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Large Area Laser Conditioning of Dielectric Thin Film Mirrors

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The laser conditioning of dielectric thin film HR coatings has been studied as a practical method for the improvement of the damage thresholds of large area (1.1 m dia.) high power 1064 nm laser mirrors on the LLNL 120 kJ, 100 TW Nova laser system. Both HfO_2/SiO_2 and ZrO_2/SiO_2HR coatings were conditioned by rastering with a small (~0.2 mm) diameter beam from a pulsed (18 Hz, 8 ns) Nd-YAG laser (1064 nm). The samples were rastered at various fluences below the unconditioned damage threshold and subsequently damage tested. Large area conditioning studies were also performed using a large aperture beam of the Nova laser. The laser conditioning effect was found to be permanent. Improvements in damage threshold due to conditioning were as high as a factor of 2.7 and were dependent on the conditioning parameters. A model for the conditioning effect is proposed based on the emptying of electronic defect levels within

1. Introduction

The cost of optical components for high power laser systems, such as those used in fusion energy research, increases dramatically with the size of the optic. In order to keep the power delivered by the laser high while keeping the cost of the system low, high damage threshold optical materials are needed. Presently, increases in the output of the 120 kJ Nova laser system used for inertial confinement fusion research at Lawrence Livermore National Laboratory are limited in part by the damage threshold of the dielectric multilayer turning mirrors. These mirrors have diameters of 96 and 109 cm and are deposited on 16 cm thick BK-7 glass substrates.

Over the last two decades many researchers have reported that the laser damage threshold of both bulk [1-5] and thin film [4-10] optical materials can be increased by first illuminating the

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material at a sub-threshold fluence. Threshold increases have been observed for photon wavelengths ranging from 10.6 μm [5] to 0.248 μm [6]. This sub-threshold illumination has been referred to as "laser conditioning" or "laser annealing". Increases in damage thresholds by a factor of three are typical but increases as high as a factor of 10 have also been reported [5]. A few studies have attempted to determine which conditioning parameters provide the largest increase in the damage threshold. Arenberg et al. [9] have studied the laser conditioning effect as a function of the conditioning fluence for 1064 nm/532 nm antireflection coatings of undisclosed composition. Laser conditioning at 1064 nm increased the 1064 nm damage threshold by 40% but did not influence the 532 nm threshold. The probability of damage occurring at fluences slightly above the unconditioned damage threshold was found to decrease as the conditioning fluence approached the unconditioned damage threshold. The conditioning effect in Arenberg's study was also found to last only 4-5 days. The 532 nm damage threshold was not influenced by conditioning at either 532 nm or 1064 nm. The authors suggested that the conditioning effect was due to removal of water from the films. Stewart et al. [8] have studied the effect of rastering single layer dielectric films with a CW CO_2 laser. For fluences ranging from 25 W/cm^2 to 100 W/cm^2 they observed indications, from both optical and structural measurements, of recrystallization of the dielectric materials. They reported a correlation between the crystallization and a small (< 40%) increase in the damage threshold for thin films of rf-sputtered Ta_2O_5 and sol-gel TiO_2. Areas conditioned in these earlier studies were typically the size of the damage test laser beam, no larger than a few mm in diameter. To our knowledge, the only direct test of the practicallity of laser conditioning large area optical materials was a study of KDP crystals [3]. It was shown that the 1064 nm damage threshold of KDP could be increased by rastering a large area of the crystal with a small area beam from a rep-rated laser. The conditioning effect was observed for sub-threshold fluences of either 1064 or 350 nm light. In contrast to Arenberg's AR coatings, the conditioning effect on KDP has been shown to be permanent over more than a month [2]. Clearly the laser conditioning phenomena is complex and generalizations must be made carefully.

This paper presents the preliminary results of a study to determine how the laser conditioning effect could be used to increase the damage threshold of the Nova turning mirrors. Laser conditioning of 1064 nm dielectric high reflective coatings was first reported by Wilder and Thomas [10]. In a companion paper in the present volume, Wolfe et al. [11] has reported on the influence of materials and coating design on the increase in the laser damage threshold due to laser conditioning. Here we concentrate on large area conditioning studies on two types of HR coatings: a) the present Nova mirrors: ZrO_2/SiO_2 reflectors designed for 1064, 532, and 355 nm light, and b) R&D HfO_2/SiO_2 reflectors designed for 1064 nm light. Both coatings were deposited by OCLI* using electron beam deposition in a 3-m diameter planetary coater. This production coater is designed to handle up to three 1-m diameter substrates and was purchased and installed by LLNL during the construction of the Nova laser. The ZrO_2/SiO_2 coatings were made in 1983 while the HfO_2/SiO_2 coatings were made in 1989. The two principal large area conditioning methods examined were i) rastering a small area beam back and forth across the sample surface, and ii) illuminating a large area optic using a large aperture laser beam such as that available on the Nova laser. Laser conditioning parameters examined included the

*Optical Coatings Laboratories Inc., Santa Rosa, Ca illumination fluence and the number of illumination pulses. We also performed preliminary conditioning tests using broadband flashlamps.

Several mechanisms have been proposed in the literature to explain the conditioning phenomenon observed for bulk materials, surfaces, and thin films. These mechanisms include the desorption of water or other contaminants from the surface [7,9], melting or recrystallization of structural defects [8], and the slow volatilization of absorbing inclusions from within the films [10]. Wolfe et al. [11] has experimentally demonstrated that for the HR coatings of interest here the first two of these mechanisms do not seem to apply. Edwards et al. [12] has similarly presented arguments against the applicability of the absorbing inclusion model to damage in the Nova mirrors of interest here. We instead propose that the conditioning effect in the dielectric HR coatings is related to the emptying of electronic defect states in the bandgap. These electronic defects serve as the source of conduction band electrons required to produce damage in the dielectric layers. We will discuss this damage/conditioning mechanism in detail in Section 6.

2. Standard damage testing of present and R&D Nova mirror coatings:

All damage tests were made using a 1064 nm Nd:YAG laser with a beam diameter of 0.2 mm at 80% of the peak fluence. The pulse length was 8 ns and the repetition rate was 18 Hz. The damage threshold was chosen as the lowest fluence which caused a light flash at the coating surface and a visible change in the oxide surface properties, as determined by the sensitive "breath test" [13]. The breath test relies on water vapor condensation patterns to identify damage areas. The damage thresholds obtained in this way are in good agreement with those obtained using x100 Nomarski microscopy. Two types of damage tests were performed using the 18 Hz laser:

S-on-1: multiple shots of the same fluence at a single site.

R-on-1: multiple shots of increasing (ramped) fluence at a single site.

For the R-on-1 tests the laser fluence was increased at ~0.2 J/sec until damage was observed. This rate corresponds to a fluence increment per shot of ~0.013 J/cm². For S-on-1 tests the samples were illuminated for about 30 seconds (~530 shots) unless damage was observed, in which case illumination was stopped immediately. In nearly all S-on-1 tests where damage was observed it occurred during the first couple of pulses. The damage threshold values reported are ±15%. Each reported threshold represents the average of 1 to 4 tests.

S-on-1 damage tests showed that the two HR coatings studied had similar thresholds (fig. 1). The thresholds at 8 ns were 12 J/cm² for the present Nova coating and 16 J/cm² for the R&D coating. These values are essentially the same given the accuracy of the measurement. The R-on-1 tests, however, produced quite different results for the two coatings. For the present Nova coatings the R-on-1 threshold was 18.5 J/cm², a factor of 1.5 increase over the S-on-1 (i.e. unconditioned) threshold. For the new coatings the R-on-1 threshold was 44 J/cm², corresponding to a factor of 2.7 increase in the damage threshold. In most cases the damage in these coatings is observed to occur at microscopic (< 50 μm) defects in the coatings. (The 8 ns R-on-1 and S-on-1 thresholds reported here for the R&D coatings agree well with values of 16 (S-on-1) and 37 (R-on-1) J/cm² predicted from data obtained at different pulse lengths on other LLNL damage test systems [11]).

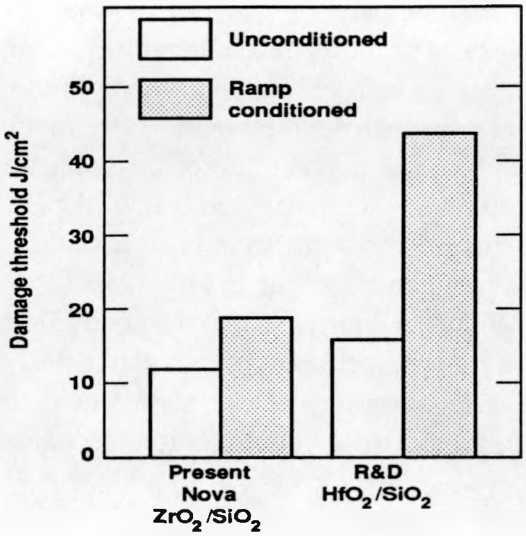

Figure 1: Unconditioned and ramp conditioned 1064 nm damage thresholds (18 Hz, τ_p=8ns) of Nova ZrO_2/SiO_2 and R&D HfO_2/SiO_2 HR coatings. Conditioning performed using damage test laser.

The R-on-1 tests clearly showed that laser conditioning had a larger effect on the R&D coatings than on the present Nova coatings. There are three major differences between the R&D and current Nova HR coatings that may cause the differences in their damage performance: i) change of high index material (HfO_2 vs. ZrO_2), ii) change of high reflectivity design wavelength, and iii) decreases in the size, density, and perhaps type of film defects due to advances in coating technology since the present Nova coatings were made. Damage measurements on R&D HfO_2/SiO_2 and ZrO_2/SiO_2 of various designs indicate that the material or design dependence of the conditioning effect is small [11]. Therefore we conclude that items (i) and (ii) above have a negligible effect on the conditioning of the films used in this study. This leaves item (iii), differences in defects, as the likely explanation for the conditioning effect differences. This also agrees with our observation that damage in both films (R&D and Nova) typically originate at the site of visible defects.

Measurements were made of the film defect sizes using dark field, bright field, and Nomarski microscopy. All three techniques showed that the defects in the R&D coatings were smaller than those in the Nova coatings: nominally 5 to 10 μm vs. 10 to 30 μm, respectively. The R&D coatings also had a slightly lower defect density (about 30 to 80 per mm^2) compared to the current Nova coatings (about 100 per mm^2). It is unlikely that these modest changes in size or areal density of the defects, per se, influences the damage threshold. Rather, these differences probably indicate different types of defects, with one type of defect being more susceptible to conditioning than the other.

Differences in the performance of the two coatings is also indicated by the dependence of their damage threshold on laser pulse length. For the present Nova mirrors no pulse length dependence is observed [14]. For the HfO_2/SiO_2 R&D coatings, however, the damage threshold, D_T (J/cm^2) is dependent on the pulse length, τ_p(ns) as [11]

$$D_T = 7.1\ \tau_p^{0.355}. \qquad (1)$$

The differences in the pulse length dependence and the extent of threshold enhancement due to conditioning for the two coatings may indicate a change in the laser damage mechanism. It should be emphasized that without conditioning the damage thresholds of the two films studied are approximately the same at 8 ns. The threshold improvements for the R&D coating is apparent only after conditioning.

3. Large Area Conditioning via Raster-scanning:

In the R-on-1 tests described above an area only the size of the test beam (~0.2 mm) was conditioned. We are interested, however, in laser conditioning coatings the size of the Nova mirrors (1.1 m), therefore other, more practical, methods of laser preconditioning were studied. Here we present the results of conditioning studies performed by rastering a large coating surface with a small area beam (~0.2 mm) at laser fluences below the S-on-1 damage threshold. The rastering was done using the damage test laser and a programmable x-y stage. The x-y stage velocity was chosen such that the sample was shot every 0.1 mm in both the x and y directions. This scan rate corresponds to four shots/site for a 0.2 mm diameter beam. Areas of ~4 cm^2 were rastered with various fluences below the S-on-1 damage thresholds of both coatings. Four types of pre-conditioning programs were examined in this study:

a) raster at 10% of the S-on-1 threshold

b) raster at 63% or 55% of the S-on-1 threshold

c) raster at 85% of the S-on-1 threshold

d) consecutive rasterings at five fluences increasing from 37 to 85% of the S-on-1 damage threshold (hereafter referred to as "step conditioning").

These conditioning programs, along with that for ramp conditioning, are shown graphically in fig. 2. For the 5-step conditioning the time between individual illuminations was approximately 1 hr. This is in contrast to the ramp conditioning where the time between shots is ~0.1 s. Note also that the increment in fluence between shots in the ramp is only ~0.05% of the S-on-1 damage threshold.

For both the R&D and present Nova coatings, single or multiple fluence raster conditioning resulted in an increase in the S-on-1 threshold. The average damage thresholds measured for the different conditioning programs are shown in fig. 3. Conditioning increased the damage threshold of the present Nova mirror by a factor of 1.2 to 1.3. For the R&D coatings, however, conditioning increased the threshold by a factor of 1.2 to 2.4. It is not clear at this time which type of raster conditioning program would provide the largest increase in the damage threshold. It appears, however, that no clear advantage is gained by step conditioning. The most important conclusion reached was that for both coatings <u>all</u> raster conditioning programs resulted in conditioning factors <u>less</u> than that obtained by the ramped fluence technique (i.e. R-on-1).

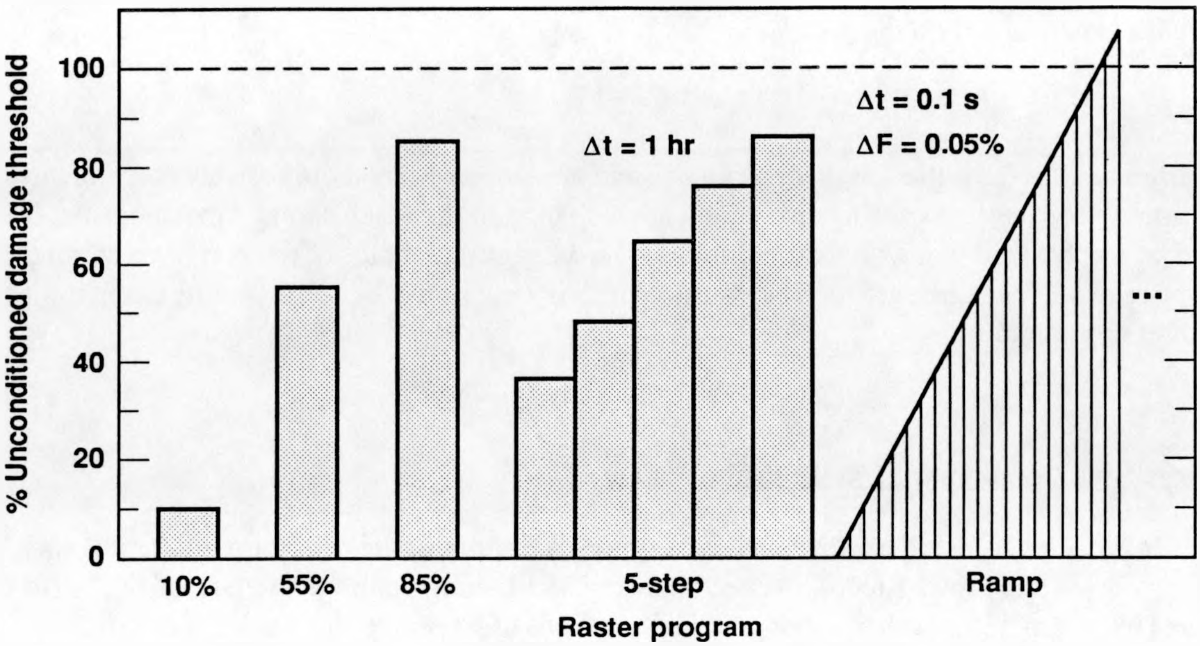

Figure 2: Laser conditioning program used in raster conditioning and ramp conditioning experiments.

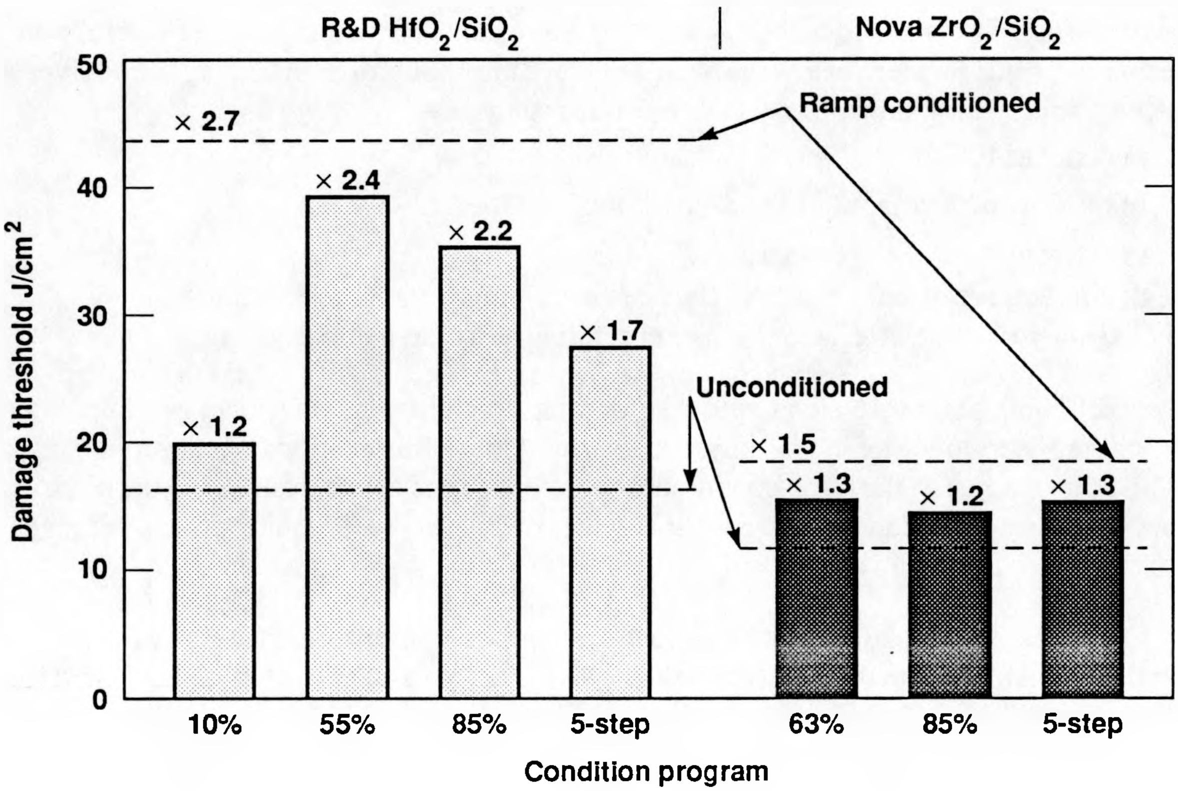

Figure 3: Conditioned 1064 nm damage thresholds (18 Hz, τ_p= 8ns) of Nova ZrO_2/SiO_2 and R&D HfO_2/SiO_2 HR coatings for various raster conditioning programs. Unconditioned and conditioned thresholds are included for reference.

In all tests we defined the damage threshold as the lowest fluence at which damage occurred. Below that threshold we assume that there is zero probability of damage. As the fluence is increased above the threshold the probability of damage increases until a fluence is reached at which any location would damage. We observed that the range of fluences over which the damage probability changed from 0% to 100% was dependent on the conditioning history of the sample. For S-on-1 thresholds the 0-100% damage probability transition range was ~10 J/cm2, while for the R-on-1 tests the range was > 40J/cm^2. For raster conditioned samples the range was intermediate between the S-on-1 and R-on-1 cases. The change in the abruptness of the damage threshold indicates that the film properties which control the damage threshold after conditioning are not uniform across the sample. It should be noted that since the damage threshold is not abrupt for the conditioned samples, the choice of the lowest damage fluence as the reported damage threshold results in a conservative value for the conditioned damage threshold. In some areas R-on-1 testing increased the damage threshold by more than a factor of four.

4. Large Aperture Nova Conditioning

Using the beam size and raster rate used above, it would take nearly two months to raster a 109 cm diameter mirror. Obviously a more practical large area conditioning technique is required. We therefore next examined the effectiveness of using a large aperture beam from the Nova laser (1ns, 1064 nm) for the conditioning illumination. If this method is effective, Nova mirrors can be conditioned in-situ. Two 5-cm samples were examined in this study: a HfO_2/SiO_2 1064 nm HR and a ZrO_2/SiO_2 1064 nm HR. It has been shown that the 1-on-1 (single pulse at a given site) damage thresholds for these two coatings at 1064 nm are both ~7 J/cm^2 at 1 ns [11]. During testing the coating samples were mounted down line from a condensing lens which focussed a mid-chain Nova beam down to a 4 cm-diameter spot. Shot energies were measured using a calorimeter and the beam profile was recorded on film. Densitometer traces of the developed film were used to measure beam modulation and the average fluence. After each shot the sample was removed from the holder and visually inspected under a microscope at magnifications up to 40X using bright-light illumination. The whole coating surface was also photographed for macroscopic changes using a 35-mm close-up camera. At the completion of inspection, the sample was drag-wipe-cleaned using methanol and remounted in the test system. A fiducial mark was used to insure the sample alignment remained the same from one shot to the next. At the completion of the tests on Nova, the samples were again photographed at magnifications up to 400X using both Nomarski and bright and dark field illumination.

A total of seven laser shots were fired at the HfO_2/SiO_2 and one at the ZrO_2/SiO_2 coating. Figure 4 shows the illumination history in terms of the average fluence for each shot and fig. 5 shows a typical fluence profile for the Nova beam. Note that the peak-to average modulation of the beam intensity is about 1.3-to-1. In the case of the HfO_2/SiO_2 coating, we slowly increased the laser fluence from a value of about 3.5 J/cm^2 up to about 12 J/cm^2; 12 J/cm^2 is about 1.5 to 2 times the 1-on-1 damage threshold. Microscopic and large area inspection of the HfO_2/SiO_2 coating after each shot showed no change. Furthermore, the "breath-test" also showed no change in the sample. The final Nova shot was fired on the ZrO_2/SiO_2 coating. This single shot, having a mean fluence of about 10.6 J/cm^2 was significantly above the single-shot damage threshold (7 J/cm^2). As expected, the sample damaged; this was clearly seen by both our microscopic

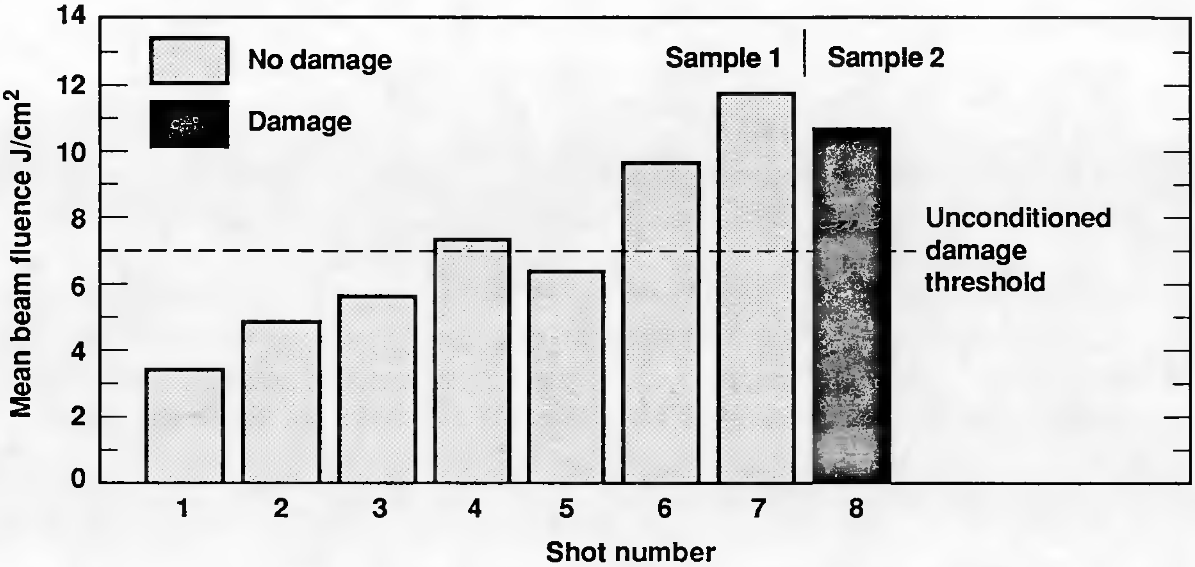

Figure 4: Beam fluence vs. shot number for large aperture Nova conditioning experiment. λ=1064nm, τ_p= 1 ns.

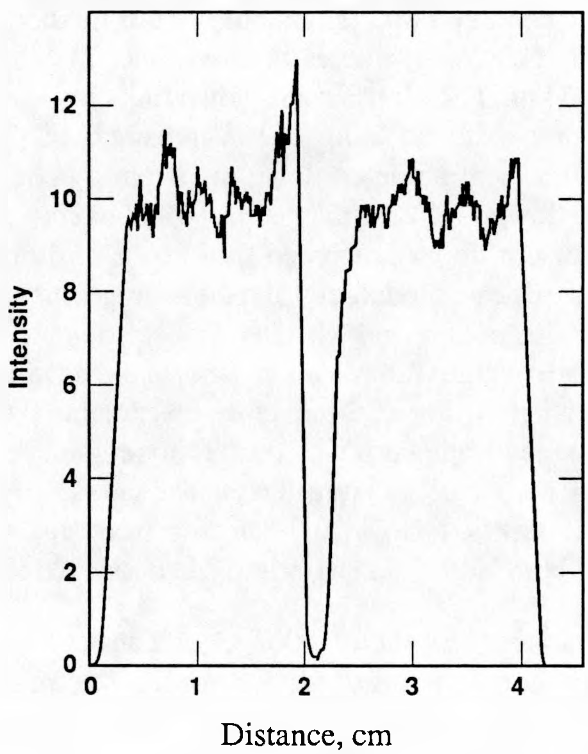

Figure 5: Example of typical Nova arm-9 beam profile showing degree of modulation. The split down middle of beam is due to an apodizer.

inspection and the "breath-test". These Nova test results show that large area optics can be conditioned using the Nova laser beam.

Previous small-area damage tests had shown that the conditioned damage threshold for the HfO_2/SiO_2 coating should be about 18-20 J/cm^2 (at 1-ns) vs. an unconditioned (1-on-1) threshold of 6-8 J/cm^2. We decided not to test the HfO_2/SiO_2 sample on Nova above about 12 J/cm^2. This was for two reasons: first, it provided us with a conditioned, yet undamaged large area sample that could subsequently be tested to determine if the conditioning effect was permanent. Second, because of beam modulation the peak fluence seen by the test sample may have been as much as 1.3-times the mean fluence. Thus at a fluence of 12 J/cm^2, some regions for the sample could be subjected to fluences near the maximum damage threshold expected from conditioning.

In order to compare the damage thresholds obtained by Nova and raster conditioning we damage tested, at 8 ns, the Nova conditioned sample. Figure 6 shows that the Nova conditioned sample has a damage threshold in the range obtained by raster conditioning. Note once again that all the large-area conditioned thresholds are lower than that obtained by ramp conditioning.

The HfO_2/SiO_2 coating that was conditioned on Nova was further damage tested to determine if the effect was permanent. These damage tests were done at 1064 nm and 10 ns; the results are shown in fig. 7. Tests conducted over a period of about 10 weeks showed no drop in the conditioned damage threshold.

Independent conditioning tests performed by Floch (at Commissariat a l'Energie Atomique, France) using HfO_2/SiO_2 coatings prepared by Matra (France) showed no change in damage threshold for up to six weeks [15]. Damage threshold improvements of a factor of 2-3 were observed in the French study.

5. Flashlamp Conditioning Experiments

Besides the raster and Nova conditioning methods, we also attempted to condition the thin film dielectrics by broadband flashlamp illumination. Broadband illumination is commonly used to decompose or outgas contaminants from vacuum systems. Similarly, we intended this process to remove organic contaminants from our thin films. The flashlamp study consisted of illuminating a HfO_2/SiO_2 HR sample with 20 flashes of a Xenon arc lamp. The illumination intensity was about 10 J/cm^{2}for each shot and the pulse length was 0.5 ms. The spectral output of the lamp is given in fig. 8. Subsequent S-on-1 damage tests to the sample showed that flashlamp illumination did not change the damage threshold of the HR coatings. Two obvious differences between the flashlamp and the laser illumination are the range of photon wavelengths involved and the magnitude of the electric field produced in the sample. The long pulse length of the flashlamp results in a low electric field since

$$E=[2 F_L/ \tau_p n y]^{0.5} \qquad (2)$$

where E is the electric field (V/cm), F_L is the fluence (J/cm^2), τ_p is the pulse length (sec.), n is the refractive index (1.45 for SiO_2), and y is the admittance in free space (2.66x10^{-3} F/s). For F_L=10

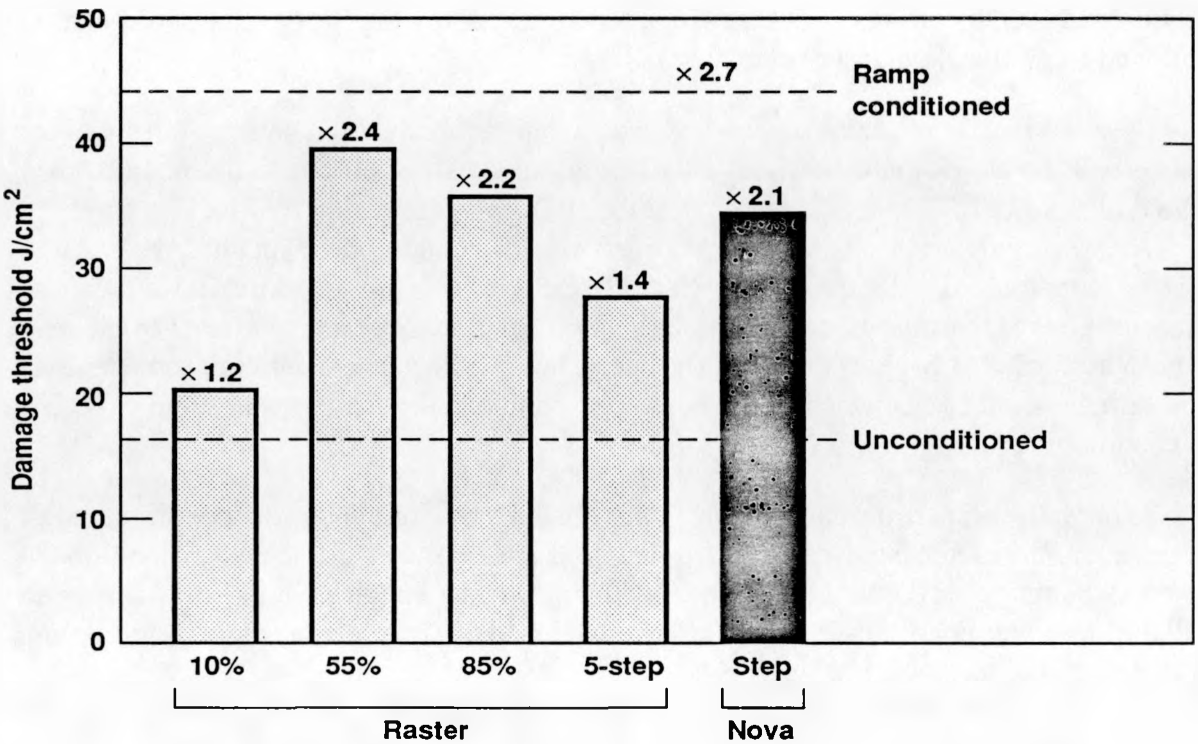

Figure 6: 1064 nm damage thresholds (18 Hz, τ_p=8ns) of R&D HfO_2/ SiO_2 HR coatings conditioned by raster scanning and large aperture Nova illumination.

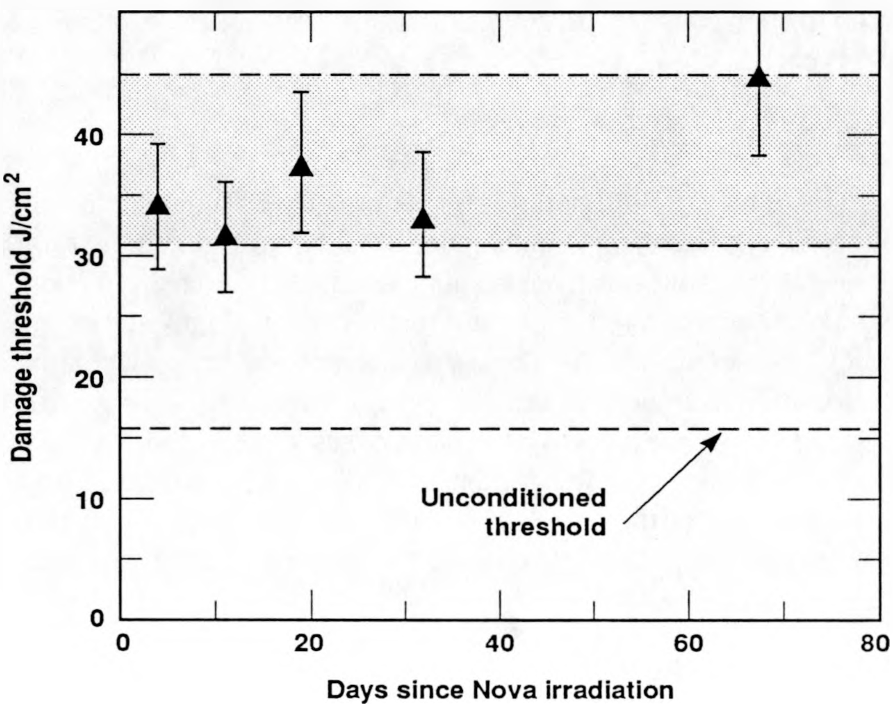

Figure 7: 1064 nm damage thresholds (τ_p = 10 ns) vs. time after conditioning for the R&D HfO_2/SiO_2 HR coatings illuminated on Nova.

J/cm² and τ= 5x10^{-4} sec., the electric field is 3x10^{3} V/cm. This field is less than 1% of the field associated with an 8 ns laser pulse of the same fluence. Possible connections between illumination wavelength, electric field, and the conditioning effect are discussed in Section 6.

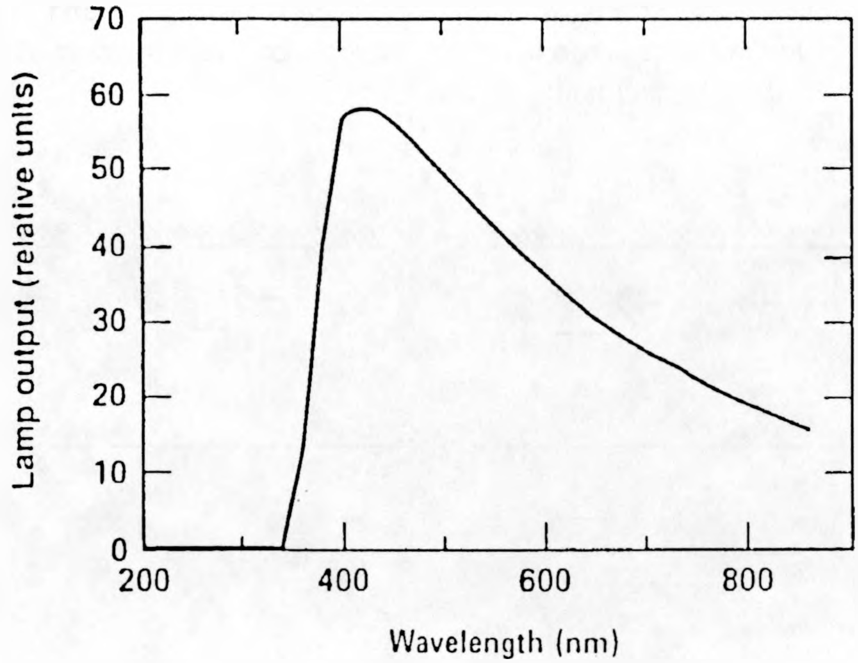

Figure 8: Time integrated Xe flashlamp output spectra [36]. Outut below 350 nm is suppressed by Ce dopant contained in the flashlamp envelope.

6. Electron Defect Model

Several different mechanisms for laser conditioning have been suggested in the literature (film crystallization, water desorption, etc.). Different mechanisms may apply for different combinations of materials, deposition methods, illumination wavelength, etc.. A complete review of the conditioning mechanism literature is outside the scope of this text. We are interested here primarily in the laser conditioning of 1064 nm dielectric HR films of HfO_2/SiO_2 deposited by e-beam evaporation.

We are presently examining a possible mechanism for laser induced optical damage in which conduction band electrons are heated by interaction with the laser beam and subsequently transfer energy to the crystal lattice. Damage occurs when the film temperature reaches some critical value such as the melting point of the dielectric material. There are two conditions that must be met for film damage to occur: (i) electrons must be available in the conduction band, and (ii) the laser intensity must be high enough to transfer sufficient energy to the lattice to cause damage. We propose that the source of conduction band electrons is the photo-excitation of electrons from shallow defect levels located below the conduction band edge. We further propose that laser conditioning occurs due to the removal of this source of conduction band electrons. When the dielectric material is illuminated at a low fluence, the electrons in the defect levels are excited to the conduction band. Since the optical electric field is not large enough to cause damage the electrons decay into deep levels from which they cannot be easily excited into the conduction band on subsequent illuminations. A diagram of the proposed band structure for the unconditioned and conditioned dielectrics are shown in fig. 9. When the 'conditioned' dielectric is subsequently illuminated at intensities above the unconditioned damage threshold, the number of electrons available for transfer to the conduction band is low and, therefore, the net energy transfered to the lattice is too low to cause damage. This increase in the damage threshold is the observed laser conditioning effect.

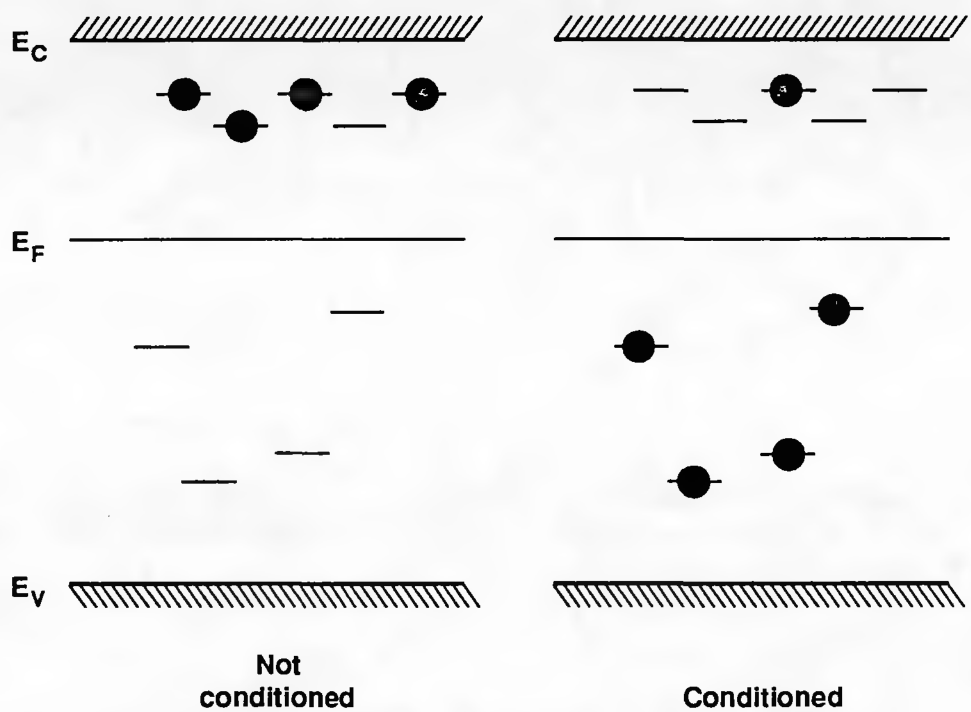

Figure 9: Schematic energy band diagram of the location of electrons (•) in traps (-) for unconditioned and laser conditioned dielectric films.

The importance of conduction band electrons to optical damage to bulk dielectric samples has been demonstrated by other investigators. Jones et al. [16] have shown that no heating of a-SiO_2 occurred by 1064 nm illumination unless the sample was simultaneously illuminated with 266 nm light. The 266 nm light provided conduction band electrons by multiphoton excitation from the valance band. Once these electrons were present in the conduction band, they could be heated by the 1064 nm photons (i.e. free carrier absorption). Similarly, Kerr et al. [17] has shown that the 10.6 μm damage threshold for silicon and glass is decreased by simultaneous illumination by UV light. Also, Soileau et al. [18] has shown that the damage threshold of bulk fused SiO_2 can be decreased by inducing electronic defects in the material by gamma irradiation. These defect levels serve as a source of conduction band electrons leading to laser damage. In that study the electrons were excited to the conduction band by two photon absorption of 532 nm photons. In the following paragraphs we consider the nature of the defect levels in the HR films of interest to Nova and discuss the mechanisms by which energy is transferred from the laser pulse to the lattice via the conduction band electrons.

6.1. Free carrier generation

Assuming a one photon (1064 nm) excitation process, the defect states contributing electrons to the conduction band of our dielectric films could be up to 1.2 eV below the band edge. In the presence of the large optical electric field (~10^6 V/cm^2) produced by the laser pulse, activation barrier lowering associated with the Poole-Frenkel effect may occur however [19]. The magnitude the the barrier lowering, ΔE_b (eV), is given by

$$\Delta E_b = [e^3 E/\pi\varepsilon_0\varepsilon]^{1/2} \quad (3)$$

where E is the magnitude of the electric field (V/cm), e is the charge on an electron, and ε is the dielectric constant, and ε_0 is the permitivity of vacuum (F/cm). The resulting decrease in the activation energy of the trap-to-conduction band transition would be as much as 0.6 eV for the materials of interest here. The Poole-Frenkel effect would therefore allow a 1064 nm photon to excite electrons from states nearly 2 eV below the conduction band edge.

Electron paramagnetic resonance has been used to demonstrate that occupied defect levels may be present between the Fermi level and conduction band in amorphous SiO_2 [20]. If the defect levels are occupied by only one electron they are paramagnetic and produce an EPR signal. Stathis et al. [21] has shown that these defect levels in high quality a-SiO_2 are normally empty but can be filled by illumination with UV photons. One particular type of defect, generally associated with a peroxide radical, can be made paramagnetic by illumination with 7.6 eV photons. If the electrons excited into the defects by the 7.6 eV photons come from the valance band, these defect levels must be about 1-2 eV below the conduction band of the ~ 9 eV bandgap SiO_2. It should therefore be possible to excite the electrons from these paramagnetic states into the conduction band by the absorption of a single 1064 nm photon (1.2 eV).

In its most stable state high purity a-SiO_2 should not have any occupied electronic levels above the Fermi level. Occupied states can be induced in this material by UV, x-ray, or charged particle irradiation. Schwartz et al. [22] has shown, however, that paramagnetic bonding defects are present in some as-deposited thin film SiO_2. Since e-beam and rf-sputter deposition techniques are accompanied by soft x-rays and energetic particles, electrons and holes can be generated during deposition. These charge carriers could then become trapped at appropriate precursor sites resulting in the formation of paramagnetic point defects. For techniques such as hot wall low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD), which do not have attendant soft x-rays or energetic particles, no paramagnetic states are observed. Cold wall LPCVD, which produces non-equilibrium films, have paramagnetic states but they can be annealed out by heating the samples to 300°C. Optical absorption measurements on rf-sputtered films of SiO_2 have also shown that the electronic properties of thin films are dependent on deposition parameters [23]. Paramagnetic defect densities on the order of $10^{16}/cm^2$ have been measured [21].

It has often been suggested that damage in dielectric multilayers occurs first in the high index material. Studies of single layer materials have shown that the damage threshold of HfO_2 and ZrO_2 are typically below that of SiO_2 [24]. Unfortunately there is little information available in the literature regarding defect levels in HfO_2 and ZrO_2. It has been shown, however, that structural defects produced by ion implantation can reduce the bandgap of HfO_2 by as much as 2 eV [25]. In general, the electronic band structure of materials are more sensitive to long range structural disorder the smaller their bandgap [26]. Therefore the electronic properties of HfO_2 and ZrO_2 are more likely to be influenced by structural defects than those of SiO_2. For the HfO_2/SiO_2 films studied here, x-ray diffraction studies have shown that the SiO_2 layer is amorphous. The HfO_2 layer, however, is amorphous at the SiO_2 surface but as the HfO_2 layer thickens, oxide with a predominantly monoclinic structure is produced [27]. This same type of structural transition has been reported for thin films of ZrO_2 [28].

The model presented here assumes that charged defects are the primary source of conduction band electrons in the dielectric films. There are, however, four other sources of conduction electrons which we must consider:

1. Thermal detrapping from shallow levels in the dielectric. Since the large bandgap insulators of interest have very low conductivities, this source of electrons is unlikely.

2. Multiphoton absorption by valance band electrons. For the 1064 nm irradiation 5 photons would be needed for ionization in HfO_2 and 8 photons would be required for SiO_2. It has been suggested in the literature that multiphoton ionization is unlikely for $n>4$ [16]. Photoacoustic measurements by Jones et al. [16] have indicated that no multiphoton ionization occurs in high purity a-SiO_2 for 1064 nm photons. Three photon absorption is observed however for 266 nm light. The number of photons required for multiphoton absorption in SiO_2 and HfO_2 given above are based on the bandgaps of the near perfect crystalline materials. These bandgaps are 9.0 eV and 5.1 eV, respectively. For highly defective thin films, however, bandgaps several eV lower have been measured for both HfO_2 [25] and SiO_2 [23]. For these lower bandgap films multiphoton processes may become more significant. Photoacoustic measurements are planned which will determine if multiphoton absorption is important at 1064 nm for the e-beam films of interest here.

3. Electron-impact ionization and subsequent avalanche formation. Recent photoacoustic measurements [16] indicate that avalanche ionization does not occur in KBr, NaCl, KI, or a-SiO_2. Furthermore, experimental and computer modeling studies by DiMaria et al. [29,30] have shown that the distribution of energies of conduction electrons in SiO_2 is not high enough to allow impact ionization to occur. No comparable measurements have yet been reported on HfO_2 or ZrO_2, however.

4. Electrons produced by laser induced defect formation (i.e. F-centers). It is believed that if F-centers were produced by the laser pulse illumination, an accumulation effect would be apparent, i.e. single shot damage thresholds would be higher than multiple shot thresholds [16].

Such an accumulation effect has not been observed for the dielectric stacks of interest here, but has been observed in sol-gel processed TiO_2 coatings [31].

Based on the available literature, it therefore seems likely that laser damage in our dielectric materials is associated with conduction band electrons and that the source of these electrons is shallow defect levels.

6.2.. Energy transfer

There are three commonly discussed mechanisms for transfer of energy between the laser beam and the crystal lattice of a dielectric material. In the classic electron-avalanche model of Bloembergen and Yablanovitch [32], the lattice heating mechanism was taken from the Drude model for AC conductivity in metals [33]. In the Drude model, electrons are accelerated by the optical electric field and then lose energy to the lattice by electron-phonon interaction (i.e. Joule heating). The other two mechanisms for lattice heating: (a) free-electron heating and (b) polaron heating, involve the direct absorption of photons and subsequent transfer of energy to the lattice by electron-phonon interactions. Free electron heating is more likely for the ionic materials and the short wavelengths of interest here [16]. The three mechanisms can be experimentally differentiated by the relationship between the energy absorbed and the laser pulse energy. For example, the energy absorbed by the free-electron model has a non-linear dependence on pulse energy while for the polaron mechanism the dependence is linear. Jones et al. [16] have shown that for SiO_2, and for many alkali-halides, lattice heating occurs by the electron-heating mechanism.

7. Discussion of Results

The laser conditioning experiments reported here demonstrated that the damage thresholds of the dielectric multilayer stacks could be increased as a result of as few as one subthreshold illumination pulse. Based on the simple laser conditioning mechanism discussed above, it might be expected that the effect of conditioning should increase with fluence or number of pulses until the cumulative photon flux has removed all the electrons from the defect levels near the conduction band. Further illumination should have little effect. Some of our data suggests this picture is correct whereas other results suggest that the conditioning mechanism is more complex than this. Clearly more data is required in order to understand the relationship between the conditioning program and the increase in the damage threshold fluence.

We have observed that damage in the dielectric stacks tends to occur at the sites of film defects visible by Nomarski microscopy. The defect driven damage is likely the result of either of two mechanisms: (i) the defects are regions of high concentrations of occupied defect levels which serve as the source of conduction band electrons, or (ii) the defect areas are regions of enhanced electric fields, as described by Bloembergen [34], and therefore allow damage to occur at lower fluences than that of a perfect material.

An interesting observation reported by Wolfe et al. [11] is that the pulse length dependence of the damage threshold for both unconditioned and ramp conditioned materials are the same. The thresholds are proportioned to τ_p^x where x is approximately 0.3. This result may suggest that the damage mechanism remains the same after conditioning.

Our attempts to condition the HR films by flash lamp illumination were not successful. There are three possible explanations for this lack of a damage threshold increase. The first explanation is related to the broadband nature of the flashlamp. The optical film is simultaneously being irradiated with both UV and IR irradiation. Stathis [35] has shown that paramagnetic states can be generated by UV illumination. The UV photon may therefore counter the emptying effect of the IR illumination. The second explanation is related to the low electric field produced by the long pulse length (~1 ms) flashlamp output The field produced by the flashlamp is a factor of 10^3 lower than that of the 8 ns laser pulses. If barrier lowering by the Poole-Frenkel mechanism is required for the excitation of trapped electrons, then the flashlamp illumination would not result in a conditioning effect. Third, the flashlamp output produces a much lower energy density over a given wavelength interval than does a laser. Consequently, if the absorption cross section associated with the conditioning process is small (and wavelength specific) then the effect of the flashlamp would be expected to be negligible. In addtion, flashlamp illumination has also been shown not to alter the damage threshold of laser conditionable KDP [2].

It may be possible to empty the paramagnetic defects by thermal excitation as well as optical excitation. Several paramagnetic states in a SiO_2 can be emptied by thermal treatments at temperatures below 700°C [35]. No information is available on thermal detrapping from states in HfO_2. For dielectric multilayers thermal conditioning is limited by thermal stress build up and may not be practical for thin films prepared by physical vapor deposition methods.

8. Conclusions

The damage threshold of HfO_2/SiO_2 high reflection coatings can be increased by a factor of about 2.7 by ramped-fluence laser conditioning (i.e. R-on-1 damage tests). This laser conditioning effect can be used to permanently increase the damage threshold of large area optics. Large areas were conditioned by either rastering a surface with a small beam or by illumination with a large aperture beam such as that available on the Nova laser. In order to be practical, these large area conditioning methods require illumination in fairly large incremental steps in laser fluence. Such discrete illumination techniques produced smaller increases in damage threshold than can be obtained by the small step, ramped-fluence techniques. Increases of a factor of about 2 can be expected for discrete step, large area conditioning. Further study is needed to determine the optimum discrete fluence illumination program. In the case of practical conditioning of Nova turning mirrors, the large aperture conditioning procedure is the most attractive since the mirrors can be conditioned in-situ on Nova. In contrast, raster conditioning of a 1.1 m diameter mirror with the damage test beam would take several weeks and a dedicated facility.

The mechanism proposed here for the laser conditioning phenomenon is based on the presence of sub-bandgap electronic defect levels that are intrinsic to the e-beam deposition process. This is in contrast to extrinsic mechanisms, such as absorbing inclusions and water contamination, that have been suggested in the past. The move toward intrinsic mechanisms may indicate that thin film processing techniques have improved over the years, as should be expected. We are currently involved in using the EPR technique to identify the electronic defects that are present in the dielectric films and to determine if the charge state of the defects are altered by the sub-threshold conditioning illumination. If the electronic defect model is correct, further improvements in film properties might be gained by using deposition techniques that are more "equilibrated" (in a structural or electronic sense). Plasma-assisted CVD is one such possible coating method.

References:

1. B. Newnam, A. Nowak, and D. Gill, " Short pulse CO_2-laser damage studies of NaCl and KCl windows",Laser Induced Damage in Optical Materials: 1979, NBS Spec. Pub. 620, p. 209.

2. J. Swain, S. Stokowski, D. Milam, and G. Kennedy, The effect of baking and pulsed laser irradiation on the damage threshold of potassium dihydrogen phosphate crystals", Appl. Phys. Lett. 41 (1982) 12.

3. R. Gonzales, M. Staggs, M. Singleton, D. George, C. Weinzapfel, S. Weinzapfel, "Variations with laser pulse duration of the thresholds at 350 nm and 1064 nm for bulk damage in crystals of KDP", UCLR-95284, presented at the Boulder Damage Conference, 1986.

4. V. Wang, J. Rudisill, C. Giuliano, M. Braunstein and A.Braunstein, "Pulsed CO_2 laser damage in windows, reflectors and coatings", Laser Induced Damage in Optical Materials: 1974, NBS Spec. Pub. 414, p. 59

5. B. Brauns, D. Schafer, R. Wolf, and G. Zscherpe, "Effect of the substrate preparation with CO_2 laser radiation on the laser resistance of optical layers", Thin Solid Films, 138 (1986) 157.

6. F. Rainer, D. Milam, and W. Lowdermilk, "Laser damage thresholds of thin film optical coatings at 248 nm",Laser Induced Damage in Optical Materials: 1981, NBS Spec. Pub. 638, p. 339.

7. J.E. Swain, W.H. Lowdermilk, and D. Milam, "Raising damage thresholds of gradient - index antireflecting surfaces by pulsed laser irradiation" Appl. Phys. Lett. 41 (1982) 782.

8. A. Stewart, A. Guenther, F. Domann, "The properties of laser annealed dielectric films", Laser Induced Damage of Optical Materials: 1987, NBS Spec. Pub. 756, p. 369.

9. J. W. Arenberg and D. Mordaunt, "Experimental investigation of the role of wavelength in the laser conditioning effect", Laser Induced Damage in Optical Materials: 1988, NBS Spec. Pub. (to be published).

10. J. Wilder and I. Thomas, "Effect of n-on-1 laser treatment on damage threshold of selected optical coatings", Laser Induced Damage of Optical Materials: 1988, NBS Spec. Pub. (to be published).

11. C. R. Wolfe, M. Kozlowski, J. Campbell, F. Rainer, A. Morgan, and R. Gonzales, "Laser pre-conditioning of optical thin films", Laser Induced Damage of Optical Materials: 1989, NBS Spec. Pub. (to be published).

12. G. Edwards, J. Campbell, R. Wolfe, and E. Lindsey, "Damage Assessment and possible damage mechanisms to 1-meter diameter Nova turning mirrors" Laser Induced Damage of Optical Materials: 1989, NBS Spec. Pub. (to be published).

13. T.J. Baker, "Breath figures", Phil. Mag., 44 (1922) 752.

14. G.R. Wirtenson and F. Rainer, LLNL intermal memorandum SOC 88-005 (Feb. 1988).

15. Herve Floch, Commissariat a l'Energie Atomique, Villeneuve Saint Georges, France, private communication.

16. S. Jones, P. Braunlich, R. T. Casper, X.-A. Shen, and P. Kelly,"Recent progress on laser-induced modifications and intrinsic bulk damage of wide-gap optical materials", Optical Engineering 28 (1989) 1039.

17. N. C. Kerr, S. E. Clark, and D. C. Emmony, "UV seeding of IR laser induced damage" abstracts to the Laser Induced Damage of Optical Materials: 1989, Boulder CO., Oct. 1989.

18. M. J. Soileau, N. Mansour, E. Carlo, and D. L. Griscom, "Effects of radiation induced defects on laser-induced breakdown in SiO_2", Mat. Res. Soc. Symp. Proc., Vol. 61 (1986) 205.

19. A. R. Newark and U. Stimming, "Photoinduced electron transfer involving localized electronic states", Electrochimica Acta, 32 (1987) 1217.

20. E.P. O'Reilly and J. Robertson, "Theory of Defects in Vitreous Silicon Dioxide", Phys. Rev. B, 27 (1983) 3780.

21. J. H. Stathis and M. A. Kastner, "Photoinduced Paramagnetic Defects in Amorphous Silicon Dioxide", Mat. Res. Soc. Symp. Proc., Vol. 61 (1986) 161.

22. R. N. Schwartz, M. D. Clark, W. Chamulitrat, and L. Kevan, "Electron Papamgnetic Resonance Studies of Intrinsic Bonding Defects and Impurities In SiO_2 Thin Solid Films" in 'Defects in Glasses', Mat. Res. Soc. Symp. Vol. 61 (1986), 359.

23. T. Hickmott and J. Baglin, "Stoichiometry and atomic defects in rf-sputtered SiO_2", J. Appl. Phys., 50 (1979) 317.

24. A. Guenther and T. Humphreys, "Physical aspects of laser-induced damage of optical materials" , Proc. SPIE, Vol. 401 (1983) p. 247.

25. J. W. Schultze, B. Danzfuss, O. Meyer, and U. Stimming, "Electrochemical investigations of ion-implanted oxide films", Mat. Sci. Eng. 69 (1985) 273.

26. J. Tauc, "Optical properties of non-crystalline solids" in Optical Properties of Solids, F. Abeles ed.,North Holland Pubs., Amsterdam, 1972.

27. Tom Allen, Optical Coatings Laboratory Inc., private communication.(1989).

28. N.V. Krizosheen, N.N. Zapleshko, and N.F. Fedorov, "Interrelationship between the structure and optical properties of zirconium dioxide thin films", Inorg. Mater., 19 (1983) 825.

29. D. J. DiMaria and M. V. Fischetti, "Hot electrons in silicon dioxide: Balistic to steady-state transport", Appl. Surface Sci., 30 (1987) 278.

30. D. J. DiMaria, M. V. Fishetti, M. Arienzo, and E. Tierney, "Electron heating studies in silicon dioxide: Low fields and thick films", J. Appl. Phys. 60 (1986) 1719.

31. I.M. Thomas, J.G. Wilder, and R.P. Gonzales, "HR coatings prepared from colloidal suspensions", Laser Induced Damage of Optical Materials: 1987, NBS Spec. Pub. 756, p. 286.

32. E. Yablonovitch and N. Bloembergen, "Avalanche Ionization and the limiting diameter of filaments induced by light pulses in transparent media", Phys. Rev. Lett. 29 (1972) 907.

33. N.W. Ashcroft and N.D. Mermin, Solid State Phyics, Saunders College, Philadelphia (1976).

34. N. Bloembergen, "Role of Cracks,Pores, and Absorbing inclusions on laser induced damage thresholds at surfaces of transparent dielectrics", Applied Optics, 12 (1973) 661.

35. Stathis, J. H., "Identification of native defects in a-SiO_2" in 'The Physics and Technology of Amorphous SiO_2', Edited by R. Devin (Plenum Publ. Corp., 1988), p. 141.

36. C.R. Wolfe, J.H. Campbell, R.E. Lyon, J.H. Pitts, H.T. Powell, "Optical damage in epoxy polymers by millisecond light pulses", Laser Induced Damage in Optical Materials: 1986, NBS Spec. Pub. 752, p. 194.