Impact of contamination and aging effects on the long-term laser damage resistance of SiO₂/HfO₂/TiO₂ high reflection coatings for 1054 nm

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Abstract. The laser damage thresholds of optical coatings can degrade over time due to a variety of factors, including contamination and aging. Optical coatings deposited using electron beam evaporation are particularly susceptible to degradation due to their porous structure. In a previous study, the laser damage thresholds of optical coatings were reduced by roughly a factor of 2 from the years 2013 to 2017. The coatings in question were high reflectors for 1054 nm that contained SiO_2 and HfO_2 and/or TiO_2 layers, and they were stored in sealed PETG containers in a class 100 clean room with temperature control. At the time, it was not certain whether contamination or thin-film aging effects were responsible for the reduced laser damage thresholds. Therefore, to better understand the role of contamination, the coatings were recleaned and the laser damage thresholds were measured again in 2018. The results indicate that the contamination played the most dominant role in reducing the laser damage thresholds of these optical coatings, even though they were stored in an environment that was presumed to be clean. © *The Authors. Published by SPIE under a Creative Commons Attribution 4.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI.* [DOI: 10.1117/1.OE.58.10.105105]

1 Introduction

Optical coatings with high resistance to laser damage are integral to the operation of the Z-Backlighter laser facility[1] at Sandia National Laboratories. The Z-Beamlet kJ-class laser operates with nanosecond pulses in the terawatt peak power range at both 1054 and 527 nm, and the Z-Petawatt laser operates with nanoseconds to subpicosecond pulses at 1054 nm. Our large optics coating system[2] utilizes electron beam evaporation to produce optical coatings that usually consist of HfO_2 and SiO_2 layers to achieve high laser-induced damage thresholds (LIDTs).

In previous studies,[3,4] we experimented with replacing HfO_2 layers with TiO_2 layers in mirror coatings to increase high reflection bandwidth and angle-of-incidence (AOI) flexibility at 1054 nm. However, TiO_2 has a lower bandgap and exhibits lower LIDTs compared to HfO_2.[5] We also discovered that the LIDTs of both HfO_2- and TiO_2-based mirror coatings from 2013 degraded even more after the coatings were stored for 4 years in sealed PETG containers in a temperature-controlled, class 100 clean room environment.[6] At the time, it was unclear whether contamination and/or thin-film aging effects were responsible for the reduced LIDTs, although both phenomena were suspected.[6] Therefore, the aim of this study was to better understand whether contamination influenced the lower LIDTs. In a nutshell, this was accomplished by cleaning the aged coatings and then measuring the LIDTs again to determine if laser damage resistance was improved by the cleaning.

2 Method

The mirror coatings that were tested in this study were first produced in 2013.[3] They are all 42 layers, quarter-wave stack designs, for 1054 nm, 45 deg AOI, P-polarization, with a half-wave outer layer of SiO_2 to improve resistance to laser damage.[7] SiO_2 was used for the low index layers, and HfO_2 and/or TiO_2 were used for the high index layers. The model in Fig. 1 shows that electric field intensities diminish near the substrate. The TiO_2 layers replaced HfO_2 layers near the substrate to afford more protection from the high electric field intensities since TiO_2 has a lower LIDT compared to HfO_2.

Of the five coatings produced in 2013, they contained either 7, 10, 13, 16, or 21 inner TiO_2 layers, with the coating containing 21 TiO_2 layers having no HfO_2 layers. An example of the layer thicknesses of the coating containing 10 inner TiO_2 layers is shown in Fig. 2. Also, a sixth coating was added to this study at a later time: in 2014, we produced a coating of the same design containing just HfO_2 and SiO_2 layers to use for comparison.

The coating process was electron beam evaporation in our custom chamber,[2] with ion-assisted deposition (IAD) from a 16-cm diameter RF ion source. The coating parameters are presented below in Table 1. In addition to IAD, the HfO_2 and TiO_2 layers were deposited with a backflow of oxygen gas into the coating chamber. The total pressure in the coating chamber during the deposition of HfO_2 and TiO_2 layers in 2013 was 1.5×10^{-4} Torr, but this pressure measurement is suspected 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 1.2×10^{-4} Torr during the deposition of the HfO_2 layers. The deposition temperature was 200°C for all coatings. In addition, the coating system used masking to maintain uniformity, planetary rotation, and quartz crystal monitoring for layer thickness control.

Following deposition, each coated sample was cleaned. Previous studies have shown that LIDTs can degrade due to environmental factors such as contamination, but, in some

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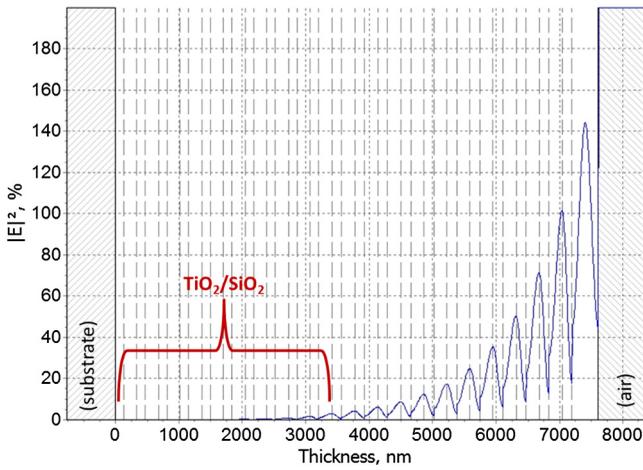
Fig. 1 Electric field intensity model at 1054 nm, 45 deg AOI, P-polarization, in mirror coating containing 10 inner TiO_2 layers and 11 outer HfO_2 layers. Vertical dashed lines indicate layer boundaries. The electric field intensity diminishes near the substrate. Using the TiO_2 layers near the substrate in the area of lowest electric field intensity is a strategy to protect TiO_2 layers from laser damage. This model was generated with Optilayer software.[8]

cases, the LIDT recovered to the original values after the coatings were cleaned in an alcohol/deionized water bath[9,10] or baked.[11] However, our lab is not equipped to accommodate the cleaning and bakout processes described in Refs. 9–11 if they are applied to meter-class optics. Therefore, we utilized our standard cleaning process instead, because it scales up to cleaning meter-class optics with our existing equipment. Our standard cleaning process involves washing the optic by hand with deionized water and Micro 90 detergent.[12]

Following cleaning, all samples were sent to Spica Technologies[13] for initial LIDT testing in 2013 or 2014. Since then, all samples were stored in clean polyethylene terephthalate-G (PETG) plastic containers in our class 100 clean room, which is temperature controlled. When LIDT testing occurred again in 2017, the samples were not cleaned, and testing was performed in a different quadrant of the sample compared to before. The results in 2017 revealed that the LIDTs of each coating diminished significantly, often by a factor of 2, and this LIDT decline occurred regardless of the number of TiO_2 layers in the coating.[6] Because contamination was a suspected cause of the LIDT decline, in 2018, the samples were cleaned with Micro 90 detergent and deionized water and sent to Spica Technologies again for
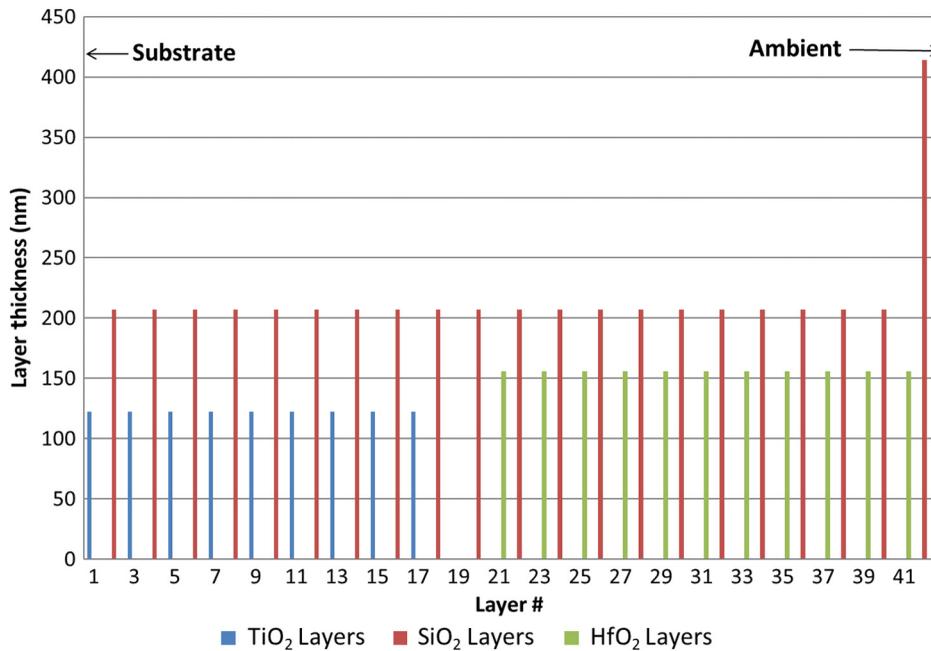
Fig. 2 Layer thicknesses of mirror coating containing 10 inner TiO_2 layers and 11 outer HfO_2 layers.

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

laser damage testing in a different quadrant. In total, each sample has undergone three LIDT tests: 2013 or 2014 (after cleaning), 2017 (no cleaning), and 2018 (after cleaning).

The LIDTs were measured at 1064 nm, 45 deg AOI, in P-polarization. The LIDT tests were conducted according to the NIF-MEL protocol.[14] Single transverse mode (Gaussian) and multilongitudinal mode laser pulses of 3.5 ns duration 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 (grow in size) as the laser fluence increases. These nonpropagating (NP) damage sites tend to be caused by the interaction of the laser field with nanodefects (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.[15]

According to the NIF-MEL damage criterion, the LIDT is reached at the fluence at which one 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 initial LIDT tests conducted in 2013/2014 were performed in the ambient environment (i.e., some humidity was present), whereas the tests conducted in 2017 and 2018 were performed in a dry nitrogen environment (0% humidity present). Ideally, all of the laser damage tests would have been performed in a dry nitrogen environment, because moisture in the coating can lead to higher LIDT.[16]

3 Results

The spectral transmission characteristics of each coating are shown in Fig. 3. The coating containing 21 TiO$_2$ layers (0 HfO$_2$ layers) has an high reflection (HR) bandwidth of 232 nm, whereas the coating containing 0 TiO$_2$ layers (21 HfO$_2$ layers) has an HR bandwidth of 77 nm (HR bandwidth is taken as interval, where transmission is <0.5%). Between 2013 and subsequent measurements in 2017, the coatings experienced a spectral shift due to aging, and the 2017 measurement of the coating containing 21 TiO$_2$ 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. There is a spectral shift of 31 nm, which is 2.85% larger than the original 1088-nm bandwidth. However, the HR bandwidth of this coating still encompasses the LIDT test wavelength of 1064 nm.

The spectral shift to longer wavelengths is not a surprise. Due to their porosity, coatings deposited with electron beam
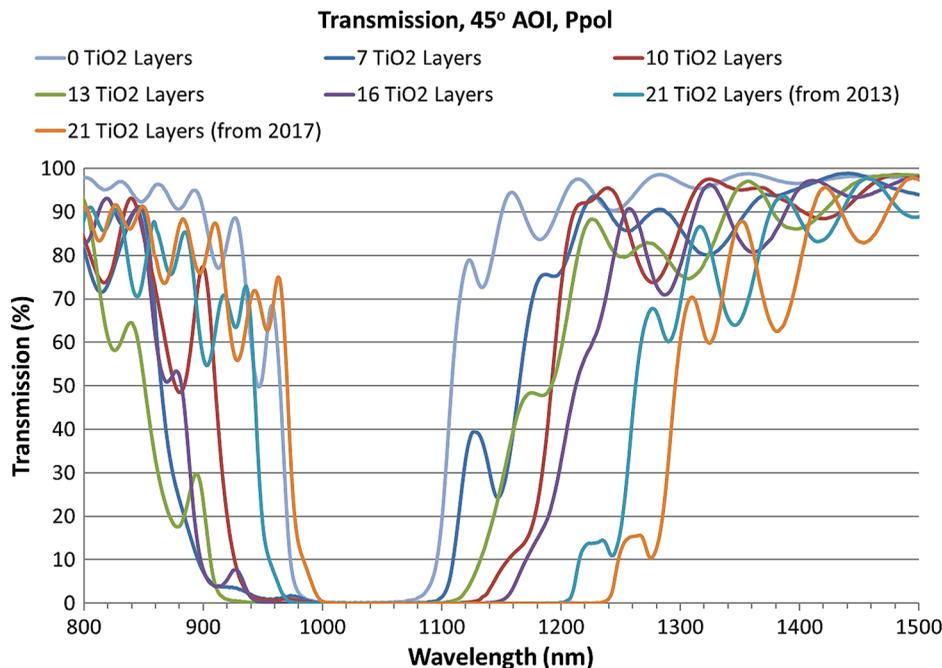
Fig. 3 Transmission spectra of all mirror coatings at 45 deg AOI, P-polarization. Between 2013 and 2017, the coatings experienced a spectral shift, and the coating containing 21 TiO$_2$ layers is shown as an example.

Laser Damage Thresholds
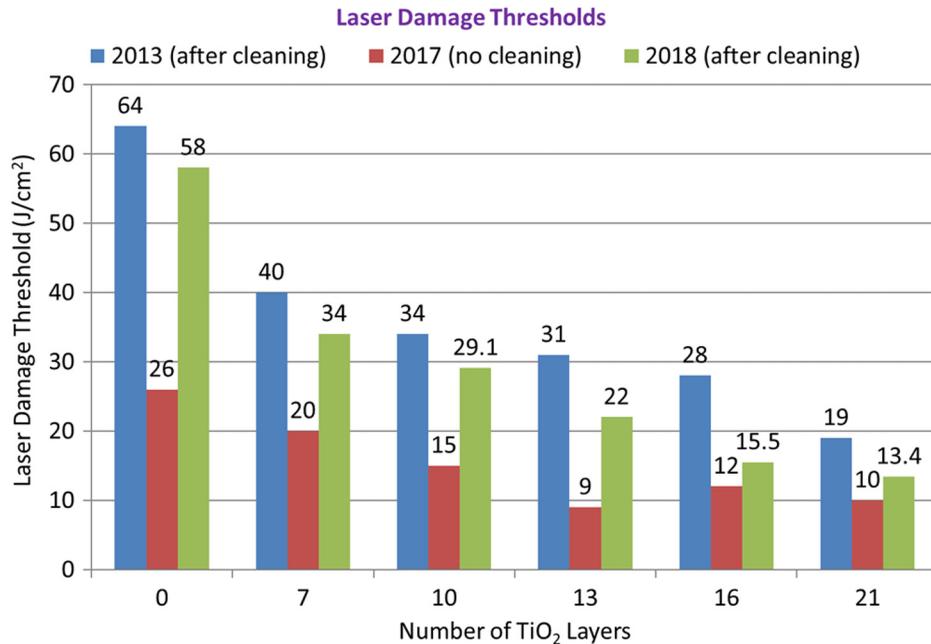
Fig. 4 LIDT of each mirror coating taken at 1064 nm, 45 deg AOI, in P-polarization. The measurement error is ± 1 J/cm^2. The LIDT degradation between the initial tests and the later tests taken in 2017 is an apparent characteristic of every coating.

evaporation undergo a spectral shift to longer wavelength, often referred to as "aging." Aging mostly occurs within the first month of deposition. This means the center of the HR bandwidths in 2013 is lower than those in 2017, and this hampers our ability to make a straightforward comparison between the initial LIDT tests and the LIDT tests that occurred in 2017 and 2018. Furthermore, the difference in humidity between the initial LIDT tests (ambient humidity) and the 2017/2018 tests (0% humidity) also limit our ability to directly compare LIDT results. Therefore, the LIDT results from 2013/2014 are suitable mostly as an approximation. In other words, we do not expect the LIDT measurements of the recleaned samples from 2018 to exactly recover to the original 2013/2014 values. The primary focus is the improvement in LIDT between 2017 and 2018 that occurred as a result of cleaning the samples with just mild detergent and deionized water.

The LIDT of each coating is shown in Fig. 4. These results indicate that LIDTs can be improved significantly by cleaning the coatings with mild detergent after they have spent years in storage. This suggests that contamination can accumulate in storage after long periods even if the storage method was reputed to be cleaned (sealed PETG containers, class 100 clean room, temperature control). The fact that the LIDTs improved after cleaning with just mild detergent and deionized water indicates that most of the contamination was weakly attached to the surface. In addition, because the coatings are porous, some water retention from the cleaning process is expected, especially because the samples were not laser damage tested in vacuum. That being said, the laser damage tests occurred in a dry nitrogen-filled environment, so the effect of moisture on the LIDT results is presumed to be minimal.

Overall, coatings containing lower numbers of TiO$_2$ layers exhibited the largest LIDT improvements between 2017 and 2018. Specifically, the coatings containing 0,

7, 10, and 13 TiO$_2$ layers experienced the largest LIDT improvement between 2017 and 2018: the 2018 LIDTs increased by roughly a factor of 2 from 2017. When the number of TiO$_2$ layers increased to 16 and beyond, large improvements in LIDT between 2017 and 2018 are no longer observed. This indicates that TiO$_2$ may not be a robust coating material for long-term use, but further studies are required to understand all the factors that contribute to this.

As mentioned previously, the NIF-MEL protocol tracks the number of NP defects present in the coating at the damage fluence. The number of NP defects observed for each coating is shown in Fig. 5. The initial LIDT tests have an NP defect distribution that appears random, regardless of the number of TiO$_2$ layers in the coating. However, the additional LIDT data from 2017 and 2018 indicate a trend toward higher numbers of defects in coatings that contain more TiO$_2$ layers. This again questions the robustness of TiO$_2$ for long-term use in laser systems. Interestingly, cleaning the coatings in 2018 in most cases did not reduce the number of defects present, even though laser damage thresholds improved. This suggests that contamination may not be fully responsible for NP defects. Intrinsic properties that change over time, particularly in the coatings that contain more TiO$_2$ layers, may be responsible for the escalation of NP defects.

4 Conclusion

HfO$_2$/TiO$_2$/SiO$_2$ mirror coatings can be exposed to contamination even if the storage method is presumed to be clean (PETG containers, class 100 clean room, temperature control). Surface contaminants significantly lowered the LIDTs of the coatings, but the LIDTs were improved by cleaning the coatings with just mild Micro 90 detergent and deionized water. The coatings containing higher proportions of HfO$_2$ layers as the high index material benefitted the most from cleaning, and LIDTs improved by about a factor of 2. The coatings containing mostly TiO$_2$ layers as the high index
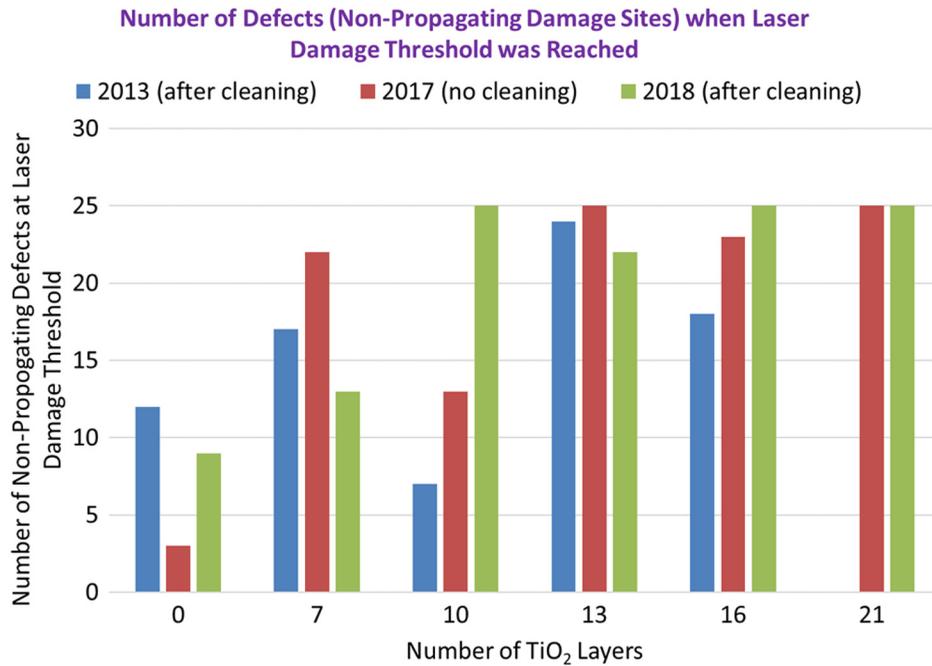
Fig. 5 Number of NP defects present at the laser damage threshold fluence in each mirror coating.

material experienced the lowest LIDT improvements after cleaning and continued to exhibit the highest numbers of NP defects. This questions the robustness of TiO₂ coatings for long-term use in high fluence laser systems. Further studies could be devoted to improving the quality of the TiO₂ films to decrease the long-term growth of defects. Also, if the LIDT tests had been conducted in the femtosecond regime, this could have helped to identify the impact of intrinsic thin film properties on the reduction of LIDTs over time since ultrafast LIDTs depend mainly on intrinsic properties of the coating materials rather than extrinsic problems such as contamination.[17,18]

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