Absorption and thermal conductivity of oxide thin films measured by photothermal displacement and reflectance methods

Z. L. Wu, M. Reichling, X.-Q. Hu, K. Balasubramanian, and K. H. Guenther

Photothermal reflectance and photothermal displacement measurements of optical absorption and thermal conductivity are reported for electron-beam- (EB) deposited and ion-plated (IP) thin films of TiO_2, Ta_2O_5, and ZrO_2. Of the particular set of samples investigated, the EB films have higher absorption than the IP films. The absorption of the EB samples decreases over a period of ~90 min on irradiations with an Ar-ion laser of 488-nm wavelength. By contrast, the absorption of the IP samples changes insignificantly or not at all. Photothermal displacement area scans of coating surfaces yield lower defect densities for the IP samples compared with the EB samples for all three oxide materials. The feasibility and limitations of photothermal measurements for thin-film optical and thermal characterizations are discussed.

Introduction

Thin films in optical coatings used for laser applications need to have low optical absorption to ensure a high laser damage threshold.[1] Heat generated by even very low but finite absorptance[2] [$A > 10$ parts in 10^6 (ppm)] of laser pulse energy needs to be dumped quickly and efficiently to avoid thin-film damage by local overheating that may cause recrystallization, melting, or evaporation. Thus the thermal conductivity of the films toward the substrate needs to be high. In comparison, lateral thermal conductivity is less important as heat is generated over the full area of the spot size (which can be several hundred micrometers or even several millimeters). Thus the distance of an individual pointlike heat source within the laser beam spot to the cooler nonirradiated film is large compared with the distance to the substrate, which is a heat sink. Despite the importance of absorption and thermal conductivity of thin films for laser applications, surprisingly little reliable data are available. Those few measurements of thermal conductivity of evaporated thin films reported in the literature show that it can be one or two orders of magnitude lower than that of the same bulk material.[3-7]

The photothermal displacement technique[8,9] (PDT) has been shown to work well for measuring the absorptance of optical thin films.[10,11] It provides a noncontact and nondestructive tool with high sensitivity.[12-14] High spatial resolution is also desirable for the complete characterization of a thin film. Otherwise, any measured residual absorptance will be the result of averaging over more strongly absorbing point defects and less absorbing defect-free areas of the thin film. It is known that defect density plays a decisive role for laser-induced damage,[15] and hence the separation of absorption caused by defects and by intrinsic properties of a thin film is important. Localized absorption caused by defects can be mapped with photothermal microscopy at micrometer resolution.[16,17]

In this paper we report the results of a comparative study of the thermal and the absorption properties of various oxide thin films deposited by electron-beam (EB) deposition and reactive low-voltage ion plating (which here we abbreviate as IP). Measurements include thermal conductivity, spatially resolved ab-

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When this research was performed Z. L. Wu and M. Reichling were with the Fachbereich Physik, Freie Universität Berlin, Arnimalle 14, D-1000 Berlin 33, Germany. X.-Q. Hu, K. Balasubramanian, and K. H. Guenther were with the Center for Research in Electro-Optics and Lasers, University of Central Florida, 12424 Research Parkway, Orlando, Florida 32826. Z. L. Wu is now with the Institute for Manufacturing Research and the Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48202. X.-Q. Hu is now with the Eyeonics Corporation, Tualatin, Oregon 97062. K. H. Guenther is also with the Department of Electrical and Computer Engineering and the Department of Physics, University of Central Florida.

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sorptance, and changes of film properties on irradiation with an Ar-ion laser beam.

Theory

The principle of thermal conductivity measurement by photothermal reflectance (PTR) is based on the observation that the optical reflectance of a surface depends to a certain extent on its temperature.[18,19] The surface temperature of a sample irradiated with an intensity-modulated pump-laser beam (Fig. 1) varies temporally in amplitude. The phase of the modulated surface temperature with regard to the pump beam intensity depends on the modulation frequency. For bulk materials, a monotonous frequency spectrum is observed both for the amplitude and the phase of the photothermal signal. The amplitude saturates for low frequencies and is proportional to the inverse modulation frequency in the high-frequency limit, while the phase changes smoothly from 0° to $-90°$. By contrast, irradiating a thin film on a bulk substrate results in a frequency-dependent surface temperature. The frequency spectrum of its phase will have a well-pronounced structure showing a transition from bulk to thin-film behavior. This transition occurs in the frequency range where the thermal diffusion length l_{th} in the sample is equal to the thin-film thickness L. Thus, when this transition is observed experimentally and compared with a theoretical model, the thermal conductivity of the thin film can be evaluated, if the thickness of the coating is known, and vice versa.

The surface temperature rise is accompanied by a thermal deformation (bulging) of the sample surface that can be monitored by a probe-laser beam; this is the basis of the cw photothermal deformation technique (PTD), also referred to as photothermal displacement technique. The PTD signal, as predicted by theory and proved by experiments, also has a well-pronounced transition in its modulation frequency-dependent phase behavior. Thus, by measuring the frequency-dependent PTD signal, one may deduce the thermal conductivity of the film sample. A big advantage of PTD over PTR is that for dielectric thin films the PTD technique does not require any sample preparation, while the PTR technique usually needs a thin metal overcoat on the sample surface to enhance the signal.

The measurement of weak absorption by PTD is possible because at a low modulation frequency the amplitude of the PTD signal is proportional to the absorption in the thin film if the absorption of the substrate is much lower. If the substrate contribution is also important, then by varying the experimental parameters like the modulation frequency and the pump beam size one can, in principle, separate the contribution of the film from that of the substrate. In this work, we assume that the substrate absorption is negligible, based on preliminary measurements of typical bare substrates. The PTD signal obtained from those measurements was approximately an order of magnitude smaller than that of typical thin-film samples.

Theoretical modeling of the harmonic heat flow in the thin-film samples[20] (required for data interpretation of heat conductance measurements) was accomplished with an algorithm that gives exact solutions for the temperature of a surface irradiated by a modulated Gaussian beam. The computer code gives the complete solution of the three-dimensional equation of heat conduction with the boundary conditions for continuous temperature and heat flux at the interfaces inside the thin-film system.

Experiments

The measurement of thermal conductivity and low absorption values is very difficult in a stationary mode because the necessary thermal equilibrium requires effective shielding from thermal disturbances in the ambient environment. Adiabatic calorimeters have been built inside high vacuum chambers to isolate effectively the sample from thermal fluctuation transferred by convection in air.[21] A thermal comparator used in earlier investigations[4,5] demanded careful thermal insulation and a rather long time to reach thermal equilibrium. Steady-state thermal measurements suffer from uncertainties in radiant heat loss and conductive drain at the sample edges. Modulating the pump beam overcomes these problems and provides extremely high sensitivity for the detection of small amounts of deposited energy.[22]

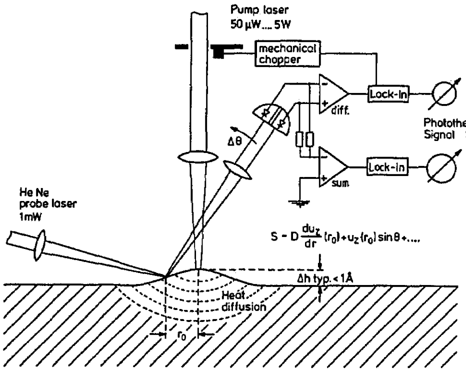


Fig. 1. Principle of high-frequency PTR and PTD measurements.

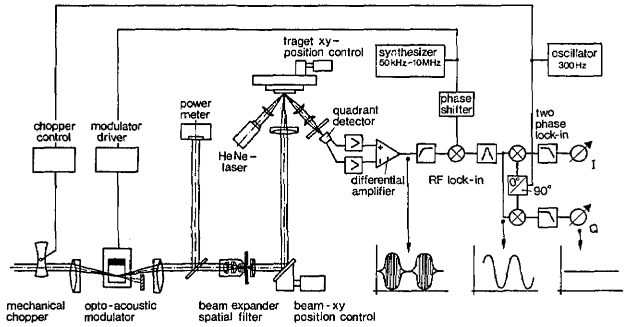


Fig. 2. Schematic of apparatus used for PTR and PTD measurements at the Physics Department, Free University in Berlin (Germany).

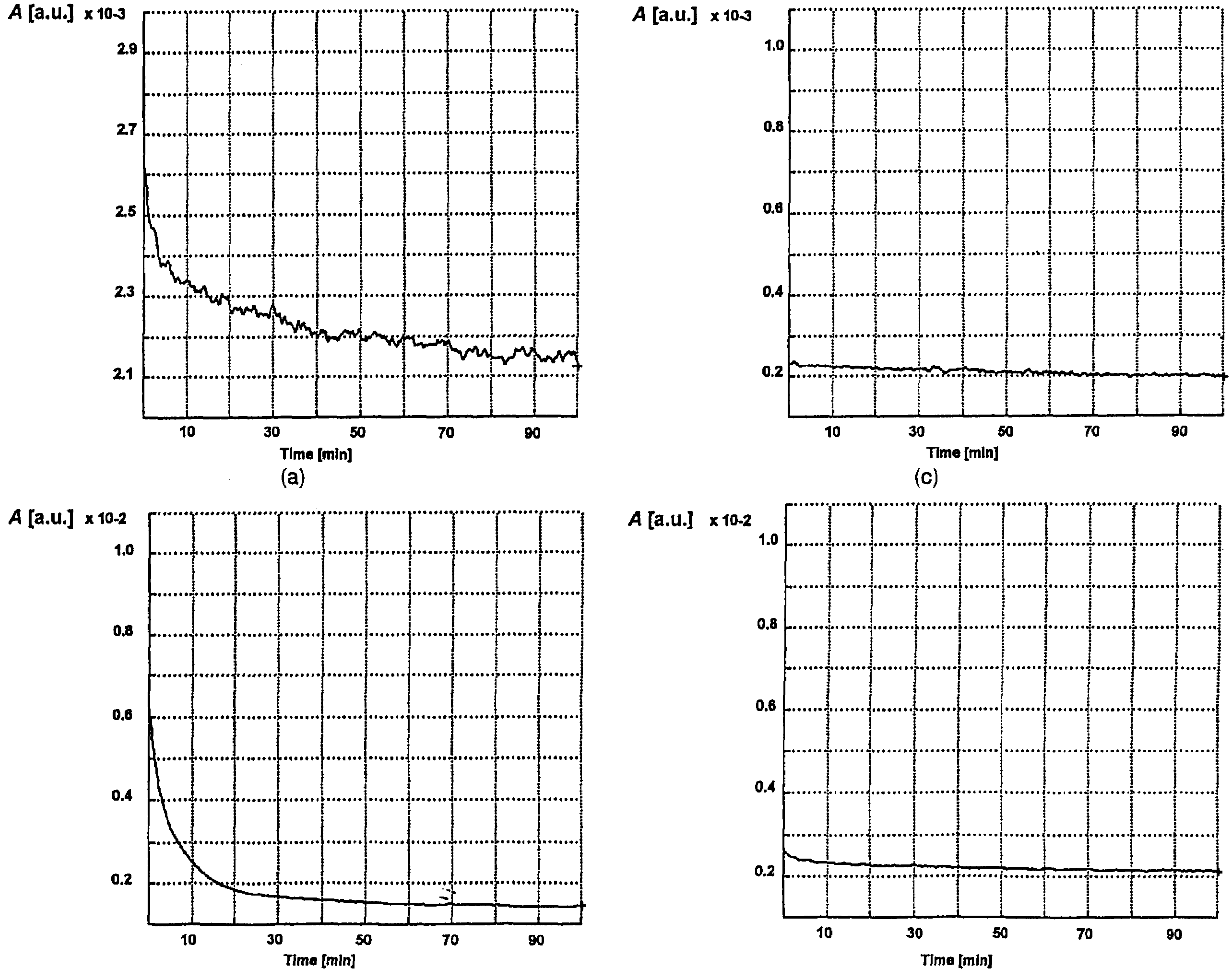
Table 1. Optical Absorption A (at 514 nm, Measured by PTD) and Thermal Conductivity k (Measured by PTR) of Thin Oxide Films

Thin-Film Material	Deposition Process	Absorption A (parts in 10^6) Before[a]	After[a]	Thermal Conductivity k ($W\,m^{-1}\,K^{-1}$)
TiO_2	EB	1280	356	0.25
	IP	105	105	0.45
Ta_2O_5	EB	685	203	0.20
	IP	235	235	0.35
ZrO_2	EB	294	176	0.05
	IP	115	123	0.20

[a] Irradiation with a 488-nm argon-ion laser, 0.2 W (at the sample).

We measured the thermal conductivity of several oxide thin films deposited by conventional EB evaporation and by reactive low-voltage IP[23] with modulated PTR and PTD techniques. Both types of measurement are based on noncontact probing of the surface with a tightly focused He–Ne laser beam and can be performed in the same apparatus shown schematically in Fig. 2. The sample is harmonically heated by an Ar-ion laser beam (at a 514-nm wavelength) and is intensity modulated by a rotating chopper and an acousto-optic modulator. The probe beam is reflected from the bulging sample surface onto a quadrant photodetector connected to a phase-sensitive detection system. In PTR operation, the signals from all four quadrants are added for measurement of the modulated part of the reflected lsaer light intensity. In the PTD operation, the angular deflection of the probe beam induced by the surface displacement (see Fig. 1) is obtained by substracting signals from quadrants opposite to each other.

A motorized sample stage allows for two-dimensional (2-D) mapping of absorption and defect scanning with micrometer spatial resolution. Measurements include the detection of thermal waves and the analysis of their frequency-dependent phase behavior for frequencies from 100 Hz up to 10 MHz. This large frequency range is necessary for scanning the



(a) (c)

(b) (d)

Fig. 3. PTD amplitude (a.u., ∝ absorption) measured for the following thin-film samples: (a) EB Ta_2O_5, (b) EB ZrO_2, (c) IP Ta_2O_5, (d) IP ZrO_2.

thermal diffusion length from values below to values above the film thickness (where film and substrate effects dominate, respectively, thus yielding a pronounced effect in the frequency response). Above 50 kHz, a double-modulation technique that uses a rf lock-in mixer in addition to the conventional lock-in amplifier enhances the signal-to-noise ratio and avoids false signals that are due to stray fields at high frequency. The system has a dynamic range of 140 dB. It also permits the measurement of optical absorption, which is proportional to the amplitude of the PTD signal.[24,25]

Results

By making multiple measurements with individual samples, we found that PTR and PTD techniques and PDT's, properly implemented, permit the measurement of optical absorption and thermal conductivity of thin film-samples with reasonable accuracy (< 20%). These measurements show that the particular set of IP thin films deposited at the Center for Research in Electro-Optics and Lasers has lower absorption and higher thermal conductivity than the comparative set of EB-deposited thin films (from the Shanghai Institute of Optics and Fine Mechanics). Table 1 also shows that the absorption of the EB coatings decreased after irradiation with 0.2 W (at the sample) of 488-nm Ar-ion laser radiation for 90 min [Figs. 3(a) and 3(b)]. The absorption of IP thin films remained pratically unchanged [Figs. 3(c) and 3(d)]. The absorption in Fig. 3 is plotted in arbitrary units (a. u.) as we are interested in relative changes for the duration of the pump irradiation only. The calibration of PTD measurements to obtain absolute absorption values is possible but was considered immaterial in this case.

A localized deviation of, say, ±20% from the average PTD signal indicates either a pinhole type (minus deviation) or a nodule- or spatter-type[26] defect (plus deviation). To investigate the defect densities of the various samples, 2-D PTD scans were performed for each sample at different modulation frequencies. Typical maps of the defect distribution show a lower defect density for IP films than for EB films [see Fig. 4(a) for ZrO_2 thin films deposited by IP and EB, and Fig. 4(b) similarly for TiO_2 films]. The square area in Fig. 4(a) (EB sample of ZrO_2 thin film) had been preconditioned by Ar-ion laser irradiation (at a 488-nm wavelength to enhance photon interaction with latent absorbing sites),[27] resulting in lower average absorption and defect density. Table 2 gives defect counts for various samples at two different modulation frequencies. IP coatings show typically lower defect counts than EB coatings; this corresponds with the lower loss measured by an optical waveguide technique.[28] All samples have higher defect counts at the higher modulation frequency because distortion of the pump-beam-induced thermal wave that is due to local absorption or thermal inhomogeneities becomes more noticable, and local deviations of the photothermal amplitude meet the criterion of a defect, as mentioned above, more frequently.

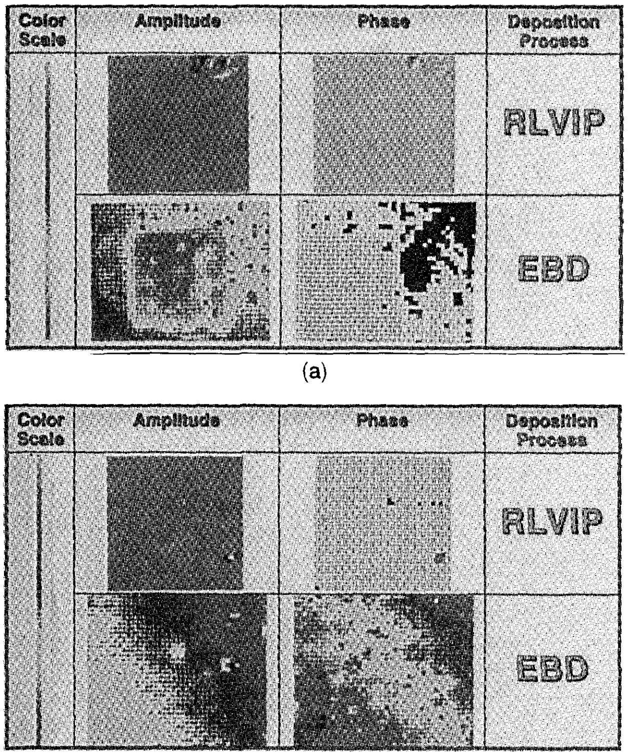


Fig. 4. Defect maps of IP and EB thin films of (a) ZrO_2 and (b) TiO_2 obtained by the PTD area scans. The square area at the center of the EB ZrO_2 sample had been preconditioned with Ar-ion laser irradiation (0.2 W, 488-nm wavelength). Scale of scanned area, 3.6 mm = 0.1 mm on the film surface.

Discussion and Conclusions

Lower absorption and higher (or at least equal) thermal conductivity was obtained for IP oxide coatings compared with EB-deposited films of the same material. From these findings, we would expect higher laser-induced damage thresholds (LIDT's) for IP thin films. This is, however, contradictory to earlier measurements of LIDT of similar samples that were EB deposited at the Lawrence Livermore National Laboratory (LLNL), and IP deposited at the Center for Research in Electro-Optics and Lasers.[29] The different origin of the EB coatings and the

Table 2. Defect Density (in inverse square millimeters) of Various Optical Coatings Measured by PTD Techniques

Thin-Film Material	Deposition Process	Modulation Frequency 120 Hz	Modulation Frequency 100 kHz
TiO_2	EB	96.8	117.9
	IP	25.3	39.8
Ta_2O_5	EB	62.5	84.3
	IP	3.8	12.5
ZrO_2	EB	75.3	98.4
	IP	10.2	42.5

nonavailability of the LLNL EB coatings for this study did not permit a direct comparison. Consequently, more measurements with additional samples, including LIDT testing and conditioning experiments, are necessary.

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