Contamination Resistant Sol-Gel Antireflective Coatings by Vapor-Phase Silanization

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Abstract

Silica-based sol-gel antireflective (AR) optical coatings are critical components of high peak power laser systems. Water vapor and volatile organic compounds can contaminate these coatings, reducing both their antireflective efficiency and laser-damage resistance. Previous work has shown that alkylation of free hydroxyl groups on the silica sol-gel with organosilicon compounds in solution can improve the contamination resistance of silica sol-gels. In this work, alkylation with organosilanes in the vapor state was studied as an alternative to solution-based methods. Sol-gel AR coatings were vapor-phase treated with hexamethyldisilazane (HMDS), tetramethyldisilazane (TMDS) and bis-(trifluoropropyl)-tetramethyldisilazane (FTMDS), at both room temperature and 50˚C. Contact angle measurements were taken to discern the degree of silanization as a function of exposure time to the reactive silane vapor. The contamination resistance of these vapor-phase treated sol-gels was determined by exposing them to a saturated vapor environment of a common organic contaminant (vacuum pump oil) at 60°C and 80 mtorr for 24 hrs. Results suggest that elevated temperatures enable higher degrees of silanization and therefore increase contamination resistance. Contamination testing suggests that HMDS treatment is more effective than TMDS and FTMDS treatments. However, none of the vapor phase techniques have provided as good protection against vacuum pump oil contamination as solution-based methods.

I. Introduction

The Laboratory for Laser Energetics (LLE) at the University of Rochester houses the OMEGA and OMEGA EP laser systems. The facility engages in research involving high-energy-density physics and laser-induced fusion. OMEGA and OMEGA EP are high-peak-power laser systems used to irradiate and compress targets composed of deuterium and tritium (hydrogen isotopes). The resulting fusion reaction yields helium and energetic neutrons. The immense amount of energy released during this process can be captured and converted into other energy forms such as electricity. Ultimately, LLE aims to develop fusion energy as an alternative energy source. However, the current goal is to produce more energy than what is consumed by the laser. These high-power laser systems employ a large number of optical components. To increase the efficiency of laser-induced fusion, it is important that these optics function to transmit as much light energy as possible.

Differences between the indices of refraction of air (1.0) and of the fused silica glass (1.5) used in the optics result in a portion of the light incident on the glass being reflected. Accordingly, each optical element will experience a 4% loss of transmission (Fresnel loss) for each surface exposed to air. To avoid these losses, thin-film anti-reflection (AR) coatings are applied to the optical surfaces to gradually change the refractive index between the air and the substrate. Two common methods for achieving this goal are vacuum deposition of metal oxide layers and solution deposition of silica nanoparticles formed by the sol-gel process[1]. This gradual change results in a much lower transmission loss (as low as 0.1%)[2]. The sol-gel process is generally preferred for AR coatings in high-peak-power systems because of the ease of deposition, higher laser damage thresholds, and ease of removal from the optical element in the event of coating damage. However, because of their porous and particulate nature, sol-gel AR coatings are susceptible to contamination by trace amounts of water vapor and other volatile organic compounds that accumulate with time in the laser and target bays. This absorption not only modifies the refractive index of the sol-gel coating, which in turn reduces its AR efficiency, but also lowers the laser damage resistance of the AR coating. Because of the large number of coated optics in these laser systems (200-300 elements), replacement of contaminated optics becomes a substantial labor and cost burden.

Earlier work done at LLE has shown that chemical treatment of colloidal silica sol-gels with alkoxy silanes in a solution-based process is an effective method for increasing their resistance to water vapor and volatile organic contaminants without compromising their AR capabilities and laser damage threshold[6]. This work investigates an alternative process, vapor phase silanization, which is simpler and more convenient to implement than the currently used solution-based silanization methods and could yield AR coatings with equivalent or superior resistance to airborne contaminants.

a. Sol-Gel Formation

Silica-based sol-gels are formed by alkaline hydrolysis of tetraorthosilicate (TEOS) with NH_4OH in ethanol solution (Fig. 1). The resulting reaction cleaves off the ethoxide groups, and in the presence of a base the free hydroxyl groups on adjacent molecules combine ("condense") to form a larger molecule. This "condensation" reaction continues in three dimensions until all of the reactants are consumed to form colloidal silica particles.(3, 4) After removal of excess base, the colloidal silica particles can be deposited on a substrate by either dip-coating or spin-coating to produce an AR coating.

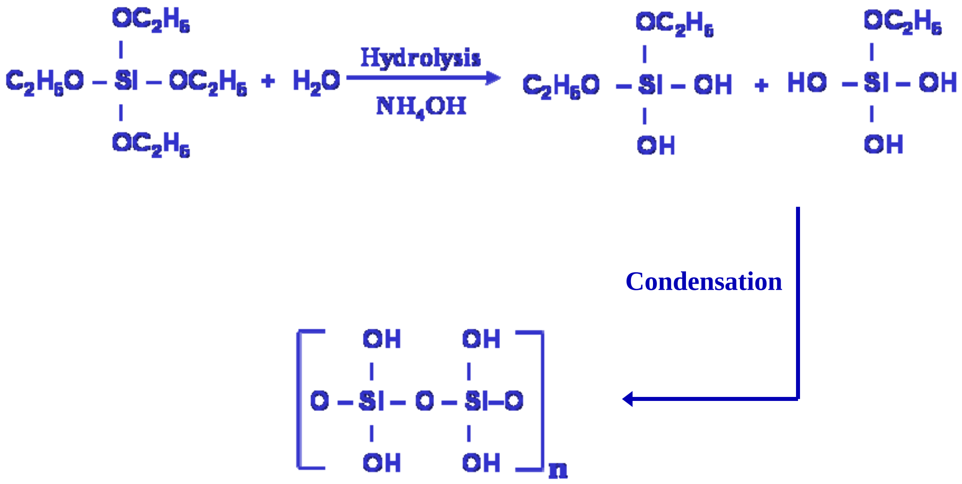


Fig.1: Formation of a silica sol-gel by alkaline hydrolysis of TEOS in ethanol solution.

b. Solution-Based Silanization Methods

By reacting silica sol-gel particles with organosilanes, absorption of contaminants such as water vapor and organic compounds can be inhibited. The organosilanes bond with the available polar hydroxyl groups of the sol-gel, (Fig. 2), resulting in a hydrophobic outer shell that resists water vapor absorption, reduces the number of sites available for hydrogen bonding with polar species, and produces a more tightly woven sol-gel particle, preventing the penetration of larger contaminants.(3, 5)

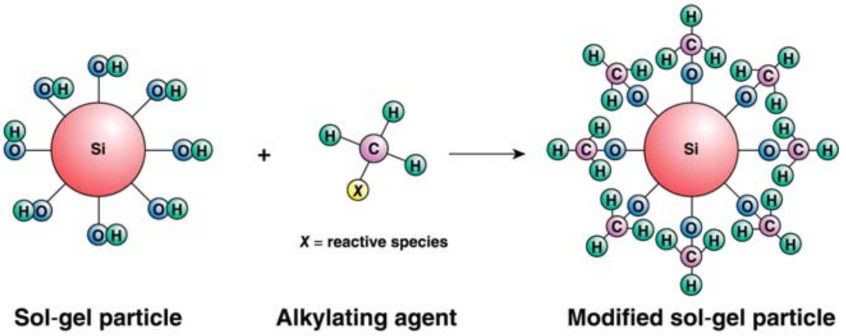


Fig. 2: Reaction of a sol-gel particle with a reactive organosilane aklylating agent. The reactive species X can be any organosilicon compound that is capable of reacting with surface hydroxyl groups.

Previous work done at LLE has shown that treatment of colloidal silica sol-gels with alkoxysilanes such as methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DDS) is an effective method for increasing their resistance to water vapor and volatile organic contaminants. The AR properties at 351 nm of sol-gel coatings prepared by treatment of conventional silica sol-gel particles with these organosilanes remain unchanged after exposure to a fully saturated vapor-state environment of vacuum pump oil for twenty-four hours at 80 mtorr and 60°C, while the transmission of conventional sol-gel coatings drops by up to 4% [6]. These remarkable results, along with the high laser damage resistance of these solution-based silanized coatings[6] have resulted in their recent implementation as the new base-line sol-gel AR coating formulation in OMEGA and OMEGA EP.

c. Vapor-Phase Sol-Gel Silanization

Silanization of silica-based materials using a reactive silane such as hexamethyldisilazane (HMDS) in the vapor state is an alternate process for increasing the contamination resistance of silica-rich surfaces. The molecular structure of HMDS is shown in Fig. 3.

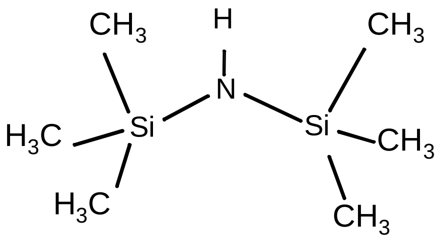
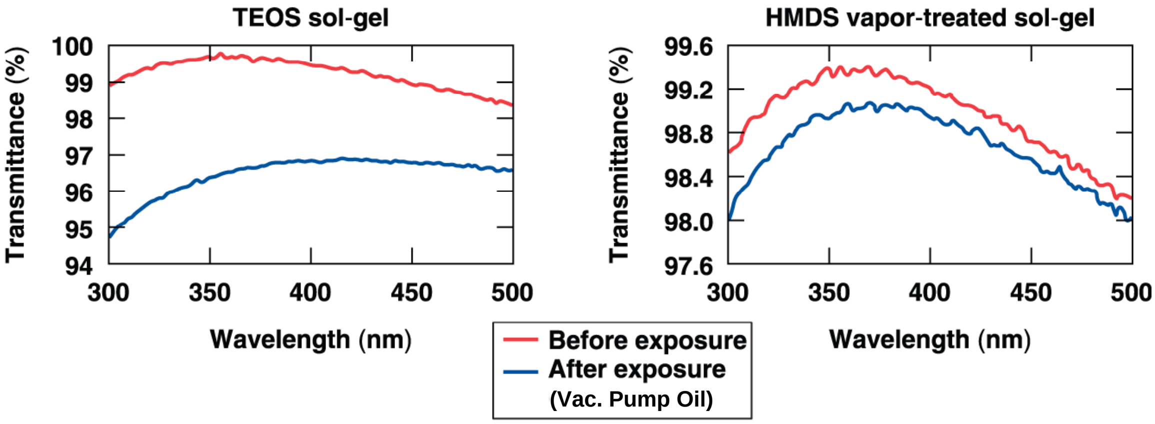


Fig 3: The molecular structure of the reactive silane HMDS.

Vapor-phase silanization has a number of advantages over solution-phase silanization. Only pure vapor comes into contact with the surface to be modified, which eliminates any higher-molecular-weight impurities that could compromise the laser damage threshold of the modified coating (similar to distillation). Any excess of unreacted material that could potentially cause changes in the AR properties of the coating with time is avoided, as only the amount needed to fully functionalize the coating surface is deposited. The vapor-phase process is exceedingly simple to implement as well; the untreated sol-gel AR optic is exposed to organosilane vapor either at ambient or at elevated temperature for an extended period of time. This method of deposition is a distinct advantage over solution deposition techniques, especially for the very large optics that would be employed in OMEGA EP. The chemical composition of the hydrocarbon layer can be easily adjusted by co-depositing several different organosilane materials simultaneously. Achieving the same results with a solution-based process requires preparation and deposition of separate sol-gel optical coatings for each composition to be evaluated, which is a much more complex and lengthy process.

Silica sol-gels treated with HMDS in the vapor phase experienced < 1% loss in transmission after exposure to a vapor-saturated environment of vacuum pump oil at 60°C and 80 mtorr for 24 hrs, while the transmission of untreated sol-gel control samples dropped approximately 3.5 % under the same exposure conditions (Fig 4)[6].



60º C for 28 hr at ~ 80 mtorr

Fig. 4: Transmission spectra contrasting the contamination resistance of standard silica sol-gel AR coatings versus those treated with HMDS in the vapor phase ~~[6]~~.

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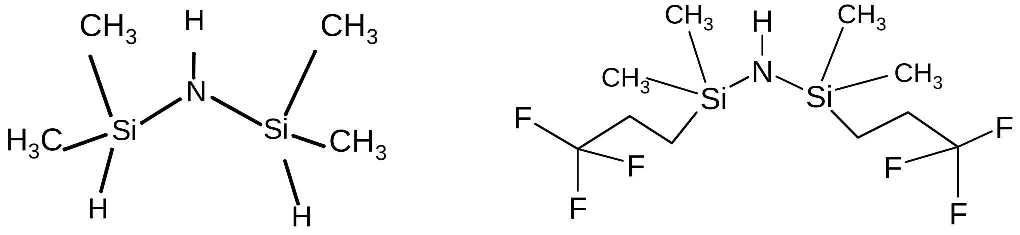
Figure 4 shows that, unlike for the solution-based silanized sol-gel AR coatings currently in use, the HMDS treated sample does shows a discernable drop in transmission when exposed to a saturated vacuum pump oil environment. The goal of this work was aimed at identifying other volatile organosilanes that may be more effective than HMDS in increasing sol-gel AR contamination resistance. Two such materials, tetramethyldisilazane (TMDS) and bis (trifluoropropyl)-tetramethyldisilazane (FTMDS), were selected for this study.

d. Chemistry of TMDS and FTMDS

TMDS is structurally similar to HMDS, but contains fewer bulky methyl groups than HMDS. In theory, because of the smaller molecular size of TMDS, it should be able to penetrate more deeply into the pores of the sol-gel coating and thus be more effective than HMDS at preventing contamination from larger organic molecules. FTMDS is a fluorocarbon known for being exceptionally hydrophobic, which would allow sol-gels treated with FTMDS to effectively resist contamination from polar substances such as water vapor. The molecular structures of TMDS and FTMDS are shown in Fig 5.



TMDS FTMDS

Fig. 5: Molecular structures of TMDS and FTMDS used for vapor phase silanization. The molecular structure for HMDS can be compared in Fig 3.

The effect on laser damage resistance at 351 nm of modifying the surfaces of high-peak-power laser optics using organic materials is always a concern. For HMDS, TMDS and FTMDS , previous work has shown that surface modification of multi-layer deposited (MLD) gratings does not reduce their laser damage thresholds, and in certain cases actually increased the laser damage threshold of these optics[7].

II. Experimental

Sol-gel coated optics (approx 2” dia) prepared by LLE’s Optical Manufacturing Group were treated with TMDS and FTMDS both at room temperature and at 50˚C to determine the effect of higher temperatures on organosilane saturation in the treatment chamber. Elevated temperatures increase the amount of reactive silane in the vapor phase, and this higher degree of vapor saturation would be expected to provide more opportunities for the organosilane molecules to react with the sol-gel. Vapor-phase treatment was conducted in the large glass chambers shown in Fig 6. The sol-gel coated optics were held in Teflon racks and placed in the chamber with the liquid organosilanes contained in 10 ml glass beakers. For elevated temperature studies, the chambers were placed on a digital hotplate set at 50°C.

Fig. 6: General silanization setup used for all experiments. The substrates are held in Teflon racks and placed into the large glass chambers for silanization. The reactive silane is placed in the chamber and the chamber is covered. For elevated temperature studies, the chambers were place on a digital hotplate (not shown).

a. Contact Angle Measurements

Contact angle measurements of a droplet of water on the treated sol-gel surface were taken using the VCA 2500XE contact angle instrument (AST Products, Inc) to identify the degree of silanization, or how completely the organosilanes had reacted with the surface hydroxyl groups of the sol-gel particles. A schematic diagram of the contact angle instrument is shown in Fig 7.

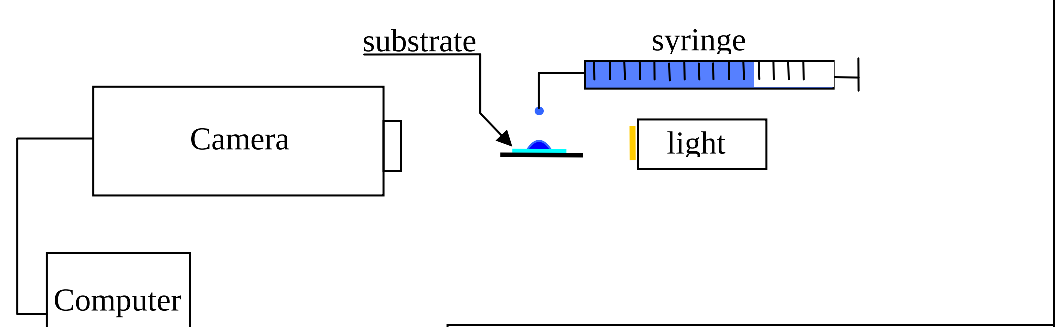


Fig. 7: The water contact angle meter setup

The contact angle measures the degree of hydrophobicity, or resistance to water, of a material. A higher contact angle indicates a greater resistance to water. As the organosilanes react with the sol-gel particles, the outer shell of the sol-gel particles become increasingly hydrophobic, tapering off to a maximum value when all of the surface hydroxyl groups have been consumed in the silanization reaction. Therefore, the contact angle can be used as a measure of the extent of silanization.

Contact angle measurements were taken at 24 hour intervals for sol-gel coated substrates exposed to TMDS and FTMDS vapor for 96 hrs at both ambient temperature and 50^{o}C. The data, shown in Fig 8, implies that, for FTMDS, elevated temperatures during vapor phase silanization resulted in a substantially more complete reaction of the silanes with

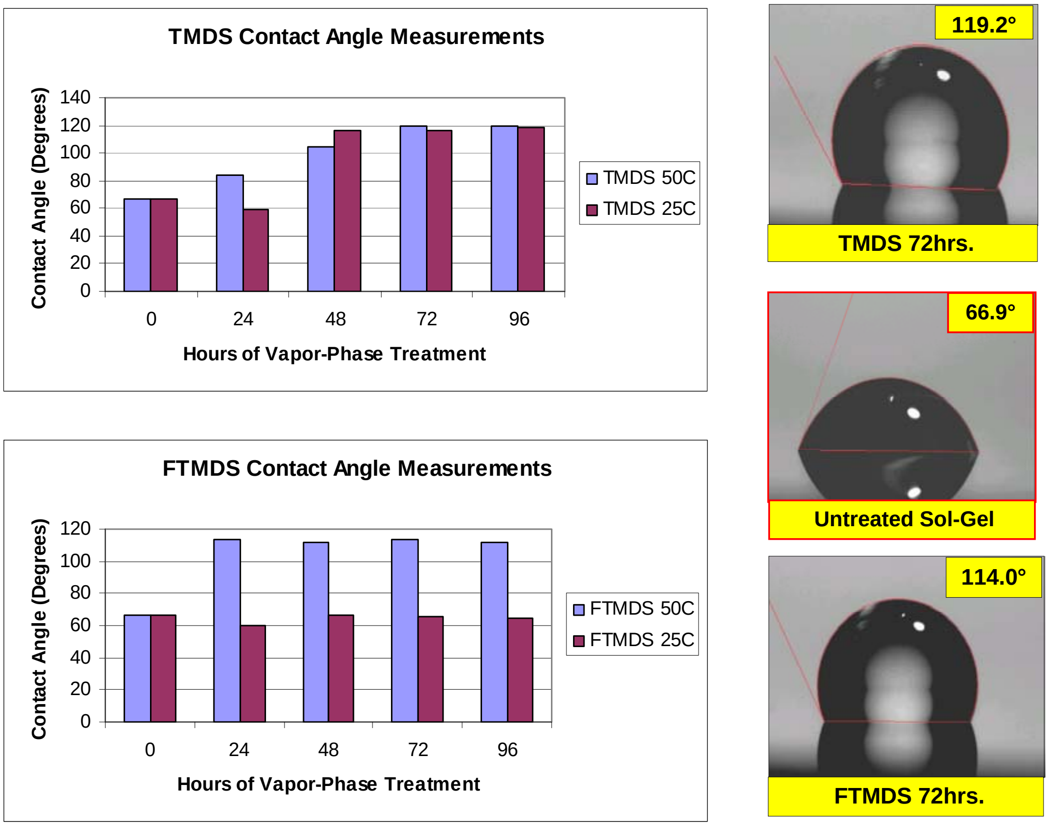


Fig. 8: (Left) - results of TMDS and FTMDS contact angle measurements;
(Right) - photographs of contact angles of a water droplet on treated and untreated sol-gel surfaces.

surface hydroxyl groups, while for TMDS only a small difference was observed at higher temperatures. With respect to length of exposure, the FTMDS-treated optic reaches its optimum contact angle (and thus complete saturation of the sol-gel surface) only at 50 ^{o}C and within 24 hrs. In contrast, TMDS reaches its peak contact angle after about 48 hrs of treatment at room temperature and, due to its higher vapor pressure, elevated temperature has little effect on the rate of silanization. Sol-gel AR-coated optics treated with TMDS and FTMDS displayed higher contact angles (119.2^{o} and 114.0^{o}, respectively) than reported for HDMS in earlier studies (107.7^{o}). These results can be interpreted to mean that TMDS and FTMDS form a denser layer over the surfaces of the sol-gel particles, and should therefore provide increased contamination resistance.

This hypothesis was tested experimentally by exposing both TMDS and FTMDS vapor-phase treated sol-gel AR coatings to an environment saturated with vacuum pump oil at 60^{o}C and 80 mtorr, using the same testing methodology as implemented earlier for both HDMS vapor-phase silanized sol-gels and the baseline solution-silanized sol-gel coatings. The transmission spectra of these samples before and after exposure to the saturated vacuum pump oil environment are shown in Fig 9. Both TMDS and FTMDS do provide a significant level of protection against vacuum pump oil vapor as compared to the untreated sol-gel control sample shown earlier in Fig. 4. The transmittance of the vapor-phase treated sol gels in Fig. 9 drops ~ 1.5% for TDMS and ~2.3% for FTMDS, while the transmission of the untreated control sample drops ~3.5 to 4% (Fig 4). Under the same conditions, the sol-gels treated with HMDS in the vapor state exhibited a change in transmission of < 1%.

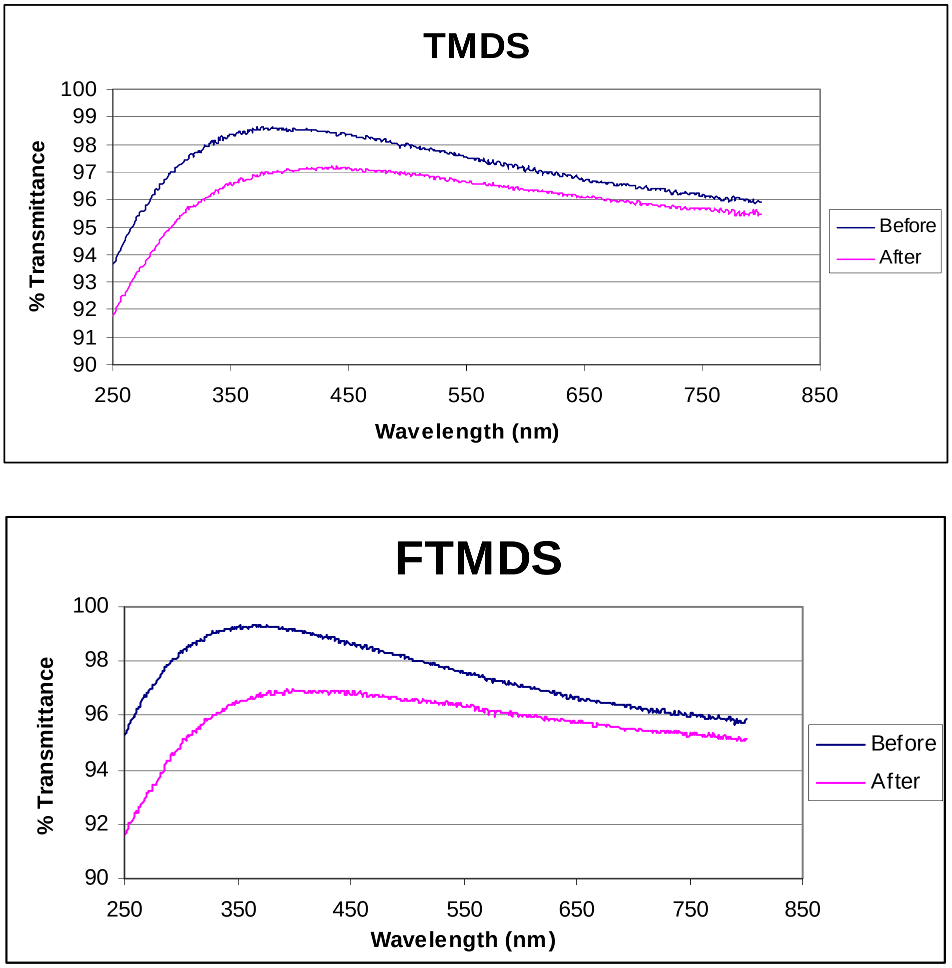


Fig. 9: Transmission spectra for sol-gel coated optics treated with TMDS and FTMDS before and after exposure for 24 hrs to an environment saturated with vacuum pump oil vapor (60°C, 80 mtorr)

III. Discussion

Comparison of the results from Fig 9 with the contact angle measurements in Fig 8 shows some correlation between contact angle and resistance to vacuum pump oil contamination for TMDS and FTMDS vapor-phase treated sol-gel AR coatings. The TDMS-treated samples, which showed a 1.5 % drop in transmission, possessed a contact angle of 119.2°, while the FTMDS-treated sample showed a drop of 2.3% and a contact angle of 114°. These results support, to some extent, the prediction that higher contact angles are representative of increased reactions between the organosilane and sol-gel, and therefore improved contamination resistance. However, HMDS treated sol-gels have a lower contact angle (107°) than either TMDS or FTMDS, yet show a smaller transmission loss (<1%). This result is somewhat counter-intuitive, as one would expect that the smaller molecular size of TMDS (which allows it to penetrate deeper into the porous sol-gel structure) and the fluorinated groups on FTMDS (which are extremely hydrophobic) would do a better job of blocking access of contaminants to the pores on the sol-gel particles than would HMDS.

Taken at face value, the relatively higher contact angle measurements of TMDS and FTMDS suggests that they had reacted with the sol-gel particle more effectively than HMDS. However, the contact angle measurements only measure the hydrophobic nature of the *surface* of the modified sol-gel particle. These measurements give no good indication of how far or how well the organosilanes have reacted with the interior of the sol-gel particles. The sol-gel particle surface is not uniform and smooth, and contains numerous channels to the interior which would also be susceptible to contamination. One potential cause of the poorer performance of FTMDS as compared to HMDS may be attributed to the inability of the larger organosilane to penetrate and react with the interior of the sol-gel particle.

IV. Conclusions

Vapor-phase silanization of sol-gel AR coatings using TDMS and FTMDS was studied for the purpose of providing a greater degree of contamination resistance than could previously be attained using HMDS. The observed poorer performance of TMDS and FTMDS vapor-treated sol-gels to vacuum pump oil contamination is related in part to their apparent inability to reach and protect the interior of the sol-gel particle. Although for less volatile organosilanes like FTMDS elevated temperatures do result in higher contact angles, the contact angle data might not be accurately reflecting the degree of silanization of the entire sol-gel particle, particularly the interior. A different means must be used to assess the degree of silanization of the entire sol-gel particle, not only its surface.

It is important to note that the contamination-testing conditions used in this study (a saturated environment of vacuum pump oil vapor at 60˚C and 80 mtorr) are far more severe than what any optical element would ever experience in OMEGA and OMEGA EP over even a 10 yr life cycle. Even though the TMDS- and FTMDS vapor-treated sol-gels examined in this study were not as resistant to oil contamination as HMDS vapor-treated or alkoxysilane solution-treated optics, their resistance may still be good enough for them to be used successfully in many applications areas in OMEGA and OMEGA EP. Additionally, since the complete nature of all contaminants that could be inadvertently introduced into these large laser systems is not well understood, TMDS and FTMDS vapor-treatment may be more effective than HMDS vapor-treatment or alkoxysilane solution-based methods in increasing resistance against these yet-to-be-identified contaminants. Future efforts should be directed toward studying the interaction of suspected potential contaminants with these two organosilanes (and others) to develop treatment processes that will protect against a broad range of contaminants. For organosilanes that have low volatility, both higher reaction temperatures and lower pressures during the vapor-phase silanization process should be investigated in order to increase their concentration in the vapor state and allow maximum saturation of the sol-gel AR coating in the treatment chamber. Mixtures of multiple organosilanes with different molecular structures should also be tested to determine if simultaneous treatment increases the contamination resistance of sol-gels.

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