- mechanisms in diamonds," *IEEE J. Quantum Electron.*, vol. QE-14, pp. 574-576, 1978.
- [14] I. M. Catalano, A. Cingolani, M. Ferrara, and M. Luga, "Multiphoton cross-section determination by means of luminescence experiments," *Opt. Acta*, vol. 27, pp. 625-635, 1980, and references cited therein.
- [15] E. P. Pokatilov and V. M. Fomin, "Multiphoton absorption by free carriers in semiconductors," *Phys. Status Solidi B*, vol. 73, pp. 553-564, 1976.
- [16] W. L. Smith, J. H. Bechtel, and N. Bloembergen, "Picosecond laser-induced breakdown at 5321 and 3547 Å: Observation of frequency-dependent behavior," *Phys. Rev. B*, vol. 12, p. 706, 1975.
- [17] E. W. Van Stryland, M. J. Soileau, A. L. Smirl, and W. E. Williams, "Pulse-width and focal-volume dependence of laser-induced breakdown," *Phys. Rev. B*, vol. 23, pp. 2144-2151, 1981.
- [18] A. Schmid, P. Bräunlich, and P. Rol, "Multiphoton-induced directional emission of halogen atoms from alkali halides," *Phys. Rev. Lett.*, vol. 20, pp. 1382-1385, 1975.
- [19] V. D. Frechette and C. Cline, "Stimulation of thermoluminescence in LiF by ruby laser light," *Appl. Phys. Lett.*, vol. 10, pp. 39-40, 1967.
- [20] P. J. Kelly, D. S. Ritchie, P. F. Bräunlich, A. Schmid, and G. W. Bryant, "Deformation of intense laser beams tightly focused inside NaCl: A comparison of the multiphoton-polaron and avalanche models of optical breakdown," presented at the 1980 Boulder Conf. High Laser Power Opt. Mater.; also, this issue, pp. 2027-2033.

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Pulsed Laser-Induced Damage to Thin-Film Optical Coatings—Part I: Experimental

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Abstract—We report a parametric investigation of the damage threshold and morphology of nine frequently employed dielectric coatings as a function of pulse length (5 and 15 ns), frequency (1.06, 0.53, 0.35, and 0.26 μm), and film thickness. A vidicon camera and computer were used to obtain real-time laser spatial profiles for each testing event. This technique greatly reduced the time required to obtain damage thresholds and enabled a large matrix of data to be obtained. The data and damage morphologies are discussed and several important conclusions are drawn concerning pulsed laser-induced damage to optical materials in thin-film form.

I. INTRODUCTION

THE limitations imposed by laser-induced damage to optical thin-film coatings have been recognized for a long time. High-power laser systems used in fusion and high-energy

systems for weapons are required to operate over long periods of time without appreciable degradation in performance. The optical coatings employed in these lasers have proven to be very expensive and greatly impact not only the design but the operation of these systems as well. The onset of even small damage sites within an optical coating can eventually degrade the beam quality sufficiently to prevent optimum laser operation. Although there have been many *a posteriori* efforts to develop improved coatings, insufficient progress has been made in elucidating the actual damage mechanism because the factors affecting laser-induced damage of coatings are not well understood.

In order to develop quality coatings, one needs to understand the fundamental damage processes and how they vary with frequency and pulse length [1]. The three most frequently proposed processes by which laser energy can be coupled into a thin-film material are avalanche ionization, multiphoton ionization, and absorption by impurities within the films. Avalanche ionization occurs when an electron in the conduction band of a material absorbs enough energy from the electromagnetic field to impact ionize a valence electron. The two electrons can undergo the same process to produce four

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conduction electrons, and so on. The number density of electrons in the conduction band grows exponentially with time until an absorbing plasma is formed. The plasma more efficiently absorbs energy from the electromagnetic field and catastrophic damage to the material occurs from the locally deposited energy. Multiphoton ionization can also produce a plasma; however, in this case the electrons are promoted from the valence to the conduction band by direct absorption of two or more photons. The number of photons required for each ionization depends on the bandgap of the material and the laser wavelength. Impurity-dominated damage is a thermal process and takes place when an impurity in the film absorbs enough laser radiation to produce melting or fracture of the host material or ensues from plasma formation in a manner described above.

An extensive amount of research has been conducted in an attempt to validate one or another of the theories. The research usually involves studying breakdown as a function of laser wavelength [2]–[15], pulse length [16]–[19], or film thickness [20]–[24]. The frequency dependence of laser damage has frequently been proposed as the main theoretical benchmark in distinguishing between the competing processes [2]–[15], [25]–[26]. This results in part because avalanche and multiphoton ionization theories predict conflicting laser wavelength dependencies, while previously proposed theories of impurity-dominated damage predict little or no wavelength dependence. However, if the Mie absorption coefficient is included in an impurity model, there is no longer a definitive distinction between the wavelength predictions of the multiphoton and impurity models. This lack of distinction arises because the films can only be tested at a few discrete points across the frequency spectrum (because of available lasers). Furthermore, both theories predict a general decrease in damage threshold with an increase in laser frequency.

In general, studies of breakdown as a function of only one parameter cannot be expected to uncover the dominant mechanism of laser damage. In fact, single parameter studies have often engendered controversy, a fact supported by numerous publications in which the conclusions drawn from experimental data are in total conflict [7], [9], [26], [27].

Unfortunately, it is not possible to correlate the results of past research efforts to obtain a multiparameter study of the breakdown process. Each individual experiment was performed on a different set of films and usually under sufficiently different experimental conditions. The investigated films varied in method of substrate preparation, film thickness, quality of starting materials, and deposition technique. The last two conditions are of vital importance in determining the type, size, and distribution of impurities in a film.

In the research reported herein, the experimental procedure employed was designed to study laser-induced damage to thin films as a function of laser wavelength, pulsewidth, film material, and film thickness.

II. EXPERIMENTAL

Experimental Arrangement

The dielectric coatings that were tested were selected to provide a wide range of material parameters (bandgaps, thermal properties, and refractive index). Additionally, different film

Fig. 1. Experimental setup for measuring the damage thresholds of optical thin-film coatings.

thicknesses were tested to provide data on the effects of different standing-field patterns in the dielectrics.

The experimental arrangement is shown in Fig. 1 and was designed to divide the laser beam into three separate paths. Path A contains more than 99.9 percent of the energy after it is reflected by a dichroic beamsplitter (location 1). This is the high-energy path and is used to irradiate the filmed side of the thin-film samples placed at location (3). Path B, which contains less than 0.1 percent of the energy was used to measure the spatial profile of the beam. Path C contains less than 0.01 percent of the energy and was used to measure the temporal profile of the laser pulse with a biplaner photodiode (location 7).

The dichroic beamsplitters (locations 1 and 2) shown in Fig. 1 were designed to reflect one of the harmonics ($R > 99.9$ percent) of $1.06 \mu\text{m}$ and transmit all others ($T > 99.9$ percent). Thus, there was a set of beamsplitters designed to reflect either 1.06 , 0.53 , 0.35 , or $0.26 \mu\text{m}$ radiation and transmit the others. They served the necessary function of filtering any of the unwanted harmonics from Paths A and B in the experiment. The beamsplitter at location (1) also acted as an attenuator and reduced the number of filters needed in front of the detectors at locations (4) and (7). This minimized the amount of spatial distortion introduced by filters.

Diagnostics and Calibration

The temporal behavior of the pulse was recorded with fast biplaner photodiode detectors. An ITT F112 detector was used to record the time profiles of 1.06 and $0.53 \mu\text{m}$ laser pulses; at 0.35 and $0.26 \mu\text{m}$, an ITT F4000 detector was used. The rise time of each detector, controlled by applying a bias voltage, was less than 0.5 ns . The output signal of the detector was then processed by a transient digitizer¹, a high-speed signal acquisition instrument that digitizes an input analog signal. The digitized signal is then displayed at a slower speed on a video monitor and transferred to a computer², which was programmed to calculate the full width at half maximum (FWHM) of the laser pulse. Fig. 2 shows the computer output for a 6 and 16 ns laser pulse.

¹Tektronix Model 7912.

²Tektronix Model CP 4165.

Fig. 2. Laser output of a 6 ns (upper trace) and a 16 ns (lower trace) pulse.

The spatial profile of the beam was obtained with an optical multichannel analyzer (OMA)³, which consists of a vidicon, an electronic camera, and a microprocessor. The active area of the vidicon is 12.5×12.5 mm. The purpose of the camera and the microprocessor is to scan an electron beam across the vidicon detector surface in any desired pattern and to store the resulting data in a usable format. During the experiment the vidicon target was scanned by the electron beam in horizontal paths or tracks, as shown in Fig. 3. Each track contained a maximum of 250 data points across the active surface area and a total of forty tracks could be programmed into the OMA.

The maximum resolution of the vidicon at the detector surface was $25 \times 25 \mu\text{m}$ (set by one electron-beam diameter) and was in practice not sufficient to adequately determine the laser profile. The laser spot size (FWHM) on the thin-film samples ranged between $170 \mu\text{m}$ at a $0.26 \mu\text{m}$ laser λ wavelength and $380 \mu\text{m}$ at a $1.06 \mu\text{m}$ laser wavelength. At $170 \mu\text{m}$, only about seven data points would span the total laser profile. To obtain a better resolution, the beam spot was magnified and reimaged on the vidicon. With sufficient magnification, the output of most of the photodiode elements in an area of 4×4 electron-beam diameters could be integrated together while still improving the effective profile resolution to $8.5 \times 8.5 \mu\text{m}$. Integrating the response over a larger vidicon area aided in reducing the background noise while increasing the dynamic range of the OMA. During an experiment each data point represented a physical area of $100 \times 100 \mu\text{m}$ at the vidicon surface.

³Princeton Applied Research Model 1215.

Fig. 3. Optical multichannel analyzer (OMA) scan pattern of the vidicon electron beam (upper drawing) and OMA output of a laser beam spatial profile (lower drawing).

The following technique was used to magnify and reimage the laser spot in the diagnostic path *B*. Location (5) (see Fig. 1) is the equivalent focal plane in path *B* to that in path *A* at the thin-film sample surface (location 3). The object distance is between the focal plane (location 5) and the lens at (location 6); the image distance is between the lens (location 6) and the vidicon (location 4). The lens (location 6) had a focal length of 10 mm and the object distance was set to produce a magnification of about 12. Exact determination of the magnification was made by placing a thin wire ($98.4 \mu\text{m}$) in the beam path at location (5) and measuring the diameter of the wire shadow on the vidicon. Two different vidicons were used in the experiment to cover the wavelength range, a PAR 1252 employed at 1.06 and $0.53 \mu\text{m}$ and a PAR 1254E at 0.53, 0.35, and $0.26 \mu\text{m}$. The overlap in wavelength at $0.53 \mu\text{m}$ between the two detectors provided a cross calibration of the two detectors. Both detectors were linear over the range of incident intensities and exhibited the same ± 7 percent uniformity in sensitivity.

It was found that at $0.26 \mu\text{m}$ the damage morphology of hafnium oxide (HfO_2) films showed a uniform removal of the thin-film materials from the substrate. This is in contrast to the isolated circular pits observed at longer wavelengths. This uniform removal appeared to reproduce the beam profile contour quite closely. Noting this, the laser beam was purposefully distorted in the near field to produce random "hot spots" of energy in the far field, and the HfO_2 samples were subjected to damaging pulses. The damage sites were photographed through a Nomarski microscope and the complete intensity

Fig. 4. Nomarski photograph of damage site on HfO_2 film and an energy contour map of the vidicon output (units are arbitrary).

profiles were recorded with the OMA in the diagnostic path B. The comparison of an actual damage site with the vidicon output is shown in Fig. 4. The contour lines of constant energy per unit area are drawn on the vidicon output. It is clear that the distributions are essentially identical and that areas of high material removal correspond to areas of high-energy deposition. This served as one of the checks to insure that the focal planes at locations (3) and (4) in Fig. 1 were equivalent. The vidicon allows real-time damage analysis with the same degree of accuracy as much slower photographic film techniques, and enables a very large amount of data to be taken in a short time [28].

The laser system⁴ employed in the study has an Nd-YAG oscillator and preamplifier, while an Nd^{3+} -doped silicate glass rod is used as a double-pass amplifier. Its TEM_{00} output has a maximum energy of 2 J in a 20 ns pulse. The laser was passively Q-switched with a saturable dye Bis-(4-dimethylamino-dithiobenzil)-nickel (BDN) placed in the oscillator cavity. The output pulse length of the laser was controlled by the dye concentration and the cavity length of the oscillator. Two different mirrors could be rotated into and out of the beam path to afford a variation in cavity length. A short cavity with the proper dye concentration produced the nominal 5 ns pulse used in the experiments. A longer cavity produced 15–18 ns pulses in a stable and reproducible manner.

KDP nonlinear crystals were employed for frequency multiplication and had a conversion efficiency of about 20 percent. The second harmonic of $1.06 \mu\text{m}$ was produced by frequency doubling using a KDP crystal, and the third harmonic at $0.35 \mu\text{m}$ was produced by sum frequency generation using a second KDP crystal with the first. This crystal combined the fundamental ($1.06 \mu\text{m}$) and the second harmonic ($0.53 \mu\text{m}$) to produce $\omega + 2\omega = 3\omega$ ($0.35 \mu\text{m}$). The fourth harmonic at $0.26 \mu\text{m}$ was obtained by frequency doubling the second harmonic. The temperature-stabilized crystals were angle tuned for index matching.

Samples

The thin-film target samples were mounted into a holder which allowed the samples to be rotated around an axis paral-

lel to the beam axis. In this way new sites on the target could be rotated into the beam path. The holder also had three-axis translational control so that the sample could be initially positioned and, once a circular ring was completely filled by laser shots, it could be moved to start a new row. For this experiment, a duplicated sample holder was made for the Nomarski microscope, which allowed the sample to be removed from the experiment and examined under the microscope for damage.

The thin-film materials used in the experiment were thorium fluoride (ThF_4), calcium fluoride (CaF_2), magnesium fluoride (MgF_2), silicon dioxide (SiO_2), hafnium oxide (HfO_2), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), zirconium dioxide (ZrO_2), and magnesium oxide (MgO). These films were chosen based on their use as dielectric coatings in the visible range and because their range of ultraviolet (UV) cutoffs (0.31 – $0.15 \mu\text{m}$) permitted an evaluation of multiphoton effects. Each film was deposited in five different optical thicknesses, which, at $1.06 \mu\text{m}$, were 1λ , $1/2\lambda$, $1/4\lambda$, $1/6\lambda$, and $1/8\lambda$, to within about ± 10 percent.

The absorptance was determined by

$$a = (Tu + Ru) - (Tc + Rc) \quad (1)$$

where Tu and Ru are the transmittance and reflectance of the uncoated samples and Tc and Rc are the same quantities obtained after coating. This method was used to assess the film absorptance and, although the procedure employed is not the most sensitive technique, it allows one to rank films qualitatively.

Each film was deposited by Perkin-Elmer on a fused silica substrate⁵ in a cryogenic vacuum system. All substrates were polished in an identical manner and cleaned before film deposition. In addition to absorptance measurements, each film was characterized by residual stress, light scattering, and index of refraction at or near each of the four wavelengths. The data for each of the thin-film samples is given in Tables I–V. Fig. 5 shows a typical stress measurement made on each sample.

Prior to each damage experiment the samples were cleaned with spectral grade ethanol. An ethanol-dampened lens tissue paper was placed on the film and carefully pulled across the surface and the residual ethanol film was allowed to evaporate.

Damage Threshold Determination

Visual inspection for damage using a Nomarski microscope at 500X was employed to determine the onset of damage. Magnifications of up to 500X allowed sites less than $1 \mu\text{m}$ in diameter to be easily identified and located.

A single test run on a specific dielectric thin-film sample at one pulsewidth and wavelength consisted of between 25 and 30 laser irradiations with a plane-polarized beam, 3° off normal, in a one-on-one format. After the first damaging shot, the next five shots were distributed uniformly over a range from very low energy to an energy at which a visual plasma could barely be detected. The five sites were examined under the microscope and the highest energy at which no damage occurred and the lowest energy at which damage occurred were noted. The next five shots were placed within this range

⁴Quantel Corporation Model NG-24B.

⁵Suprasil type T20.

TABLE I
MgF₂ AND ThF₄ THIN-FILM DEPOSITION AND OPTICAL PARAMETERS

MgF ₂ Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	λ ₁ (μm)	n(λ ₁)	λ ₂ (μm)	a(λ ₂)
Ultimate pressure = 8x10 ⁻⁷ torr		1100		0.035	0.35	1.539	1.339	1.167	0.0015
Deposition pressure = 2x10 ⁻⁶ torr		1101	1.102λ @ 1.06μm	0.034	0.36	0.946	1.351	0.789	0.0058
No O ₂ bleed		1202		0.036	0.17	0.668	1.390	0.585	0.0055
		1203	0.572λ @ 1.06μm	0.032	0.28	0.519	1.387	0.469	0.0067
		1404	0.558λ @ 0.530μm	0.032	0.040	0.425	1.392	0.393	0.0076
		1405		0.036	0.042	0.361	1.385	0.337	0.024
		1606	0.537λ @ 0.353μm	0.036	0.020	0.315	1.427	0.297	0.033
		1607		0.038	0.034	0.279	1.426	0.265	0.036
		1808		0.036	0.036	0.251	1.432		
		1809	0.419λ @ 0.265μm	0.034	0.030				

ThF ₄ Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	λ ₁ (μm)	n(λ ₁)	λ ₂ (μm)	a(λ ₂)
Ultimate pressure = 2x10 ⁻⁶ torr		2110	0.953λ @ 1.06μm	0.030	0.028	1.384	1.548	1.016	0.0049
Deposition pressure = 3x10 ⁻⁶ torr		2111		0.032	0.038	0.827	1.565	0.685	0.0080
No O ₂ bleed		2212	0.500λ @ 1.06μm	0.040	0.040	0.581	1.549	0.506	0.000
		2213		0.034	0.028	0.450	1.561	0.406	0.000
		2414	0.437λ @ 0.530μm	0.030	0.026	0.371	1.563	0.341	0.013
		2415		0.032	0.034	0.317	1.550	0.295	0.013
		2616		0.034	0.034	0.277	1.572	0.260	0.012
		2617	0.494λ @ 0.353μm	0.030	0.028	0.245	1.582		
		2818	0.483λ @ 0.265μm	0.034	0.028				
		2819		0.032	0.028				

TABLE II
CaF₂ AND Al₂O₃ THIN-FILM DEPOSITION AND OPTICAL PARAMETERS

CaF ₂ Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	λ ₁ (μm)	n(λ ₁)	λ ₂ (μm)	a(λ ₂)
Ultimate pressure = 1x10 ⁻⁶ torr		5140	0.964λ @ 1.06μm	0.035	0.050	1.328	1.292	1.022	0.0008
Deposition pressure = 5x10 ⁻⁶ torr		5141		0.035	0.042	0.821	1.331	0.696	0.0064
No O ₂ bleed		5242	0.443λ @ 1.06μm	0.030	0.030	0.591	1.393	0.522	0.0097
		5243		0.034	0.036	0.461	1.406	0.420	0.019
		5444		0.030	0.022	0.380	1.418	0.353	0.027
		5445	0.525λ @ 0.530μm	0.030	0.034	0.318	1.462		
		5646	0.535λ @ 0.353μm	0.030	0.020	0.279	1.475		
		5647		0.034	0.022				
		5848		0.032	0.020				
		5849	0.482λ @ 0.265μm	0.035	0.056				

Al ₂ O ₃ Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	λ ₁ (μm)	n(λ ₁)	λ ₂ (μm)	a(λ ₂)
Ultimate pressure = 1x10 ⁻⁶ torr		4130	0.972λ @ 1.06μm	0.036	0.06	1.35	1.570	1.03	0.005
Deposition pressure 1x10 ⁻⁵ torr		4131		0.034	0.046	0.836	1.621	0.684	0.007
O ₂ bleed at 1x10 ⁻⁵ torr		4232	0.491λ @ 1.06μm	0.034	0.038	0.588	1.621	0.515	0.006
		4233		0.036	0.046	0.459	1.648	0.414	0.009
		4434	0.580λ @ 0.530μm	0.036	0.056	0.379	1.652	0.348	0.020
		4435		0.034	0.06	0.323	1.661	0.302	0.042
		4636	0.554λ @ 0.353μm	0.034	0.038	0.284	1.653	0.268	0.086
		4637		0.034	0.042	0.254	1.658	0.243	0.151
		4838		0.036	0.042				
		4839	0.638λ @ 0.265μm	0.036	0.045				

TABLE III
ZrO₂ AND MgO THIN-FILM DEPOSITION AND OPTICAL PARAMETERS

MgO Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	$\lambda_1(\mu\text{m})$	$n(\lambda_1)$	$\lambda_2(\mu\text{m})$	$a(\lambda_2)$
Ultimate pressure = 2×10^{-6} torr		0190		0.036	0.040	1.507	1.608	1.118	0.000
Deposition pressure = 5×10^{-5} torr		0191	1.055λ @ 1.06μm	0.033	0.048	0.892	1.642	0.747	0.000
O ₂ bleed at 3×10^{-5} torr		0292	0.531λ @ 1.06μm	0.040	0.024	0.623	1.628	0.544	0.021
		0293		0.036	0.020	0.483	1.636	0.435	0.028
		0494		0.032	0.024	0.398	1.633	0.365	0.034
		0495	0.530λ @ 0.530μm	0.032	0.025	0.344	1.643	0.322	0.026
		0696		0.038	0.016	0.302	1.656	0.284	0.035
		0697	0.575λ @ 0.353μm	0.038	0.022	0.269	1.687	0.256	0.032
		0898		0.035	0.018	0.245	1.717		
		0899	0.551λ @ 0.265μm	0.036	0.020				

ZrO ₂ Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	$\lambda_1(\mu\text{m})$	$n(\lambda_1)$	$\lambda_2(\mu\text{m})$	$a(\lambda_2)$
Ultimate pressure = 3×10^{-6} torr		7160	1.058λ @ 1.06μm	0.037	0.012	1.52	1.749	1.122	0.000
Deposition pressure 5×10^{-5} torr		7161		0.038	0.016	0.896	1.856	0.753	0.000
O ₂ bleed at 3×10^{-5} torr		7262	0.571λ @ 1.06μm	0.035	0.014	0.633	1.985	0.551	0.0067
		7263		0.035	0.020	0.492	1.979	0.444	0.018
		7464	0.500λ @ 0.530μm	0.036	0.020	0.406	1.994	0.374	0.038
		7465		0.035	0.020	0.349	1.833	0.327	0.079
		7666	0.514λ @ 0.353μm	0.036	0.014	0.309	1.817	0.292	0.162
		7667		0.032	0.010	0.279	1.805	0.267	0.205
		7868		0.034	0.010	0.257	1.790	0.248	0.321
		7869	0.551λ @ 0.265μm	0.033	0.010				

TABLE IV
HfO₂ AND TiO₂ THIN-FILM DEPOSITION AND OPTICAL PARAMETERS

HfO ₂ Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	$\lambda_1(\mu\text{m})$	$n(\lambda_1)$	$\lambda_2(\mu\text{m})$	$a(\lambda_2)$
Ultimate pressure = 8×10^{-7} torr		9180	0.943λ @ 1.06μm	0.036	0.04	1.33	1.932	1.00	0.004
Deposition pressure 1×10^{-5} torr		9181		0.038	0.07	0.080	1.981	0.670	0.002
No O ₂ bleed		9282	0.472λ @ 1.06μm	0.036	0.07	0.582	2.003	0.510	0.001
		9283		0.034	0.05	0.457	2.038	0.412	0.012
		9484		0.036	0.07	0.381	2.030	0.350	0.032
		9485	0.508λ @ 0.530μm	0.036	0.07	0.326	2.109	0.306	0.067
		9686		0.034	0.07	0.289	2.148	0.274	0.107
		9687	0.623λ @ 0.353μm	0.036	0.07	0.262	2.201	0.250	0.192
		9888		0.038	0.06				
		9889	0.511λ @ 0.265μm	0.036	0.06				

TiO ₂ Deposition Analysis		Sample	Film Optical	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
Substrate temperature = 250°C		Number	Thickness	Uncoated	Coated	$\lambda_1(\mu\text{m})$	$n(\lambda_1)$	$\lambda_2(\mu\text{m})$	$a(\lambda_2)$
Ultimate pre-sure = 2×10^{-6} torr		6150	0.990λ @ 1.06μm	0.035	0.026	1.412	1.932	1.050	0.000
Deposition pressure = 5×10^{-5} torr		6151		0.038	0.014	0.857	1.848	0.725	0.000
O ₂ bleed at 5×10^{-5} torr		6252		0.035	0.020	0.606	1.732	0.541	0.031
		6253	0.498λ @ 1.06μm	0.035	0.020	0.485	1.825	0.444	0.065
		6454		0.040	0.022	0.411	0.804	0.387	0.133
		6455	0.418λ @ 0.530μm	0.036	0.026	0.369	1.739		
		6656		0.037	0.010				
		6657	0.524λ @ 0.353μm	0.035	0.010				
		6858	-λ/8 @ 1.06μm	0.034	0.010				
		6859		0.036	0.010				

TABLE V
SiO₂ THIN-FILM DEPOSITION AND OPTICAL PARAMETERS

SiO ₂ Deposition Analysis	Sample Number	Film Optical Thickness	Percent T.I.S. @ 6328μm		Refractive Index Data		Absorbance Data	
			Uncoated	Coated	λ ₁ (μm)	n(λ ₁)	λ ₂ (μm)	a(λ ₂)
Substrate temperature = 250°C	3120	0.963λ @ 1.06μm	0.030	0.036	1.303	1.387	1.007	0.000
Ultimate pressure = 2x10 ⁻⁶ torr	3121		0.052	0.032	0.819	1.418	0.715	0.0045
Deposition pressure = 5x10 ⁻⁵ torr	3222		0.034	0.022	0.585	1.453	0.531	0.0053
O ₂ bleed at 3x10 ⁻⁵ torr	3223	0.458λ @ 1.06μm	0.040	0.040	0.490	1.456	0.376	0.0052
	3424	0.395λ @ 0.530μm	0.042	0.030	0.412	1.428	0.320	0.032
	3425		0.032	0.022	0.346	1.413	0.281	0.082
	3626	0.492λ @ 0.353μm	0.035	0.028	0.298	1.397	0.251	0.171
	3627		0.40	0.020	0.265	1.398		
	3628		0.034	0.028	0.239	1.430		
	3829	0.498λ @ 0.265μm	0.036	0.022

Fig. 5. Stress in MgF₂ versus thin-film thickness.

and the process repeated. The damage threshold was assigned a value determined by

$$\text{energy/area} = \frac{E_n + E_d}{2} \quad (2)$$

where E_n is the highest energy density at which no damage occurs and E_d is the lowest energy density at which damage occurs. The spread in threshold is taken as

$$E_s = \frac{2|E_n - E_d|}{(E_n + E_d)} \quad (3)$$

The spread given by E_s is usually taken as a semiquantitative measure of the statistical nature of the breakdown process, but some care must be taken in this interpretation. The principal experimental errors are those arising from the energy measure-

ment, the vidicon response variation, and the measurement of the system magnification (spot size). These errors are expressed as fractional standard deviations and were 5, 7, and 5 percent, respectively. The fractional standard deviation (fsd) of the experiment can be determined from

$$\frac{\delta (\text{energy/area})}{\text{energy/area}} = \frac{\left[\left(\frac{\partial f}{\partial M} \right)^2 (\delta M)^2 + \left(\frac{\partial f}{\partial C} \right)^2 (\delta C)^2 + \left(\frac{\partial f}{\partial x} \right)^2 (\delta x)^2 \right]^{1/2}}{f(M, C, x)} \quad (4)$$

where M = energy (E)/vidicon counts (C) and is the calibration factor for the vidicon. The function $f(M, C, x)$ for this experiment is

$$f(M, C, x) = \frac{MC}{x^2} \quad (5)$$

where x is the effective element width, determined from the wire calibration. In using (4) it is assumed that the errors in M , C , and x are statistically independent. The final calculated fractional standard deviation was 13.1 percent.

The precision found in the damage thresholds by (3) was generally better than 13 percent. In fact, the average variation for the different materials ranged from 7.1 to 10.3 percent and the average for all of the materials was 9.2 percent. In this effort it was not possible to ascribe the variation of the breakdown threshold to the statistics of the damage, as opposed to the statistics of the experimental error.

III. RESULTS

Since the tested films were deposited in different thicknesses and covered a wide range of indexes of refraction, the standing electromagnetic wave formed inside the films had to be considered. The equation for calculating the standing-field patterns has been given by Newnam *et al.* [20]. The calculated ratio of the peak internal field to the peak incident field was squared to obtain the ratio for the peak energies per unit area internal to and incident onto the film. The measured energy/area incident onto the film was multiplied by this ratio to obtain the threshold internal energy densities shown in Tables VI-X.

TABLE VI
MgF₂ AND ThF₄, DAMAGE THRESHOLDS (J/cm²) AS A FUNCTION OF LASER WAVELENGTH, PULSE LENGTH, AND FILM THICKNESS
(THE CONVERSION FACTORS TO OBTAIN INCIDENT J/cm² ARE GIVEN IN THE PARENTHESES)

		1.06 μm		0.53 μm		0.353 μm		0.26 μm	
		5 ns	15 ns	5 ns	15 ns	5 ns	15 ns	5 ns	15 ns
		λ (at 1.06 μm)							
MgF ₂	1	9.2 $\pm$ 1.0 (0.96)	13.1 $\pm$ 0.9	3.6 $\pm$ 0.4 (0.97)	7.9 $\pm$ 0.8	3.6 $\pm$ 0.4 (0.97)	4.2 $\pm$ 0.3	2.9 $\pm$ 0.2 (0.98)	2.4 $\pm$ 0.4
	1/2	- (0.96)	15.8 $\pm$ 0.8	6.9 $\pm$ 1.0 (0.97)	12.1 $\pm$ 1.2	-	-	- (0.99)	2.0 $\pm$ 0.2
	1/4	11.5 $\pm$ 2.0 (0.94)	16.9 $\pm$ 1.2	7.2 $\pm$ 0.8 (0.98)	14.4 $\pm$ 0.4	2.7 $\pm$ 0.4 (0.96)	4.7 $\pm$ 0.1	1.9 $\pm$ 0.3 (0.98)	2.9 $\pm$ 0.3
	1/6	-	-	8.1 $\pm$ 0.8 (0.98)	14.4 $\pm$ 1.2	2.8 $\pm$ 0.2 (0.98)	5.7 $\pm$ 0.6	1.8 $\pm$ 0.1 (0.98)	3.0 $\pm$ 0.1
	1/8	27.4 $\pm$ 5.7 (1.05)	37.0 $\pm$ 6	8.9 $\pm$ 0.4 (0.98)	13.9 $\pm$ 1.8	2.3 $\pm$ 0.2 (0.96)	5.4 $\pm$ 0.5	1.3 $\pm$ 0.2 (0.99)	3.0 $\pm$ 0.1
ThF ₄	1	6.9 $\pm$ 0.0 (0.97)	12.2 $\pm$ 1.2	3.5 $\pm$ 0.4 (1.00)	8.9 $\pm$ 0.6	4.3 $\pm$ 0.0 (1.00)	5.6 $\pm$ 0.1	1.5 $\pm$ 0.1 (1.02)	2.1 $\pm$ 0.0
	1/2	- (0.96)	13.0 $\pm$ 1.8	6.1 $\pm$ 0.6 (0.98)	12.6 $\pm$ 3.5	-	-	- (1.00)	2.3 $\pm$ 0.3
	1/4	28.0 $\pm$ 5.6 (1.00)	34.7 $\pm$ 3.3	7.6 $\pm$ 0.8 (0.98)	19.0 $\pm$ 2.0	3.1 $\pm$ 0.2 (1.00)	7.4 $\pm$ 0.2	1.3 $\pm$ 0.0 (1.01)	-
	1/6	-	-	24.1 $\pm$ 7.0 (1.00)	42.1 $\pm$ 3.7	4.6 $\pm$ 0.5 (0.99)	8.6 $\pm$ 0.2	1.7 $\pm$ 0.1 (1.02)	3.8 $\pm$ 0.0
	1/8	30.5 $\pm$ 0.1 (0.98)	55.8 $\pm$ 5.5	29.2 $\pm$ 1.9 (1.00)	47.0 $\pm$ 3.8	7.9 $\pm$ 0.4 (1.00)	10.3 $\pm$ 1.4	1.8 $\pm$ 0.3 (1.00)	5.3 $\pm$ 0.2

TABLE VII
CaF₂ AND Al₂O₃, DAMAGE THRESHOLDS (J/cm²) AS A FUNCTION OF LASER WAVELENGTH, PULSE LENGTH, AND FILM THICKNESS
(THE CONVERSION FACTORS TO OBTAIN INCIDENT J/cm² ARE GIVEN IN THE PARENTHESES)

		1.06 μm		0.53 μm		0.353 μm		0.26 μm	
		5 ns	15 ns	5 ns	15 ns	5 ns	15 ns	5 ns	15 ns
		λ (at 1.06 μm)							
CaF ₂	1	12.8 $\pm$ 0.6 (0.94)	16.6 $\pm$ 1.3	5.0 $\pm$ 1.0 (1.00)	10.5 $\pm$ 0.7	3.2 $\pm$ 0.2 (1.00)	4.2 $\pm$ 0.1	2.7 $\pm$ 0.1 (1.03)	4.6 $\pm$ 0.8
	1/2	- (0.95)	19.2 $\pm$ 0.8	6.4 $\pm$ 0.0 (1.00)	11.9 $\pm$ 1.0	-	-	1.3 $\pm$ 0.5 (1.03)	-
	1/4	16.3 $\pm$ 1.5 (0.92)	27.2 $\pm$ 7	12.1 $\pm$ 1.0 (1.00)	18.0 $\pm$ 0.4	2.6 $\pm$ 1.0 (1.01)	4.9 $\pm$ 0.5	2.2 $\pm$ 0.0 (1.03)	3.6 $\pm$ 0.0
	1/6	-	-	9.9 $\pm$ 1.2 (0.90)	18.4 $\pm$ 0.5	5.9 $\pm$ 0.2 (1.01)	9.9 $\pm$ 0.2	2.3 $\pm$ 0.3 (1.02)	4.7 $\pm$ 0.6
	1/8	20.2 $\pm$ 2.8 (1.04)	31.6 $\pm$ 1.3	14.2 $\pm$ 0.6 (0.98)	22.8 $\pm$ 0.7	9.2 $\pm$ 0.6 (1.01)	18.0 $\pm$ 1.8	2.5 $\pm$ 0.0 (1.03)	5.8 $\pm$ 0.2
Al ₂ O ₃	1	11.4 $\pm$ 1.0 (0.94)	15.1 $\pm$ 2.3	- (0.93)	13.2 $\pm$ 1.3	3.2 $\pm$ 0.3 (0.93)	6.6 $\pm$ 1.5	1.5 $\pm$ 0.1 (0.94)	2.3 $\pm$ 0.1
	1/2	- (0.94)	16.3 $\pm$ 2.0	6.5 $\pm$ 0.0 (0.93)	11.7 $\pm$ 1.2	-	-	-	-
	1/4	13.5 $\pm$ 0.1 (0.98)	20.1 $\pm$ 1.8	7.3 $\pm$ 0.4 (0.94)	13.2 $\pm$ 0.8	2.7 $\pm$ 0.3 (0.95)	6.0 $\pm$ 0.6	2.2 $\pm$ 0.1 (0.99)	2.0 $\pm$ 0.2
	1/6	-	-	7.1 $\pm$ 1.0 (0.96)	13.8 $\pm$ 1.1	3.2 $\pm$ 0.5 (0.93)	5.1 $\pm$ 0.5	- (0.99)	2.5 $\pm$ 0.4
	1/8	20.0 $\pm$ 3.0 (0.97)	21.5 $\pm$ 0.2	8.5 $\pm$ 0.3 (0.97)	14.0 $\pm$ 2.4	2.9 $\pm$ 0.3 (0.93)	5.9 $\pm$ 0.6	1.7 $\pm$ 0.3 (0.97)	2.3 $\pm$ 0.3

TABLE VIII
ZrO₂ AND MgO, DAMAGE THRESHOLDS (J/cm²) AS A FUNCTION OF LASER WAVELENGTH, PULSE LENGTH, AND FILM THICKNESS
(THE CONVERSION FACTORS TO OBTAIN INCIDENT J/cm² ARE GIVEN IN THE PARENTHESES)

		1.06 μm		0.53 μm		0.353 μm		0.26 μm	
		5 ns	15 ns	5 ns	15 ns	5 ns	15 ns	5 ns	15 ns
		λ (at 1.06 μm)							
ZrO ₂	1	8.3 $\pm$ 0.8 (0.78)	-	4.4 $\pm$ 0.6 (0.93)	-	1.1 $\pm$ 0.0 (0.95)	-	0.8 $\pm$ 0.0 (0.93)	0.7 $\pm$ 0.06
	1/2	10.0 $\pm$ 0.5 (0.84)	-	-	-	1.5 $\pm$ 0.5 (0.95)	-	- (0.96)	0.5 $\pm$ 0.1
	1/4	10.0 $\pm$ 1.2 (0.94)	9.5 $\pm$ 0.1	6.7 $\pm$ 0.1 (0.76)	6.2 $\pm$ 0.8	1.3 $\pm$ 0.1 (0.94)	2.2 $\pm$ 0.0	0.5 $\pm$ 0.2 (0.90)	-
	1/6	-	-	4.2 $\pm$ 0.2 (0.86)	4.9 $\pm$ 0.6	1.4 $\pm$ 0.0 (0.83)	-	0.9 $\pm$ 0.2 (0.94)	1.1 $\pm$ 0.2
	1/8	10.6 $\pm$ 0.6 (0.89)	10.9 $\pm$ 1.6	6.0 $\pm$ 0.3 (0.92)	6.9 $\pm$ 0.2	2.7 $\pm$ 0.2 (0.86)	2.6 $\pm$ 0.1	0.7 $\pm$ 0.0 (0.88)	1.0 $\pm$ 0.05
MgO	1	-	-	- (0.95)	11.4 $\pm$ 2.2	-	-	-	-
	1/2	10.2 $\pm$ 0.1 (0.92)	9.8 $\pm$ 0.4	6.1 $\pm$ 0.9 (0.94)	10.0 $\pm$ 1.2	-	-	-	-
	1/4	14.9 $\pm$ 0.9 (0.97)	15.0 $\pm$ 1.0	8.8 $\pm$ 0.6 (0.93)	16.2 $\pm$ 0.5	2.8 $\pm$ 0.3 (0.98)	3.9 $\pm$ 0.0	1.3 $\pm$ 0.1 (0.95)	2.3 $\pm$ 0.1
	1/6	-	-	7.8 $\pm$ 0.8 (0.95)	14.3 $\pm$ 1.0	3.1 $\pm$ 0.4 (0.95)	5.5 $\pm$ 0.8	2.1 $\pm$ 0.0 (0.98)	2.9 $\pm$ 0.2
	1/8	12.2 $\pm$ 0.5 (0.95)	12.8 $\pm$ 0.7	10.6 $\pm$ 1.8 (0.98)	14.2 $\pm$ 0.7	2.8 $\pm$ 0.7 (0.95)	4.3 $\pm$ 0.4	1.6 $\pm$ 0.4 (0.93)	2.6 $\pm$ 0.4

TABLE IX
HfO₂ AND TiO₂ DAMAGE THRESHOLDS (J/cm²) AS A FUNCTION OF LASER WAVELENGTH, PULSE LENGTH, AND FILM THICKNESS
(THE CONVERSION FACTORS TO OBTAIN INCIDENT J/cm² ARE GIVEN IN THE PARENTHESES)

		1.06 μm		0.53 μm		0.353 μm		0.26 μm	
		5 ns	15 ns	5 ns	15 ns	5 ns	15 ns	5 ns	15 ns
λ (at 1.06 μm)									
HfO ₂	1	12.8 $\pm$ 1.3 (0.79)	-	3.9 $\pm$ 0.8 (0.77)	-	0.9 $\pm$ 0.05 (0.77)	-	1.2 $\pm$ 0.07 (0.94)	1.1 $\pm$ 0.09
	1/2	-	-	5.0 $\pm$ 0.5 (0.76)	-	-	-	-	-
	1/4	8.5 $\pm$ 1 (0.91)	13.1 $\pm$ 0.5	1.7 $\pm$ 0.6 (0.75)	9.2 $\pm$ 1.2	3.4 $\pm$ 0.2 (0.93)	4.3 $\pm$ 0.9	0.7 $\pm$ 0.07 (0.8)	1.4 $\pm$ 0.08
	1/6	-	-	0.4 $\pm$ 0.04 (0.81)	0.7 $\pm$ 0.07	0.7 $\pm$ 0.08 (0.83)	-	0.3 $\pm$ 0.0 (0.82)	0.2 $\pm$ 0.0
	1/8	5.4 $\pm$ 0.2 (0.83)	7.9 $\pm$ 0.6	3.4 $\pm$ 0.1 (0.93)	5.4 $\pm$ 0.4	1.6 $\pm$ 0.03 (0.85)	2.7 $\pm$ 0.2	0.4 $\pm$ 0.02 (0.71)	0.7 $\pm$ 0.02
TiO ₂	1	8.8 $\pm$ 1 (0.81)	-	4.3 $\pm$ 1.3 (0.89)	-	0.1 $\pm$ 0.01 (0.97)	-	-	-
	1/2	11.4 $\pm$ 1 (0.8)	-	4.8 $\pm$ 0.4 (0.86)	-	-	-	-	-
	1/4	14.9 $\pm$ 0.4 (0.93)	13.8 $\pm$ 2	6.6 $\pm$ 0.3 (0.85)	11.8 $\pm$ 0.4	0.1 $\pm$ 0.01 (0.96)	-	-	-
	1/6	-	-	5.2 $\pm$ 0.5 (0.91)	8.8 $\pm$ 0.3	0.1 $\pm$ 0.0 (0.90)	-	-	-
	1/8	10.0 $\pm$ 1 (0.92)	9.8 $\pm$ 0.7	6.4 $\pm$ 1.4 (0.95)	10.8 $\pm$ 0.1	0.6 $\pm$ 0.0 (0.95)	-	-	-

TABLE X
SiO₂ DAMAGE THRESHOLDS (J/cm²) AS A FUNCTION OF LASER WAVELENGTHS, PULSE LENGTH, AND FILM THICKNESS
(THE CONVERSION FACTORS TO OBTAIN INCIDENT J/cm² ARE GIVEN IN THE PARENTHESES)

		1.06 μm		0.53 μm		0.353 μm		0.26 μm	
		5 ns	15 ns	5 ns	15 ns	5 ns	15 ns	5 ns	15 ns
λ (at 1.06 μm)									
SiO ₂	1	-	-	-	-	-	-	-	-
	1/2	-	-	7.8 $\pm$ 0.5 (1.03)	-	-	-	-	-
	1/4	22.4 $\pm$ 0.0 (1.00)	45.0 $\pm$ 5.4	9.4 $\pm$ 1.4 (1.03)	19.6 $\pm$ 1.1	5.6 $\pm$ 0.6 (1.00)	10.7 $\pm$ 0.2	0.9 $\pm$ 0.1 (0.95)	1.6 $\pm$ 0.2
	1/6	-	-	-	-	-	-	1.3 $\pm$ 0.1 (0.96)	-
	1/8	41.4 $\pm$ 0.4 (1.03)	47.3 $\pm$ 4.7	21.1 $\pm$ 2.7 (1.03)	48.4 $\pm$ 2.0	- (0.99)	13.5 $\pm$ 1.4	2.2 $\pm$ 0.2 (0.97)	2.5 $\pm$ 0.3

The numbers shown after the data represent the spread in the experimental data given by (3) in Section II. The interpretation of these numbers was discussed at the end of the last section and should not be confused with the experimental error, which was 13.1 percent.

Damage Threshold Changes with Film Thickness

Newnam [20] reported a dependence of the breakdown threshold of TiO₂ films on film thickness. This dependence was attributed to the different field strengths in the films and the thresholds were found to correlate with the internal field strengths. It can be seen in the reported data for TiO₂, which has been corrected for the internal-field strength, that there is very little difference in thresholds. The fact that the film thickness dependence of damage to TiO₂ disappears when the data is corrected for the internal-field strength would seem to support the conclusions of Newnam. However, an examination of all the data for the different film materials reveals that there remains an additional thickness dependence of damage in many of the materials after standing-field corrections are made. For example, at 15 ns and 1.06 μm , the 1/8 λ ThF₄ film damage threshold is more than four times greater than the 1 λ -thick film. Since the data has been corrected for the inter-

nal-field strengths, this film thickness dependence of damage is unexplained.

All of the fluoride films show a marked increase in damage threshold with decrease in film thickness. This phenomenon is usually weaker and in some cases apparently nonexistent in the oxide films. For example, Al₂O₃, MgO, and SiO₂ all had a slight film thickness dependence of damage; however, ZrO₂, HfO₂, and TiO₂ showed essentially no dependence.

The film thickness dependence of damage is further complicated by changes in the laser wavelength and pulse length. All of the data shows that the thickness dependence in fluorides is strong at 1.06 μm for 15 ns FWHM laser pulses and becomes progressively weaker at shorter wavelengths and pulse lengths. In fact, there is no thickness dependence in ThF₄ at 0.26 μm for 5 ns pulse lengths. SiO₂, Al₂O₃, and MgO damage thresholds exhibited a weaker but similar trend with changes in wavelength and pulse length.

Damage Threshold Dependence on Pulse Length

The MgO and TiO₂ thin-film damage contain another important feature. There is essentially no laser pulse length dependence in the TiO₂ films at 1.06 μm ; however, at 0.53 μm the damage threshold is higher for 15 ns than for 5 ns laser pulses.

The MgO films behave the same at 0.53, 0.35, and 0.26 μm in that they show a pulsewidth dependence at these wavelengths, but not at 1.06 μm .

The fluoride films show a much stronger dependence of damage on pulsewidth at 0.26 μm than the oxides. In fact Al_2O_3 , SiO_2 , and ZrO_2 film data indicate a weak laser pulsewidth dependence at 0.26 μm . The only oxide films which exhibit a marked time dependence at 0.26 μm are MgO and HfO_2 .

Damage Threshold Dependence on Wavelength

The most important aspect of the data is the information relating a change in damage threshold with laser wavelength. In most cases the threshold drops as the laser wavelength decreases. There are a few exceptions to this observation; at 15 ns the $1/8\lambda$ ($\lambda = 1.06 \mu\text{m}$) TiO_2 and the $1/8\lambda$ and $1/4\lambda$ MgO films do not decrease in damage threshold between 1.06 and 0.53 μm , but at 5 ns the damage thresholds of all the films decrease as the laser wavelength decreases. In no case does the threshold increase as one proceeds to shorter wavelengths.

The variation of damage threshold with wavelength can also be seen to be a function of the film thickness. For example, the $1/8\lambda$ CaF_2 film decreases by a factor of about fifteen in going from 1.06 to 0.26 μm , whereas the 1λ film only decreased by a factor of about three. This phenomenon is seen to hold true for all of the materials except TiO_2 (which was not tested at 0.26 μm), ZrO_2 , and MgO.

To summarize the observations made to this point, we can say that in general the films exhibit a thickness dependence on damage threshold which cannot be explained by the different internal electromagnetic fields in the films. This influence of the film thickness on damage is further affected by the laser pulsewidth and wavelength. This can be clearly seen in the data on the dependence of damage threshold on laser pulsewidth. The phenomenon has been reported in other research [3], [19], [21]–[25]. The present effort is unique in that a large number of different thin-film materials (nine) have been tested at two different laser pulsewidths over a range of different film thicknesses and wavelengths.

The pulse length dependence is stronger for the fluoride films than for the oxide films. We note, for example, that at 1.06 μm the CaF_2 data show a consistent increase in damage threshold at all film thicknesses in going from 5 to 15 ns. The same behavior is less marked in the Al_2O_3 , TiO_2 , MgO, or ZrO_2 data. The large matrix of data obtained should aid in evaluating the physical causes of the influence of laser pulsewidth on the breakdown threshold.

Observations on Damage Morphology

Material, wavelength, pulse length, and film thickness are all important parameters which have been observed to influence the damage threshold of thin films. There is another parameter which can be utilized to provide clues to the nature of the breakdown mechanism. This is the observation of the damage site morphology. In Fig. 6 a sequence of four damage sites for MgO is shown. Each photograph was taken on the same MgO film at the same magnification. The damage sites were produced by 5 ns laser pulses at wavelengths of 1.06, 0.53, 0.35, and 0.26 μm . The two most obvious features of the

Fig. 6. MgO damage morphology due to laser radiation at 1.06 μm (a), 0.56 μm (b), 0.35 μm (c), and 0.26 μm (d).

morphology are the decrease in damage-site size and increase in the number density of sites as the laser wavelength decreases. The same general behavior of the morphology was observed in all the thin films, although the change was not as dramatic in the oxide films as in the fluoride films, except for MgO.

At 0.26 μm , there was an additional change in the oxide film damage morphology. At the longer wavelengths the morphology was that of individual cratered sites, as shown in Fig. 6. At 0.26 μm , the damage morphology became more uniform in appearance. The damage at 0.26 μm for Al_2O_3 , SiO_2 , HfO_2 , and ZrO_2 is shown in Fig. 7. For completeness, the damage sites in ThF_4 at different wavelengths are shown in Fig. 8. The individual crater sites, which are evident in the damage at 0.26 μm , were observed for all fluoride films and MgO as opposed to the uniform and diffuse damage in the remainder of the oxide films tested.

An additional point concerning the TiO_2 films involves the absorption edge of bulk TiO_2 which is at 0.3 μm , close to the 0.35 μm laser radiation. It can be seen from the data that the damage threshold drops by more than an order of magnitude in going from 0.53 to 0.35 μm . The measured absorbance is a factor of four higher at 0.35 than at 0.53 μm ; a similar change for the other oxides occurs between 0.35 and 0.26 μm . At 0.26 μm , the laser radiation photon energy is well past the absorption edge of TiO_2 and damage can be ascribed to linear absorption. The damage morphology of TiO_2 goes from single site to uniform morphology just as the other oxide films; however, in the case of TiO_2 , the change occurs at 0.35 μm rather than at 0.26 μm . The TiO_2 damage at 0.35 μm looks the same as the ZrO_2 damage at 0.26 μm shown in Fig. 7. Between 1.06 and 0.53 μm TiO_2 films show the same decrease in damage-site size and increase in site density as the other materials.

Summary of Observations

The observations made above can be summarized as follows:

1) In general, films exhibit a damage threshold which depends on film thickness in a way that cannot be explained totally by internal electromagnetic fields.

Fig. 7. Laser damage from 0.26 μm radiation to TiO_2 (a), HfO_2 (b), ZrO_2 (c), and SiO_2 (d).

Fig. 8. Laser damage to ThF_2 with 1.06 μm (a), 0.53 μm (b), 0.35 μm (c), and 0.26 μm (d) laser radiation.

2) The fluoride films show a stronger dependence of damage threshold on film thickness than the oxide films.

3) For MgO and TiO_2 , the damage thresholds have no pulse-width dependence at 1.06 μm but do at shorter wavelengths.

4) The damage thresholds of fluoride films show a stronger laser pulsewidth dependence than those of oxide films.

5) ZrO_2 damage thresholds have essentially no pulsewidth dependence at any wavelength.

6) There is essentially no film thickness dependence of damage in ZrO_2 films.

7) Al_2O_3 , SiO_2 , and ZrO_2 damage thresholds exhibit little or no pulsewidth dependence at 0.26 μm .

8) MgO and HfO_2 damage thresholds have a marked time dependence of 0.26 μm .

9) The thin-film damage thresholds decrease with decreasing laser wavelength.

10) In general, the film thickness dependence becomes weaker at shorter wavelengths. That is, the decrease in damage threshold is more pronounced for thin films than for thick films.

11) The individual damage-site size decreases and the num-

ber density of damage sites increases with decreasing laser wavelength.

12) The change in site size with wavelength is not as pronounced for the oxides as for fluorides except in the case of MgO .

13) The damage morphology of most oxide films changes at 0.26 μm from individual craters to a uniform damage area.

14) The damage morphology of TiO_2 films changes at 0.35 μm .

15) The damage morphology of the $1/6\lambda$ ($\lambda = 1.06 \mu\text{m}$) HfO_2 film is the same at all wavelengths and looks similar to the 0.26 μm damage morphology of the oxides shown in Fig. 6. Also, the damage threshold of the $1/6\lambda$ HfO_2 is much lower than any other HfO_2 film.

IV. CONCLUSIONS

The damage thresholds of thin-film coatings to laser radiation represent a complex interplay among material properties, laser wavelength, pulsewidth, and film thickness, among others. Presented here is the first comprehensive self-consistent body of carefully obtained data on extremely well characterized samples. All of these many parameters are varied in such a way that the relative effect of each upon the damage threshold may be unambiguously assessed. This data should enable a rational test of competing theoretical models for pulsed laser-induced damage processes in dielectric thin films. We will test various theoretical models against this data in the following paper.

REFERENCES

- [1] A. H. Guenther, *10th Symp. Optical Materials High Power Lasers*, Introduction, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 541, 1978.
- [2] A. G. Molchanov, "Development of avalanche ionization in transparent dielectrics under the action of a light pulse," *Sov. Phys.—Solid State*, vol. 12, no. 3, pp. 749–750, 1970.
- [3] A. S. Epifanov, "Avalanche ionization induced in solid transparent dielectrics by strong laser pulses," *Sov. Phys.—JETP*, vol. 40, no. 5, pp. 897–902, 1974.
- [4] W. L. Smith, J. H. Bechtel, and N. Bloembergen, "Picosecond laser-induced breakdown at 5321 and 3547 Å: Observation of frequency dependent behavior," *Phys. Rev. B*, vol. 15, no. 8, pp. 4039–4055, 1976.
- [5] A. V. Vinogradov and F. S. Faizullov, "Role of many-photon and impact ionization in the breakdown of dielectrics by picosecond laser pulses," *Sov. J. Quantum Electron.*, vol. 7, pp. 650–652, 1977.
- [6] A. Schmid, P. Kelly, and P. Braunlich, "Multiphoton theory of optical breakdown in alkali halides," A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication, 1977, pp. 465–472.
- [7] A. S. Epifanov, A. A. Manenkov, and A. M. Prokhorov, "Frequency and temperature dependences of avalanche ionization in solids under the influence of an electromagnetic field," *Sov. Phys.—JETP Lett.*, vol. 21, no. 8, pp. 223–224, 1975.
- [8] B. G. Gorshkov, Yu K. Danileiko, A. S. Epifanov, V. A. Lobachev, A. A. Manenkov, and A. V. Sidorin, "Laser induced breakdown of alkali halide crystals," *Sov. Phys.—JETP*, vol. 45, no. 3, pp. 612–618, 1977.
- [9] M. J. Soileau and M. Bass, "Optical breakdown in NaCl and KCl from 0.53 to 10.6 μm ," *Appl. Phys. Lett.*, vol. 35, no. 5, pp. 370–371, 1979.
- [10] D. W. Fradin and E. Yablonovitch, "Comparison of laser induced bulk damage in alkali halides at 10.6, 1.06 and 0.69 microns," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 372, 1972, pp. 27–39.
- [11] M. Bass and H. H. Barrett, "Laser induced damage probability at 1.06 and 0.69 μm ," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 372, 1972, pp. 58–69.

- [12] J. O. Porteus, M. J. Soileau, H. E. Bennett, and M. Bass, "Laser damage measurements at CO₂ and DF wavelengths," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 435, 1975, pp. 207-215.
- [13] B. E. Newnam and D. H. Gill, "Spectral dependence of damage resistance of refractory oxide optical coatings," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 362, 1976, pp. 292-300.
- [14] J. O. Porteus, T. M. Donovan, J. L. Jernigan, and W. N. Faith, "Multithreshold evaluation of 100 nanosecond pulsed laser damage to coating materials at 2.7 and 3.8 μm wavelengths," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 541, 1978, pp. 202-211.
- [15] B. E. Newnam and D. H. Gill, "Ultraviolet damage resistance of laser coatings," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 541, 1978, pp. 190-201.
- [16] J. M. McMahon, "Damage measurements with sub-nanosecond pulses," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 372, 1972, pp. 100-103.
- [17] V. Wang, C. R. Guiliano, and B. Garcia, "Single and multilongitudinal mode damage in multilayer reflectors at 10.6 μm as a function of spot size and pulse duration," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 435, 1975, pp. 216-229.
- [18] J. R. Bettis, R. A. House, II, and A. H. Guenther, "Spot size and pulse dependence on laser induced damage," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 462, 1976, pp. 338-345.
- [19] D. Milam, "1064-nm laser damage threshold of polished glass surfaces as a function of the pulse duration and surface roughness," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 541, 1978, pp. 164-167.
- [20] B. E. Newnam, D. H. Gill, and G. Faulkner, "Influence of standing-wave fields on the laser damage resistance of dielectric films," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 435, 1975, pp. 254-271.
- [21] J. H. Apfel, J. S. Matteucci, B. E. Newnam, and D. H. Gill, "The role of electric field strength in laser damage of dielectric multilayers," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 462, 1976, pp. 301-309.
- [22] L. G. DeShazer, B. E. Newnam, and K. M. Leung, "The role of coating defects in laser induced damage to dielectric thin films," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 387, 1973, pp. 114-123.
- [23] J. H. Apfel, "Further studies of the role of electric field strength in laser damage of dielectric layers," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 509, 1977, pp. 251-254.
- [24] D. H. Gill, B. E. Newnam, and J. McLead, "Use of non-quarter wave designs to increase the damage resistance of reflectors at 532 and 1064 nanometers," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 532, 1977, pp. 260-270.
- [25] A. A. Manenkov, "New results on avalanche ionization as a laser damage mechanism in transparent solids," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication, 1978, pp. 455-464.
- [26] M. J. Soileu, M. Bass, and E. W. Van Stryland, "Frequency dependence of breakdown fields in single crystal NaCl and KCl," in *Laser Induced Damage in Optical Materials*, A. J. Glass and A. H. Guenther, Eds. US GPO Washington, DC: NBS Special Publication 541, 1978, pp. 309-317.
- [27] I. V. Aleshin, A. A. Doman, and Ya. A. Imas, "Optical breakdown of glass by a sharply focused laser beam," *Sov. Tech.-Phys. Lett.*, vol. 4, no. 7, pp. 348-349, 1978.
- [28] W. L. Smith, A. J. DeGroot, and M. J. Weber, "Silicon vidicon system for measuring laser intensity profiles," *Appl. Opt.*, vol. 17, no. 24, pp. 3938-3944, 1978.

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