

# Femtosecond laser damage resistance of oxide and mixture oxide optical coatings

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We report on the laser damage resistance of ion beam—sputtered oxide materials ( $\text{Al}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{HfO}_2$ ,  $\text{SiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ) and mixtures of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ ,  $\text{Nb}_2\text{O}_5$ - $\text{SiO}_2$ ,  $\text{HfO}_2$ - $\text{SiO}_2$ ,  $\text{Ta}_2\text{O}_5$ - $\text{SiO}_2$ , and  $\text{ZrO}_2$ - $\text{SiO}_2$ , irradiated by single 500 fs pulses at 1030 nm. Laser-induced damage threshold (LIDT), refractive index, and bandgaps of the single-layer coatings are measured. For pure oxide materials a linear evolution of the LIDT with bandgap is observed. The results are in accordance with our simulations based on photo-ionization and avalanche-ionization. In the case of mixtures, however, deviations from the previous behaviors are evidenced. The evolution of the LIDT as a function of the refractive index is analyzed, and an empirical description of the relation between refractive index and LIDT is proposed. © 2012 Optical Society of America

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In the development of femtosecond lasers and their applications, laser-induced damage to optical components is a main limitation. This issue inhibits the available power and long-term resistance of short-pulse laser systems. In these complex systems the coatings are often the weakest part when the laser damage resistance is concerned. It therefore drives strong effort of research in the field of thin films to reduce the cost and increase the lifetime of the coatings. Progress on this particular topic requires available experimental data on the laser-induced damage threshold (LIDT) of optical coating materials and fundamental knowledge of the laser damage mechanisms. Despite common characteristics with bulk materials, the laser damage of dielectric thin films has peculiarities that need to be taken into account: specific optical, mechanical, thermal, and electronic properties affecting the resistance of components under laser exposition, these properties being very dependent on the deposition conditions. Different studies on femtosecond laser damage of oxide optical coatings have been performed, mostly at 800 nm, where the Ti:sapphire laser operates. In particular, a linear scaling of the breakdown fluence with bandgap energy has been reported, and a phenomenological model for the pulse duration dependence has been obtained [1]. The extension of these results to wavelengths of 1030–1050 nm, where ytterbium-doped gain media lasers operate and where very high power—class lasers are under development, is of particular interest. An additional possibility exists for the fabrication of high-power optics using mixtures of oxides. These materials have several advantages, the most important being the tailoring of optical constants and the ability to produce continuous spatial variation of the refractive index. With an adapted design, the use of mixture materials can lead to subsequent enhancement of the LIDT of multilayer systems compared to the use

of pure-material systems [2]. The LIDT of mixture coatings in the femtosecond regime has however been the object of very few studies. The work of Nguyen *et al.* [3] dealing with ion-beam sputtering (IBS)-deposited  $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$  coatings, and our previous work [4], reports on the LIDT versus bandgap energy of mixed oxide films in the femtosecond regime. In this letter the laser damage characteristics of composite films are compared to the properties of pure oxide materials.

Different samples of oxide materials ( $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ) and mixtures of these materials ( $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ ,  $\text{Nb}_2\text{O}_5$ - $\text{SiO}_2$ ,  $\text{HfO}_2$ - $\text{SiO}_2$ ,  $\text{Ta}_2\text{O}_5$ - $\text{SiO}_2$ , and  $\text{ZrO}_2$ - $\text{SiO}_2$ ) were deposited on fused silica samples, applying an IBS process with a zone-target assembly. The samples were manufactured on two deposition plants using the same principle of operation:  $\text{Nb}_2\text{O}_5$ - $\text{SiO}_2$  and  $\text{ZrO}_2$ - $\text{SiO}_2$  with an optical thickness of  $6\lambda/4$  [4] and  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ ,  $\text{HfO}_2$ - $\text{SiO}_2$ , and  $\text{Ta}_2\text{O}_5$ - $\text{SiO}_2$  with a thickness of  $2\lambda/4$  [5,6].

The transmittance and reflectance spectra of the samples at close to normal angle of incidence were measured by spectrophotometry. Afterward, the refractive index and physical thickness analysis was carried out in the low-absorptance spectral region with a numerical method. The optical bandgap values were determined from the absorption coefficient  $\alpha$  by plotting  $(\alpha E)^{1/2}$  as a function of the photon energy and extrapolating the linear curve progression.

The damage test facility and methods are described in [7]. The source is a commercial diode-pumped ytterbium-amplified laser with a Gaussian spatial profile. The wavelength is 1030 nm with 5 nm bandwidth. The pulse duration has been set to 500–20 fs and measured with a single-shot autocorrelator. The beam, linearly polarized, was focused at normal incidence on the front face of the sample, with a beam diameter of  $53 \mu\text{m}$  at  $1/e$ . For the

fluence determination we used the effective spot size as defined in the International Organization for Standardization (ISO) standard [8] and the energy given by a calibrated detector placed behind a beam splitter. To establish the uncertainty of the fluence value we took into account relative errors introduced by the measured energy variation and the beam diameter fluctuations. Single shots were used in our experiments in order to avoid any incubation or fatigue effects. A statistical approach involving 50 tested sites at each fluence was used to test the sample. Damage in our study is defined as an irreversible modification detected by a Nomarski microscope at higher magnification ( $\times 100$  objective). The results are given in term of “internal” LIDT, using

$$\text{LIDT} = |E_{\text{max}}/E_{\text{inc}}|^2 \times \text{LIDT}_{\text{measured}}, \quad (1)$$

with  $E_{\text{max}}/E_{\text{inc}}$  being the ratio of the maximum of the standing-wave electric field distribution in the film to the incident field. This ratio is calculated numerically based on the determined refractive index and thicknesses.

On the different samples that were tested, the transition of damage probability from 0 to 1 was very sharp, less than few percent in fluence. This indicates that the LIDT is determined by intrinsic material properties rather than by the defects and impurities due to imperfections in the manufacturing process [1]. As previously explained, the main intrinsic property that drives the laser damage resistance is the absorption gap. The LIDTs are then reported on Fig. 1 as a function of the measured gap.

A linear dependency of the threshold with the gap is observed. The linear equation coming from [1] (obtained at 800 nm) is also plotted in Fig. 1, using our pulse duration as an input. Our results exhibit a good agreement with this phenomenological law. In comparison to this last reference, where  $\text{SiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{HfO}_2$  were studied at 800 nm, these materials and also  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  are shown to exhibit the same tendency at

1030 nm. As a consequence, a clear material classification is possible for optical coating materials using the following formula (500 fs, 1030 nm):

$$\text{LIDT} = 0.63(\pm 0.031 \text{ J cm}^{-2} \text{ eV})Eg - 1.61(\pm 0.14 \text{ J cm}^{-2}), \quad (2)$$

with  $Eg$  the absorption gap of the coating material (eV).

In order to understand this behavior we used physics-based models to relate the LIDT to the bandgap of the material. In the femtosecond regime the damage of dielectric materials can be understood as a result of pure electronic processes [9]. Free electrons will be generated during the laser pulse up to a level where the electron density in the conduction band reaches a critical density. The simplest way to describe this free-electron generation is to use the rate equation,

$$dN/dt = W_{\text{PI}}(E) + W_{\text{AI}}(E, N) - W_{\text{Loss}}(N). \quad (3)$$

The variation in the free electron density,  $N$ , in the material as a function of time and the electric field,  $E$ , depends on the rate of photo-ionization ( $W_{\text{PI}}$ ), the rate of avalanche ionization ( $W_{\text{AI}}$ ), and a relaxation rate ( $W_{\text{Loss}}$ ) that takes into account relaxation of electrons from the conduction band to lower electronic states. Predictions of the femtosecond-damage threshold have been demonstrated by means of the following rate equation [1,10], even when complex interference effects affect this result, as is the case in optical thin films [11]. A complete description of the model can be found in [10]. The different parameters used in this equation are not perfectly known, especially for coating materials. In our simulations the effective electron mass and the decay term in the relaxation rate have been set as fitting parameters. A variation of the refractive index with the gap based on our measurements has been used:  $n = 2.86 - Eg/(5.39 \text{ eV})$ . In Fig. 1 the results of the simulation are shown, with the effective electron mass set to  $0.5m_e$  (with  $m_e$  the free electron mass) and a decay term of 1 ps. A good description of the experimental observations is obtained. There is of course no physical reason for these parameters to be the same for the different materials, however the effective mass that was found corresponds to a mean value of what can be observed in these dielectric materials. Simulations for different effective masses were conducted in order to illustrate the effects of changes from material to material. It is interesting to note that the 1 ps value that was found for the decay term corresponds to the time scale of the formation of self-trapped excitons in similar coatings [12].

The case of mixture materials is shown on Fig. 2. For these materials the absorption gap is changing with the ratio of high- and low-index material content, and so is the LIDT. These materials have the interesting possibility of a tunable gap, refractive index, and LIDT. In the case of  $\text{HfO}_2\text{-SiO}_2$  and  $\text{Al}_2\text{O}_3\text{-SiO}_2$  a similar behavior as has been measured and simulated for pure oxide is evidenced. The difference between the high- and low-index material gap in these two cases is relatively moderate. In the case of larger differences ( $\text{Ta}_2\text{O}_5/\text{SiO}_2$ ,  $\text{Nb}_2\text{O}_5/\text{SiO}_2$ ,

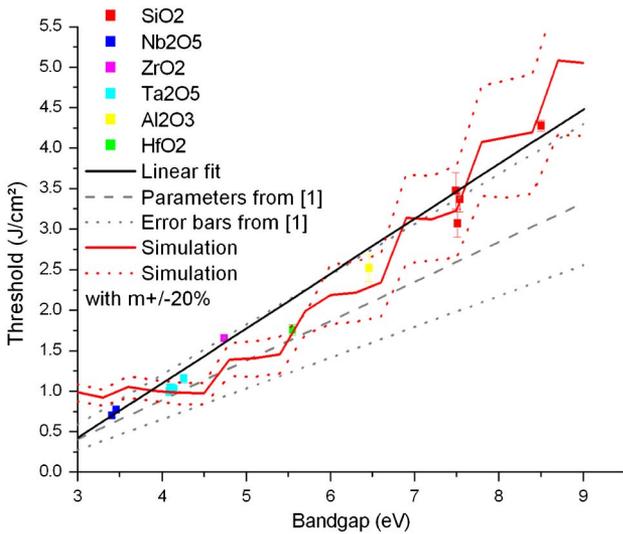


Fig. 1. (Color online) LIDT of IBS oxide materials measured at 1030 nm, 500 fs in 1-on-1 mode as a function of the measured absorption gaps. Plain black line: linear fit of the experimental data; dashed lines: linear equation from [1] with the error bars given in this reference; plain red line: result of our simulations.

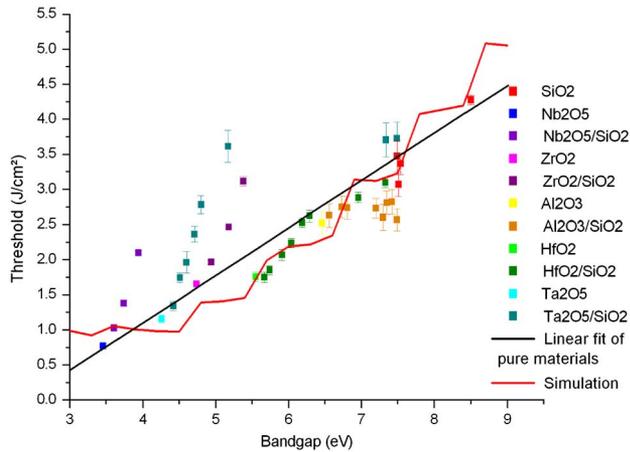


Fig. 2. (Color online) LIDT of IBS oxide and mixtures of oxide materials measured at 1030 nm, 500 fs in 1-on-1 mode as a function of the measured absorption gap. The data points, the linear fit, and the simulation results of Fig. 1 are also reported.

and  $\text{ZrO}_2/\text{SiO}_2$ ) a strong deviation is observed: slopes of LIDT versus  $Eg$  are different from pure oxides, and a decrease in slope at high  $\text{SiO}_2$  content can also be noted. In order to confirm this result, the  $\text{Ta}_2\text{O}_5/\text{SiO}_2$  absorption gaps were measured again with another method using the Tauc—Lorentz approach [13]. Similar gaps were found. Then the previous empirical linear law and the model based on constant parameters (electron mass and decay term) cannot describe the observed behaviors. More knowledge about the electronic properties of these materials, such as the band structure and the different defect states, is certainly needed. However, up to now these materials are totally unknown on these points. Our results indicate that the estimated absorption gap, derived from spectrophotometric measurements, cannot be used to obtain predictive values of LIDT, contrary to the case for pure oxide materials.

For applications, the interesting material parameter for the design of multilayer optical component is the refractive index. We report in Fig. 3 the LIDTs and their relation to the refractive index with experimental data that involve more than 50 samples.

The results are found to be very consistent: a continuous evolution is found independently of the sample nature. Using different simple laws to describe this behavior, we found that the results can be described by:

$$\text{LIDT} = 12/n^3 \text{ J cm}^{-2}. \quad (4)$$

This law has no physical meaning in our present knowledge, but it can describe the results and might be helpful in the process of coating design.

We have reported on the laser damage resistance of optical coatings at a wavelength and in a range of materials where no data were available. In the case of pure oxide materials the dependence of the LIDT on the gap was in good accordance with physics-based models that rely on the electronic rate equation. In the case of

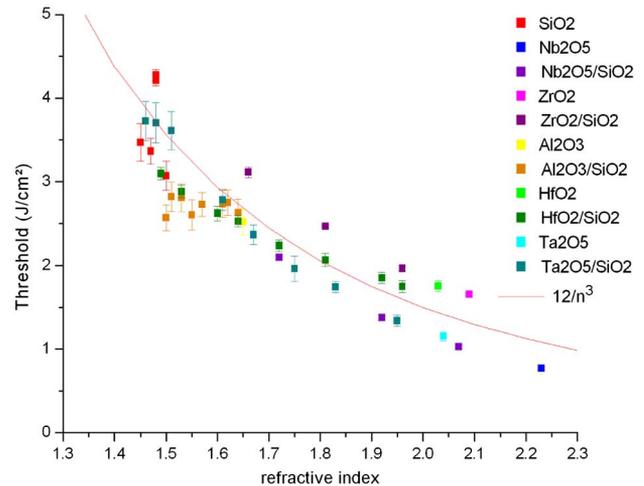


Fig. 3. (Color online) Measured LIDT (1030 nm, 500 fs) as a function of the refractive index at 1030 nm.

mixtures, deviations from the model and from previous reported results were evidenced. The knowledge of the absorption gap and electronic properties of mixtures appears to be the critical point for an understanding of the physical effects involved. An empirical law based on an exhaustive studied was derived to relate the LIDT to the refractive index. This can be taken into account by scientist when designing damage-resistant coatings.

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