ELSEVIER

Thin Solid Films 253 (1994) 333–338

thin solid films

Photoacoustic studies of laser damage in oxide thin films

M. Reichling[a], J. Siegel[a], E. Matthias[a], H. Lauth[b], E. Hacker[b]

[a]*Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*
[b]*JENOPTIK Technologie GmbH, Prüssingstrasse 41, 07739 Jena, Germany*

Abstract

Laser damage thresholds of ZrO_2, TiO_2 and HfO_2 films of optical thickness λ ($\lambda = 248$ nm) evaporated on quartz glass substrates were investigated with the photoacoustic probe beam deflection technique in a 1-on-1 irradiation mode for a range of fluences from below to above the thin-film laser damage threshold. In addition, irradiated spots were investigated systematically by a video imaging difference technique. It is demonstrated that the photoacoustic technique allows a more sensitive and precise determination than optical inspection of the onset of damage. An exponential dependence of damage thresholds on the apparent band gap of the respective thin-film material, as determined by optical absorption spectroscopy, was found. Results for amorphous and polycrystalline films on BK7 glass and SQ1 quartz substrates are compared and the influence of a SiO_2 protective coating on the laser-damage threshold is investigated.

Keywords: Band structure; Laser ablation; Optical coatings

1. Introduction

Thin films of refractory oxides are important materials for the fabrication of optical coatings and their properties have been studied for many years [1]. An important field of application is the use of oxide thin films in multilayer systems designed as high-reflective mirrors for UV–laser systems. The major figure-of-merit for such mirrors is the laser damage threshold if they are used in high-power laser systems [2]. Up to now laser damage in oxide thin films has mainly been discussed in terms of a phenomenological description of thin-film absorption and thin-film thermomechanical response [3, 4], while the origin of the absorption and the primary interaction of the laser light with the thin-film system and its defects have been studied less extensively.

The work presented in this paper is part of an ongoing study of laser damage and pre-damage phenomena in oxide thin films that aims at elucidating the main laser–thin film interaction mechanisms and consecutive processes leading to material failure. Here we concentrate on the investigation of simple model systems (i.e. single layers) and investigate their damage behaviour with the pulsed photoacoustic beam deflection (PBD) technique that is based on the mirage effect in the air above the sample surface [5]. By comparing results from oxide materials with different intrinsic material properties and system designs we try to elucidate the role of thin-film defects in the damage process.

2. Experimental

Measurements were performed on a set of 24 oxide samples with λ ($\lambda = 248$ nm) optical thickness deposited by electron beam evaporation. The process conditions were adjusted to obtain either a polycrystalline or an amorphous film structure. Furthermore, each material was deposited on SQ1 quartz and BK7 glass substrates for comparison, and the series was duplicated in order to study the influence of an optically inactive $\lambda/2$ protective SiO_2 overcoating.

Two different techniques were applied to measure the laser damage threshold: the pulsed photoacoustic mirage deflection and a video image difference technique. The principle of the mirage detection is given in Fig. 1. The damaging laser pulse from the excimer laser (pump laser) passes a variable attenuator to adjust the laser intensity and is focused on the sample surface into a spot of ca. 450 μm. Measurement of the incident laser pulse energy with a pyroelectric detector and of the beam profile by a CCD camera system allows an accu-

0040-6090/94/$7.00
SSDI 0040-6090(94)04690-8

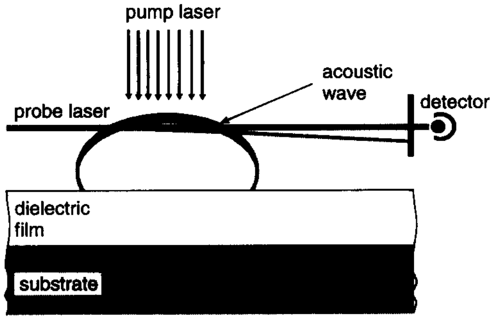

Fig. 1. Detection scheme for pulsed photoacoustic mirage measurements.

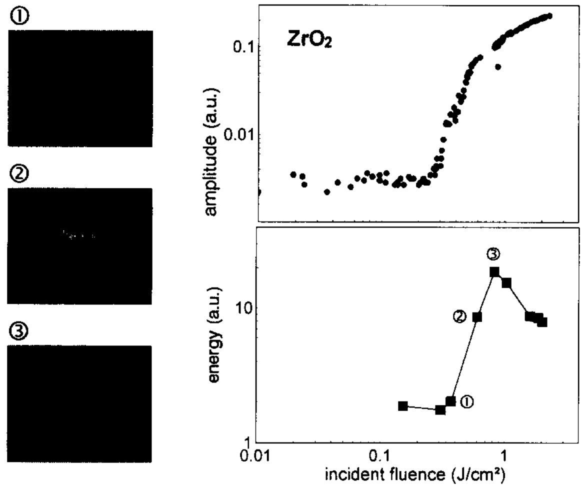

Fig. 2. Comparison of laser-damage threshold determination by mirage detection (top right) and the video image difference technique (bottom right). The frames on the left represent difference images (before and after irradiation) taken for three representative fluence values marked in the brightness energy graph.

rate determination of the incident laser fluence. All measurements were done in a 1-on-1 irradiation mode.

The transient change of the refractive index in the ambient air resulting from the plasma-induced supersonic pressure wave leads to a mirage deflection of a He–Ne laser beam (probe laser) aligned parallel to the sample surface. For the present purpose, data analysis of the mirage signal is restricted to deriving the deflection amplitude (peak to peak) of the acoustic pulse. More details of the experimental apparatus and threshold determination and also other applications of the mirage technique can be found elsewhere [6, 7].

The video imaging system is not only utilized for beam-shape measurements but also for damage threshold determination by detection of scattering centres. To accomplish such optical threshold measurement, video images of the sample surface (frames) are taken prior to and after irradiation with the excimer laser light. Any change in surface reflectivity or its scattering properties appears as a brightness contrast in a difference image taken from the two frames.

To obtain a quantitative measure for the damage, we calculate the rms value integrated over all pixels of such a difference image. This rms value represents the brightness energy of the image and is indicative of damage if its value exceeds the noise level. The numerical analysis of the video images allows a more sensitive and error-free detection of the onset of damage than video techniques presented earlier, where damage detection was based on the visual impression of the experimentalist [8].

3. Detection sensitivity

In previous work, the sensitivity of the pulsed photoacoustic mirage technique was compared with results from various other measurement schemes [9]. It was found that the mirage method provides the most sensitive tool for threshold detection. To complete this series we installed the video detection system yielding a quantitative measure of optically detected damage.

A typical example for ZrO_2/BK7 is shown in Fig. 2, where the graph on the lower right shows the dependence of brightness energy on incident laser fluence and clearly exhibits threshold behaviour. As an illustration for the data analysis scheme, three difference images are shown on the left. Whereas the topmost near-threshold image is dominated by noise, the lower images show high contrast over the damaged regions and thus yield brightness energies far above the noise level.

A comparison of the fluence-dependent energy data with the mirage data shown on the upper right of Fig. 2 reveals that the latter yields a lower value for the threshold and, therefore, represents a more sensitive method for the detection of damage onset. Furthermore, it should be noted that, for a given time and computational resources, we are able to collect much more data points with the mirage method than with the video technique, resulting in a higher precision for thresholds determined by the mirage technique.

4. Oxide materials

One aim of our ongoing studies is to find correlations between the laser light absorption properties and the apparent damage thresholds for different oxide materials. For the samples investigated here we expect different mechanisms for the primary interaction of the 248 nm (5 eV) laser light with the thin-film material. Whereas a linear absorption process via interband transitions is expected for TiO_2, the band gap energies of ZrO_2 and HfO_2 are larger than the photon energy, implying a non-linear, probably defect-mediated, process for the interaction. This expectation is experimen-

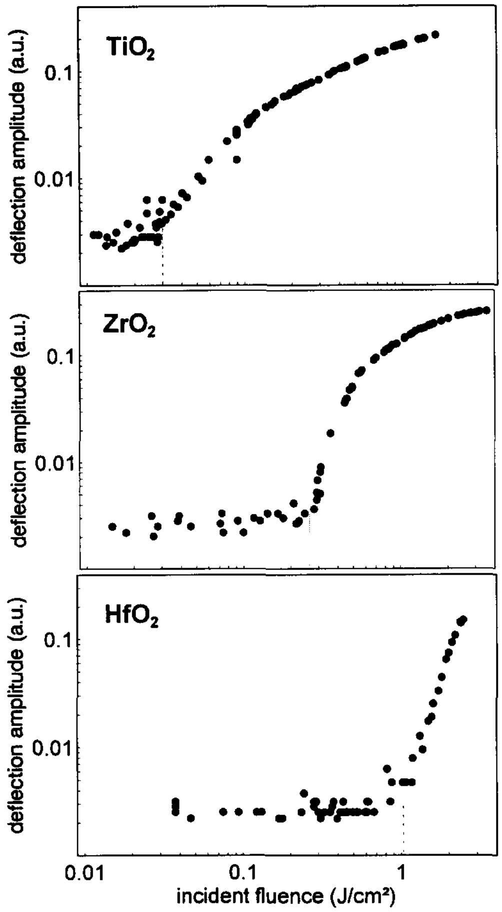

Fig. 3. Fluence-dependent mirage signal amplitudes for three oxide thin films. Threshold fluences: TiO_2, 0.030 ± 0.005; ZrO_2, 0.27 ± 0.03; HfO_2, 1.0 ± 0.1 J cm^{-2}.

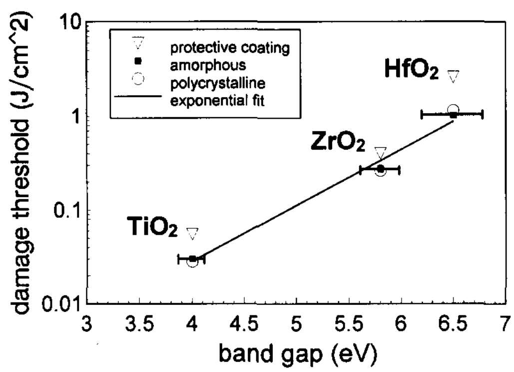

Fig. 4. Correlation between the experimentally determined band gap energy and the apparent laser damage threshold at 248 nm (5 eV) for the oxide thin films. Different symbols refer to preparation conditions and system design while the solid line represents a best exponential fit to data for amorphous single layers without a protective coating.

tally confirmed by the mirage results in Fig. 3. The smooth increase in fluence-dependent mirage deflection amplitude above the damage threshold measured for TiO_2 contrasts well the sharp change in curvature and steep rise in signal amplitude observed for the other two materials. The nature of the light–thin film interaction process can be roughly judged from the slope of the above threshold increase of the mirage deflection amplitude. Although a precise signal interpretation would require complicated plasma effects to be included, which is beyond the scope of this paper, it can be assumed that a moderate increase in deflection amplitude with incident fluence results from mostly linear absorption of the laser light (TiO_2), while a steep signal increase indicates high non-linearity (ZrO_2, HfO_2).

A clear correlation between thin-film electronic properties and the damage threshold can be deduced from the graph in Fig. 4, where the threshold fluence is plotted against the gap energy as determined by optical absorption spectroscopy. The straight line included in the semi-logarithmic plot represents a best exponential fit to the data and describes the results well, within experimental error. The exact origin of this simple dependence, however, is not yet clear and needs to be elucidated in more detail by complementary measurements on other oxide materials and a careful study of defect properties. It has been shown earlier that the apparent damage threshold in wide band gap multilayer systems depends strongly on the content and structure of defects rather than on intrinsic electronic properties of the thin-film materials [10]. Therefore, defect-induced states have to be incorporated into any model aimed at a prediction of the threshold in cases of non-linear laser light absorption.

5. Thin-film preparation and system design

In addition to film material, there may be other factors determining the apparent laser damage threshold of a thin-film system. In the following we describe the investigation of some parameters with the pulsed mirage technique.

Fig. 5 shows fluence-dependent mirage amplitudes for three different ZrO_2 coatings. For the first sample the evaporation conditions were adjusted to obtain an amorphous thin-film structure while the second sample was grown polycrystalline. As can be seen from the graph, there is no influence of the preparation method on the damage threshold. Since we expected a change in electronic properties and, hence, at least a slight change in damage threshold from one material modification to the other, which did not occur, the experimental result is indicative of a damage threshold determined by extrinsic defects. This interpretation is supported by the results shown in the bottom graph in Fig. 5. This curve represents data obtained from a polycrystalline sample covered with an additional optically inactive $\lambda/2$ SiO_2 overlayer. The purpose of such an overlayer is to protect the film underneath from environmental influences. Since the electric field in the

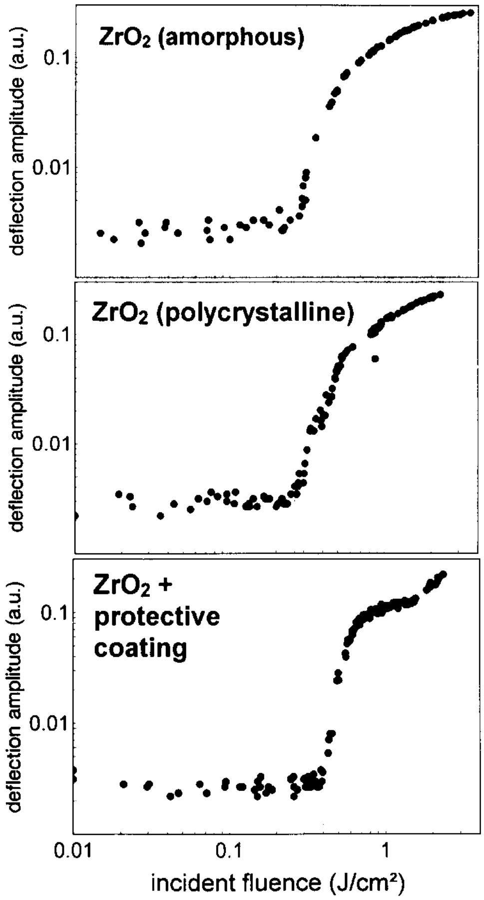

Fig. 5. Comparison of damage results for different modifications of the ZrO_2 thin-film system.

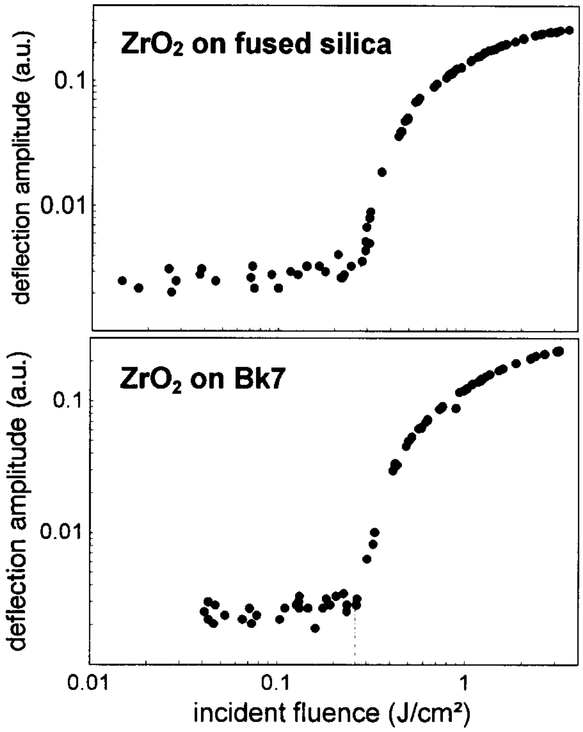

Fig. 6. Comparison of damage results for ZrO_2 deposited on SQ1 quartz and BK7 glass substrates.

topmost $\lambda/2$ layer of such a system is small, no degradation of the damage threshold due to absorption in this layer is expected. However, the overcoat could prevent the penetration of atmosphere contaminants into the ZrO_2 film, which has a high porosity. In fact, the damage threshold of the overcoated system is twice as high as the threshold for the single layer design, yielding evidence for effective protection by the overlayer. A more detailed inspection of the curves in Fig. 5 reveals that in addition to the increased damage threshold there is another feature characterizing data for the protected system. The increase in deflection amplitude above the damage threshold is considerably steeper than for the other unprotected systems. This is indicative of a higher order process typical of the interaction with high-purity material where the interaction process is more dominated by intrinsic material properties, while a moderate increase in amplitude corresponds to defect-related absorption with lower order processes similar to those in small band gap materials.

Such comparative measurements were performed for all oxide thin-film systems and the results are summarized in Fig. 4. Obviously, threshold data described in detail for ZrO_2 are not singular but the other materials exhibit identical trends.

As the last parameter for a possible change in damage threshold, we investigated the influence of the substrate material. A change in damage threshold might result from laser light absorption in the substrate and consecutive heating at the interface, from changing thin-film adhesion properties or from substrate-dependent defect properties. In our case we studied films evaporated on SQ1 substrates that are highly transparent for the 248 nm excimer laser light and films evaporated on BK7 glass substrates with a strong absorption at this wavelength. Results from a comparative study again on ZrO_2 films are displayed in Fig. 6. As a typical result also found for the other oxides, there is virtually no difference in the damage threshold for the two substrate materials. Apparently, absorption in the film dominates the damage process even for a wide band gap material such as HfO_2. This observation again emphasizes the role of defect-mediated processes for the determination of the damage threshold in these oxide thin-film systems.

6. Discussion

One major result of the mirage data analysis presented here is the strong dependence of the apparent thin-film damage threshold on the band gap energy. At first sight this seems to imply a dominance of intrinsic thin-film properties for the damage, which is in contradiction with other results and earlier studies where extrinsic defect states appeared to determine the damage behaviour [10]. Although a fully conclusive quantitative interpretation of the experimental results cannot yet be presented, we give a self-consistent, tentative interpretation for our observations that explains all features. The key assumption of this interpretation is that the primary process of interaction of laser light with materials with band gap energies larger than the photon energy is a linear absorption by defect states. An absorption process finally resulting in damage occurs when an electron is transferred from the valence band or an occupied defect state into the conduction band [11]. Depending on the energetic position of the defect levels and their density of states, this may be accomplished by a simple absorption process, a multiphoton process or cascading processes involving several energy levels. Such a mechanism has been demonstrated by Dickinson and co-workers, who were able to correlate the presence of cleavage-induced defects and laser damage at 248 nm in MgO single crystals [12, 13]. The degree of non-linearity of the overall behaviour is mainly determined by the density of defect centers and the position of their energy levels. For wide band gap, high-purity materials such as a protected HfO_2 coating, the thresholds are high but when the threshold fluence has been exceeded the energy input leads to avalanche breakdown with a high degree of non-linearity [14]. High defect densities, on the other hand, provide a high electronic density of states in the band gap leading to a high energy input and damage at lower intensities. The dominance of linear absorption by the defect states results in a moderate overall non-linearity similar to the situation in a small band gap material such as TiO_2. Such a change in damage behaviour can be followed when a high-purity dielectric material is irradiated with energetic photons, creating a definite density of point defects in the crystal [15].

To explain the band gap energy dependence of the threshold fluence even in the case of wide band gap materials, we recall that the density of defect states is correlated with the band gap of the host material. Any material-dependent shift in the energetic position of valence or conduction bands will automatically also rearrange the defect states and, therefore, shift the defect-related damage threshold. Hence, the exact position of the apparent damage threshold is determined by the density and specific electronic structure of the defect states, and depends on how deep the tail of defect density of states extends into the band gap region [13]. The knowledge of the density of states is, therefore, the clue to a quantitative description of the functional dependence of the threshold energy on the band gap.

7. Conclusions

The laser damage thresholds at 248 nm for three oxide thin-film systems were measured by a photoacoustic probe beam deflection technique. It was found that thresholds for TiO_2, ZrO_2 and HfO_2 depend exponentially on the respective band gap energies as determined by optical absorption spectroscopy. The primary interaction process of the laser light with the thin-film material is attributed to absorption by defect states in the band gap, and their energetic position near the edges of the bands of the host material accounts for the observed relation between band gap and damage threshold. The role of absorption by intrinsic and defect states in wide band gap materials could roughly be judged by the slope of the above threshold fluence-dependent increase in probe beam deflection amplitude. The transition from a more intrinsic to a more defect-related behaviour was demonstrated for thin films covered with an optically inactive protective coating. An increase in damage threshold by a factor of two was found for all oxides. No change in damage threshold was found on altering the structural properties of the films and depositing on different substrate materials.

Acknowledgement

This work was supported by the Sonderforschungsbereich 337 of the Deutsche Forschungsgemeinschaft.

References

[1] H. A. Macleod, *Thin-Film Optical Filters*, Adam Hilger, Bristol, 2nd edn., 1986, p. 504.
[2] M. R. Kozlowski, I. M. Thomas, J. H. Campbell, F. Rainer, in K. H. Guenther (ed.), *Thin Films for Optical Systems*, Proceedings of SPIE 1782, SPIE, Bellingham, 1993, p. 105.
[3] M. R. Lange, J. K. McIver and A. H. Guenther, *Thin Solid Films*, *125* (1985) 143.
[4] H. L. Gao and N. Y. Wang, *Appl. Opt.*, *32* (1993) 7084.
[5] S. Petzoldt, A. P. Elg, M. Reichling, J. Reif and E. Matthias, *Appl. Phys. Lett.*, *53* (1988) 2005.
[6] E. Matthias, M. Reichling, J. Siegel, O. W. Käding, S. Petzoldt, H. Skurk, P. Bizenberger and E. Neske, *Appl. Phys.*, *A*, *58* (1994) 129.
[7] E. Matthias, J. Siegel, S. Petzoldt, M. Reichling, H. Skurk, O. Käding and E. Neske, *Thin Solid Films*, in press.
[8] K. Mann and H. Gerhardt, in H. E. Bennett, L. L. Chase, A. H.

Guenther, B. E. Newnam and M. J. Soileau (eds.), *Laser Damage in Optical Materials*, Proceedings of SPIE 1438, SPIE, Bellingham, 1990, p. 39.
[9] J. Siegel, M. Reichling, E. Matthias, E. Hacker and H. Lauth, *J. Phys. (Paris), Colloq.*, in press.
[10] A. Bodemann, N. Kaiser, M. Reichling and E. Welsch, *J. Phys. (Paris), Colloq.*, in press.
[11] S. C. Jones, P. Braunlich, R. T. Casper, X.-A. Shen and P. Kelly, *Opt. Eng.*, *28* (1989) 1039.
[12] R. L. Webb, S. C. Langford, L. C. Jensen and J. T. Dickinson, *Mat. Res. Soc. Symp. Proc.*, *236* (1992) 21.
[13] J. T. Dickinson, L. C. Jensen, R. L. Webb, M. L. Dawes and S. C. Langford, *J. Appl. Phys.*, *74* (1993) 3758.
[14] A. S. Epifanov, *Sov. Phys. JETP*, *40* (1975) 897.
[15] R. L. Webb, L. C. Jensen, S. C. Langford and J. T. Dickinson, *J. Appl. Phys.*, *74* (1993) 2338.