Abrasion Resistant Anti-Reflective Sol-Gel Coatings

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Abstract:

Anti-reflective sol-gel coatings are deposited on many of the optical surfaces in both the OMEGA and OMEGA EP laser systems. These coatings are responsible for yielding the maximum transmission of UV light as it passes from air into the glass optics. One issue with these coatings resides in their lack of abrasion resistance. An unmodified sol-gel coating will be scratched if subjected to a very small mass dragged across its surface (~ 6 g), making it necessary to handle optics containing these coatings with extreme caution during installation and alignment.

In an effort to increase the abrasion resistance of sol-gel coatings, organosilane modified sol-gel particles have been crosslinked with dithiols. This process increases abrasion resistance because the dithiol crosslinkers bond sol-gel particles to each other and to the coated substrate, resulting in a robust sol-gel network that can withstand greater abrasive forces. The most promising results have been demonstrated using a 15 mol% solution of the organosilane modifier 3-methacryloxypropyltriethoxysilane (MOTOS) in combination with the crosslinker pentanedithiol. A substrate coated with this solution demonstrated little to no damage after a mass of 36 g was dragged across its surface (simulating abrasive forces that the coating may endure during handling) while maintaining 96% transmission. A reduction in transmission of the coating was observed with increasing abrasion resistance

Introduction:

Optics in the OMEGA and OMEGA EP laser systems rely on sol-gel coatings to reduce transmission losses. Each time that the laser beam comes in contact with an air-glass interface, there is the opportunity for losses in transmission (called Fresnel losses) due to the difference in refractive indices of the air and glass. Fresnel loss accounts for roughly a 4% transmission loss for each air/substrate interface. By depositing a coating on the substrate surfaces, the difference in refractive indices between the coating and the air is decreased, which helps to maintain maximum transmission. For a given wavelength range of light, the optimum refractive index of the coating is equal to the square root of that of the glass (1). For the substrates used in this work, the glass has an index of refraction of 1.51, and therefore, the coating should have a refractive index of 1.26. While sol-gel coatings based on tetraethyl-orthosilicate (TEOS) have proven effective in maintaining high transmission, they are easily damaged through incidental, frictional contact with masses of only 6 g. To increase abrasion resistance, experiments involving the chemical modification of sol-gel coatings with organosilanes and crosslinking with dithiols have been performed. The chemical modification and crosslinking within the coating produces a robust network of bonds. This network provides for an increase in abrasion resistance because the crosslinked bonds not only join the particles to each other, but also help to adhere the coating to the glass substrate. A standard alkoxysilane, tetraethyl orthosilicate (TEOS), is used to create the sol-gel through a condensation reaction that is triggered by the presence of a base catalyst (ammonium hydroxide).

In previous work, difunctional aldehydes, specifically glyoxal and glutaraldehyde, were used as cross-linking agents to improve the abrasion resistance of TEOS-based sol-gel coatings (2). The advantage of using organosilane modifiers and dithiol crosslinking agents resides in the ability to conduct the crosslinking reaction by UV irradiation at room temperature. Glyoxal and glutaraldehyde both require a 90 min baking cycle at 130° C to initiate crosslinking.

Experimental

To prepare the standard, unmodified sol gel solution, 23 mL of TEOS is mixed into 220 mL of ethanol and stirred constantly at room temperature. Water from the atmosphere triggers a hydrolysis reaction in the solution and ethanol is liberated from the TEOS leaving silicon with four hydroxyl groups. (2,3) This solution undergoes a base catalyzed polycondensation reaction once 7 mL of ammonium hydroxide are added. The polycondensation reaction results in the formation of silica oxide (SiO_2) particles, which continue to grow in diameter as the solution ages for one week. This reaction continues until the ammonia in solution is refluxed out of the system at the conclusion of the week. At this point, the SiO_2 particles have grown to 20 nm and are left suspended as a colloid in the ethanol solution. Figure. 1 shows this series of reactions.

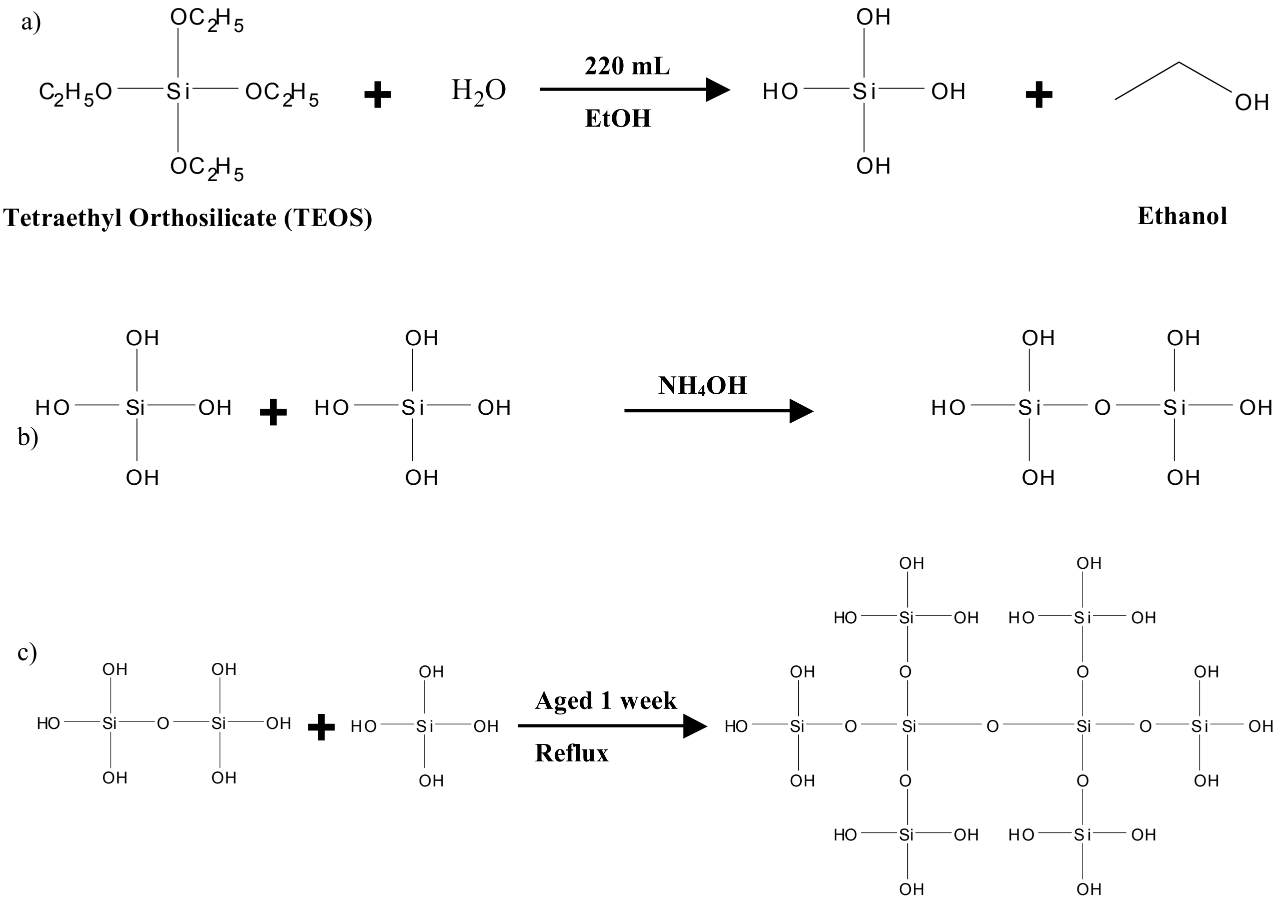

Fig. 1: Formation of silica oxide particles via the sol-gel process. a) TEOS is hydrolyzed, liberating ethanol. b) A polycondensation reaction occurs in the presence of a base catalyst (ammonium hydroxide). c) Polycondensation results in the formation of silica oxide particles after one week, at which point the ammonium hydroxide is removed from solution by reflux as ammonia gas.

The colloidal suspension of SiO_2 particles is modified using the organosilane 3-methacryloxypropyltriethoxysilane (MOTOS), which attaches to the surface of the SiO_2 particle. The modifiers allow for more bonds between particles as crosslinking agents can attack the carbon-carbon double bonds on the modifiers. Fig. 2 shows a MOTOS molecule, while Fig. 3 shows a schematic of a TEOS-based sol-gel particle modified by organosilanes reacted with cross-linking agents.

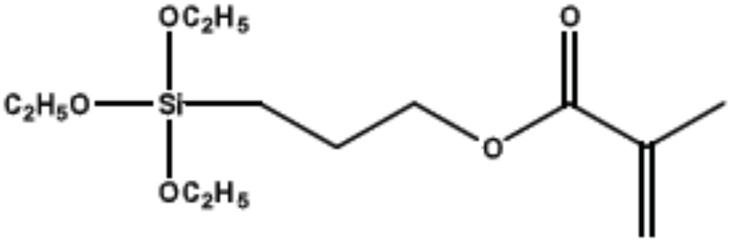

Fig. 2: 3-Methacryloxypropyltriethoxysilane (MOTOS). The carbon-carbon double bond (vinyl group) on MOTOS provides an opportunity for a crosslinking agent to create bonds between SiO_2 particles

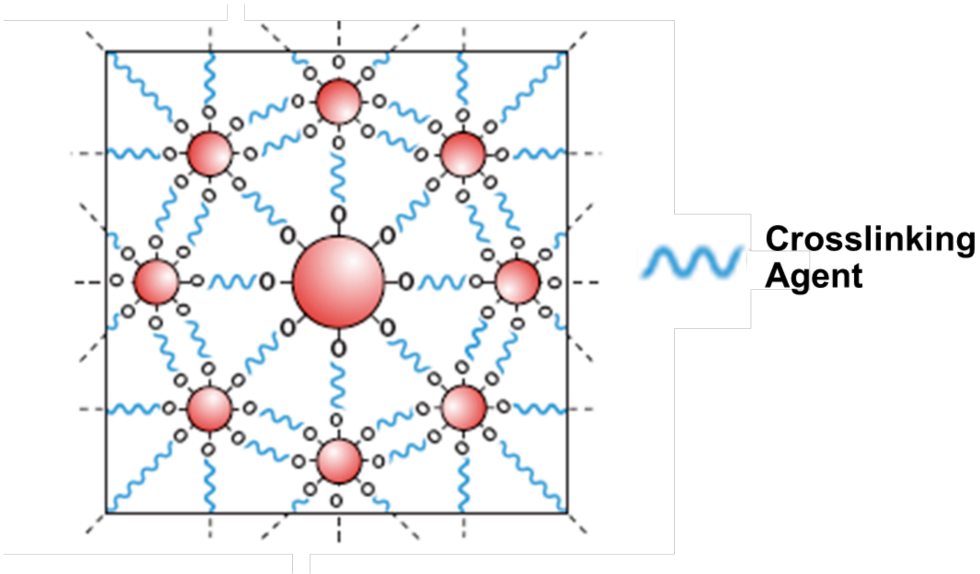

Fig. 3: Modified, crosslinked silica oxide particle. The silica oxide particles have been modified, allowing the crosslinking agent to create bonds between particles forming a robust network.

Dithiol crosslinking agents are added to the solution containing these organosilane-modified SiO_2 particles in a slightly less than a 2:1 molar ratio of organosilane to dithiol to ensure that cross-linking occurs between two SiO_2 particles Three dithiol crosslinking agents (propanedithiol, butanedithiol, and pentanedithiol) were initially used in this study. Crosslinking occurs when the nucleophilic dithiol attacks the electron-rich vinyl groups of the MOTOS organosilane molecules bonded to the SiO_2 particles, resulting in a network of bonds (4,5). This reaction is triggered when the coating is exposed to 254 nm UV light for 30 min. Fig. 4 shows the photoinitiated reaction.

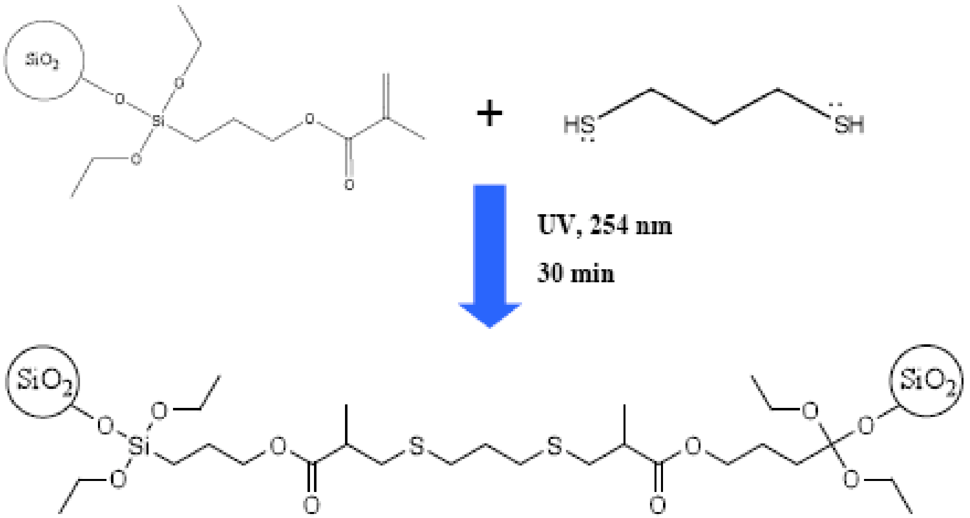

Fig. 4: Photoinitiated crosslinking reaction. The nucleophilic dithiol (propanedithiol) reacts with two different modified SiO_2 particles, forming a network of bonds between SiO_2 particles.

Solutions were prepared in a Class 100 vertical laminar flow exhaust hood housed inside a Class 10,000 clean room. After mixing the TEOS, MOTOS, and dithiol, the solutions were left to stir for several hours. Additional stirring was necessary prior to spin-coat deposition to ensure an even distribution of particles in the solution. The solutions were applied to the optics via a spin-coating process in the vertical laminar flow exhaust hood. The coating solution was deposited onto the optic in 0.5 mL quantities- or enough to cover the surface of the substrate- from glass syringes fitted with a submicron particle filter and the substrate was spun at 3000 RPM for 40 seconds. After a two-day drying period in air, the substrates were placed under a 254 nm UV lamp for 30 minutes to complete the crosslinking reation before any tests were run.

Sol-gel coatings prepared from all three dithiols with MOTOS were evaluated for their transmission characteristics. Coatings prepared using propanedithiol and butanedithiol did not display any anti-reflection properties (i.e., showed little to no improvement in transmission as compared to the transmission of an uncoated optic). For this reason, only pentanedithiol was pursued further as a cross-linking agent for these coatings.

To test the abrasion resistance of the pentanedithiol-crosslinked coatings, the coated substrate was placed with the coated side up between two sheets of clean-room wipes as seen in Fig. 5. Square substrates (~6 g each) were stacked on top of clean-room wipes one at a time. Before the addition of each new substrate, the wipe carrying the applied mass was dragged across the surface of the coated substrate and then the mass of the stack of substrates was determined. The coating on the substrate was then observed by eye for any gross damage. If scratches could be seen, the dry wipe test was complete and the final mass of the stack of square substrates was measured. If there was no damage observed, another square substrate was placed on top of the stack and the procedure was repeated. Substrates with coatings that showed no observable damage when mass loads $\geq$100g were dragged across their surfaces were viewed under a microscope at 100x magnification for any small-scale damage. No damage was evident at this magnification.

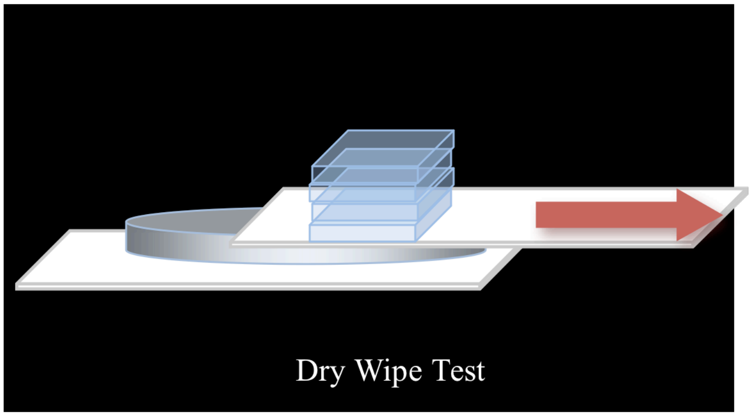

Fig. 5: Dry wipe test diagram for abrasion resistance of a coating. The top clean-room wipe carrying a stack of substrates was dragged in a straight line across the surface of the coated substrate, which was then observed with the naked eye for any scratches.

The abrasion resistance results for the pentanedithiol-crosslinked coatings are shown in Table 1, along with optical transmission data for each substrate tested. Coatings modified with 15 mol% MOTOS solutions and pentanedithiol exhibited transmission results that are comparable to those of the standard TEOS coatings currently employed in the OMEGA and OMEGA EP laser systems. These coated substrates also showed an abrasion resistance six times stronger than that of the TEOS coatings. When experiments were run using the 25 mol% concentrated MOTOS-pentanedithiol solutions, a higher abrasion resistance was achieved (100 g dragged across the surface did not scratch the coating), but there was also a large decrease in transmission as compared to coatings with a lower MOTOS/pentanedithiol concentration. Because an abrasion resistance of over 100 g would not be necessary for sol-gel coatings in OMEGA or OMEGA EP (where optics are routinely handled with considerable care due to their size, weight, and high replacement cost) it would be prudent to sacrifice some abrasion resistance for improvements in transmission.

When the abrasion and transmission results on MOTOS-pentanedithiol modified coatings are compared to those for the glutaraldehyde and glyoxal systems, it is evident that equivalent results can be obtained through the use of MOTOS-pentanedithiol solutions (Table 1). The crosslinking with dithiols achieves the same or better abrasion resistance at room temperature deposition as with elevated temperature using reactive dialdehydes, therefore enabling easier application of coatings onto the optics.

Sol-gel composition (mol%)	**% Transmission at AR (λ_{max})**	**Mass required to scratch coating (g)**
TEOS (100%)	**96.641 (1073 nm)**	**≤ 7**
MOTOS-pentanedithiol (15%)	**96.175 (882 nm)**	**36**
MOTOS-pentanedithiol (25%)	**93.904 (1358 nm)**	**100+**
Glutaraldehyde (50%)	**96.120 (532nm)**	**30**
Glyoxal (50%)	**96.447 (660 nm)**	**37**

Table 1: Transmission and abrasion resistance for various cross-linked sol-gel coating compositions. Data for standard TEOS sol-gel coatings is included for reference.

Figure 6 compares the transmission of an uncoated optic, an optic coated on one side with the 15 mol% MOTOS/pentanedithiol crosslinked sol-gel solution and the calculated transmission of an optic coated on both sides with the same solution. The calculated transmission was obtained by multiplying the magnitude of the difference in transmissions of the uncoated and single side coated optics by 2 and then adding the transmission of the uncoated optic.

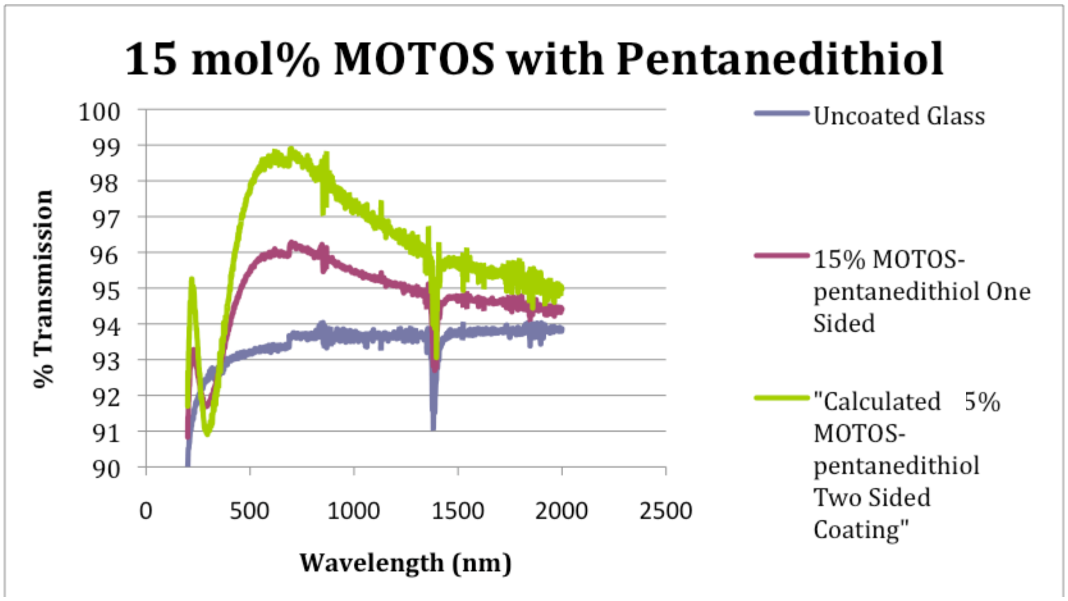

Fig. 6: Calculated transmission of a substrate with both sides coated compared to the measured transmission of uncoated and single-side-coated substrates. Transmission increases from the uncoated glass to the double coated glass as the coatings reduce Fresnel loss by narrowing the gap in refractive indices of the air and the glass.

Conclusion:

Optical elements were coated with sol-gel solutions containing 3-methacryloxypropyltriethoxysilane and crosslinking dithiols at concentrations of 15 mol% and 25 mol% via spin coating. Abrasion resistance of the coatings was tested using a dry-wipe protocol. The best results were obtained with coatings prepared from 15 mol% MOTOS-pentanedithiol solutions. These new coatings not only display excellent abrasion resistance but also provide the added benefit of a simple, room temperature deposition process. No high temperature bake is required as is needed for previously studied abrasion-resistant sol-gel coatings employing glutaraldehyde and glyoxal as cross-linking agents. Additional research remains to be done to determine the contamination resistance, hydrophobicity, and laser damage resistance of these new coatings (the latter is a key requirement for deployment in OMEGA and OMEGA EP), as well as to understand the mechanism driving the reduction in transmission with increasing abrasion resistance. Once these issues are better understood, work can progress toward optimizing deposition parameters for application of these coatings to apertures suitable for future deployment in OMEGA and OMEGA EP.

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