Protective Polymer Coatings for Laser Optics

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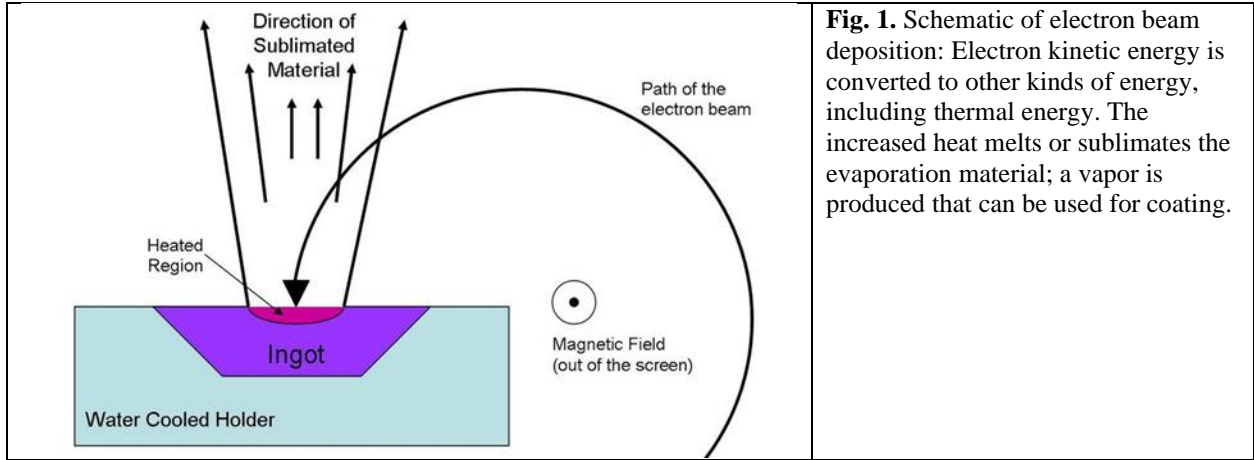Rochester NY, 14534

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Abstract

Mirrors and laser glass used in OMEGA and OMEGA EP are sensitive to water. When water vapor works its way into the pores of high-reflectance mirror coatings, the wavelength of peak reflectance shifts, leading to a reduced reflectance at the intended beam wavelength. Water exposure leads to pitting and eventually clouding on phosphate laser glass, causing light from the laser beam to scatter. Both of these effects ultimately lead to a loss of energy as the beam makes its way to the target. Different organosilanes and coating processes were tested on both mirrors and phosphate laser glass with the overall goal of slowing the absorption of water into the samples. An effective coating process was found for the mirrors that involves vapor depositing organosilanes in a nitrogen-purged atmosphere. Although vapor depositing organosilane coatings onto laser glass did not afford a sufficient level of protection from water vapor, polydimethylsiloxane (PDMS) applied by rod-coating was found to effectively protect the glass from water damage in an environment of 99% relative humidity.
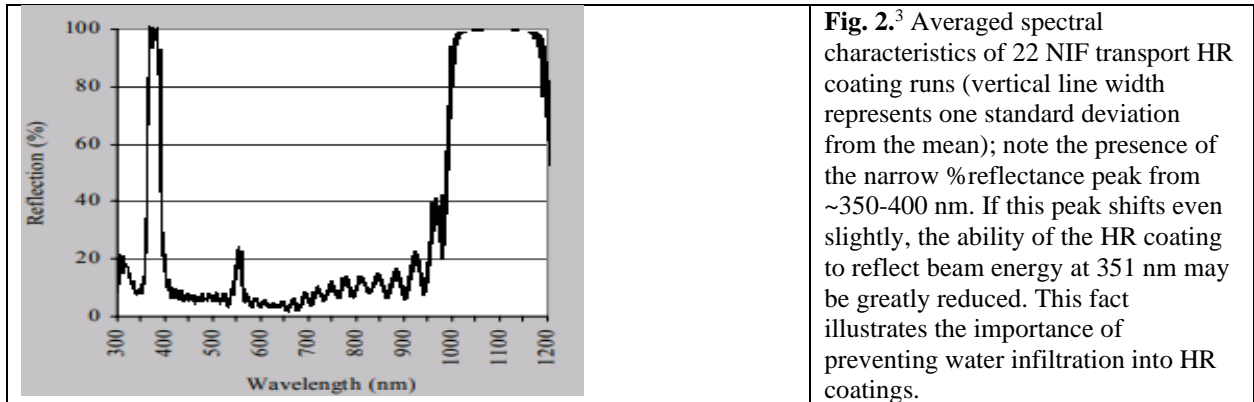
1. Introduction: Importance of the Sensitivity of Optics to Water Vapor

1.1 High Reflective Coatings

High power lasers are used to investigate the use of fusion as a practical source of energy. Many of these lasers use high reflective (HR) coatings composed of hafnia and silica layers on a glass substrate as mirrors to redirect the laser beam. Various methods of coating the substrate with hafnia and silica layers (sputtering, ion assisted deposition, e-beam deposition) can result in porous coatings. Electron beam deposition (**Fig. 1**) is the coating method primarily used at the Laboratory for Laser Energetics (LLE) for OMEGA and OMEGA EP, the Lawrence Livermore National Laboratory for the National Ignition Facility (NIF), and the Megajoule Laser Facility for CEA in France.[1, 2]

Fig. 1. Schematic of electron beam deposition: Electron kinetic energy is converted to other kinds of energy, including thermal energy. The increased heat melts or sublimates the evaporation material; a vapor is produced that can be used for coating.

Because deposition of the hafnia and silica is not uniform, many pores exist in the HR coatings for water vapor to infiltrate. When water works its way into the pores of the HR coating, both the refractive index and the narrow absorption band of the coating change (example shown in **Fig. 2**), which leads to major energy losses as the beam travels to the target.

Fig. 2.[3] Averaged spectral characteristics of 22 NIF transport HR coating runs (vertical line width represents one standard deviation from the mean); note the presence of the narrow %reflectance peak from ~350-400 nm. If this peak shifts even slightly, the ability of the HR coating to reflect beam energy at 351 nm may be greatly reduced. This fact illustrates the importance of preventing water infiltration into HR coatings.

HR coatings in the OMEGA and OMEGA EP lasers redirect laser beams primarily at 351 nm and 1054 nm wavelengths. The HR coating samples experimented with are intended for use with a 351 nm laser pulse. However, these coatings could also be used with a 1054 nm laser pulse, where they have a higher laser damage threshold.
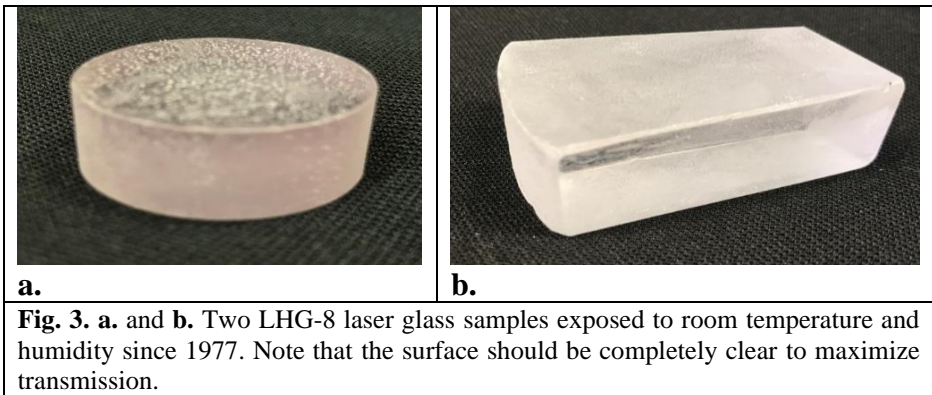
1.2 Laser Glass

LHG-8 is a phosphate-based laser glass used in many high-peak-power lasers (OMEGA, OMEGA EP, the NIF, Gekko-XII, LFEX (PW), Vulcan, and LIL[4]) as a gain medium to amplify

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the beam. This glass was chosen, in part, for its athermal properties. LHG-8 has a nearly zero temperature coefficient of optical path length ($+0.6 \times 10^{-6}$ / °C). This property is important because repeated laser shots raise the temperature of the glass, causing a change in optical path length and disturbance in the spatial oscillation pattern and overall oscillation performance of the beam.[5]

LHG-8 laser glass possesses desirable athermal properties, but it is sensitive to water vapor. The rods and disks in OMEGA and OMEGA EP experience "chalking" and pitting (**Fig. 3**), due to incremental lapses in atmospheric control of the nitrogen environment that the equipment is housed in.[6, 7] The chalking is a

Fig. 3. a. and **b.** Two LHG-8 laser glass samples exposed to room temperature and humidity since 1977. Note that the surface should be completely clear to maximize transmission.

result of leaching and pitting, and is caused by network dissolution.[8, 9] In the laboratory, some degree of macroscopic chalking was observed on laser glass samples kept at room temperature and humidity only two weeks after polishing. After this observation, freshly polished laser glass samples were housed in a desiccator at ~25% relative humidity (RH).

The overall effect of chalking and pitting on the laser glass surface is a loss of beam energy. The chalking lowers the sample's %transmission and the pitting causes the beam to scatter. To minimize the effect of chalking and pitting, a 50/50 mixture of ethylene glycol and water is used to cool the LHG-8 rods in the OMEGA laser, which significantly reduces (but does not completely eliminate) degradation of the optical quality of the laser glass rods.

2. Methodology: Vapor Phase Organosilylation

To combat water sensitivity of both the HR coatings and LHG-8 laser glass, coatings that render the surface hydrophobic by preventing the penetration of water were developed. Organosilazanes were first investigated for generation of hydrophobic coatings because of their successful application as contamination-resistant coatings on multi-layer dielectric gratings.[10, 11] Silazanes, a subcategory of silanes, are hydrides of silicon and nitrogen (analogous to siloxanes with -NH- replacing -O-). Hexamethyldisilazane (HMDS), tetramethyldisilazane (TMDS), bis(trifluoropropyl)-tetramethyldisilazane (FTMDS), and trimethylchlorosilane (TMCS) were chosen specifically due to their high laser damage threshold performance on these MLD gratings.[10, 11]

Organosilanes chemically modify surfaces containing hydroxyl groups through the process of silylation (**Fig. 4**). HR coatings are known to have surface hydroxyl groups due to hydration of their hafnium oxide and silica oxide composition. The LHG-8 laser glass composition also indicates that surface hydroxyl groups are present for silylation to take place (**Fig. 5**).[4]
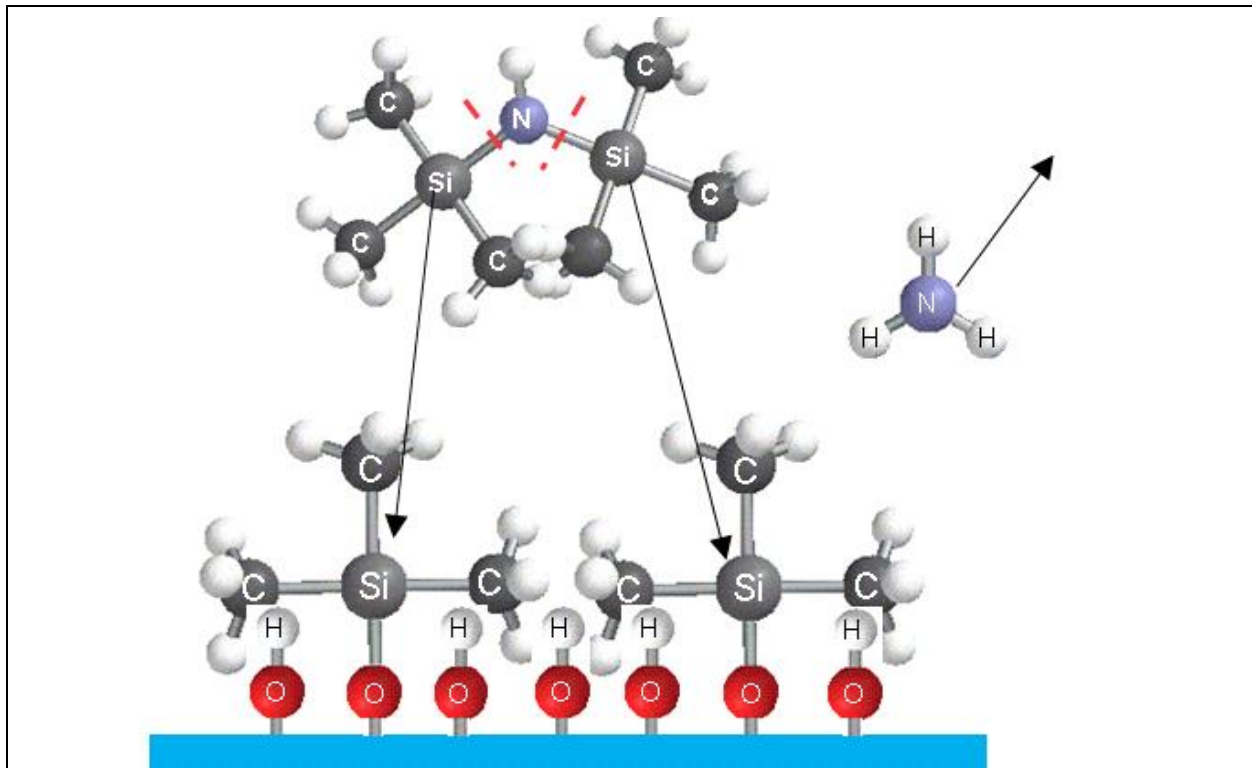
Fig. 4. Silylation occurs when silane groups break off from the disilazane and bond to hydroxyls on the substrate's surface; ammonia is produced as a byproduct. It should be noted that TMCS reacts with the surface hydroxyl groups by depositing a single trimethylsilane group through a similar (but simpler) one-step process, forming hydrogen chloride gas as a byproduct.

Component oxide equivalent (mol%)	LHG-8 [8]	LG-770 [8]	LG-750 [8]	HAP-3 [52]	Nd-SG [78]
P_2O_5	55-60	58-62	55-60	60	-
Al_2O_3	8-12	6-10	8-12	10	1.64
SiO_2	-	-	-	15	98.1
K_2O	13-17	20-25	13-17	-	-
Li_2O	-	-	-	13	-
BaO	10-15	-	10-15	-	-
MgO	-	5-10	-	-	-
Nd_2O_3[a]	0-2	0-2	0-2	0-2	0.23
Other	<2	<2	<2	<2	0
O/P ($\pm$0.1)	3	3	3	3.2	NA

[a] Nd-doping levels vary depending on use.

Fig. 5.[4] Representative compositions of commercial Nd-doped laser glasses and one developmental glass. The boxed compounds indicate compounds that form surface hydroxyl groups, enabling silylation to occur.

The vapor deposition experimental setup initially followed the same procedure as used to coat MLD gratings[10] and consisted of a sealed jar containing either an HR-coated substrate or a piece of polished laser glass and a 5 mL beaker with 1-2 mL of the chosen organosilane (**Fig. 6**). Most of the organosilanes used are volatile enough to vaporize at room temperature and then deposit on the surface of the sample as a vapor, inducing silylation. In some experiments, increased heat (50ºC) was applied by a programmable hot plate, and a watch glass replaced the screw-on lids in order to prevent a pressure buildup within the glass jars. Both reflectance and transmission spectra were taken using a Perkin Elmer Lambda 900 UV-VIS NIR spectrophotometer equipped with an integrating sphere detector or a 6º fixed spectral reflectance accessory for the HR coatings before and after
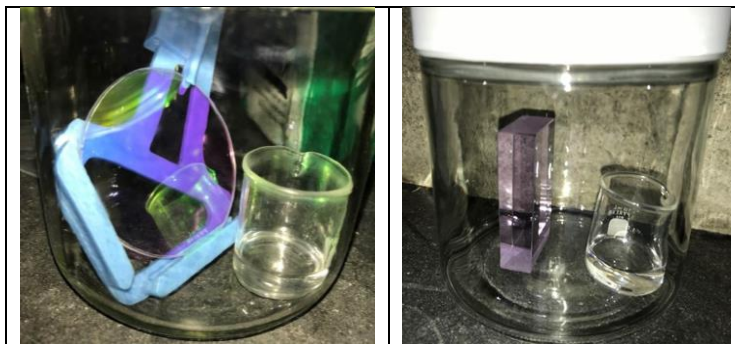
Fig. 6. Original silylation setup. HR coating on left and laser glass sample on right. Same size glass jars and glass beakers were used.

silylation, and then again after an interval of exposure in either a room-temperature humidity chamber (99% RH) or a "vapor temp" chamber (saturated humidity environment at 50ºC) to determine the effectiveness of the organosilane coatings. For HR coating samples, a fully effective coating would result in no changes in either the magnitude or location of the reflectance and transmission peaks before and after humidity exposure. For the LHG-8 laser glass, only transmission spectra were taken, because laser glass reflectance properties are not essential to the functioning of the lasers. For these samples, analysis of the surface quality of the laser glass by Nomarski differential interference contrast (DIC) microscopy (Zeiss AxioScope A.1) in reflection was used as a measure of coating effectiveness. If the average number of microscopic surface pits

per viewing area increased after humidity exposure, then the coating did not effectively protect the laser glass from water vapor.

The results obtained from this initial experimental setup were unexpected for both HR coatings and laser glass. Both the reflectance and transmission peaks for the organosilylated HR coatings shifted after exposure to humidity (explanatory results shown in **Fig. 7**). Microscopy observations showed an increased number of pits on the organosilane-coated laser glass surfaces after humidity exposure, with a resulting drop in the transmission of the sample. These results were similar for almost every organosilane attempted, even when increased temperature was employed during the vapor deposition coating process. Attempts to dip-coat the samples with HMDS and FTMDS did not yield coatings with improved hydrophobic properties.

In the one of the initial experiments, vapor-phase organosilylation of HR coatings was first undertaken by exposure to a saturated environment of HMDS at room temperature for 30 hours. The contact angle of a droplet of water was measured before and after HMDS exposure using an AST contact angle goniometer instrument (the contact angle is the angle between a line tangent to the droplet's surface and the sample surface and is a useful metric for determining the hydrophobicity and surface energy of the substrate surface—here, the contact angle measurement was used to determine the presence of a hydrophobic coating on the HR coatings and laser glass samples). There was a significant increase in the contact angle of the HR coating after HMDS exposure (from below the instrument's level of detection to 100.5º). The sample was then moved to the humidity chamber, and both reflectance and transmission spectra were measured after 23 hours of humidity exposure. The results (**Fig. 7**) showed a horizontal shift to the left in both the reflectance and transmission peaks from the initial time=0 reading to after the coating was applied, then a horizontal shift back to the right after 23 hours in the humidity chamber. These results

indicate that the HMDS coating, which is assumed to be present based on the increased contact angle, is not sufficiently effective to prevent water vapor infiltration into the sample.
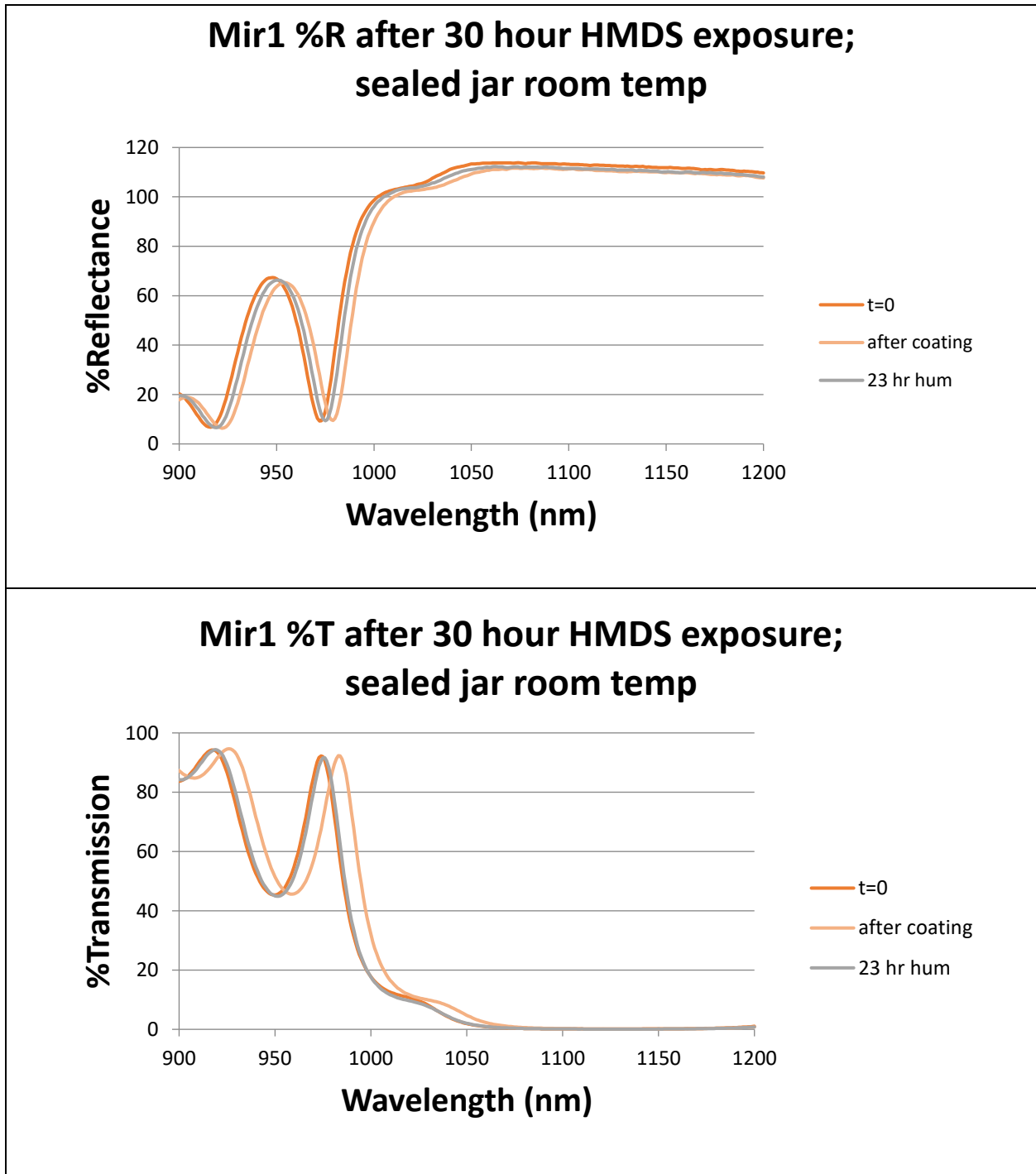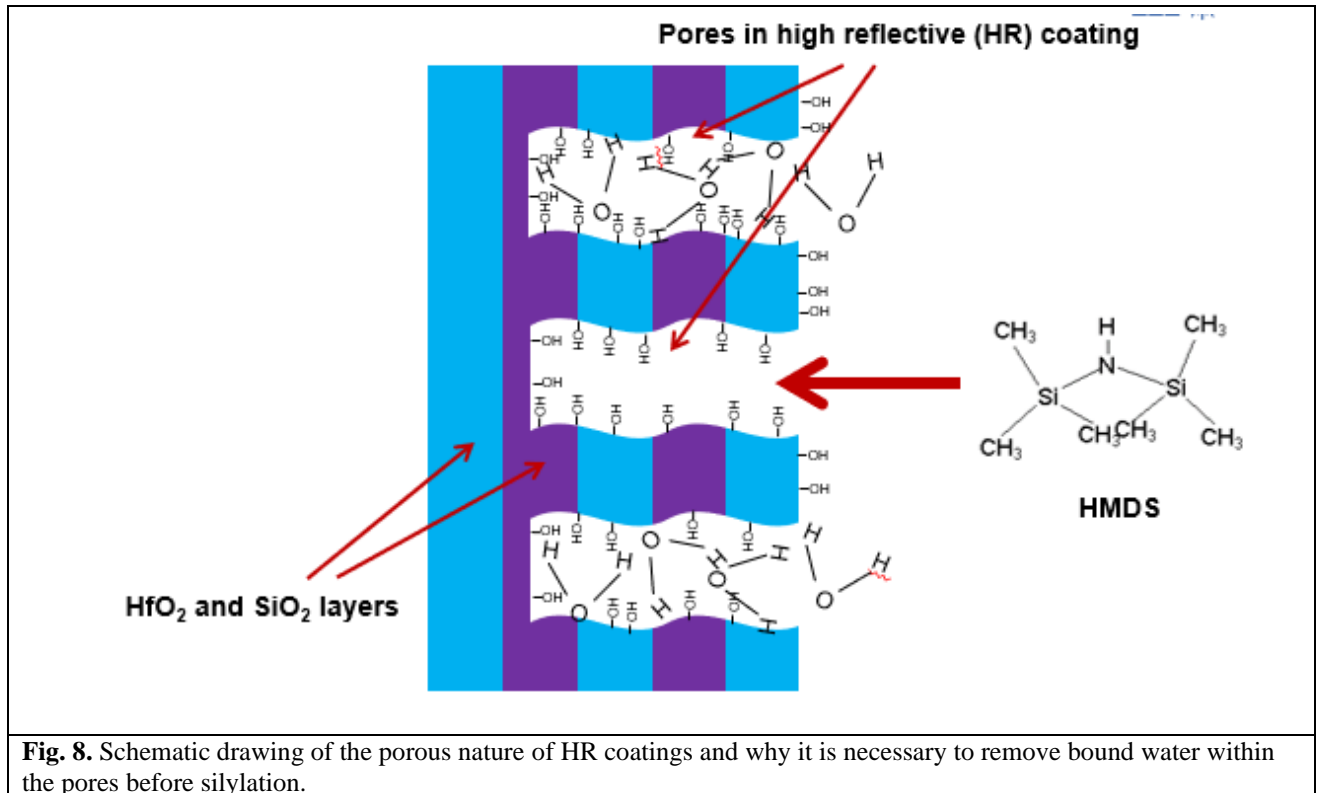

Fig. 7. Reflectance and transmission spectra of an HMDS-treated HR coating sample at (1) time=0 (when the sample was initially obtained from LLE's Optical Manufacturing group), (2) after 30 hours of HMDS vapor exposure at room temperature, and (3) after 23 hours in the humidity chamber. It should be noted that the reflectance readings are shown to surpass 100%, because the aluminum surface used to calibrate the spectrophotometer was less reflective than the HR coatings for the approximate wavelength range 1000-1200 nm.

The poor performance of these vapor-phase deposited HMDS coatings points to the possibility that there may have been water molecules bound to the OH groups on the coating surface that were reacting with the HMDS and consuming a sufficient quantity of organosilane to slow down the silylation rate or reduce the effective HDMS concentration available at the surface. Disilazanes react *non-selectively* with surface hydroxyl groups and water (both bound and un-bound) in a porous coating. To overcome this problem, vapor-phase depositions were conducted under a nitrogen atmosphere as described in Section 3 below.

3. Nitrogen Atmosphere Silylation of HR Coatings

Because the presence of bound surface water to the hydroxyl groups on the HR coatings can interfere with the silylation process, samples were equilibrated in a purged nitrogen atmosphere prior to vapor deposition of HMDS in a dry, oxygen-free environment (**Fig. 8**).

Fig. 8. Schematic drawing of the porous nature of HR coatings and why it is necessary to remove bound water within the pores before silylation.

Fig. 9 displays the setup for the nitrogen purge and silylation process at room temperature. The following procedure was used:

- The sample was placed in the silylation chamber and the chamber stopcocks were opened, allowing the chamber to be purged with nitrogen for 24 hours. This caused any water molecules in the pores of the coating to be removed.

- The nitrogen flow was turned off at the regulator, both chamber stopcocks were closed, and 10 ml of organosilane was added to the gas bubbler reservoir in order to introduce the HR coatings to the desired organosilane.

- Both chamber stopcocks were opened, and nitrogen was bubbled through the silylating agent until the contents of the gas bubbler were depleted to saturate the chamber atmosphere with organosilane.

- The nitrogen flow was turned off and both chamber stopcocks were closed; the sample was allowed to equilibrate in a disilazane-saturated environment for 24 hours.

- Both chamber stopcocks were opened, and the chamber was purged with nitrogen to expel all remaining silylating agent before the sample was removed.

**Fig. 9.** Setup for nitrogen purge at room temperature.
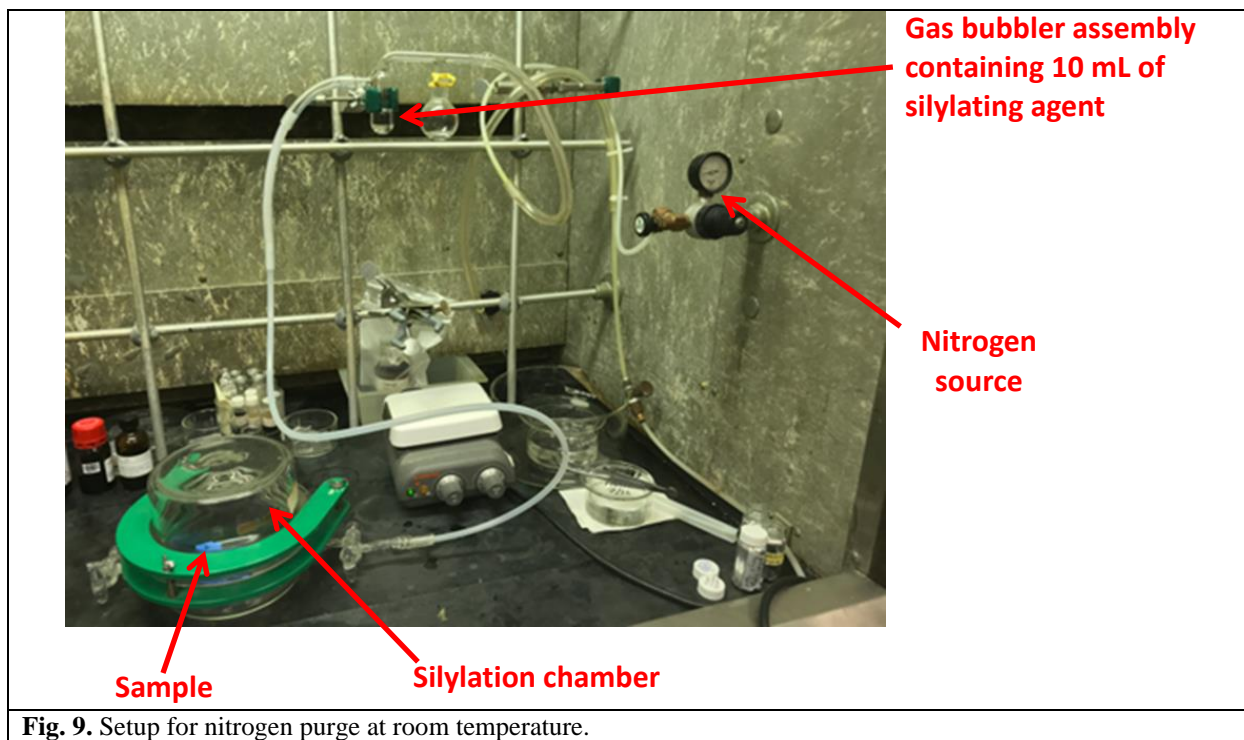
Fig. 10 compares the reflectance spectra for HR samples before and after silylation with HMDS, as well as after exposure to high relative humidity environments. For HR samples silylated in air, peaks in the spectra shifted significantly after humidity exposure, whereas the spectra for those samples that were silylated after 24 hours equilibration in dry nitrogen were essentially unchanged. These results imply that nitrogen purging before HMDS silylation is much more effective in protecting HR coatings from moisture-induced changes in optical properties. Similar results were also obtained with other disilazane materials (TMDS and FTMDS).
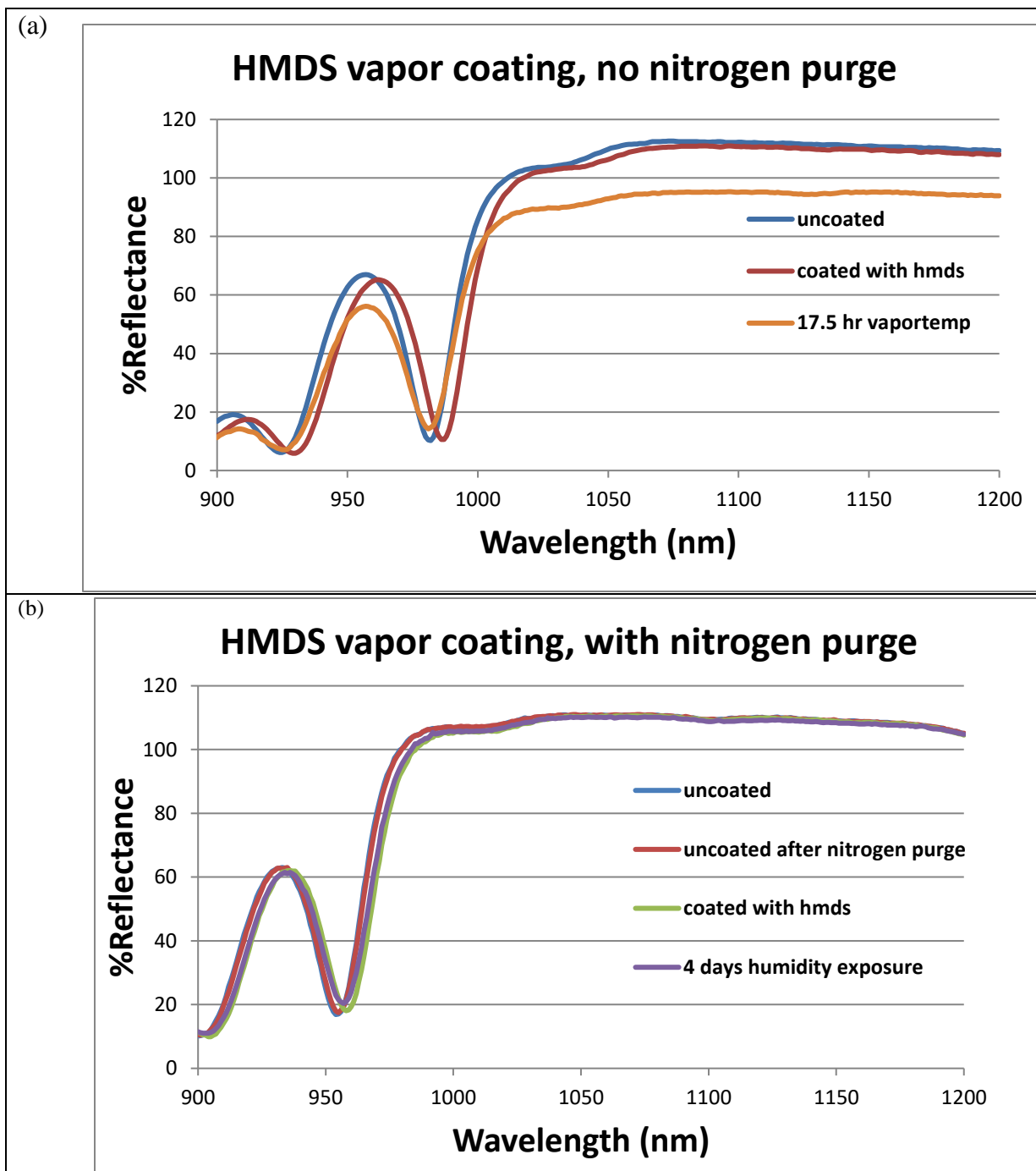
Fig. 10. Reflectance spectra for two samples coated with HMDS, (a) without and (b) with a nitrogen purge. Samples equilibrated in nitrogen exhibited superior performance to samples that had been silylated directly. TMDS and FTMDS coatings also show superior performance when the nitrogen purge coating method is used.

4. Hydrophobic Organosilane Laser Glass Coatings

Unlike for HR coatings, neither vapor-phase deposited nor dip-coated disilazane coatings could prevent pitting of LHG-8 phosphate laser glass at the long term, high humidity exposure levels (10-day 99% RH exposure at 25 °C) used in accelerated aging tests (**Fig. 11**). Microscopic analysis shows that the average number of pits per microscope frame for samples coated with silazanes increased after intense exposure to humidity. Under less harsh conditions, these materials may provide sufficient protection for day-to-day laser bay operations, but more work must be done to verify the level of protection possible. In terms of other optical properties, a 4% increase in transmission through the laser glass was observed after disilazane application, implying that disilazanes can act as anti-reflective coatings (**Fig. 12**). Transmission peaks generally increase after the laser glass is coated, showing that disilazanes are acting as anti-reflective coatings. These increases in transmission peaks were consistent for HMDS and FTMDS, on both vapor deposition and dip-coated surfaces.
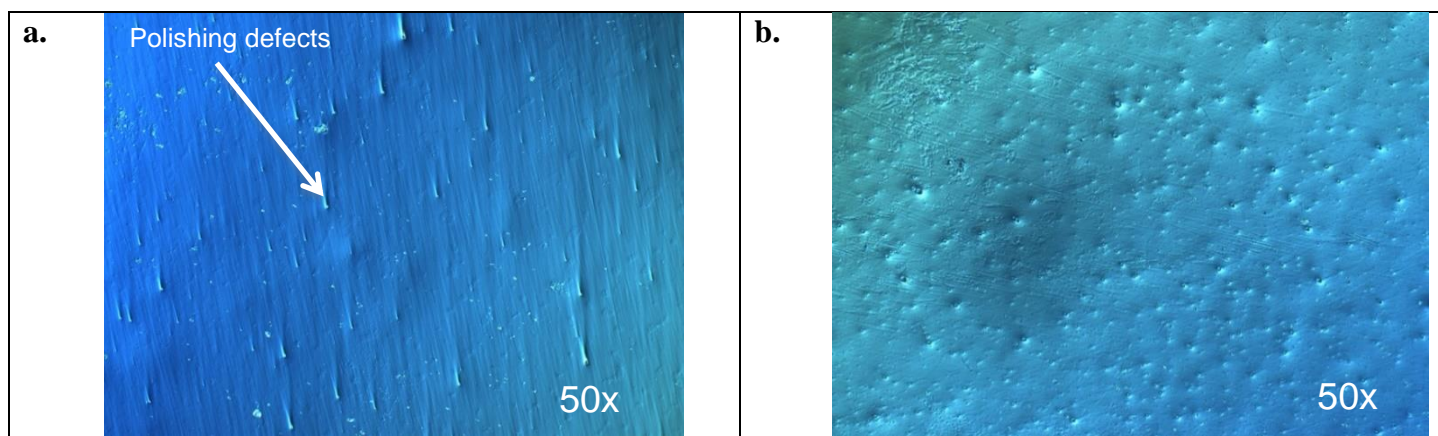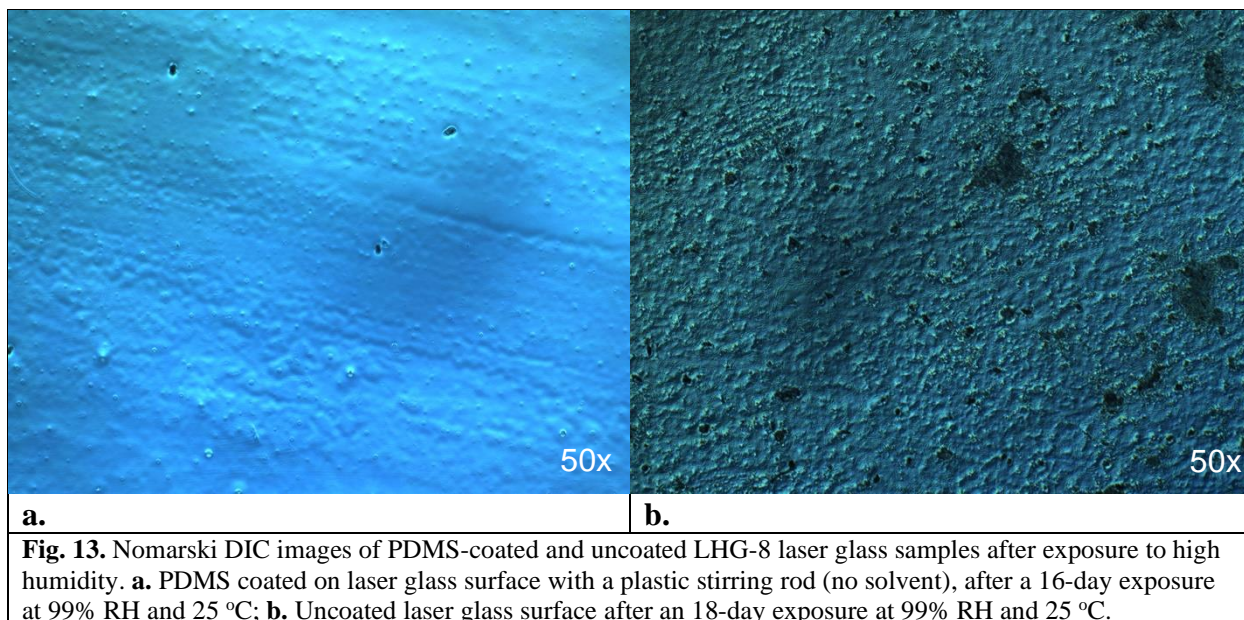

Fig. 11. a. Control sample before exposure; surface is covered with regular microscopic polishing defects. **b.** Sample vapor-phase coated with HMDS after 10 day 99% RH exposure at 25 °C.

HMDS vapor deposition and dip-coat on laser glass
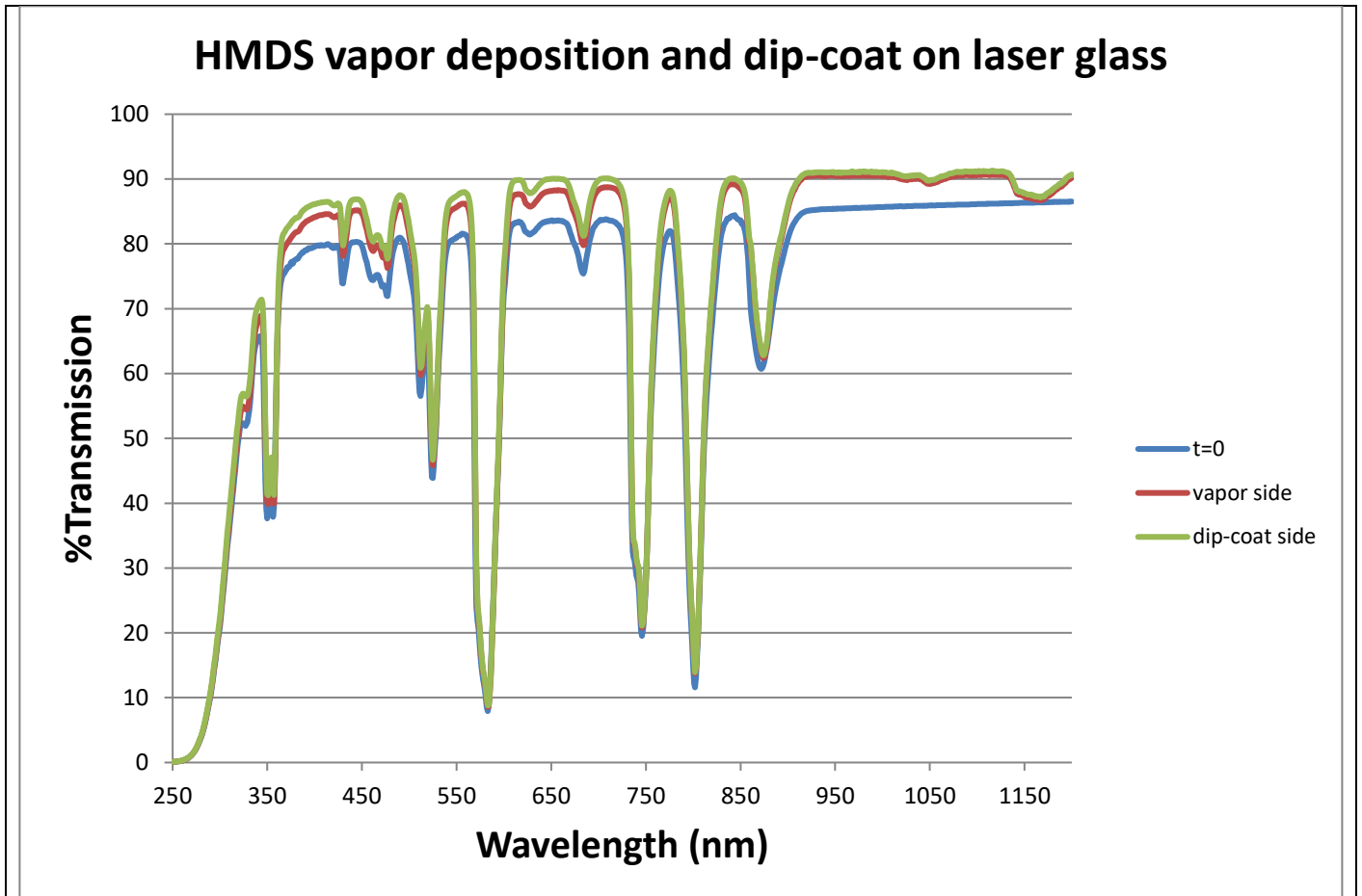
Fig. 12. The transmission spectra for a laser glass sample (rectangular prism shape) with a vapor-deposited coat of HMDS on one half and a dip-coating of HMDS on the other half. A time=0 reading was taken when no coating was present on the sample. Notice that the transmission peaks increased after the sample received the HMDS coating.

Additional experiments were conducted using Dow Corning Sylgard polydimethylsiloxane (PDMS) elastomer applied to polished laser glass surfaces by rod-coating. This material provided adequate protection of the polished LHG-8 surface from pitting over a 16-day exposure at 99% RH and 25 °C (**Fig. 13**). In addition to providing a good level of protection from water vapor damage under harsh environmental conditions, this coating is transmissive and shows anti-reflective properties at an average thickness of ~ 3.2 µm.

Fig. 13. Nomarski DIC images of PDMS-coated and uncoated LHG-8 laser glass samples after exposure to high humidity. **a.** PDMS coated on laser glass surface with a plastic stirring rod (no solvent), after a 16-day exposure at 99% RH and 25 ºC; **b.** Uncoated laser glass surface after an 18-day exposure at 99% RH and 25 ºC.

5. Conclusion

Many organosilanes were investigated to coat laser optics (HR mirrors and laser glass) in order to protect them from humidity damage. At first, organosilanes were vapor coated onto both kinds of optics. However, the HR coatings required a nitrogen purge prior to vapor deposition to remove water already present in the coatings' pores in order to produce an effective hydrophobic organosilane coating. In the case of laser glass, organosilanes (both vapor deposited and dip-coated) did not protect samples under extreme conditions from humidity damage. PDMS was found to provide a sufficient hydrophobic coating on laser glass.

These experiments determined that effective coatings (no changes in reflectance or transmission peak positions upon humidity exposure) can be produced when water molecules are removed from porous HR coatings prior to vapor phase deposition of disilazanes. Although disilazane coatings deposited on LHG-8 phosphate laser glass did not provide a sufficient level of protection from water vapor under extreme humidity conditions, Sylgard PDMS coatings virtually eliminated surface pitting of the laser glass when exposed to a prolonged saturated humidity

environment. More investigations are needed on the effectiveness of PDMS coatings at different thicknesses, RH levels, and lengths of humidity exposure.

Future experiments should also include optical characterization and damage threshold testing on both Sylgard PDMS and vapor-phase deposited organosilane HR coatings for eventual application in OMEGA and OMEGA EP. Other materials may prove to be even more effective and should be investigated. For example, another well-know and widely characterized "glassy" polysiloxane resin, GR-650, which in the past has been used as a protective coating for hygroscopic potassium dihydrogen phosphate (KDP) frequency conversion crystals on OMEGA and other large high-peak-power lasers, is a promising candidate. Additionally, multifunctional organosilane compounds that react with both the laser glass surface and cross-link among themselves (e.g., derived from efforts at LLE to develop contamination-resistant and abrasion-resistant sol-gel anti-reflective coatings)[12, 13] should be considered.

Acknowledgements

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