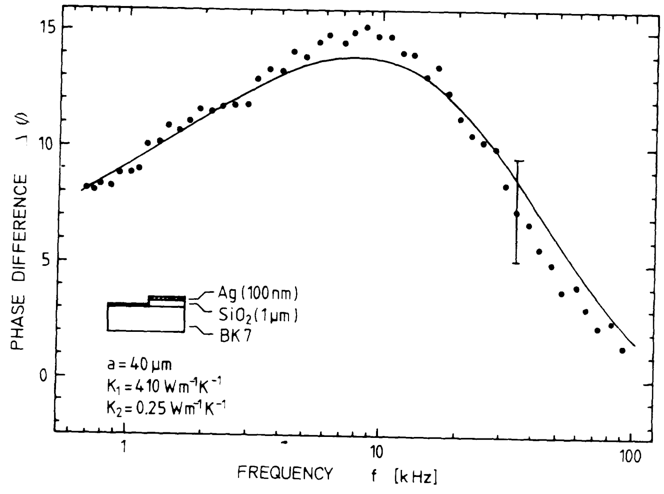

Fig. 7. Measured phase behaviour of the PTR signal of the 100 nm Ag overcoated 1 μm SiO_2 thin film on BK_7 substrate. The error bar in the figure corresponds to an uncertainty of ±20%.

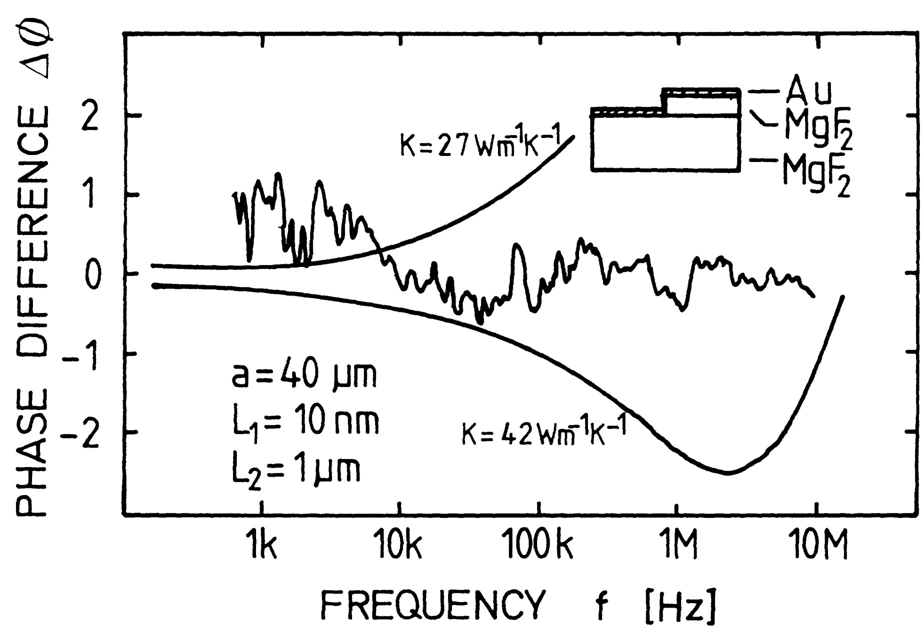

Fig. 8. Experimental results of a Au overcoated 1 μm MgF_2 substrate, which were normalized against the data of the Au overcoated MgF_2 substrate. The smooth solid lines are theoretical calculations of the normalized signal with thermal conductivities of the MgF_2 films indicated in the figure.

is normalized against the data of the Au overcoated MgF_2 substrate. The fact that the phase difference is about zero in the whole frequency range demonstrates again a bulk-like behaviour in the thermal conductivity of the MgF_2 film.

The PTR technique, though has been demonstrated a sensitive tool for thermal conductivity investigation of optical coatings, has an unfavorable limit in that it needs an extra metallic overcoat when applied to dielectric thin films. This overcoat makes the technique actually a contact and damage technique since the overcoat in this case is a part of the probe and can not be removed from the dielectric film without damaging it.

Therefore, we apply also PDT in our experiments for dielectric thin films. Compared with PRT, the PDT method has a much higher sensitivity for dielectric materials [4].

Fig. 9 demonstrates a PDT measurement on a ZrO_2 film on BK_7 glass. The thickness of the film is 1 μm. As expected by model calculation in Fig. 4, the signal shows a local maximum at 10 KHz, which corresponds to a thermal diffusion length equal to the film thickness, as discussed in Eq. (1). Assuming that the density and the specific heat of the ZrO_2 film is the same as its bulk value, we obtain a thermal conductivity of 0.06 $Wm^{-1}K^{-1}$, very close to the result of 0.05 $Wm^{-1}K^{-1}$ from the PTR measurements on the same film but with a 100 nm Ag overcoat. The mutual agreement gives us faith to the model calculation and the experimental methods. More results from PDT measurements performed on other coatings are summarized in Table 1. For comparison we also list the PTR data, previously reported results of similar coatings [1,7,19,20], as well as the values of the corresponding bulk materials [1,20]. With the exception of MgF_2, we have observed for all the 1 μm films a reduced thermal conductivity compared to bulk values.

5. CONCLUSIONS

In conclusion we have demonstrated by experiments that:

1) Both PTR and PDT methods can be applied to thermal conductivity measurements of optical coatings.

2) For both of the techniques the phase behaviour is more sensitive to the thermal properties of the thin film.

3) Though the PTR method is easier to handle, especially at high modulation frequencies where for PDT the differenciating and dividing electronics suffer from poorer performance, it has a unfavorable limit when applied to transparent dielectric thin films. In this case one has to introduce either an additional absorbing overcoat which makes the method practically a

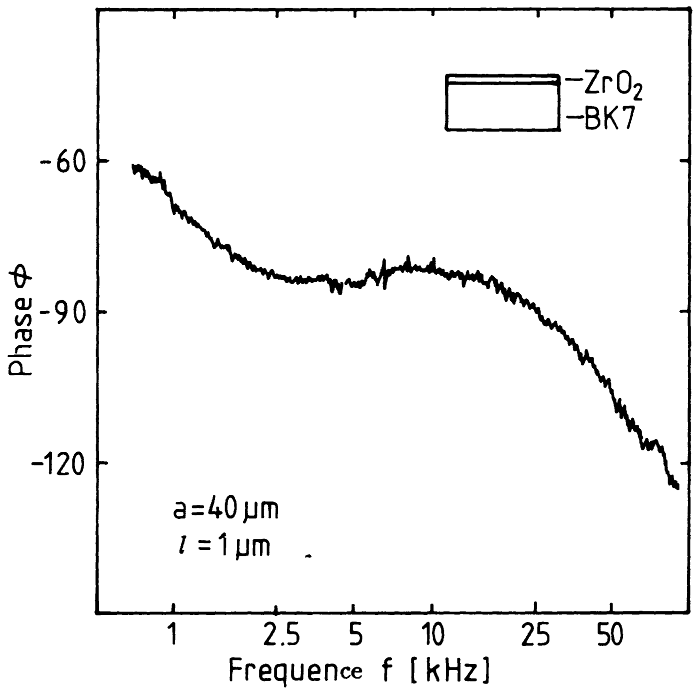

Fig. 9. Measured frequency dependent phase of the PDT signal of the 1 μm ZrO_2 film on BK_7 substrate, with the pump beam radius of 40 μm. The local maximum at 10 kHz corresponds to the transition frequency where *Lth* = *l*.

Table 1. Thermal conductivity ($Wm^{-1}K^{-1}$) of different thin films measured by PTR and PDT. For reference previously reported data of similar coatings [7,19,20] and the corresponding bulk values [1,20] are also listed.

Film/BK7 (EB)	Present Work PTR	 PDT	Ref. /19/ (Si sub.)	Ref. /20/ (Si sub.)	Ref. / 7 / (Fused Silica)	Bulk /1,20/
SiO_2 (1 μm)	0.25	---	0.17	0.45, 0.61	0.1	1.2-10.7
ZrO_2 (1 μm)	0.05	0.06	---	0.04	0.014	---
TaO_5 (1 μm)	0.2	0.29		---	0.026	---
MgF_2 (1 μm)	bulk-like			0.58	---	14.6-30
Au (1 μm)	248	---	---	---	---	
Au (2.5 μm)	311	311	---	---	---	311

contact and damage technique, or an absorbing substrate which actually has modified the system to be measured.

4) As a comparison, the PDT approach has the following advantages:

   a. It is more sensitive, especially when applied to transparent dielectric thin films;

   b. Due to the existence of the local maximum in the frequency dependent phase behaviour, no numerical fitting is needed for the data analysis;

   c. It measures the real system, i.e. no special preparation of the sample is needed for the measurements;

   d. Since the technique is noncontact and nondamage, it is applicable for in-situ investigations;

   e. As has been demonstrated for pulsed photothermal deformation technique [8], the cw-PDT should be also sensitive to thermal anisotropy when refined by introducing thermal gratings.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1. For recent relevant reviews, see A.H. Guenther and J.K. McIver, "Understanding supports Progress in Damage-resistant Coatings", Laser Focus World, 103 (June, 1990). A.H. Guenther and J.K. McIver, "The Role of Thermal Conductivity in the Pulsed Laser Damage Sensitivity of Optical Thin Films", Thin Solid Films 163, 203(1988).

2. J.C. Murphy, J.W. MacLachlan Spicer, L.C. Aamodt, B.S.H. Royce (editors): Photoacoustic and Photothermal Phenomena II, Part III, Springer Ser. Opt. Sci. 62 (1990).

3. W.B. Jackson, N.M. Amer, A,C. Boccara, and D. Fournier, "Photothermal Deflection Spectroscopy and Detection", Appl. Opt. 20, 1333 (1981).

4. M.A. Olmstead, N.M. Amer, S. Kohn, D. Fournier, and A.C. Boccara, "Photothermal Displacement Spectroscopy", Appl. Phys. A 32, 141 (1983).

5. W.P. Leung and A.C. Tam, "Thermal Diffusivity in Thin Films Measured by Noncontact

Single-ended Pulsed-laser-induced Thermal Radiometry", Opt. Lett. 9, 93 (1984).

6. C. Karner, A. Mandel, and F. Traeger, "Pulsed Laser Photothermal Displacement Spectroscopy for Surface Studies", Appl. Phys. A 38 , 19 (1985).

7. D. Ristau and J. Ebert, "Development of a Thermographic Laser Calorimeter", Appl. Opt. 25, 4571 (1986).

8. Z.L. Wu, J. Jauregui, and E. Matthias, "Thermal Diffusivity of Thin Films and Surfaces Investigated by Transient Thermal Gratings", Laser-Induced Damage in Optical Materials: 1991, H. E. Bennett, L. L. Chase, A. H. Guenther, B. E. Newnam, M. J. Soileau, editors, Proc. SPIE 1624, to be published (1992).

9. E. Matthias and R. W. Dreyfus, "From Laser-Induced Desorption to Surface Damage", in Photoacoustic, Photothermal and Photochemical Processes at Surfaces and in Thin Films, Topics in Current Physics, 47, 89 (editor P. Hess, Springer-verlag Berlin-Heidelberg, 1989).

10. J. A. Sell and D. M. Heffelfinger, "Laser Beam Deflection as a Probe of Laser Ablation of Materials", Appl. Phys. Lett. 55, 2435 (1989).

11. P. J. Timans, R. A. McMahon, and H. Ahmed, "Time-resolved Reflectivity Techniques for Dynamic Studies of Electron Beam Crystallization of Silicon-on-insulator Films", Appl. Phys. Lett. 53, 1844 (1988).

12. Z. L. Wu, M. Reichling, Z. X. Fan, and Z. J. Wang, "Applications of Pulsed Photothermal Deflection Technique in The Study of Laser-induced Damage in Optical Coatings"' Laser-Induced Damage in Optical Materials: 1990, H. E. Bennett, L. L. Chase, A. H. Guenther, B. E. Newnam, M. H. Soileau, editors, Proc. SPIE 1441, 214 (1991).

13. R. T. Swimm and L. Hou, "Photothermal Measurement of Optical Coating Thermal Transport Properties", Laser-Induced Damage in Optical Materials: 1986, NIST Spec. Publ. 752, 251 (1988).

14. R. T. Swimm and G. Wiemokly, "Thermal Transport Studies of Optical Coatings, Interfaces and Surfaces by Thermal Diffusion Wave Interferometry", Laser-Induced Damage in Optical Materials: 1989, H. E. Bennett, L. L. Chase, A. H. Guenther, B. E, Newnam, M. J. Soileau, editors, Proc. SPIE 1438, 291 (1990).

15. A. Rosencwaig, J. Opsal, W. L. Smith, and D. L. Willenborg, "Detection of Thermal Wave Through Optical Reflectance", Appl. Phys. Lett. 46, 1013 (1985).

16. X. Su, "Theoretical Analysis and Experimental Investigation of Photothermal Signals in Optical Coatings", Master Thesis, Shanghai Institute of Optics and Fine Mechanics, Academia Sinica (Shanghai, China, May 1989).

17. H. Groenbeck, "Photothermal Temperature and Displacement Calculations on Thin Film Systems", Technical Report, Freie Universitaet Berlin (Berlin, Germany, Aug. 1991).

18. Q. Kong, J. Fischer, and F. Traeger, "Surface Temperature and Thin Film Investigations by Pulsed Laser Photothermal Displacement Spectroscopy", in Photoacoustic and Photothermal Phenomena II (J. C. Murphy, J. C. MacLachlaa Spicer, L. C. Aamodt, B. S. H. Royce, eds.), Springer Series in Optical Sciences 62, 179 (Springer-Verlag, Berlin-Heidelberg, 1990).

19. D. L. Decker, L. G. Koshigoe, and E. J. Ashley, "Thermal Properties of Optical Thin Films", Laser-Induced Damage in Optical Materials: 1984, NBS Spec. Publ. 727, 291 (1986).

20. J. C. Lambropoulos, M. R, Jolly, C. A. Amsden, S. E. Gilman, M. J. Sinicropi, D. Diakomihalis, and S. D. Jacobs, "Thermal Conductivity of Dielectric Thin Films", J. Appl. Phys. 66, 4230 (1989).

21. M. Cardona, Modulation Spectroscopy, pp117-136 (Academia, New York, 1969).

22. Z. L. Wu, M. Reichling, E. Welsch, D. Schaefer, Z. X. Fan, and E. Matthias, "Defect Characterization for Thin Films Through Thermal Wave Detection", Laser-Induced Damage in Optical Materials: 1991, H. E. Bennett, L. L. Chase, A. H. Guenther, B. E. Newnam, M. J. Soileau, editors, Proc. SPIE 1624, to be published (1992).

23. Z. L. Wu, Z. J. Wu, Z. X. Fan, and Z. J. Wang, "Photothermal Deflection Microscopy of Optical Coatings", in Optical Coatings, J. F. Tang, editors, P226 (Shanghai, China, 1989).

24. J. Opsal, M. W. Taylor, W. L. Smith, and A. Rosencwaig, "Temporal Behavior of Modulated Optical Reflectance in Silicon", J. Appl. Phys. 61, 240 (1987).

25. T. W. Walker, P. E. Nielsen, and A. H. Guenther, "Pulsed Laser Induced Damage to Thin Film Optical Coatings - Part I: Experimental", IEEE J. Quant. Electron. 125, 143 (1985).

26. M. R. Lange, J. K. McIver, and A. H. Guenther, "Pulsed Laser Damage in Thin Film Coatings: Fluorides and Oxides", Thin Solid Films 125, 143 (1985).

27. S. Jacobs, "Thermal Conductivity in Thin Films", Lab. Laser Eng. Rev.29,30(1986).