Improved Laser Damage Resistance of Multi-Layer Diffraction Gratings Vapor-Treated with Organosilanes

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Abstract

Multi-layer dielectric gratings are used in high power laser systems to compress laser energy pulses. The final power of these short pulse petawatt class systems is limited by the laser damage resistance of the optical components in the system, especially the diffraction gratings. This work was motivated by the previous discovery that vapor-treatment of gratings with hexamethyldisilazane (HMDS) can increase the damage threshold. Gratings were laser damage tested, and then a simple room temperature vapor-deposition technique was used to coat them with several different disilazane compounds. The gratings were then damage tested again to determine if an increase in damage threshold had occurred. The laser-induced damage threshold of an HMDS-treated grating increased by 4.5% in a 1-on-1 damage test, while that of a tetramethyldisilazane-treated grating increased by 16.5% in an N-on-1 damage test. Both the N-on-1 and 1-on-1 damage thresholds of a bis-(trifluoropropyl)tetramethyldisilazane-treated grating increased, by 4.8% and 5.3 % respectively. Such increases in laser damage threshold are unprecedented and counterintuitive because it is widely accepted that the presence of organic material or coatings on the surfaces of optical substrates decreases their laser damage resistance. The results are especially encouraging since they were obtained on samples of sub-optimal quality. The next logical step is to attempt to confirm this effect on high-quality, freshly cleaned grating samples.

1. Introduction

High energy petawatt (HEPW) laser systems are capable of producing beams of unprecedented intensities for high energy density physics experiments. In a number of countries around the world, these systems are being built to develop laser fusion as an alternate energy source. Laser fusion uses lasers to compress and heat targets containing hydrogen isotopes, initiating fusion - the combination of nuclei to form helium and energetic neutrons. The current goal of laser fusion research is to reach and exceed "break even"- the point at which the amount of fusion energy produced equals the energy consumed by the laser. Two HEPW systems, Japan's GEKKO Petawatt and the United Kingdom's Vulcan Petawatt are currently in operation, while several more, including the OMEGA Extended Performance (EP) laser, are under construction or in planning[1].

OMEGA EP is an addition to the existing fusion laser system, OMEGA, at the University of Rochester Laboratory for Laser Energetics (LLE). The OMEGA EP system, expected to begin operation in 2008, will have two beamlines equipped with a short pulse (1 ps to 100 ps) capability at a wavelength of 1053 nm. These two beams can be directed into the OMEGA laser's target chamber to be used for fast ignition experiments, which use a pulse of energetic electrons to heat the compressed fuel, thus igniting the fusion reaction[2], and to produce short pulses of x rays to "backlight" imploding fusion targets for diagnostic purposes. The short-pulse beams interacting with plasmas produced by longer pulses will also be used to study high energy density physics, such as high-intensity laser-matter interactions, in OMEGA EP's target chamber[3,4].

The short pulses are created by chirped pulse amplification (CPA)[5], as shown in Figure 1. To amplify the laser pulse without damaging the amplifier, a short pulse from the source is first chirped, or stretched into a longer, lower-power pulse in which the longer wavelengths travel at the front. The pulse is amplified and then compressed by a series of four diffraction gratings. The compression occurs as the longer wavelengths at the front of the amplified pulse are diffracted more and therefore forced to travel longer paths than the shorter ones, allowing all wavelengths in the pulse to arrive at the fourth grating at the same time. Because the fourth grating in the series experiences the shortest pulse length it subject to the highest fluence, or power per unit area. The damage resistance of this last grating is the limiting factor on the amount of energy that can be obtained in the compressed laser pulse. Consequently, this last grating must not only be of very high optical quality, but it must also have an exceedingly high laser damage threshold. The laser damage resistance of previous-generation gold diffraction gratings was around 0.5 J/cm^2 while the minimum requirement for the gratings to be used in OMEGA EP is around 2.7 J/cm^2 for a pulse length of 10 ps[4].

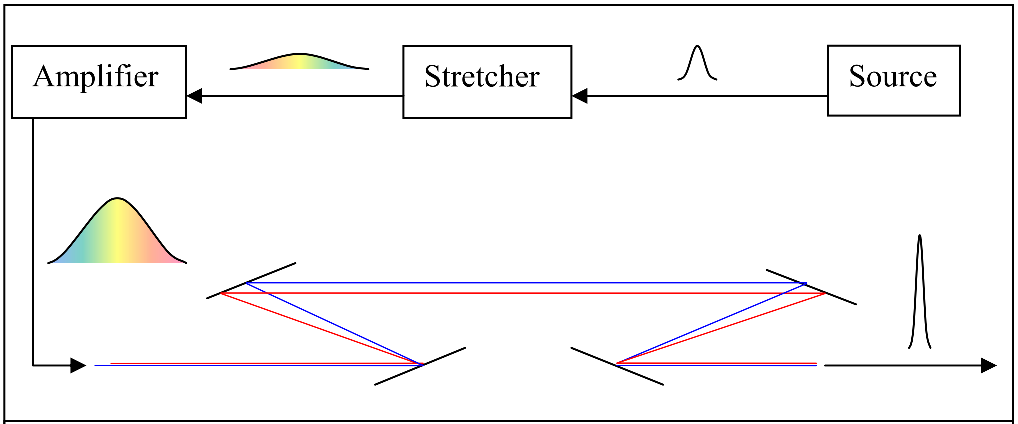


Fig 1. Schematic diagram of chirped pulse amplification

Multi-layer dielectric (MLD) diffraction gratings (see Figure 2) are composed of reflective stacks of thin (subwavelength) SiO_2 and HfO_2 layers which differ in dielectric constant. Diffraction of light is caused by the grooves etched into the top SiO_2 layer. MLD gratings are currently used because of their much higher laser-induced damage thresholds in comparison to previous gratings[6]. However, because the damage resistance of the last grating is the limiting factor on the energy of the laser, new ways to increase the damage threshold are desirable.

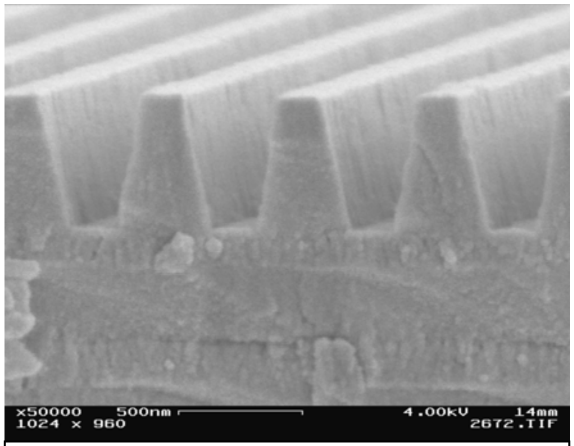


Fig 2. SEM micrograph of an MLD grating. The grooves are 500 nm deep.

In preliminary experiments by the Optics and Imaging Sciences group at LLE, gratings were exposed overnight to the organosilane compound hexamethyldisilazane, (HMDS), which is used in the semiconductor industry as a coupling agent to increase the adhesion between a silica wafer and a photoresist. Organosilanes are compounds composed of silicon atoms carrying up to four different carbon-containing functional groups. MLD gratings that were vapor treated with HMDS reproducibly demonstrated increases of >20% in laser damage thresholds[7]. This increase in damage resistance, known as “laser hardening,” was unexpected and counterintuitive, because conventional wisdom dictates that the presence of organic materials on optical components will lead to reduced laser damage thresholds. The goal of this investigation was to assess the reproducibility of the phenomenon, find the necessary conditions for the reaction, and identify whether the laser hardening effect is unique to HMDS.

During this investigation, candidate organosilanes were used to vapor treat glass slides to assess their potential for treating diffraction gratings. The chemistry of the reaction of the compounds with silica surfaces is described in Section 2. Estimates of the necessary exposure time for a saturated coating were obtained by measuring the water contact angle on the surfaces, as summarized in Sections 3 and 4. Diffraction grating samples were damage tested before and after treatment with the most promising organosilanes, as described in Section 5. Section 6 details improvements in the laser-induced damage thresholds that were found as a result of this treatment.

2. Chemistry of Organosilanes

Two different classes of organosilanes that bond easily to silica surfaces were identified. Both disilazane (silamine) and chlorosilane compounds are widely used to change the surface chemistry of silica capillary columns for gas chromatography by bonding organic functional groups with widely different polarities to the inner surface of the column[8]. Silylation occurs as the compounds react with and replace hydroxyl groups on the silica surface. The reaction utilizes the natural vapor pressure of the chemicals and proceeds in the vapor phase at room temperature and pressure. This feature makes vapor treatment with these chemicals simple, and because it does not require heat, it avoids the risk of shattering the sensitive MLD gratings by thermal shock. The disilazane compounds can react completely in a two-step mechanism with the surface silanols (see Figure 3). In this example, the HMDS first reacts with a surface hydroxide group to attach one trimethylsilane group to the substrate surface to form trimethylaminosilane, which further reacts with the surface to deposit a second trimethylsilane group, which forms ammonia as a byproduct. The overall reaction with HMDS can be written as[9]:

$$2\ \equiv\text{Si–OH} + (CH_3)_3\text{–Si–NH–Si–}(CH_3)_3 \rightarrow 2\ \equiv\text{Si–O–Si}(CH_3)_3 + NH_3 \qquad (1)$$

The chlorosilane compounds react via a simpler single step reaction shown in Figure 4. For example, a trimethylchlorosilane (TMCS) molecule interacts with the surface silanols to deposit a single trimethylsilane group, forming hydrogen chloride gas as a byproduct as shown in the equation below[10]:

$$\equiv Si–OH + (CH_3)_3SiCl \rightarrow \equiv Si–O–Si(CH_3)_3 + HCl \qquad (2)$$

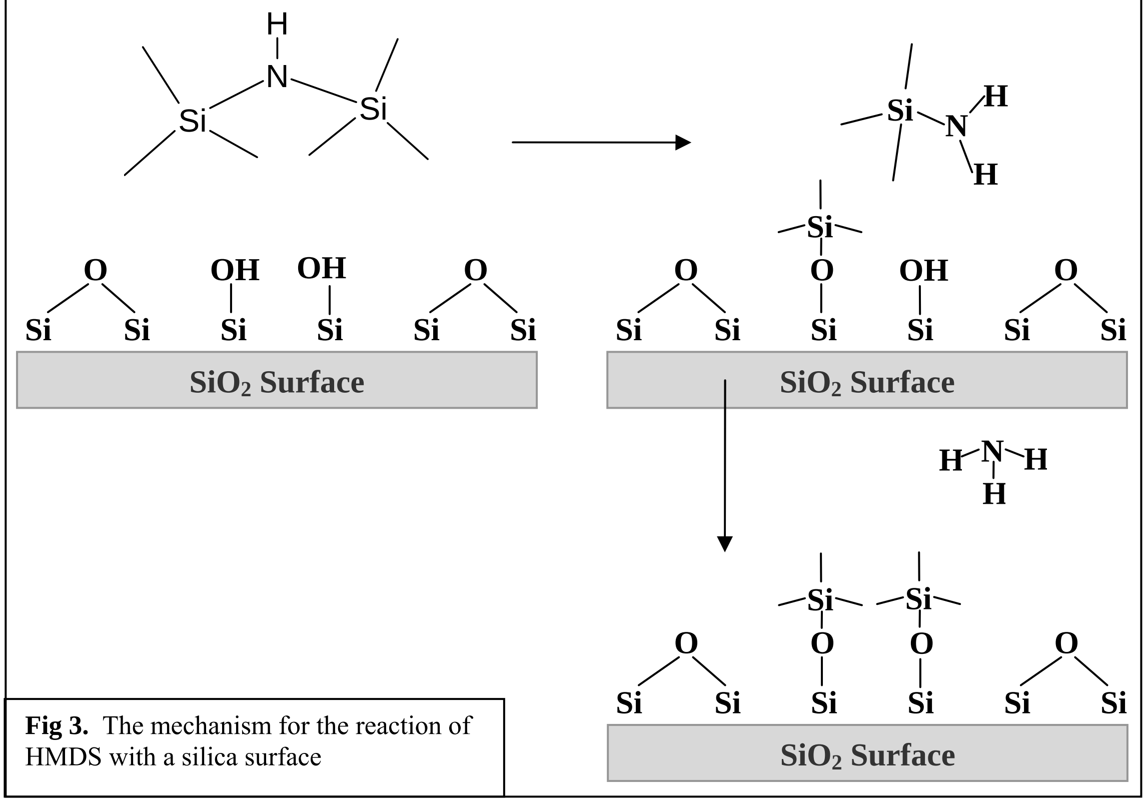
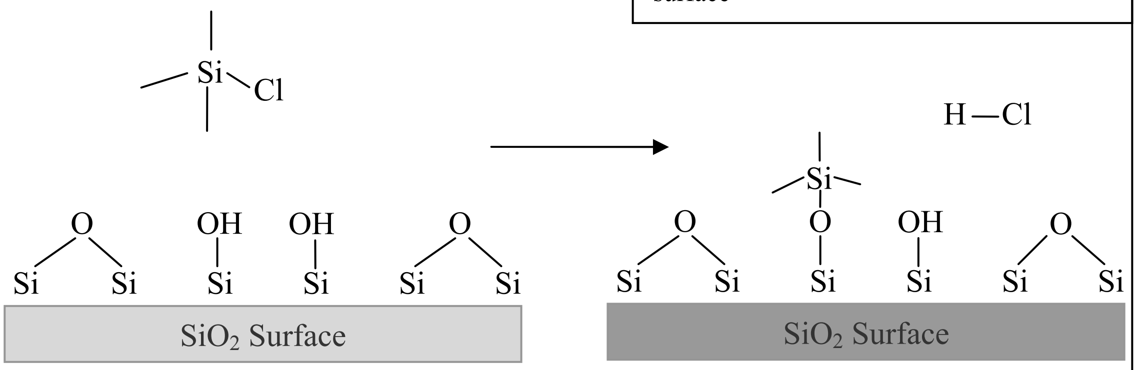


Fig 3. The mechanism for the reaction of HMDS with a silica surface

Fig 4. The reaction of TMCS with a silica surface



3. Silylation Experiments

Initial experiments investigating the reactivity of different compounds with a silica surface were performed with each candidate organosilane. Because of a very limited supply of grating substrates, initial silylation experiments were carried out on cleaned, baked dry microscope slides. The slides were treated with HMDS, tetramethyldisilazane (TMDS), 1,3-di-n-octyltetramethyldisilazane (OTMDS), bis(trifluoropropyl)tetramethyldisilazane (FTMDS) and TMCS. The HMDS was used to replicate the original experiment, the TMDS was of interest because of its close structural similarity to HMDS, and the OTMDS was chosen to investigate the effect of a longer hydrocarbon chain on the "hardening" effect. The effect of the trifluoropropyl groups in the FTMDS would show whether the laser hardening was unique to silanes with strictly hydrocarbon end groups. Finally, treatment with TMCS deposits the same trimethylsilyl groups on to the surface as does treatment with HMDS. Treatment with TMCS would therefore identify whether the silylation of the surface or the mechanism of the treatment is responsible for the increase in damage threshold. The effect of elevated temperature (50 C) on the silylation with HMDS was also investigated.

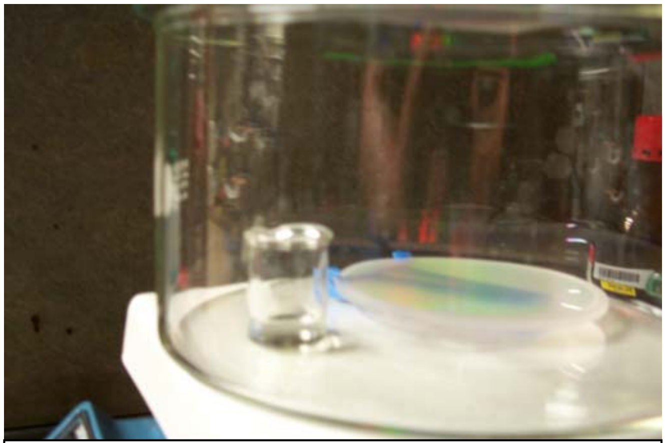


Fig 5. General silylation setup used for all experiments showing the treatment of a grating sample (flat, right) with FTMDS (beaker, left).

A simple chemical vapor deposition technique at room temperature was used to treat the slides with the silanes for different amounts of time. Samples were placed in a chamber with an open vial containing approximately 2 ml of each organosilane for 2, 4, 6, 22, and 30 hours, using the setup shown in Figure 5. Control samples consisted of both a clean, untreated glass slide and a slide assumed to be fully silylated, prepared by saturating the slide with the given compound. For the elevated temperature trials, the hotplate that was used as the work surface to support the substrates and the container holding the organosilane was turned on and regulated at 50°C.

The degree of silylation, or the amount of silane that had been deposited on the slide, was tracked by measuring the water contact angle using a VCA 2500XE contact angle instrument (AST Products, Inc), as shown schematically in Figure 6. The contact angle of a droplet of water on a surface is a measure of the hydrophobicity, or the free energy, of a surface. To measure the contact angle, a drop of water was deposited on to the substrate, and a digital photograph of the droplet profile was taken immediately.

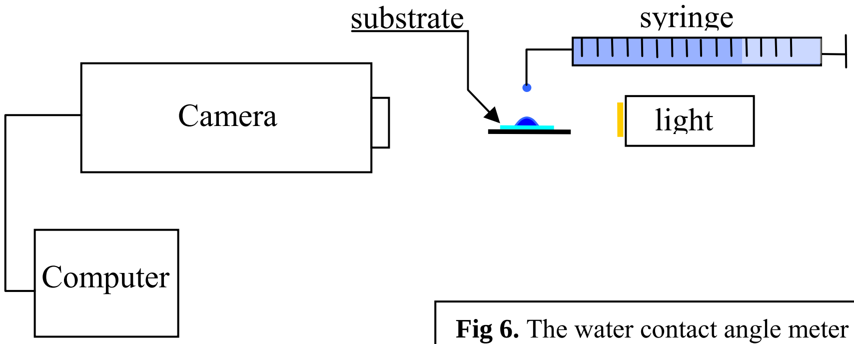


Fig 6. The water contact angle meter setup

Examples of two photographs with calculated angles, one for a TMCS treated slide and one for a clean glass slide, are shown in Figure 7. In the photographs, the droplet is outlined by the dark band, where light is refracted away from the camera. Software is used to calculate the angle between the tangent to the edge of the droplet touching the surface, and the surface. The clean glass slide exhibits a very low contact angle, because the hydrophilic hydroxyl groups on the surface cause the polar water drop to spread and flatten across the slide. Nonpolar organosilane groups deposited onto a silica surface render it more hydrophobic, repelling the water droplet and making it bead up more, which increases the contact angle. Increased surface silylation (i.e. greater density of organosilane groups deposited) increases the contact angle along with the hydrophobicity. Each reported contact angle is the average of at least five measurements taken on separate areas of the substrate.

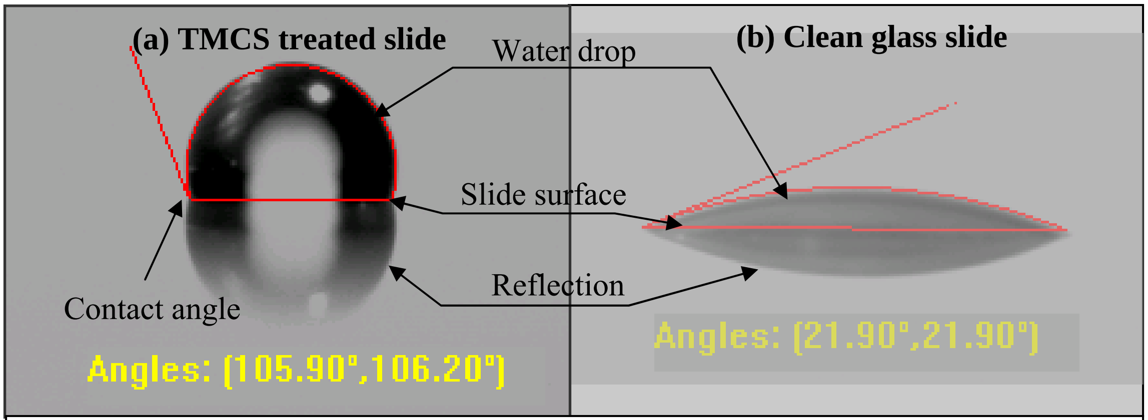


Fig 7. Photographs of water drops on (a) a TMCS treated slide and (b) a clean glass slide, showing very different contact angles.

4. Slide Silylation Results

Figure 8 plots the contact angle against exposure time to show the level of silylation as a function of time. HMDS-treated samples were fully silylated after a 30 hour exposure, as were the samples exposed to TMDS. Due to their much lower vapor pressures, both OTMDS and FTMDS failed to fully silylate the slide during the 30 hour exposure period. However, the difference between 30 hour exposure FTMDS vapor treatred sample and the fully silylated control was small. Because of the very low vapor pressure of OTMDS vapor treatment experiments will not be feasible unless an alternate method can be found to raise its vapor pressure (e.g., conducting vapor-phase exposure under reduced pressure). Since developing such a method was beyond the scope of this work due to time constraints, only FTMDS was further evaluated.

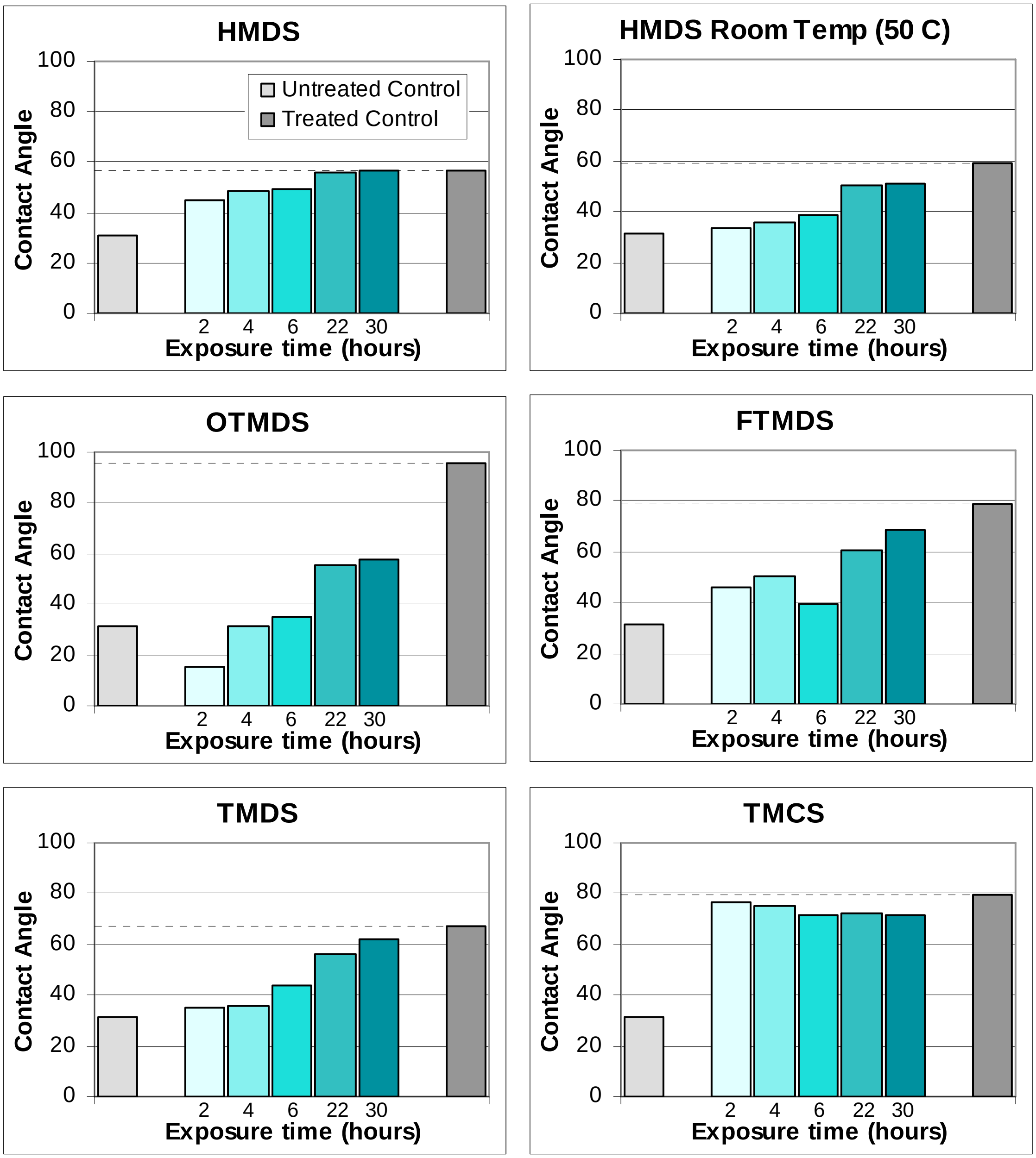


Fig 8. Contact angle as a function of exposure time for glass slides exposed to various silanes. Untreated controls are clean glass slides and treated controls are slides soaked in the silane. Because increased silylation increases surface hydrophobicity, the water contact angle is indicative of increased silylation.

The TMCS had by far the shortest silylation time of the compounds tested, reacting completely within two hours. This fast silylation rate was unsurprising because chlorine-containing organic compounds are associated with high reactivity. The resulting shorter sylilation time would be more convenient as a treatment for the full-scale gratings. Treatment with TMCS also resulted in a higher contact angle than the HMDS, indicating that it was more effective at depositing a higher number of trimethylsilane groups per unit area, perhaps due to its smaller molecular size. However, treatment with TMCS proved to be somewhat impractical for use on the gratings. The reaction of TMDS with the substrate produces HCl vapor, which forms deposits on all exposed glass surfaces to produce a cloudy, frostlike layer. Upon removal from the chamber, the HCl quickly evaporates, but an oily sheen removable with a distilled water wash remained on the surface. Application of TMCS to the MLD gratings would require an extra process step, increasing the chance of damage to the delicate gratings. Because of this complication, the chlorosilane family was not investigated further.

Water contact angle measurements were then attempted on a clean, untreated grating, but could not be obtained because the water droplets ran down the grooves. The grating sample was exposed to HMDS for 30 hours, and the water contact angle was then measured successfully. Treatment of the

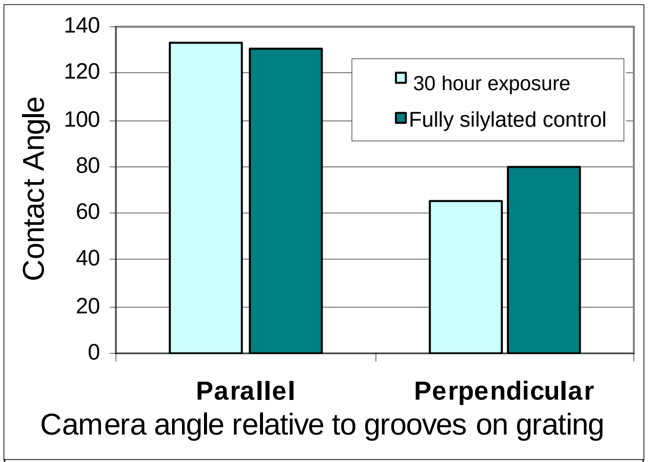
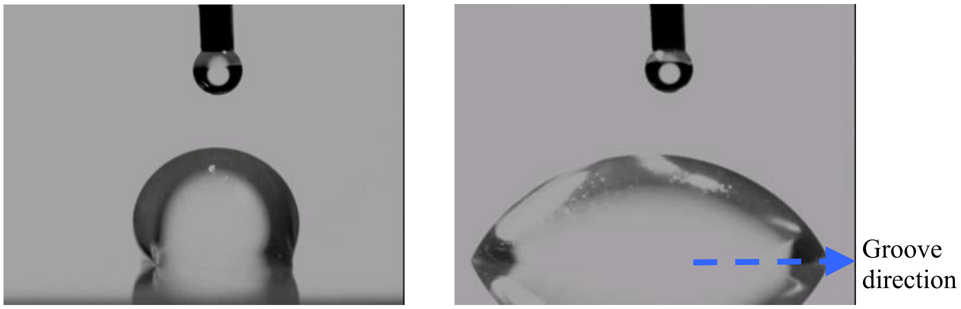


Fig 9. The water contact angle (degrees) on the vapor treated grating compared to a fully silylated control, viewed both parallel and perpendicular to the grooves.

grating surface increased its hydrophobicity, which prevented the droplets from spreading into the grooves. This observation is a clear indication that silylation had occurred. As demonstrated in Figures 9 and 10, the contact angle measurements depend on the angle of the camera relative to the direction of propagation of the grooves on the grating. Measurements obtained with the camera perpendicular to the grooves are much lower than when the image is taken parallel to the grooves. The measurements for water contact angle on the vapor-treated grating were similar to those obtained on a fully silylated grating, and indicated that as expected from the microscope slide experiments, silylation had occurred.



(a) Viewed parallel to grooves

(b) Viewed perpendicular to grooves

Fig 10. Variation of contact angle on a grating surface as viewed from different angles. In (a), the groove direction is into the page.

5. Damage Threshold Experiments

Untreated diffraction grating samples were damage tested prior to silylation. Because of limits on grating availability, the samples used were recycled from previous experiments, and had been cleaned months earlier and stored. The cleaning process uses high temperature immersion in acid piranha solution (H_2SO_4 and H_20_2).

Both 1-on-1 and N-on-1 laser-induced damage tests were performed. A 1-on-1 damage test irradiates separate sites with increasing energies until visible damage occurs, while an N-on-1 damage test irradiates a single site at progressively greater intensities until damage occurs. The second test is important because of a phenomenon called "laser conditioning," in which a higher laser damage threshold is obtained by successively irradiating the surface at increasing energies. The tests were performed at the LLE damage test facility, using a laser operating at 1054 nm with a pulse width of 10 ps and a spot size of 370 microns.

The samples were then vapor-treated for 30 hours with HMDS, TMDS, and FTMDS. Because of limitations in grating availability, time, and the availability of the damage test facility, the three organosilanes that were found to be the most promising from the initial silylation experiments were chosen to be tested. Based on both the microscope slide experiments and a trial exposure of one grating, 30 hours was the necessary time to obtain complete or almost complete silylation.

6. Damage Test Results

The results of the damage tests are shown in Figure 11. The TMDS treated sample showed the largest increase, 16.5%, from 2.12 to 2.57 J/cm^2 in the N-on-1 damage test, but the 1-on-1 damage threshold was virtually unaffected. Conversely, the 1-0n-1 damage threshold of the HMDS treated sample increased 4.5 %, while the N-on-1 damage test remained almost constant. The FTMDS treated grating was the only one to show increases in both damage thresholds (approximately 5% for each) though the increase in the 1-on-1 test was within the margin of error.

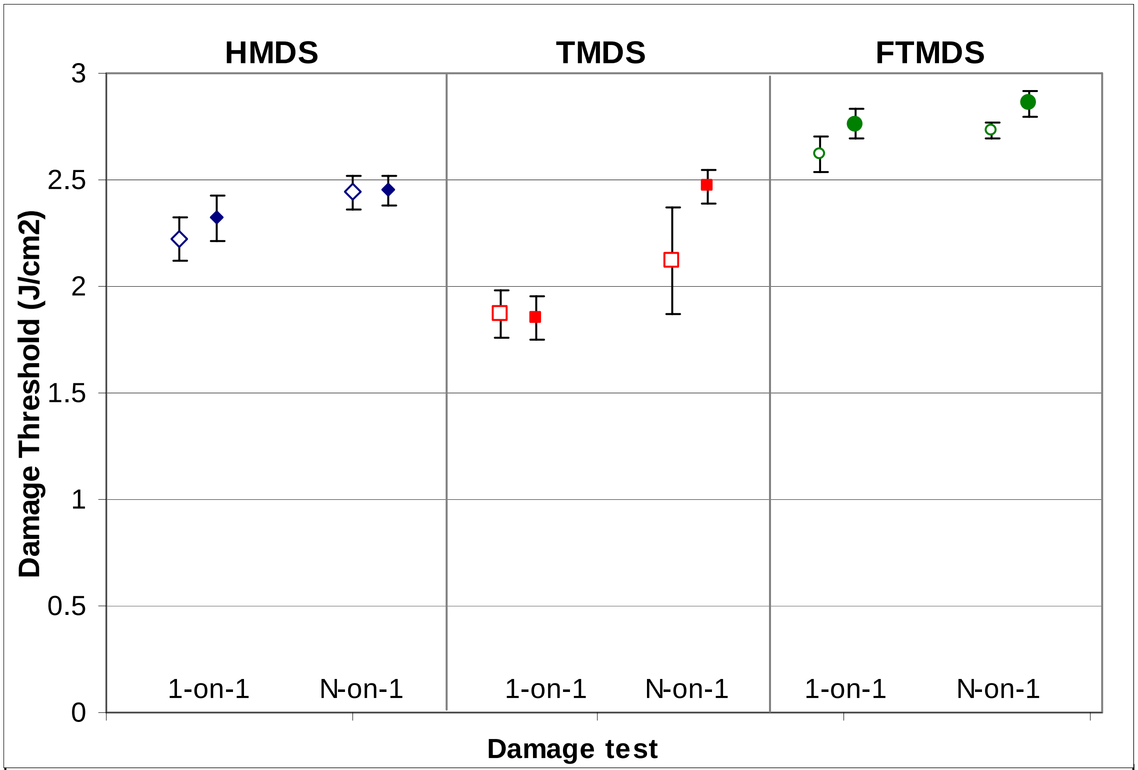


Fig 11. A comparison of the damage thresholds of MLD gratings before and after treatment with HMDS, TMDS and FTMDS, in both 1-on-1 and N-on-1 damage tests. Open symbols are thresholds before treatment, and closed symbols are after treatment. The error bars are determined from the variance from the 7-10 trials used to obtain the average value.

7. Discussion

Vapor treatment with the organosilane compounds is preferable over other surface treatment options, such as spin-coating. Spin-coating is a commonly used physical deposition technique that involves spinning the substrate at up to several thousand rpm to evenly coat the substrate with a solution. The excessive handling required by this, and most other deposition processes, risks damaging the large, delicate optics; spinning such a substrate up to thousand rpm is risky at best. The vapor treatment reaction can be carried out with minimal equipment, minimal handling of the optics, and at room temperature and pressure. The process chemically bonds only a single monolayer to the surface of the substrate, eliminating the need to control the coating thickness, the coating time, or the amount of chemical penetration into the porous surface. Because the vapor-deposition process inherently produces pure vapor that contacts the surface directly, the need to purify the chemicals before deposition is eliminated. Additionally, it would be relatively simple to implement because facilities exist to provide a similar vapor-treatment step (an ammonia hardening step of sol-gel anti-reflective optical coatings), although the toxicity and flammability of the organosilanes make them more difficult to work with.

Since Figure 11 shows that vapor treatment with all three chemicals caused increases in damage thresholds, it is now established that the "hardening" effect is not limited to HMDS. The increase in both damage thresholds obtained with the FTMDS treatment is also significant because it shows that the laser hardening phenomenon is not unique to disilazanes with only hydrocarbon groups, but applies to a wider class of compounds. An increase in both damage thresholds is desirable, because otherwise gratings would need to be conditioned before being exposed to peak intensities if the N-on-1 damage threshold were much higher than the 1-on-1 damage threshold. The large increase in the N-on-1 damage threshold obtained with the TMDS also makes it a good candidate for use.

Interestingly, this experiment did not reproduce the > 20 % increases in damage threshold obtained in the preliminary trials. The reason for this is most likely due to the physical condition and cleanliness of the available gratings. Due to limited availability of gratings, only recycled samples from previous tests, of varying age and with different handling, etch, and cleaning processes were used. It is impossible to estimate magnitude of the effect of the condition of these "recycled" gratings on the results, and any increase in damage threshold is therefore very encouraging. Since processing and cleaning methods are known to affect the damage thresholds of the gratings,[11] the history of the gratings used in further experiments should be as controlled as possible, and the gratings should be cleaned in acid piranha solution just prior to testing to make sure that all trace organic contamination has been removed. The effect of the history of the grating (such as the etch process used to make the grooves) on the hardening phenomenon should be investigated to see which processes have the greatest effect. Further study is needed to optimize treatment conditions such as time and temperature, and a wider range of organosilanes needs to be tested. In particular, TMCS should be tested because, despite the issue with the haze generated by the HCL byproducts, the faster exposure time and more complete silylation could ultimately make it more efficient to use than HMDS. The treatment would help determine whether the reaction mechanism of the disilazane family, or some other factor associated with the deposited organosilane groups, is responsible for the hardening effect.

A number of spectroscopy techniques, including Fourier transform infrared spectrometry and UV-visible-near IR spectroscopy, can be used to identify the mechanism responsible for the hardening. Surface studies of the gratings by electron microscopy or atomic force microscopy both before and after treatment, and after laser conditioning and damage testing could also provide information on maximizing the benefit of the treatment. Furthermore, the hardening effect can also be looked at as a way to revive gratings whose damage threshold is below acceptable levels, either immediately after fabrication or after use in the laser system. An increase of even ~0.3 J/cm^2 in the damage threshold, as was obtained with the TMDS, would be enough to make a marginal grating useable again, reducing the need for new gratings.

An additional benefit of the organosilane coatings studied here might be to protect the gratings of petawatt lasers against organic contamination. Trimethylsilylated MCM-41 capillary columns, used in gas chromatography, have demonstrated decreased adsorption of organic compounds in comparison to untreated columns[12]. Because the chamber containing the gratings used for laser pulse compression is operated at very high vacuum, the volatility of organic materials that may be present in equipment and fixtures will be enhanced at the low operating pressure of the chamber ("outgassing"). These materials may redeposit on nearby optical elements subjected to petawatt peak power levels, including the gratings. This vapor-deposition process of residual volatile organic components is a major potential source of laser damage. If the gratings could be treated with a material that would either prevent deposition and absorption of volatile organics on the grating surfaces (or at least facilitate easy cleaning of the gratings), major cost savings could be realized in the operation of lasers such as OMEGA EP.

8. Conclusions

Hardening of multi-layer dielectric gratings used in high-energy petawatt class laser systems has been found to be possible by vapor-phase treatment of the gratings with a number of organosilane compounds. The process is relatively simple to implement, and could provide a way to increase the damage resistance of the gratings and ultimately allow for more powerful lasers. This work has shown an increase in damage resistance using three organosilane compounds. With further investigation on higher quality samples and optimization of the process, it may be possible to implement the process on a larger scale.

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