Laser-induced damage in composites of scandium, hafnium, aluminum oxides with silicon oxide in the infrared

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The laser-induced damage of mixtures of Sc$_2$O$_3$, HfO$_2$, Al$_2$O$_3$ with SiO$_2$ has been characterized in the infrared for both nanosecond and subpicosecond pulses. Laser-induced damage thresholds (LIDTs) are reported and discussed versus band gap for different compositions. The distributions versus fluence of nanosecond damage precursor densities are extracted fitting damage probability curves. Two models are used: first, a statistical approach, i.e., direct calculation of damage precursor density from damage probability, and second a thermal model based on absorption of initiator. The results show a good agreement. The nature, shape, and size of these precursors are discussed. The critical temperature in the thermal model is dependent on the band gap energy. © 2014 Optical Society of America

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1. Introduction

For the design of optical interference coatings, the mixing of two simple materials has the competence to offer tailored refractive indices covering the range between the two materials. The employment of the mixed coatings avoids discrete layer interfaces, and some improvements compared to classical designs have been observed in physical properties, such as reduction of the residual stress. Recent studies on the properties of oxide composites indicate interesting characteristics such as reduced absorption in the UV range and enhanced laser damage resistance, particularly for subpicosecond applications as presented in the review paper [1] and the references therein.

The objectives of the present paper are first to explore the effects of the material, especially its composition and its optical band gap energy, on short pulse laser damage resistance for a variety of simple and mixed oxide thin films in the infrared and at different pulse durations (at $\lambda = 1030$ nm, 500 fs, and 1064 nm, 12 ns both in 1:1). This interest is motivated by the need to understand how to mitigate laser damage and to fabricate high laser resistance materials.

There have been numerous works that have investigated the laser damage behavior of silica and simple metal oxides and the role of defects [2]. The problem is complex because of the influence of numerous parameters that are extrinsic to the film, such as irradiation conditions (pulse duration, wavelength, laser beam diameter) and substrate properties and preparation. In the nanosecond regime, it
is well known that laser damage in high-quality thin films (low defect density and low absorption) is initiated by nanosized precursors with densities that can be very low (classically much lower than 0.1 μm$^{-2}$) so that they are generally undetectable by routine optical and physical nondestructive characterization techniques [3] and even by the more recent high resolution and high sensitivity photothermal techniques [4]. More recently, many studies are devoted to the analysis of density distribution of damage precursors versus fluence (see for example [5]). However, only a few studies concern mixed coatings [6]. Identification of the nature, geometry, and characteristics of the defects responsible for the damage initiation is essential in order to further improve the damage resistance of coating materials. Thus we will focus our interest on the extraction of the distribution of nanosecond damage precursor densities versus fluence from the damage probability curves and on discussing the nature and the size of nanosecond precursors.

We report on characterization of infrared laser-induced damage in mixtures of Sc$_2$O$_3$, HfO$_2$, and Al$_2$O$_3$ with SiO$_2$ prepared by ion beam sputtering. First, laser-induced damage thresholds (LIDTs) in the 1 on 1 mode are reported versus band gap energy and composition of the mixtures for both nanosecond and subpicosecond pulses, for the sake of comparison. The nanosecond LIDTs, as well as sub-picosecond ones, are found to be related to the band gap energy for a given kind of mixtures. The changes in morphologies of damaged areas are discussed.

Following the same procedure as in [6], the nanosecond laser damage probability curves have been fitted first by a statistical approach, i.e., direct calculation of damage precursor density from damage probability [5,7], and second by a thermal model based on absorption of initiator [8,9]. The distributions of laser damage precursor density extracted from fitting of experimental data by the two models are compared and show a good agreement. From the thermal model, another fit parameter is the critical temperature, which is a characteristic of the film. A dependence of the critical temperature on the optical band gap of the material is observed, and it is compared with that of plasma temperatures. Moreover, the thermal model has the advantage to connect damage probability to precursor physical properties, size, and complex index, and we discuss the opportunity to identify them.

2. Deposition and Nondestructive Characterization of Thin Films

The samples were deposited on fused silica substrates by ion beam sputtering. Refraction and extinction indices have been fitted from transmittance and reflectance spectra applying the Sellmeier model. The band gap values were calculated from the absorption coefficient $\alpha$ by plotting $(\alpha E)^{1/2}$ as a function of the photon energy and extrapolating the linear curve to 0 (Tauc model). The related precision is about 3%. For the Al$_2$O$_3$/SiO$_2$ and the HfO$_2$/SiO$_2$ mixtures, the compositions (atomic fraction) were determined by EDX, whereas for the Sc$_2$O$_3$/SiO$_2$ mixtures XPS-measurements are performed. Volumetric fractions were also determined from spectrophotometric measurements using the effective medium model for all three sample sets. More details about thin film deposition and optical and physical characterization can be found in [10,11]. As examples, we give here in Figs. 1 and 2 the results for scandium silicon oxide composites.

3. Measurements of LIDT and Probability Curves

The damage thresholds in nanosecond regime were studied with a Nd:YAG laser operating in the single longitudinal mode regime (Quantel YG980, wavelength 1064 nm, effective pulse duration 12 ns), in 1 on 1 mode (Fig. 3). More details about the experimental set-up and procedures can be found in [6]. The laser damage test set-up used for the subpicosecond tests at the wavelength 1030 nm and pulse duration 510 fs (diode-pumped ytterbium amplified laser) in 1 on 1 mode is described in detail in [12].
A small beam diameter (less than 100 μm at \(1/e^2\)) has been chosen in all cases to be as close as possible to intrinsic damage conditions. The spotsize dependence of the LIDT has been studied by Jensen et al. and it has been found an increase of the LIDT toward small focal spots [13]. The damage thresholds that we report are then representative of these test conditions, with an objective of making comparative studies of the intrinsic behavior of the mixtures. For applications and when functional LIDT is needed, other kinds of measurement procedure such as the damage thresholds under multiple shots or with the total surface of the sample tested (raster scan procedure [7]) can be more appropriated. The probability curves were plotted with 20 different fluences and 50 sites were tested at each fluence. LIDT is defined as the maximum fluence with zero damage probability.

4. Laser Damage Resistance

A. Relation LIDT versus Optical Band Gap

The LIDTs at 1030 nm, 510 fs, 1 on 1 are plotted in Fig. 4 as a function of the optical band gap energy of the different mixtures. For hafnium silicon oxide mixtures, we find a rather linear dependence that has been observed previously especially for simple metal oxides [6,12]. However, for aluminum and scandium silicon mixtures, there is no evident relation between LIDT and band gap energy as it has been found in [10]. We observe again that the mixtures have a more complex behavior than the simple oxides that cannot be explained by the model based on the equation rate. The mixtures of scandium and silicon oxide can have high LIDT and low values of band gap, i.e., high refractive index, and for this reason they are very interesting materials for the design of high laser resistance multilayer coatings.

The LIDTs measured at 1064 nm, 12 ns, 1 on 1 with small irradiation spots are plotted as a function of the optical band gap energy in Fig. 5 for scandium silicon oxides, in Fig. 6 for hafnium silicon oxides, and in Fig. 7 for aluminum silicon oxides. At each curve, we have associated some representative images of the damage morphologies at high fluences.
We find that the nanosecond LIDT of the mixtures is related to the band gap of the material for a given kind of mixture as it has been widely observed in the subpicosecond regime for simple metal oxides and in the nanosecond regime in [5] for ZrO$_2$/SiO$_2$ and Nb$_2$O$_5$/SiO$_2$ mixtures. In fact, this dependence could seem inconsistent with a defect-induced damage initiation, but it is not the case: The defects responsible for nanosecond damage initiation could be associated to electronic levels in the forbidden gap and their influence could be variable with the band gap energy.

Furthermore, the observation of damage morphologies shows that there is a relation between the morphology and the band gap energy. At a discontinuity or inflection of the curve LIDT-band gap energy there corresponds an important change in the morphology, evoking a change in the damage mechanism. For example, in the case of hafnium composites between the samples of band gap energy 3.2–7 eV, we have a transition from a large damage with a diameter comparable to the beam size to multiple small pits.

B. Fitting of the Nanosecond Damage Probability Curves

An example of nanosecond damage probability curves measured at the wavelength 1064 nm, with a pulse duration of 12 ns, a 1 on 1 procedure and beam diameter of 50 μm is presented in Fig. 8(a) for Sc$_2$O$_3$/SiO$_2$ mixtures of different composition. The experimental data are plotted with error bars. The set of curves reveals that the sample of higher SiO$_2$ composition is more stable and has a smaller probability to initiate damage.

Following the same procedure as in [6], the nanosecond laser damage probability curves have been fitted first by a statistical model (direct calculation of damage precursor density from damage probability), where the precursor density is proposed to follow a power law versus fluence [5,7] and then by a thermal model based on the absorption of the initiator [7,9]. These models and the fitting method used are presented in detail in [6]. Here, we just give some precisions on the fitting method by the thermal model. Many parameters are involved in the calculation of the damage probability thanks to this model. First, we have the parameters related to the absorbing defect (precursor), real and imaginary parts of its complex index, and defect density distribution versus radius (power law,$R_{\text{min}}, R_{\text{max}}$), as well as mass density and heat capacity; second, the parameters related to the matrix film, thermal conductivity, and refractive index (this last parameter has been measured for each sample); and third the critical temperature that is a parameter characteristic of the material. As most of these parameters remain unknown and could hardly be measured, we make some reasonable simplifications to reduce the number of fitting parameters. We assume that the defects in the simple materials and their mixtures own the same characteristics (complex index, size distribution) related to the deposition method and conditions. The mass density and heat capacity have a negligible influence in their variation domain; they are fixed at the value of SiO$_2$ for the whole set of probability curves. Since the values of thermal

Fig. 7. LIDT versus band gap at 1064 nm, 12 ns, 1 on 1 in aluminum silicon oxide mixtures with the increased part of SiO$_2$ (the volumetric fraction is given) and related evolution of damage morphologies (NM).

![Fig. 7](image_url)

Fig. 8. (a) Damage probability curves for scandium silicon oxide mixtures of different compositions (1064 nm, 12 ns, 1 on 1) (beam diameter 50 μm) and (b) corresponding distributions of damage precursor density versus fluence extracted from the fittings by the two models: statistical approach (dot line) and thermal model (solid line).
conductivity for the thin films tested in this paper are unknown, we keep the thermal conductivity $0.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for all the samples. The thermal conductivity of the bulk fused silica at 273 K is $1.4 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, but the thermal conductivity of materials in thin film form can be lower than those of the same bulk material. The influence of the thermal conductivity on the thermal model has been discussed in [14]; a smaller thermal conductivity results in a smaller size of the defects. With these assumptions, we are able first to evaluate the critical temperatures of each sample from its LIDT value. Then we extract the characteristics of defects (complex index and size distribution) and finally the damage precursor density versus fluence from fitting the damage probability curves.

The nature and size of the precursors will be given and discussed in the following section. The distributions of defect densities versus fluence are given for scandium silicon oxides in Fig. 8(b) (see Table 1 for the associated values of precursor size and complex index). The two models show a good agreement. The precursor density is increasing with the fluence following the power law and the maximum varies for all the samples from $10^5 \text{ cm}^{-2}$ to few $10^5 \text{ cm}^{-2}$ (or few $10^3 \text{ μm}^{-2}$). The order of magnitude is in good agreement with previous measurements in fused silica films [3] ($10^2 \text{ μm}^{-2}$). The SiO$_2$ sample has the lower density of defects and the Sc$_2$O$_3$ has the highest one, but the evolution is not monotone for intermediate compositions.

The same work has been done for hafnium silicon oxide mixtures in Fig. 9(a) and for aluminum silicon oxide mixtures in Fig. 9(b). The agreement between the two models is also good. The maximum values of densities vary from a few $10^5 \text{ cm}^{-2}$ to a few $10^6 \text{ cm}^{-2}$ for hafnium composites and from a few $10^5 \text{ cm}^{-2}$ to a few $10^5 \text{ cm}^{-2}$ for aluminum composites. These orders of magnitude are comparable to the values presented by Laurence et al. on fused silica surface at high fluences [5]. However, the evolution of defect density is not regular with film composition, and the different samples of each set have similar defect densities.

When fitting the probability curves by the thermal model, the critical temperatures for each sample are calculated from the LIDT values. Thus, critical temperature of the laser damage initiation exhibits a dependence on the band-gap of the material. The critical temperatures of the tested samples are summarized versus the band gap in Fig. 10. The expected order of magnitude is of several thousand degrees, depending on which mechanism is responsible for laser damage. It is interesting to compare these values to plasma temperatures measured by Carr et al. at 1064 nm, 3 ns in several bulk optical materials of different band gap energies [15]. They found plasma temperatures to be dependent on the band gap of the material that can be attributed to the larger energy needed to liberate an electron in a wider gap material. We observe in Fig. 10 that the critical temperatures of simple materials and their mixtures well continue the trend of the plasma temperatures; this could indicate that the critical temperature in the studied mixtures may be related to the plasma temperature. The values of critical temperatures are also in good agreement with the previous results on niobia silica and zirconia silica mixtures presented in [6].

| Table 1. Nature and Size of Precursors Obtained for Different Mixtures by Fitting Damage Probability Curves |
|-------------------------------------------------|----------------------|------------------|
| Set of Samples                                | Complex Index of Precursors | Maximum Diameter (nm) |
| Sce$_2$O$_3$/SiO$_2$ mixtures                 | $0.3 + 4 \cdot i$       | 17               |
| HfO$_2$/SiO$_2$ mixtures                      | $2 + 2 \cdot i$         | 15               |
| Al$_2$O$_3$/SiO$_2$ mixtures                  | $1.5 + 2 \cdot i$       | 12               |

C. Nature and Size of Damage Precursors

The thermal model makes it possible to connect damage probability to absorbing precursor physical properties. Thus, metallic particles and off-stoichiometric...
oxide clusters could be considered as reasonable sources of absorption, and therefore damage, in the films. We have then considered these two potential sources and tried to estimate with the thermal model if these defects could be responsible for damage, and what should be their size and absorption. We assume that the defects in the simple materials and their mixtures own the same characteristics (complex index, size distribution) related to the deposition method and conditions.

The nature and size of the defects as fitting parameters in the thermal model were obtained by the curve fitting and are shown in Table 1. We can estimate the precision to 7%. We see that for all sets of mixtures, the defects involved in the damage process have necessary a high absorptivity (metallic absorption). However, the complex index of the defect given by fitting is different from that of the metal. For example, the complex index for the defect in $\text{Al}_2\text{O}_3/\text{SiO}_2$ is found $1.5 + 2 -i$, while the index of bulk aluminum at 1064 nm is $1.2 + 11.2 - i$. Moreover, the defects involved are less than 20 nm in diameter for all the mixtures when supposing a thermal conductivity of the host material $k = 0.5 \text{ W/(m} \cdot \text{K)}$. The influence of the thermal conductivity has been discussed in [14]; a smaller thermal conductivity results in a smaller size of the defects.

In conclusion, we can say from analysis of the damage probability curves that the statistical approach gives us the density of precursors that can vary from $10^{-4}$ to $10^{-2} \text{ m}^{-2}$, and the thermal model tells us that if absorbing precursors are responsible for damage initiation, these defects are highly absorbing, with a diameter of about 20 nm and a density of about $10^{-2} \text{ m}^{-2}$. The mean distance between defects can vary from 10 to 100 μm, depending on the density.

These kinds of absorbing defects are not very different from those present in simple metal oxides, and they are not detected in these materials by techniques with sufficiently high resolution and sensitivity, which can detect 5 nm gold particles [4].

The question of an anisotropic defect geometry should be taken into consideration. Indeed in such highly absorbing defects of nanometric size, plasmonic effects can happen. The investigation of photo-induced thermal effects in arbitrary nanostructures based on the finite element method was discussed by Demésy et al. [16]. We give here in Fig. 11 an example of calculating the absorptivity of the defect and the maximum temperature inside anisotropic defects of different shapes and orientations in relation to the electric field. The absorptivity is defined as $\alpha = \sigma/(\pi R^2)$, where $\sigma$ is the absorption cross section and $R$ the particle radius. The calculation was performed for the spherical form as well as the ellipsoidal form where the major axis of the ellipsoid is kept the same as the radius of the sphere and the minor axis is reduced.

We note that the evolution of the absorptivity of the ellipsoid depends on their orientation. In Fig. 11(a), the major axis of the ellipsoid is perpendicular to the electric field. The absorptivity decreases because of the decreasing of the defect volume. But in Fig. 11(b), when the major axis of the
ellipsoid is parallel to the electric field, there is a strong plasmonic resonance: The absorptivity can be very large, even for small particles. The defects B in Fig. 11(a) and E in Fig. 11(b) have the same volume but very different absorptivities: 0.02 for B and 0.75 for E. The associated maximum temperatures are 600 K for B and 14000 K for E. This indicates that a light anisotropy of defects can change drastically the LIDT and even very small defects may be responsible for the initiation of laser damage. Therefore, because of the resonant character of plasmonic effects, it is difficult to anticipate the size of absorbing defects responsible for laser damage initiation.

5. Conclusion

The laser-induced damage of mixtures of Sc₂O₃, HfO₂, Al₂O₃ with SiO₂ has been characterized for IR nanosecond and subpicosecond pulses in 1 on 1 mode and for small beam diameters to be as close as possible to the intrinsic behavior of the films. LIDT are reported versus optical band gap energy in both nanosecond and subpicosecond regimes. If the relation between the subpicosecond LIDT performance and band gap energy is more complex for the mixtures than for simple oxides, we have observed for nanosecond LIDT’s a clear dependence on the band gap energy. This dependence indicates that the defects responsible for damage initiation could be associated to electronic levels in the forbidden gap and electronic processes.

A statistical model and a thermal model based on the calculation of the photo-induced thermal effects are employed for the interpretation of the damage probability curves in nanosecond regime. The distributions of damage precursor densities versus the fluence were obtained and both models give similar results. The order of magnitude is in good agreement with previous measurements on silica (classically lower than 0, 1 μm⁻²).

The critical temperatures in the thermal model are found to be dependent on the band gap, evoking defects related to electronic processes and they well continue for simple materials and their mixtures the trend of the plasma temperatures as a function of the band gap energy. This could indicate that the critical temperature for the damage initiation could be related to the plasma temperature.

The thermal model makes it possible to connect absorbing precursor physical properties to damage probability. The analysis of the damage probability curves by the statistical approach gives us the density of precursors that can vary from 10⁻⁴ to 10⁻² μm⁻² and the thermal model tells us that if absorbing precursors are responsible for damage initiation, these defects are highly absorbing, with a diameter lower than 20 nm and a density of about 10⁻² μm⁻². The mean distance between defects can vary from 10 to 100 μm, depending on the density. These kinds of defects should be detectable by high resolution and sensitivity characterization techniques. However, the shape of the defects is extremely critical and even lightly anisotropic particles with a metallic absorption are likely to arouse strong resonances leading to laser damage although their size is even smaller. Thus, both metallic clusters and high-density areas of electronic defects still remain hypothetical candidates as damage initiators. Further experiments and modeling are required to conclude about their respective role.

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