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Comparison of aging effects in hafnia and titania thin films on the laser damage resistance of high reflection coatings for 1054 nm

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ABSTRACT

Optical coatings deposited using electron beam evaporation are subject to aging effects that change the spectral characteristics of the optical coating. The aim of this study was to determine whether aging effects can also negatively impact the laser damage resistance of an optical coating. Maintaining high resistance to laser damage is particularly important for the performance of high fluence laser systems. In 2013, we deposited different high reflection coatings for 1054 nm containing $HfO_2/TiO_2/SiO_2$ layers. For this study, we re-measured the laser damage thresholds of these coatings at 3.5 ns to determine if aging effects cause the laser damage threshold to decline, and to compare whether HfO_2 or TiO_2 is superior in terms of long-term laser damage resistance.

Keywords: Optical Coatings, Hafnia, Silica, Titania, Laser Damage, Mirrors, Aging, Contamination

1. INTRODUCTION

The large optics coating system [1] at Sandia National Laboratories is responsible for providing coated optics with high resistance to laser damage for the Z-Backlighter laser facility [2]. The Z-Beamlet kJ-class system operates with ns pulses in the terawatt peak power range at both 1054 nm and 527 nm, while the Z-Petawatt laser operates with ns to sub-ps pulses (1054 nm).

Our coatings consist of hafnia (HfO_2) and silica (SiO_2) layers, but in 2013 we also tested coatings with titania (TiO_2) layers [3,4]. The higher refractive index of titania allowed us to develop mirrors with wider high reflection bandwidths to improve angle-of-incidence (AOI) flexibility, and compensate for the spectral shift caused by water absorption or aging. However, due to the lower bandgap of titania compared to hafnia, the laser-induced damage threshold (LIDT) of mirrors containing titania were reduced compared to mirror coatings that contained just hafnia and silica layers [3].

Due to the lower LIDT of mirrors containing titania layers, their suitability in high energy laser systems requires further investigation. One concern was whether aging effects in titania would further reduce the LIDT over time. This concern has been mentioned in the literature [5]: Lowdermilk, et al, discovered that after 1 year of storage in a laboratory environment, three titania/silica high reflection (HR) coatings had an LIDT reduction of one-half, but two of the coatings were restored to their original LIDT after baking at 275 °F for 4 hours. The LIDT of the third coating was not restored by baking, which raises more questions about the cause of LIDT degradation. For this reason, we have conducted our own LIDT degradation study using mirror coatings containing titania that we produced in 2013. We determined how much the LIDT degraded between then and now, and compared the results to the LIDT degradation of a hafnia/silica mirror that was coated in 2014. In short, the damage threshold of every coating declined over time, mostly by a factor of 2 or more, and our coatings containing titania exhibited a larger number of defects in 2017 compared to 2013. More details about these results and their significance will be explained in later sections.

To be clear, our long-term study of LIDT degradation is not about laser incubation, or in other words, a fatigue effect caused by repeated laser shots into the coating [6]. Instead, we wanted to determine whether there are changes occurring in a coating over time that would lead to lower LIDT. Also, by comparing different coatings where the high index layers were either hafnia, titania, or both, we could discern whether one of those materials may be superior in terms of maintaining long-term resistance to laser damage.

2. METHOD

In 2013, we produced 5 mirror coatings containing hafnia, titania, and silica layers using our electron beam evaporation system for large optics [3]. The coatings were 42-layers, quarter-wave stack designs, for 1054 nm, 45° AOI, P-polarization, with a half–wave outer layer of silica to improve resistance to laser damage [7]. The coatings we produced contained 7, 10, 13, 16, or 21 inner titania layers, with the coating containing 21 titania layers having no hafnia layers. In 2014, we produced a coating of the same design containing just hafnia and silica layers to use for comparison. An example of the layer thicknesses of the coating containing 10 inner titania layers is shown in Fig. 1.

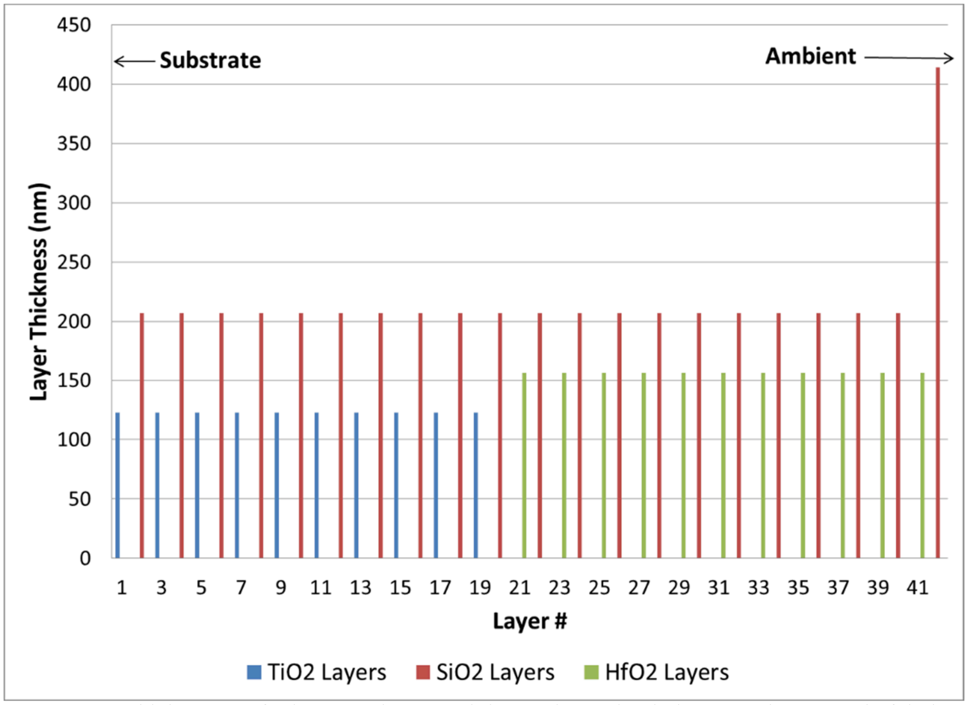

Figure 1: Layer thicknesses of mirror coating containing 10 inner titania layers and 11 outer hafnia layers.

The reason for replacing the inner, rather than outer hafnia layers with titania, was due to the lower LIDT of titania. As shown in Fig. 2, the electric field intensity diminishes near the substrate for this type of coating design (using the electric field model generated with Optilayer software [8]). Therefore, placing titania layers near the substrate is a strategy for minimizing the fluence and reducing the possibility of laser damage in the more sensitive titania layers.

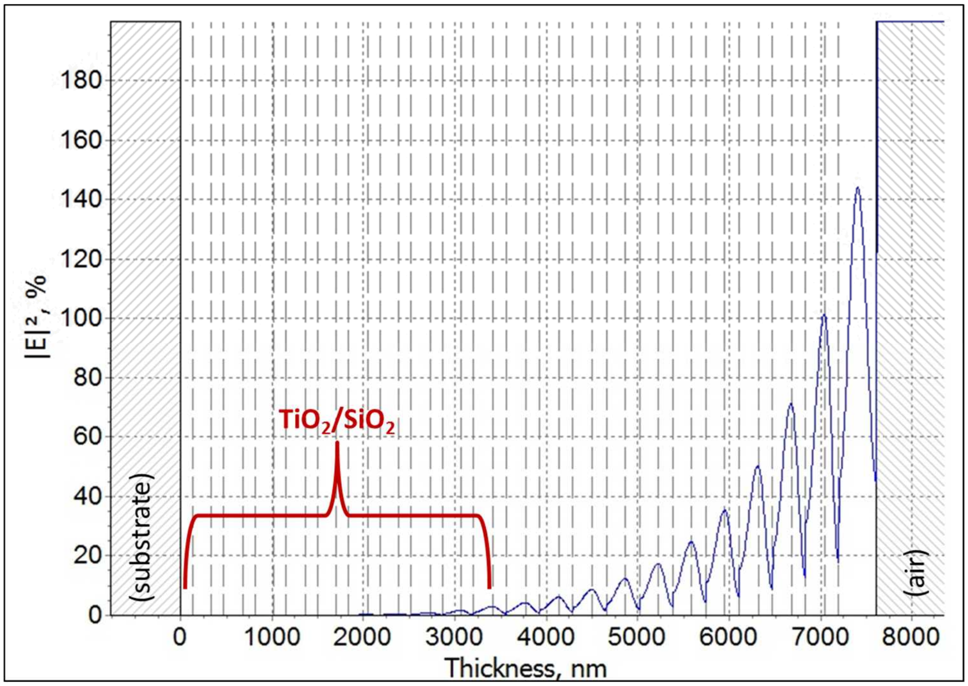

Figure 2: Electric field intensity model at 1054 nm, 45° AOI, P-polarization, in mirror coating containing 10 inner titania layers and 11 outer hafnia layers. Vertical dashed lines indicate layer boundaries. Titania has a lower badgap compared to hafnia, and therefore also a lower LIDT compared to hafnia. Using the titania layers in the area of lowest electric field intensity is a strategy to protect titania layers from laser damage.

Each coating was deposited on an optically polished fused silica substrate, 2" diameter X 0.5" thick, with the exception of the hafnia/silica coating produced in 2014: the substrate material was BK7. Prior to coating, all the substrates were cleaned using our standard process [9], which involves Micro 90 detergent, Baikalox alumina slurry, and deionized water.

The coating process was electron beam evaporation with ion-assisted deposition (IAD). The coating parameters are shown below in Table 1. In addition to IAD, the hafnia and titania layers were deposited with a backflow of oxygen gas into the coating chamber. The total pressure in the coating chamber during the deposition of hafnia and titania layers in 2013 was 1.5e-4 Torr, but this pressure measurement cannot be confirmed because our ion gauge was not calibrated at the time. In 2014, using a calibrated ion gauge, the total pressure in the coating chamber was 1.2e-4 Torr during deposition of the hafnia layers. The deposition temperature was 200° C. In addition, the coating system used masking to maintain uniformity, planetary rotation, and quartz crystal monitoring for layer thickness control.

Table 1: Coating Deposition Parameters with IAD

	Starting material	**Deposition rate (Å/s)**	**Ion beam current (mA)**	**Ion beam voltage (V)**	**Ar neutralizer flow (sccm)**	**Ar flow (sccm)**	**O_2 flow (sccm)**
SiO_2	1-3 mm granules	7	425	400	6	25	25
HfO_2	Hf shavings	3	600	400	7	0	45
TiO_2	Ti 2-3 mm granules	3	600	400	7	0	45

Following deposition, each coated sample was cleaned with Micro 90 and deionized water and sent to Spica Technologies [10] for initial LIDT testing. Since then, these samples were stored in clean polyethylene terephthalate –G (PETG) plastic containers in our class 100 clean room. When LIDT testing occurred again in 2017, the same samples were measured, but testing was performed in a different quadrant of the sample compared to before.

The LIDTs were measured at 1064 nm, 45° AOI, in P-polarization. The LIDT tests were conducted according to the NIF-MEL protocol [11]. In this protocol, the coated surface of the test optic first undergoes an alcohol drag-wipe cleaning step. Then, single transverse mode (Gaussian), multi-longitudinal mode laser pulses of 3.5 ns duration and produced at a 5 Hz repetition rate in a 1 mm diameter collimated beam are incident one at a time per site in a raster scan composed of ~ 2500 sites over a 1 cm^2 area. In the raster scan, the laser spot overlaps itself from one site to the next at 90% of its peak intensity radius. The laser fluence typically starts at 1 J/cm^2 in the cross section of the laser beam. After testing the 2500 sites at 1 J/cm^2, the fluence is increased in a 1 J/cm^2 increment and the 2500 sites are tested again. This progression repeats until the damage threshold fluence is reached.

The NIF-MEL procedure is essentially an N-on-1 test at each of the 2500 sites. Laser damage is identified as some type of melt or crater that alters the coated surface, but in some cases the damage stabilizes as a damage site that does not propagate – that is, grow in size – as the laser fluence increases. These non-propagating (NP) damage sites tend to be caused by the interaction of the laser field with nano-defects (pits, nodules, or contamination) in the coating. In other cases, the damage does propagate. Propagating damage tends to be intrinsic, governed by how the laser field interacts directly with the coating molecules.

According to the NIF-MEL damage criterion, the LIDT is reached at the fluence at which 1 or more propagating damage sites occurs, or the fluence at which the number of NP damage sites accumulates to at least 25, whichever fluence is smaller. The 25 or more NP sites are 1% or more of the 2500 sites tested and constitute about 1% or more of the 1 cm^2 coating area tested. Our reason for choosing an LIDT test with these damage criteria is the following. We know we cannot tolerate a propagating damage site in the laser beam train because it will quickly develop into catastrophic damage in the form of a large crater in the optic or worse; and 25 or more NP damage sites per cm^2, while they are benign because they may not grow, are flaws in the coating that scatter about 1% of the laser light out of the beam, and that level of loss of laser intensity is unacceptable for us.

The LIDT tests conducted in 2013 were performed in the ambient environment (that is, some humidity was present), while the tests conducted in 2017 were performed in a dry nitrogen environment (0% humidity present). However, we do not expect the lack of humidity in 2017 to have a dramatic effect on the LIDTs of our coatings. Specifically, prior to 2014, most LIDT tests for our coatings were performed in ambient air at various humidity levels, but the LIDTs of our standard coatings have remained fairly consistent between then and now.

3. RESULTS

Within a week of producing each coating, they were measured on our Perkin-Elmer Lambda 950 spectrophotometer, and the transmission characteristics are shown in Fig. 3. Between 2013 and 2017, the coatings experienced a spectral shift, and the coating containing 21 titania layers is shown in Fig. 3 as an example. The high reflection band of this coating was originally centered at 1088 nm and is now centered at 1119 nm. This is a spectral shift of 31 nm, which is 2.85% larger than the original 1088 nm bandwidth.

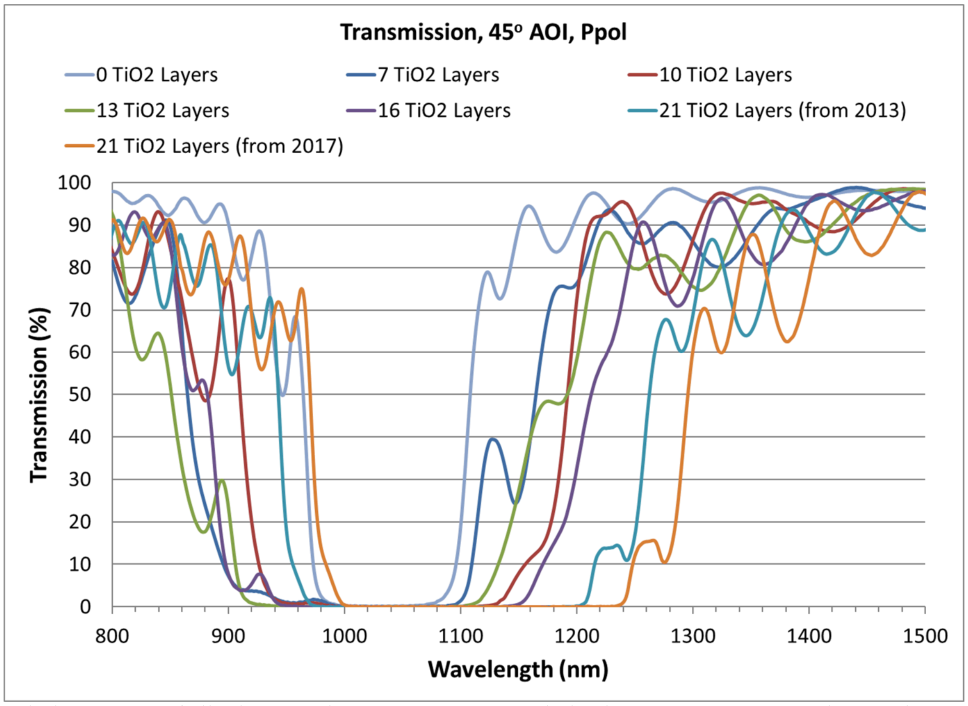

Figure 3: Transmission spectra of all mirror coatings at 45□ AOI, P-polarization. Between 2013 and 2017, the coatings experienced a spectral shift, and the coating containing 21 titania layers is shown as an example.

Although the spectral shift of 2.85% may seem large, the modeled electric field behavior of these coatings is almost identical between 2013 and 2017, as shown in in Fig. 4. Therefore, we can rule out electric field behavior as a source for any changes in LIDT from 2013 and 2017. On the other hand, the spectral shift is indicative of structural changes within the coating, which may influence LIDTs.

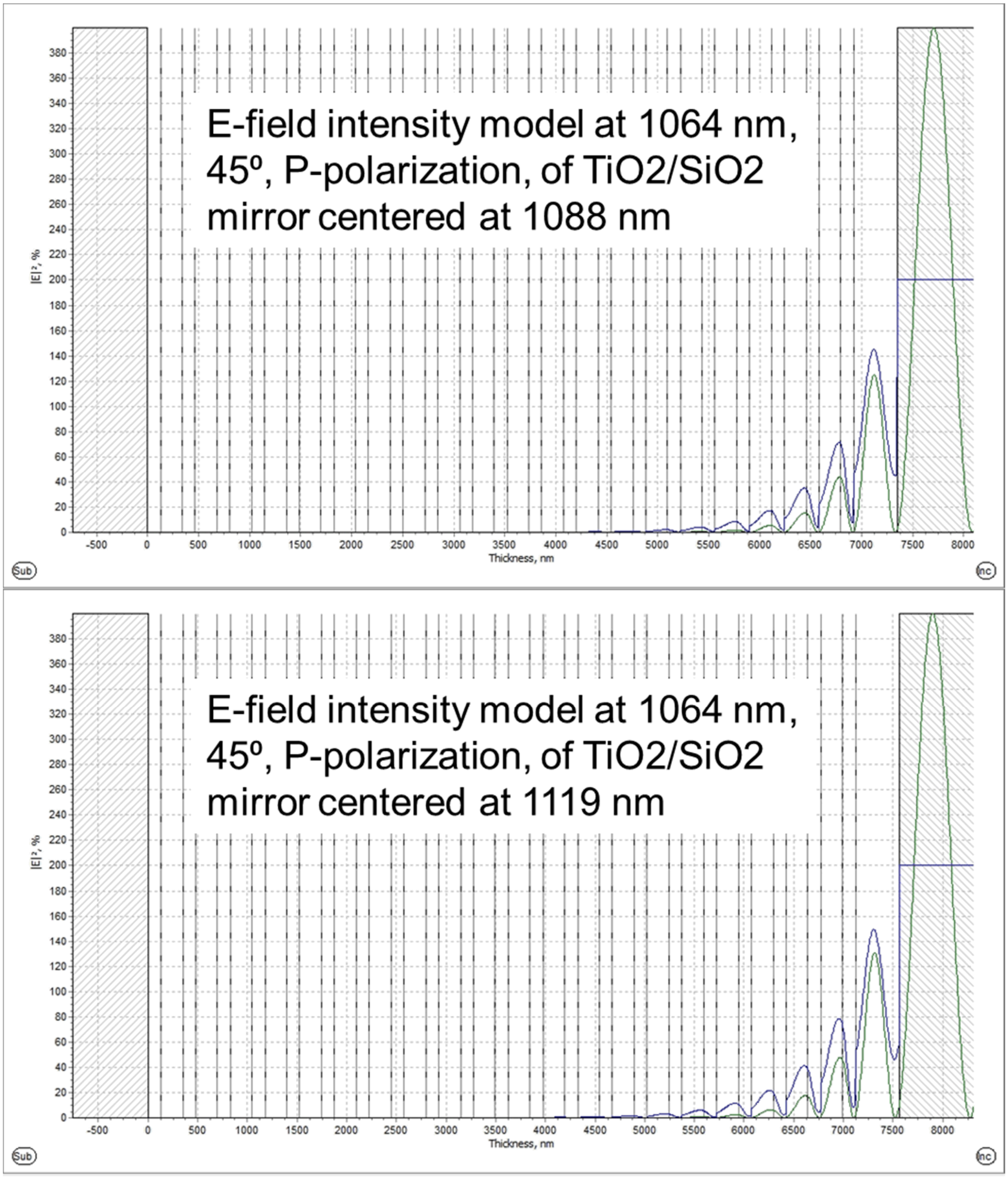

Figure 4: Electric field intensity model at 1064 nm, 45□ AOI, P-polarization of the mirror coating with 21 titania layers. The center of the high reflection band was originally at 1088 nm, but over time, it shifted to 1119 nm. However, this 2.85% spectral shift resulted in negligible electric field changes, meaning that changes in LIDT between 2013 and 2017 are likely not attributed to electric field differences.

To highlight the ability of titania layers for increasing the bandwidth of HR coatings, Fig. 5 shows HR bandwidth with respect to the number of titania layers in the coatings. The HR bandwidth is almost exactly 3 times higher in the titania/silica coating compared to the hafnia/silica coating.

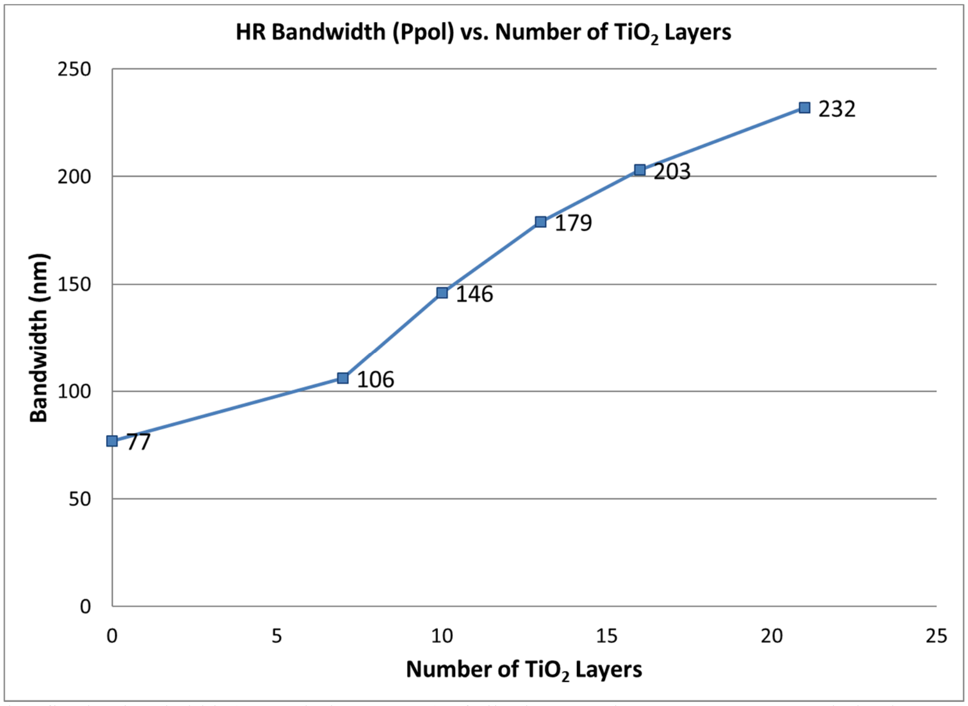

Figure 5: High reflection bandwidth (transmission < 0.5%) of all mirror coatings at 45° AOI, P-polarization, centered at 1054 nm.

The LIDT of each coating is presented in Fig. 6, and the amount of LIDT degradation is presented in Fig. 7 as a ratio of the initial LIDT over the 2017 LIDT.

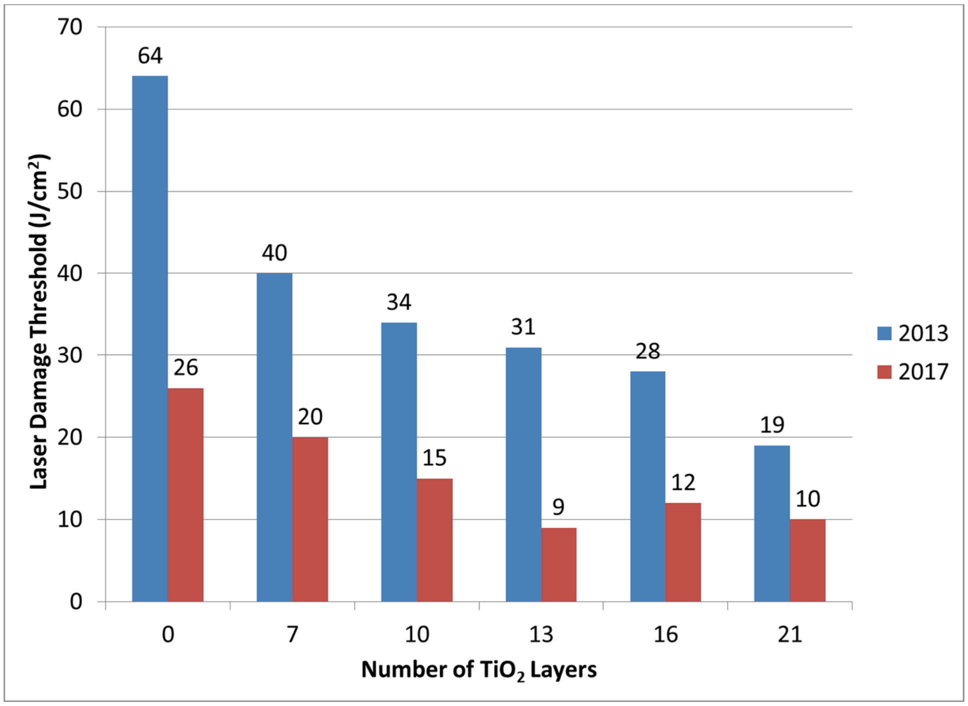

Figure 6: LIDT of each mirror coating taken at 1064 nm, 45° AOI, in P-polarization. The measurement error is +/- 1 J/cm^2. The LIDT degradation between the initial tests and the later tests taken in 2017 is an apparent characteristic of every coating.

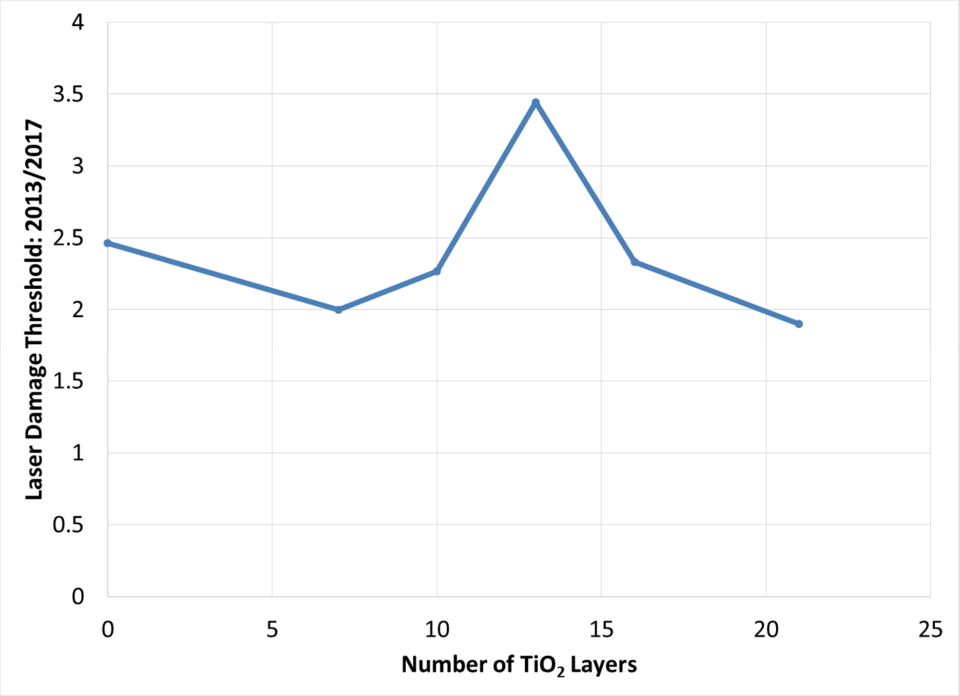

Figure 7: The LIDT degraded by a factor of 1.9 to 3.5 since initial LIDT tests were performed.

Since the initial LIDT tests were performed, Fig. 7 shows that the LIDTs have degraded by a factor of 1.9 to 3.5. Coatings containing hafnia do not have a clear advantage in terms of resisting degradation: the hafnia/silica coating degraded by a factor of 2.5, and the titania/silica coating degraded by a factor of 1.9. However, the main advantage of using hafnia, assuming the coating's spectral characteristics are suitable for the application, is that its initial LIDT is highest. This means any degradation that occurs may still result in the coating having an acceptable LIDT over time.

In order to understand the cause of the LIDT degradation, one clue is to analyze the number of NP defects in the coatings, which are indicative of contamination, or coating defects such as nodules. During the LIDT tests, the number of NP damage sites were recorded at the damage threshold fluence. Figure 8 shows the number of NP defects detected in each coating.

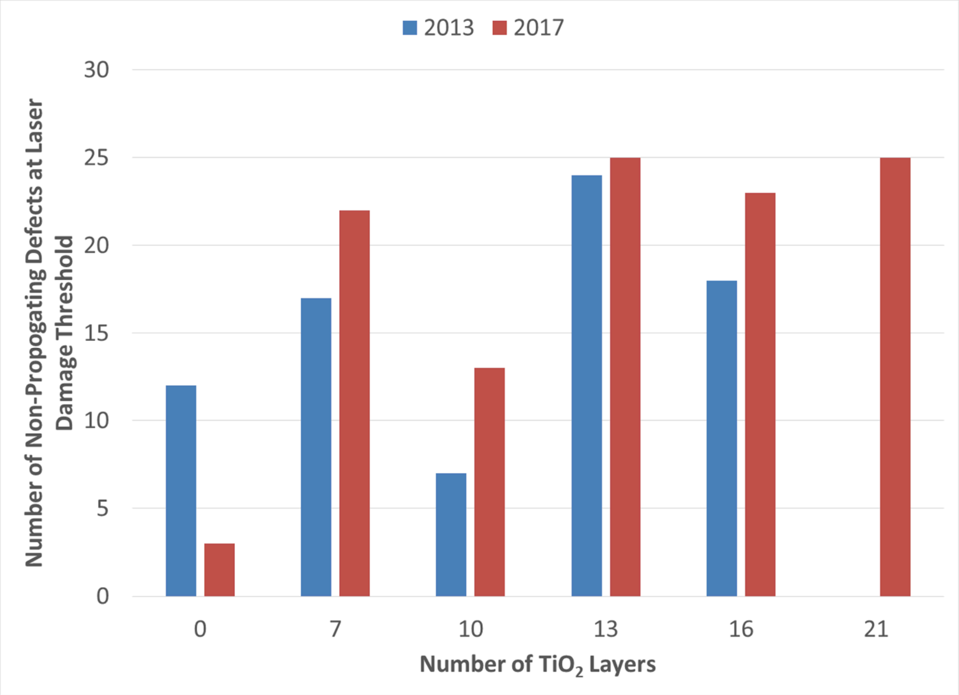

Figure 8: Number of NP defects present at the laser damage threshold fluence in each mirror coating.

The coatings containing titania have more defects in 2017 compared to their initial levels. That being said, only the coatings containing 13 or 21 titania layers reached their damage threshold due to the presence of 25 or more NP damage sites. The other four coatings reached their damage threshold due to the detection of propagating damage. Since propagating damage is usually related to intrinsic properties of the thin film rather than external problems such as contamination and nodules, this suggests that a thin film aging effect is responsible for the decreased LIDTs. The spectral shifts that occurred over time are also indicative of structural changes within the coatings, and may be related to the aging effects that reduce laser damage resistance. However, the increased number of surface defects detected in the coatings containing titania will not be ignored. In fact, contamination is a well-documented problem in optical coatings [12-15]. For this reason, in future work, we shall clean the samples using a method such as alcohol soaking [12,13] and retest to determine whether cleaning helps recover the initial LIDTs.

4. CONCLUSION

Over a period of 3-4 years, the LIDTs of hafnia/titania/silica coatings were reduced by a factor of 1.9 to 3.5. A thin film aging effect is likely responsible for this outcome, in addition to increased contamination, particularly for coatings containing titania. We have yet to test the effect of cleaning the optics to see if some recovery of the initial LIDT is possible. The implication of these results is that coatings may damage in the beam train sooner than expected. Until further studies suggest otherwise, it may be prudent to prepare optical coatings with LIDTs that are 2-3 times higher than the operating fluence of the laser system in order to compensate for LIDT degradation, and prolong the operational life of the optics.

If we had the foresight in 2013, we would have tested these samples with fs pulses, since ultrafast LIDTs depend mainly on intrinsic properties (bandgap) of the coating materials rather than extrinsic problems such as contamination [16, 17]. In other words, LIDT testing using fs pulses could help to more directly identify the contribution of thin film aging effects in LIDT degradation. In addition, it would be interesting to see if LIDT degradation is a problem with other coating technologies such as ion-beam sputtering and atomic layer deposition.

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