CONF-731054--6

UCRL-JC 114983
PREPRINT

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This paper was prepared for submittal to the
Laser-Induced Damage Conference
Boulder, CO
October 27-29, 1993

November 4, 1993

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ABSTRACT

Low absorption coatings were examined using a high repetition rate copper vapor laser to study the surface temperature as a function of incident power. Nonlinear absorption was observed in some of the coatings as a result of increased incident power. A variety of commercial coating vendors using common dielectric oxide material combinations were surveyed. Wavelength, coating material, and coating vendor were varied to study their effects on the linearity of the absorption. The films were deposited by electron beam or ion beam sputtering technologies. Changes in the film characteristics were observed after exposure to high incident power. The nature of these changes and their permanency were also examined.

Key Words: Nonlinear absorption; ion beam sputtering; electron-beam deposition; laser induced damage

Introduction

In 1931 the first theoretical work on nonlinear absorption was formulated by Göppert-Mayer.¹ Since then a wide variety of experimental and theoretical work has been done on nonlinear absorption in optical materials²⁻⁴ including semiconductors, crystals, and glasses⁵⁻¹⁹. Although some work has been done on nonlinear absorption in thin liquid films²⁰⁻²¹, little has been written about this effect for optical coatings²². Many of the early nonlinear absorption measurements consisted of determining the transmission losses through the sample for various power densities. This method is appropriate for transparent samples, but not for high reflector (HR) coatings. A variety of methods currently exist for measuring absorption in optical coatings.²³ The method used at the Atomic Vapor Laser Isotope Separation (AVLIS) Program at Lawrence Livermore National Laboratory (LLNL) is a calorimetric technique.²⁴ With this method, we can measure absorption to 10^{-6} at various wavelengths, polarization states, and power densities. This allows us the opportunity to study nonlinear absorption, below the laser damage threshold of dielectric HR coatings.

The AVLIS laser²⁵⁻²⁶ is a complicated system that requires a large volume of high quality optical components with stringent specifications.²⁷ One of the most challenging specifications is an absorption less than 10^{-5} on HR coatings used in the optical transport system. Although all HR coatings are measured for absorption, a better understanding of the effects of power density on the absorption of the coatings was necessary to assure low absorption performance in the laser environment.

Experiment

The test set up, illustrated in figure 1, consisted of copper vapor laser light with a 4.3 kHz repetition rate and approximately 50 ns pulse width imaged onto a coating sample. The temperature rise of the illuminated coating was measured with an Inframetrics IR thermal camera calibrated for temperature measurements. A video camera was used to observe the scattered light from a magnified view of the illuminated spot to low defect regions in the coating and laser damage. A beam profiler was used to determine beam diameter and uniformity. Ballistic calorimeters were used for power measurements. A more in-depth explanation of the setup is given elsewhere.²⁸ The coating was illuminated at different power levels to observe the dependence on power density. The absorption can be calculated from the following formula²⁴,

$$\text{Absorption} = .045 \frac{T^{1.11} R^{0.83}}{P^{1.05}} \quad (1)$$

where T is the peak temperature in degrees Celsius, R is the beam radius in centimeters and P is the laser power in watts. This formula is an approximation that has consistently predicted the results within 30% of TSO, a finite element analysis computer code used at LLNL to calculate the wavefront distortion of optical components with high laser power loading.²⁹

Absorption measurements were carried out on a variety of samples including production coating witnesses and development coatings which enabled a sampling of a variety of coating material combinations and coating vendors. Absorption was characterized as a function of incident power density at both 511 and 578 nm and each separate wavelength. Absorption

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measurements were conducted at single and multiple site locations. Some sites exhibited different absorption values at low power densities after being illuminated with a high power density. These parts were measured with an interferometer, optical microscope, spectrophotometer, and atomic force microscope (AFM) to observe any changes in the film after high power exposure.

Results

Theory

The attenuation of the intensity I , of a laser beam by a coating exhibiting both linear and nonlinear absorption is as follows,

$$\frac{dI}{dz} = -\alpha I - \beta_n I^n - \sigma_{ex} N_{ex} I \quad (2)$$

where α is the linear absorption coefficient, and β_n , $n = 2, 3, \dots$ are the multiphoton absorption coefficients.⁸ $\sigma_{ex} N_{ex}$ is the photogenerated carrier absorption where σ_{ex} is the total carrier cross section (holes plus electrons) and N_{ex} is the density of the carriers.¹³ Since all the measurements are made at a single pulse length, it is not possible to separate photogenerated carriers from multiphoton absorption in this study. By plotting the temperature versus power density on a log-log scale, one can determine information about the nonlinearity of the absorption from the slope of a best fit line through the data points. A slope of 1 would correspond to linear absorption whereas a slope of greater than 1 would imply nonlinear absorption. Since thin films are complex systems containing multiple states and phases of a single material as well as defects, one could expect the absorption for a given area to demonstrate a combination of linear and nonlinear absorption effects. Materials that have very good stoichiometry and low UV absorption edges like HfO_2 , SiO_2 , and ZrO_2 , would be expected to behave in a rather linear fashion. Ta_2O_5 is a material that is frequently oxygen deficient requiring a post deposition bake and has a higher UV absorption edge that could produce significant nonlinear behavior.

Production Samples

Witness samples from six years of HR production coating runs were examined for absorption at low (1-2 kW/cm²) and high (5-9 kW/cm²) power densities. The coatings are all e-beam deposited on either fused silica or zerodur substrates. Figure 2 illustrates the magnitude of change in the absorption for two vendors and various material combinations. All the coatings had an absorption of less than 30 ppm at the low power density. Although many of the coatings demonstrated little change, there were a significant number of coatings that had very drastic increases in absorption. Table 1 is a summary of two different coating types, copper and dye HR coatings, and the number of coatings where nonlinear absorption was observed. Coatings with changes in absorption of greater than 2x between low and high power densities were considered to exhibit significant nonlinear effects.

Table 1. Absorption characteristics of various HR coatings with different material combinations and coating vendors.

Vendor	Copper HR (511 & 578 nm)		Dye HR (595±35 nm)		Coating Materials
	Linear Abs.	Nonlinear Abs.	Linear Abs.	Nonlinear Abs.	
A	—	—	43	8	Ta_2O_5/SiO_2
A	29	13	—	—	$Ta_2O_5/HfO_2/SiO_2$
B	2	24	6	3	Ta_2O_5/SiO_2

* Tested at 578 nm.

The nonlinear absorption in the production coatings has a relatively strong dependence on coating material and wavelength. There is also a difference in the absorption characteristics between vendors using the same material combinations. Possible explanations for the different nonlinear behavior are differences in impurities in the starting coating materials, evaporation parameters affecting the stoichiometry of the films, defect types and sizes, and post processing of the films. The results of these measurements required a closer examination of coating material, wavelength, and vendor affects on the absorption characteristics of AVLIS coatings.

Development Samples

HR e-beam coatings from various development programs were examined for absorption at low and high power densities. A wider variety of vendors are included as well as additional coating materials as seen in figures 3a & b. All the absorption

measurements were made below the laser damage threshold of the coating. E-beam Ta₂O₅/SiO₂ coatings typically demonstrated nonlinear absorption at relatively low power densities. E-beam HfO₂/SiO₂ and ZrO₂/SiO₂ coatings exhibited both linear and nonlinear absorption. The resolution limit of the thermal camera for measuring the coating surface temperature was 0.1°C, so it was not possible to determine nonlinear absorption at low power densities for very low absorption coatings. It can be observed that some of the HfO₂/SiO₂ coatings exhibit significant nonlinear absorption at very high power densities but not at low power densities. The Ta₂O₅/SiO₂ coatings all have strong nonlinear tendencies even at relatively low power densities. The degree of nonlinearity varied from run to run and vendor to vendor for identical materials.

IBS deposited coatings were evaluated for nonlinear absorption for a variety of materials as seen in figures 4a & b. The HfO₂/SiO₂ also began exhibiting significant nonlinear behavior at high power densities but rather linear behavior at low power density. Ta₂O₅/SiO₂ coatings were the only IBS films to have significant nonlinear absorption at low power densities. Many of the IBS copper coatings had higher absorption (10-100 ppm) than the counterpart e-beam films (<10 ppm), but behaved in a more linear fashion. A summary of the average slope values of all the development samples is in table 2.

Table 2. Summary of slope values of development coatings for seven different coating vendors.

Vendor	Ta ₂ O ₅ /SiO ₂	ZrO ₂ /SiO ₂	HfO ₂ /SiO ₂	Process
A	—	—	—	e-beam
B	2.09	—	2.07	e-beam
C	2.98	1.66	1.18	e-beam
D	—	—	2.00	e-beam
E	1.55	1.23	1.30	IBS
F	2.63	—	0.92	IBS
G	—	—	0.84	IBS

Wavelength Dependencies

Typical HR coatings for the AVLIS program have slightly higher absorption at 511 over 578 nm. Measurements were made at individual wavelengths to determine if nonlinear absorption would be observed for both wavelengths and if there was a similarity in the nonlinearity. The results are summarized in Table 3. The magnitude of the absorption differed from vendor to vendor as can be seen in figures 5a & b. Generally vendor A had significantly lower absorption than vendor B. Absorption at 578 nm was always lower than the absorption at 511 nm. Since the temperature rise of the vendor A coatings at 578 nm were unmeasurable, it was not possible to see if the absorption nonlinearity was affected by wavelength. The vendor B coatings did not have significant differences in the absorption nonlinearity for the different wavelengths.

Table 3. Comparison of slope values of nonlinear absorption for different wavelengths, vendors, and incident angles.

Vendor	Slope		Incident Angle (degrees)
	511 nm	578 nm	
A	1.47	*	10
A	4.24	*	45
B	1.98	2.19	10
B	1.62	2.03	45

* Slopes could not be determined since temperature rises in the coating were below detectable limits.

Beam Footprints

A test was conducted to examine the absorption of a coating at low power density, then ramping to a high power density and returning to low power density again. Some of the samples that demonstrated nonlinear absorption had different absorption values for the same low power density when exposed to a higher power density between measurements. Figures 6a & b illustrate the results of these tests. Interestingly, some of the coatings had beam footprints that could be observed in the condensation pattern formed after breathing on the surface. The beam footprint could be observed in the condensation pattern when viewed under florescent or high intensity incandescent lighting. A number of measurements were carried out on these

footprints to begin to understand what changes had occurred in the film. Interferograms before and after exposure were taken and the reflected wavefront of the sample appeared to be unaffected. Optical microscope measurements of the sample before and after exposure also did not show any differences. AFM measurements of an exposed and unexposed were identical in surface roughness and appearance. Spectrophotometer traces in both areas also were identical. The footprints faded with time and were no longer visible in a condensation pattern on the optic after about 3 months. The parts were retested in the same location as the previous footprint and the original absorption value were observed with low power density illumination. After exposed to a high power density a new beam footprint was observed. The only change that was observable in these films was a slightly increased absorption and a footprint only observable when the coating was viewed with a condensation pattern on the surface. The changes were not permanent nor were they normally seen at these power density levels with films that did not exhibit nonlinear absorption.

Summary

Nonlinear absorption was observed in some HR coatings. $\text{Ta}_2\text{O}_5/\text{SiO}_2$ coatings had the strongest tendency to exhibit nonlinear effects although some $\text{ZrO}_2/\text{SiO}_2$ and $\text{HfO}_2/\text{SiO}_2$ coatings also had nonlinear absorption. Some of the $\text{HfO}_2/\text{SiO}_2$ films had a significant change in the nonlinearity of the absorption at power densities near the damage threshold of the coating. IBS films were generally more linear than the e-beam films possibly due to differences in the types of defects or defect densities. There did not appear to be a measurable difference in the nonlinearity of the absorption between 511 and 578 nm for the same coating although the absorption at 578 nm was always lower than at 511 nm. Beam footprints were observed on some of the coatings by observing the condensation pattern on a coating after breathing on the part. The footprint was not permanent and could also not be observed with a number of tools including an optical microscope, AFM, spectrophotometer, and interferometer. The absorption at low power density was different after the coating was subjected to a higher power density. The nature of the existence of the beam footprints and the nonlinearity of the absorption requires further study.

Acknowledgments

The following companies and individuals have contributed coatings and their expertise to make this paper possible: Steve Browning at Optical Coating Laboratory, Inc., Marc VonGunten at Spectra-Physics, Components and Accessories, Bruce Perilloux at Coherent Components Group, Paul Szczepanski at Litton Airtron, Mohammad Tehrani at Litton Guidance and Control Systems, Ramin Lalezari at Research Electro-Optics, and Ken Scribner at General Optics. This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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Fig. 1. Experimental apparatus for measuring nonlinear absorption.

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Fig. 2. Change in absorption between low and high power densities for production HR coatings.

Fig. 3a. Temperature versus power density of e-beam development dye (570–630 nm) HR coatings. Tested at 578 nm.

Fig. 3b. Temperature versus power density of e-beam development copper (511 and 578 nm) HR coatings.

Fig. 4a. Temperature versus power density of IBS development dye (570–630 nm) HR coatings. Tested at 578 nm.

Fig. 4b. Temperature versus power density of IBS development copper (511 and 578 nm) HR coatings.

Fig. 5a. Nonlinear absorption characteristics for different incident angles and wavelengths for Vendor A.

Fig. 5b. Nonlinear absorption characteristics for different incident angles and wavelengths for Vendor B.

Fig. 6a. Absorption characteristics for a ramp cycle low-high-low in power density.

Fig. 6a. Absorption characteristics of a modified ramping cycle in power density.

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