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Damage Thresholds of Thin Film Materials and High Reflectors at 248 nm*

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Twenty-ns, 248-nm KrF laser pulses were used to measure laser damage thresholds for halfwave-thick layers of 15 oxide and fluoride coating materials, and for high reflectance coatings made with 13 combinations of these materials. The damage thresholds of the reflectors and single-layer films were compared to measurements of several properties of the halfwave-thick films to determine whether measurements of these properties of single-layer films were useful for identifying materials for fabrication of damage resistant coatings.

Keywords: absorption; environmental stability; index of refraction; halfwave-thick layers; laser-induced damage; reflectors; stress; UV coating material.

1. Introduction

Because UV lasers are potentially useful for the investigation of inertial confinement fusion, we have continued development of thin-film coatings for KrF lasers. In previous experiments we tested a large number of coatings made from a limited set of thin-film coating materials, principally SiO_2, MgF_2 and Sc_2O_3, which were selected primarily because they are highly transmissive at 248 nm [1], [2]. Lengthy studies of a few materials allow optimization of the deposition parameters for these materials, and provide a sensibly large data base for evaluation of coatings made from the materials. However, since time and expense limit the number of such studies that can be performed, there is the possibility that potentially superior materials will remain unidentified. It would, therefore, be advantageous to discover relationships between damage thresholds of coatings and the physical properties of the coating materials which could be used to guide material selection. In this paper we describe a material survey whose aim was to establish such relationships.

There are two general formats for survey studies of thin-film materials. An evaluation of a large number thin-film materials can be made by studying either single-layer films of the materials or by studying properties of multilayer coatings made from the materials. Testing of halfwave-thick single layers is attractive because, in principle, the materials can be individually evaluated and because internal electric fields experienced by halfwave films during laser damage testing do not depend strongly on the refractive index of the material. The physical properties of single-layer films may, however, be affected by contact of the film with both the substrate and the atmosphere. Testing highly reflective multilayer coatings made of the materials to be evaluated eliminates the influence of the substrate, and provides direct information about a useful coating design. Also, environmental degradation or contamination of a given film layer could be prevented by overcoating the reflector with a film of a more stable material. The disadvantages of using multilayer reflectors are that the materials are tested in combinations, rather than individually, and that given a number of materials, there are many potentially interesting material combinations.

It is also important to note that a survey study of thin film materials cannot be expected to provide an unambiguous ranking of the relative worth of many coating materials. A survey, by necessity, includes only a few films of each material, but characteristics of thin films are reproducible only for those materials for which deposition has been optimized, which is the task one seeks to avoid by conducting a survey. A survey may reveal general relationships between laser damage thresholds and measured physical properties of films, and these relationships would, in turn, indicate which materials should be studied more carefully.

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We decided to evaluate the effectiveness of material surveys by testing both halfwave-thick layers of 15 oxide and fluoride materials, and highly reflective quarterwave stack reflectors made from 13 combinations of the same materials. The coatings were made at Optical Coating Laboratory, Inc. (OCLI) by electron-beam evaporation of the materials onto fused silica substrates that had been bowl-feed polished at OCLI. For single-layer films, measurements of the refractive index, absorption, stress, environmental stability and the position of the UV band edge were made. For both films and high reflector (HR) coatings, the threshold for damage by 20-ns, 248-nm KrF laser pulses was measured at Lawrence Livermore National Laboratories (LLNL). Results of these measurements and a discussion of possible correlations between the thresholds of the reflective coatings and physical parameters of the materials are presented.

2. Experimental Procedure

Damage thresholds were measured at LLNL with 20-ns, 248-nm pulses generated by a discharge-pumped KrF laser. At the surface of the sample, the beam was 1.5 mm in diameter at the e^{-2} intensity level, but the intensity distribution was nonuniform. The highest fluences in the beam occurred at isolated maxima, where fluence was uniform to within + 5% over areas not less than 0.1 mm in diameter. For each shot, the beam was photographed with Kodak 1-Z spectroscopic plates, and the intensity distribution was determined by densitometry. Peak fluence for each shot was computed by numerically integrating the intensity distribution and normalizing the integral to agree with the measured pulse energy.

The samples were mounted on a rotating stage which allowed the irradiated test site to be moved into the field of view of a Nomarski microscope. Test sites were photographed before and after irradiation at a magnification of 420. The test sites were also inspected visually using either Nomarski or bright-field microscopy, and under intense white light illumination using the unaided eye. Damage was defined to be a permanent surface alteration that was detectable by any of these inspection techniques.

Each test site was irradiated once. The average number of sites tested per sample was seven. Damage was defined as the average of the lowest fluence that caused damage and the highest fluence which did not cause damage. A detailed description of the laser system used in these tests and of our experimental procedure has been previously presented [1].

Other parameters of the coatings were measured at OCLI. Transmittance and reflectance were measured with a Cary 17-DX spectrophotometer. Index of refraction for the individual coating materials was calculated from the measured reflectance and transmittance of thick single-layer films. The absorption coefficient of a film material was measured by coating a halfwave-thick layer of the material on a high reflector and measuring the decrease in reflectance. Film stress was determined by interferometric measurements of the stress-induced flexure of coated substrates 0.38 mm in thickness. The absorption edge was defined to be the wavelength at which the transmission of a coating with a 1.5-μm optical thickness was 50%. Since tranmission measurements could not be made at wavelengths below 200 nm, the band edge could not be measured in some films. These materials were separated into two groups: those with some measurable absorption at 200 nm (absorption edge less than 200 nm) and those with no detectable absorption at 200 nm (band edge much less than 200 nm).

3. Single-Layer Films

Halfwave-thick layers of 15 oxide and fluoride films were fabricated by OCLI using electron-beam evaporation of the materials onto fused silica substrates that had been bowl-feed polished by OCLI. The films of most of these materials had generally good cosmetic appearance, and contained only isolated defects with typical dimensions of 1 μm. There were, however, some exceptions. Films of YF_3 were mosaic arrays of 10-μm-sized areas presumably caused by local stress fracture. Some areas on Na_3AlF_6 films were clean, but other areas had a streaked appearance. Films of both ZrO_2 and NaF had a hazy, fogged appearance.

We measured laser damage threshold for two halfwave-thick layers of each material. The damage thresholds are given in figure 1. The morphology of damage in each film was also recorded. Three general types of damage were observed, and the nature of the damage correlated with the measured damage threshold. In low-threshold films, damage appeared as micropits which were aligned in either straight or curved rows that resembled polishing sleeks. In medium-threshold films, damage usually was seen as a spatially uniform area (shaped like the incident laser beam) which was visible by either bright-field or Nomarski microscopy. This implies alteration of both surface texture, which effects white-light visibility, and surface height, the parameter observed in Nomarski microscopy. The altered areas also contained a few pits, which were typically 1 μm in diameter. High-threshold films, such as SiO_2 and ThF_4, had damage morphologies much like the damage that is observed on front surfaces of bare polished fused silica: pits 1 μm in diameter which are surrounded by halos at high fluences.

The damage thresholds ranged from less than 1 J/cm² in ZrO_2, which is comparable to the damage fluence for some metallic films, to 25 J/cm² in ThF_4, which is about twice the front-surface threshold of bare polished fused silica [3]. The latter is an unusual result for which we have no satisfactory explanation; thresholds of coated surfaces rarely exceed those of bare surfaces. However, the experimental observation we are reporting is straightforward. When we use the test procedure described above, we find 1) thresholds ranging from 9 to 15 J/cm² for front surfaces of bare polished silica substrates [3], 2) thresholds exceeding 20 J/cm² for some silica surfaces coated with low-index films, and 3) the same morphology of damage for both types of surfaces. It is also interesting to note that substrate structure appeared to influence damage morphology on low-threshold films, but not on moderate- or high-threshold films. Absorption by impurities trapped in polishing scratches could have caused this damage, but all substrates were similarly polished, so scratches on substrates irradiated at higher fluences should also have damaged. The implication is, therefore, that in low-threshold films, the film material itself had been influenced by the presence of the polishing sleek.

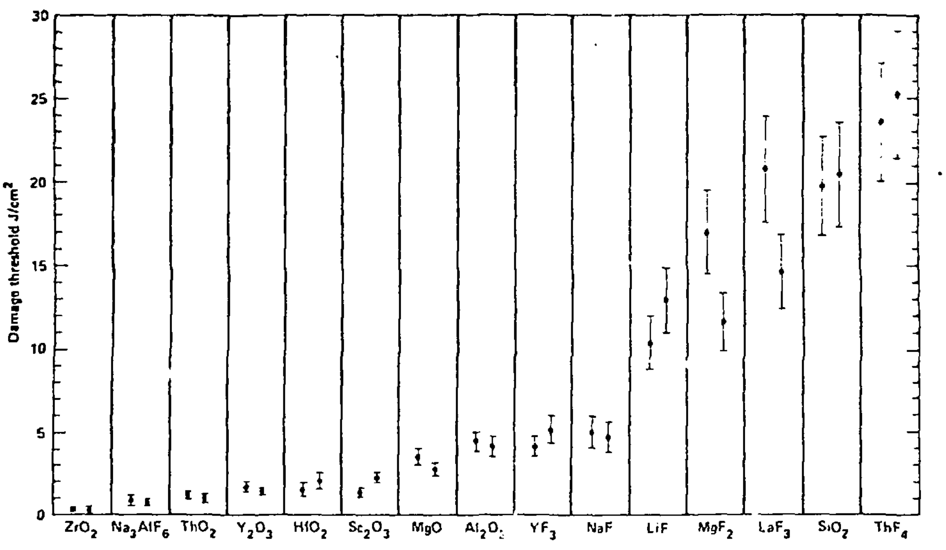

Figure 1. Laser damage thresholds (20 ns, 248 nm) of halfwave-thick films.

Next, consider the comparison of the film thresholds to physical properties of the films. In figure 2, four properties of the films are plotted as a function of the average threshold for each material. Thresholds were largest in the films with low refractive index, which (excepting SiO_2) were all fluorides. The high-index films (which were all oxides), and the films of Na_3AlF_6 (which had poor physical properties), had low thresholds. Our results are generally similar to those of Newnam and Gill who used 22-ns, 266-nm pulses to test single layers of six oxide materials and three fluoride materials [4], and those of Walker, et.al., who tested films of six oxides and three fluorides with 15-ns, 266-nm pulses [5]. Among these three studies, both the threshold ranking of individual film materials, and the absolute values of thresholds reported for a given film material, vary considerably, suggesting that it is difficult to establish true comparisons of materials in thin-film form. However, the general correlation between high thresholds and low refractive indices is present in all three studies. This correlation was first observed by Turner [6], and later developed as a threshold scaling law by Bettis, et. al. [7]. The scaling law predicts some of the results of the three UV damage studies. However, the scaling rule is based on the assumptions that damage is caused by electron avalanche and that thresholds should scale according to the strength of the local electric field. The law would not be applicable if linear absorption were the dominant mechanism for damage in UV film materials.

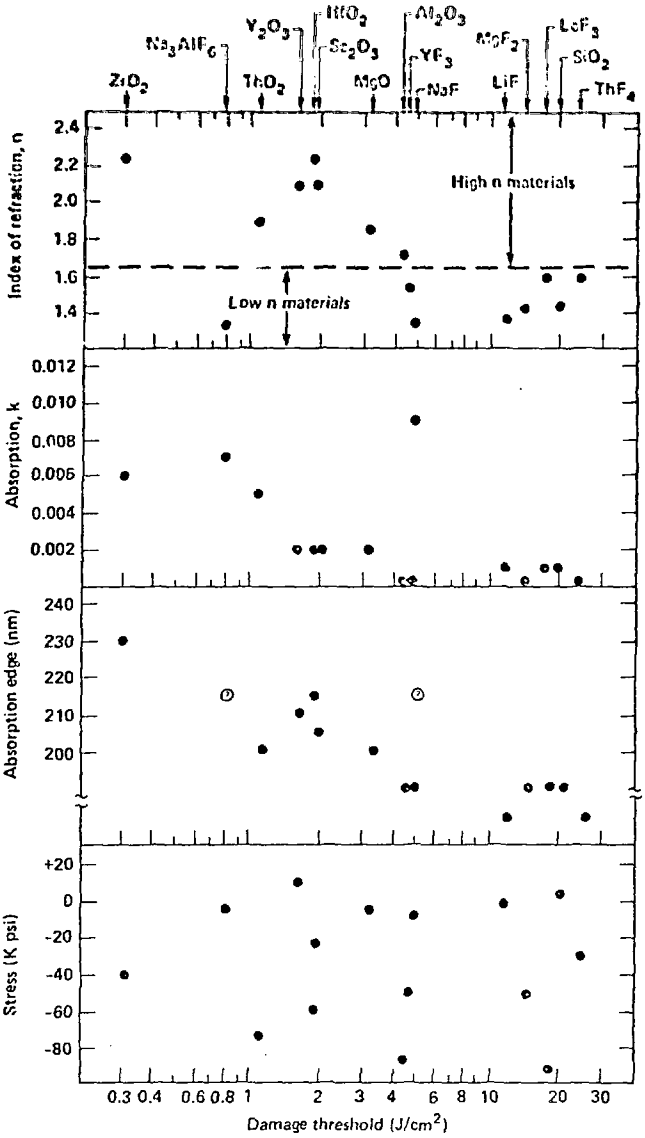

Figure 2. Index of refraction, absorption, position of the UV band edge and film stress for 15 UV coating materials plotted as a function of the average of the damage thresholds measured on two halfwave-thick samples of each material.

We also found that thresholds varied systematically with film absorption and with the spectral position of the UV band edge. Highly absorbing films had low thresholds. All low-absorption films had UV band edges below 200 nm, so absorption and position of the band edge were closely related. In fact, since the oxides were the materials which had band edges in the near UV, high absorption, and also high refractive index, it is possible that the apparent correlation between UV damage thresholds and index is accidental. Again, there were exceptions. NaF was very absorptive, but had a moderately large threshold, and scattering losses in both Na_3AlF_6 and NaF were so large that we could not measure the positions of the band edge.

The only previous study of the correlation between UV thresholds and film absorption concluded that linear absorption was responsible for damage induced by 266-nm 22-ns pulses in ZrO_2 [4].

Finally, we found no correlation between film stress and damage threshold, and a possible correlation between cosmetic appearance and threshold. The ZrO_2 and NaF films had a foggy appearance, and the film of Na_3AlF_6 exhibited streaked areas. The threshold of the ZrO_2 film was less than that of any other film tested, and these two fluoride films had thresholds less those of other materials with comparable properties.

Although the material characteristic responsible for damage in a given material is not known, trends in the entire set of data identify the characteristics that are associated with good resistance to damage by 248-nm irradiation. The film material should have low refractive index, low absorption, band edge located at a wavelength well below 248-nm, good cosmetic quality, and good environmental stability when exposed to high humidity. For single-layer films stress did not influence thresholds.

4. High Reflectors

Reflectors for use at 248 nm were fabricated by OCLI from 13 high-index/low-index combinations of the materials that were studied as single-layer films. Four reflectors of each type were made, two in each of two coating runs. Each reflector had a minimum of 15 quarterwave-thick layers and was overcoated with a halfwave-thick layer of the low-index material used in the reflector stack. The coatings were deposited onto conventionally polished substrates of BK-7.

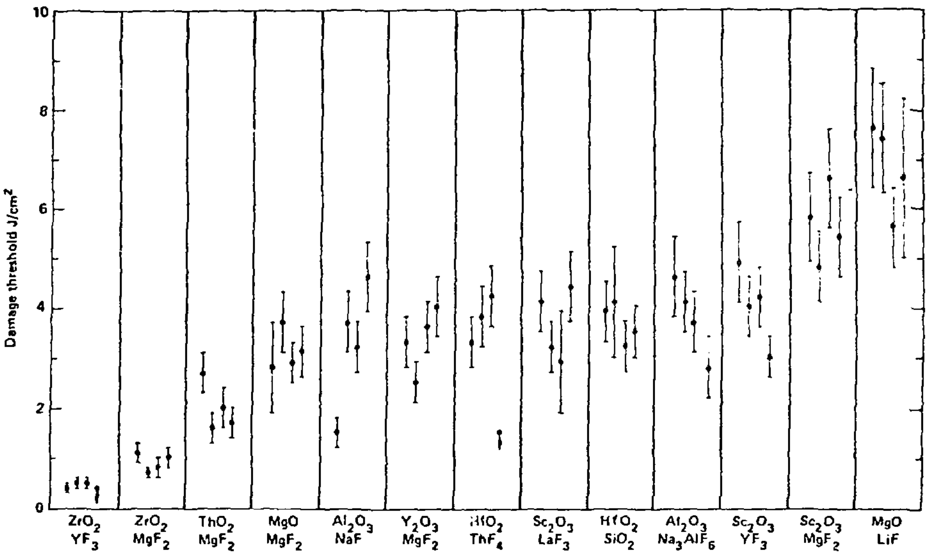

Figure 3. Laser damage thresholds (20 ns, 248 nm) of quarterwave-stack multilayer highly reflecting coatings made from 13 combinations of high-index and low-index materials.

The cosmetic appearance of most reflectors was usually like that of halfwave-thick films of its constituent materials, but the surface density of defects was slightly higher in reflectors. All reflectors with ZrO_2 and NaF had a foggy granular appearance, and reflectors with YF_3 had stress fractures. Other unusual reflectors included the following: those with HfO_2 had many cosmetic defects and sections of missing coating; those with Na_3AlF_6 were densely fogged, and had large circular voids; the ThO_2/MgF_2 reflectors appeared scuffed and nonuniform.

Damage thresholds of these reflectors, shown in figure 3, fell into three groups: below 3 J/cm^2, between 3 and 5 J/cm^2, and greater than 5 J/cm^2. Reflectors with the lowest thresholds were fabricated with high-index materials that had low thresholds when tested as single layers, ZrO_2 and ThO_2. In contrast, the low-index material Na_3AlF_6 had a low threshold when tested as a single layer, but when combined with Al_2O_3, produced a reflector with moderate threshold. Reflectors of Sc_2O_3/MgF_2 and MgO/LiF had the highest thresholds, the median values being 5.6 and 7.0 J/cm^2, respectively. It is interesting that these largest reflector thresholds were considerably greater than the thresholds of single layers of the high-index materials, and considerably less than the highest thresholds observed in single layers of the low-index materials.

Rank	High-n material	Low-n material	Index n	Abs. k	Abs. edge	Stress	Threshold	Cosmetic	Environmental	
1	MgO	LiF	●	○	●	●	○	?	○	Low-n materials
2	"	MgF_2								
1	Sc_2O_3	MgF_2	●	●	?	○	X	X	?	
2	"	YF_3								
3	"	LaF_3								
1	Al_2O_3	Na_3AlF_6	?	●	?	●	X	●	?	
2	"	NaF								
1	HfO_2	SiO_2	●	○	○	●	○	?	?	
2	"	ThF_4								
1	ZrO_2	MgF_2	●	?	?	○	●	●	?	
2	"	YF_3								
1	Sc_2O_3	MgF_2	X	●	○	X	○	●	X	High-n materials
2	Y_2O_3	"								
3	MgO	"								
4	ThO_2	"								
5	ZrO_2	"								
1	Sc_2O_3	YF_3	●	●	●	●	●	●	?	
2	ZrO_2	"								

Figure 4. Comparison of threshold ranking (high to low) of reflectors to ranking of coating materials with respect to increasing refractive index, absorption, position of band edge, and stress, and with respect to decreasing threshold of halfwave-thick films, cosmetic appearance and environmental stability. Reflectors are grouped into subsets containing a common material, and within each subset, are ranked by decreasing threshold. For each subset, we indicate whether each possible ranking of the varied materials agreed (●) or disagreed (X) with the threshold ranking. In some instances there were either minor disagreements (O) or the material ranking could not be established (?).

A major purpose of this study was to determine whether the threshold ranking of reflectors could have been predicted from either the threshold ranking of single layers of the constituent materials, or the ranking of the constituent materials in terms of their physical properties. A comparison between these rankings is shown in figure 4. The lefthand columns of Fig. 4 list the pairs of materials from which reflectors were made. The list is organized so that all reflectors containing a given material appear as a group. Groups of reflectors with a common high-index material are at the top of the figure; groups with a common low-index material are at the bottom. Inside a given group, the reflectors are ranked in order of decreasing threshold. In the righthand part of the figure, we use four symbols to indicate whether the ranking of thresholds in a group of reflectors agreed (●) or disagreed (X) with a particular ranking for the materials that were varied in that group. The open circle indicates an insignificant inconsistency between threshold rankings of reflectors and a material ranking based on only a slight difference in physical parameters or reflector thresholds. The symbol (?) indicates no material ranking was possible because material parameters were equal or unknown.

As an example, consider the set of three reflectors that contained Sc_2O_3 as the high-index material and either MgF_2, YF_3 or LaF_3 as the low-index material. Threshold ranking (high to low) for these reflectors agreed with material rankings based on increasing refractive index ($n = 1.43$ for MgF_2, $n = 1.54$ for YF_3, $n = 1.59$ for LaF_3) and increasing absorption ($k < .001$ for MgF_2, $k < .001$ for YF_3, $k = .001$ for LaF_3); disagreed only slightly with the ranking based on increasing magnitude of film stress (-50 Kpsi for MgF_2, -49 Kpsi for YF_3, -91 Kpsi for LaF_3); and strongly disagreed with the rankings based on decreasing damage thresholds of the film (14.4 J/cm^2 for MgF_2, 4.6 J/cm^2 for YF_3, 17.7 J/cm^2 for LaF_3) and decreasing cosmetic quality (the YF_3 films had stress fractures). Films of MgF_2, YF_3 and LaF_3 had comparable environmental stability and comparable positions for their UV band edges, so rankings could not be established on the basis of these properties.

The entire set of data in figure 4 shows two general trends. First, when various low-index films were used with a given high-index film (top half of figure), the highest reflector thresholds were correlated with use of the low-index material with lowest refractive index. Absorption, position of the UV band edge, and stress were reasonably good indicators of the merit of the low-index materials, whereas thresholds of single-layer films and cosmetic appearance were sometimes poor selection criteria. Attempts to correlate environmental stability with reflector thresholds were inconclusive. Second, when various high-index materials were used with a given low-index material, optimum reflector thresholds were correlated with minimal absorption and best cosmetic appearance in the high-index film. Of these, we suspect that absorption is the strongest parameter. There was also reasonable correlation between reflector thresholds and either position of the UV band edge or threshold of single-layer films of high-index materials. The refractive index, stress and environmental stability in high-index materials did not correlate with reflector thresholds.

5. Summary

We measured laser damage thresholds for halfwave-thick layers of 15 oxide and fluoride materials, and for HR coatings made from 13 combinations of these materials. Several physical properties of the single-layer films were also measured.

Of the HR coatings tested, those made of Sc_2O_3/MgF_2 and of MgO/LiF had the highest median thresholds, which were, respectively, 5.6 and 7.0 J/cm^2. The thresholds of single-layer films ranged from less than 1 J/cm^2 for ZrO_2 to more than 20 J/cm^2 for SiO_2 and ThF_4. Thresholds were greatest in films of materials for which refractive index and absorption were small, and the position of the UV edge was well below 248 nm. Thresholds of single-layers did not correlate with film stress.

Measurements of thresholds for halfwave-thick single layer films did not identify the materials from which the reflectors with greatest threshold were fabricated. The survey was moderately successful in identifying material characteristics which effect thresholds of reflectors, and identified a promising material combination, MgO/LiF, which we had not previously studied.

In reflectors made of pairs of materials having a common high-index material, and various low index materials, the largest thresholds for the reflectors correlated with use of the low-index material with lowest refractive index. In reflectors with a common low-index material, thresholds correlated with use of the high-index material with the lowest absorption.

6. Acknowledgements

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7. References

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