Contaminant Resistant Sol-Gel Coatings

Valerie Rapson
Greece Olympia High School

Advisor: Kenneth L. Marshall

University of Rochester
Laboratory for Laser Energetics
Summer High School Research Program 2005

1. Abstract

Sol-gel coatings are used on the OMEGA laser optics as anti-reflection (AR) coatings to maximize their transmittance. Over time, trace organic compounds in the laser bay contaminate these sol-gel coatings, reducing their efficiency as AR coatings. Consequently, the optics must be removed, cleaned and re-coated with the sol-gel AR approximately every three months. In April of 2005 Y. Xu *et al* [1] demonstrated that changing the chemical composition of the sol-gel would reduce its susceptibility to contamination. In the work reported here, dimethyldiethoxysilane (DDS) and methyltriethoxysilane (MTES) were used to modify standard sol-gel solutions based on tetraethylorthosilicate (TEOS) in order to increase its resistance to contamination by volatile and semi-volatile contaminants. The methyl groups in the added components reduce the number of active OH groups available for hydrogen bond formation with contaminants in the air. The resulting coatings show improved contamination resistance, can be applied to OMEGA optics with only minimal changes to the current spin-deposition process, and show equivalent or superior laser damage resistance to current sol-gel AR coatings used on OMEGA.

2. Introduction

Originally created 60 years ago, sol-gel coatings are deposited on optics to form an anti-reflective (AR) coating, which maximizes their transmittance. Sol-gel coatings are used on a substantial number of the optics that make up the OMEGA laser. Each optical element has a potential optical loss associated with it, and the sol-gel AR film helps to reduce surface reflective loss. The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). Sol-gel formation occurs when a metal alkoxide such as tetraethylorthosilicate (TEOS) is combined with an alcohol (ethanol) in the presence of either an aqueous acid or an aqueous base. The resulting hydrolysis reaction replaces the alkoxide groups (OR) with hydroxyl groups (OH). Condensation reactions involving the resulting silanol groups (Si-OH) produce siloxane bonds (Si-O-Si), with water and the alcohol (ROH) as by-products.
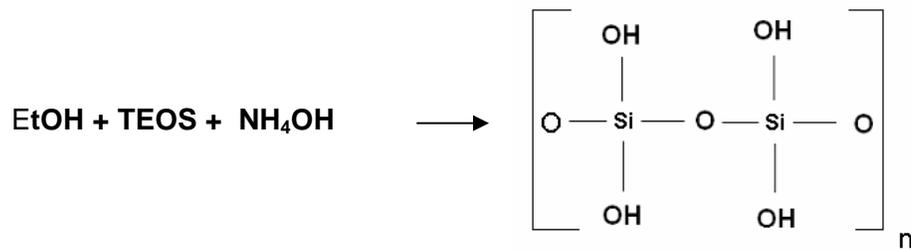

Figure 1: structure of sol-gel molecules

When the sol particles inter-twine into a network, a gel is formed. As the gel continues to dry, condensation reactions continue to occur. Water and alcohol are driven off and the network continually becomes smaller, forming what is called a "xerogel".

The characteristics and properties of the sol-gel network are determined by a number of factors that can affect the rate of both the hydrolysis and condensation reactions. These factors include pH, solution age, temperature, and drying rate or time. By controlling these factors, it is possible to vary the structure and properties of the sol-gel.

Recently, Y. Xu *et al*[1] have reported that sol-gel coatings can be made more contamination-resistant by modifying standard silica sol-gel solutions through co-hydrolysis with other organosiloxane additives. In the co-hydrolysis method, either methyltriethoxysilane (MTES) or dimethyldiethoxysilane (DDS) was added to a standard TEOS-based sol-gel solution at various molar percentages of X, where X= $M_x/(M_x + M_{TEOS})$. M_{TEOS} is the number of moles of TEOS and M_x is the number of moles of the organosiloxane additive (in this case, either MTES or DSS). Xu *et al* [1] prepared and evaluated solutions with molar percentages ranging between 10% and 50%. Their work showed that the sol-gels modified with DDS at 30 mole percent were the most contamination resistant. Based on their method, TEOS-based sol-gel coating solutions used at LLE were modified with MTES and DDS and the effectiveness of the resulting co-hydrolyzed sol-gel solutions were tested for their resistance to contamination by both moisture and volatile organic compounds. The project goal was to develop contamination-resistant AR sol-gel formulations that could be applied to OMEGA optics with minimal changes in the deposition process while at the same time maintaining or exceeding the high laser damage threshold of the standard TEOS-based sol-gel coatings currently deployed on OMEGA.

3. Experimental Data

The standard sol-gel solution used by the LLE Optical Manufacturing Group (OMAN) consists of a mixture of 22.0425 L of ethanol, 2.320 L of TEOS, and 717.5 ml of ammonium hydroxide (NH_4OH). This production batch size was scaled down to smaller amounts for the co-hydrolysis experiments. The ethanol and TEOS were added first and stirred for approximately 3 hours. Ammonium hydroxide was then added and the solution was stirred for another 2 hours. Once this was completed, the sol-gel solution was placed in a closed container and allowed to stand for 3 days. This standard TEOS-based sol-gel solution was used as the starting stock solution for preparation of the modified, co-hydrolyzed sol-gel mixtures. Six 100 ml portions of the standard sol gel stock solution were combined with solutions of 10%, 20% or 30% of either MTES or DDS in ethanol to create the co-hydrolysis mixtures. To determine the amount of each solute to use, the formula

$$X = M_x/(M_x + M_{TEOS}).$$

is solved for M_x, , where X is either 0.1, 0.2 or 0.3. To simplify the calculation, M_{TEOS} was set equal to one mole and the resulting amount for M_x was scaled down according to the actual amount of TEOS used to make each solution. To calculate how many grams of MTES or DDS are needed, the number of moles that corresponds to the weight percentage of the solute of interest was multiplied by the gram molecular weight of either MTES or DDS. The amounts of TEOS needed were scaled down from 2.320 liters to 9.2ml for a 100ml solution.

Once the co-hydrolyzed sol-gel solutions had aged for 3 days, they were spin coated onto substrates in the Optical Materials laboratory clean room. During spin

coating, the substrate is first flooded with the sol-gel and then spun at a certain rpm for a designated length of time. The thickness of the coating is affected by both the spinning speed and the time the substrate is spun for. The thickness in turn determines to a certain extent the wavelength at which the anti-reflective (AR) properties of the coating are the most efficient. The standard TEOS-based sol-gel coating was spun at 4000 rpm for 40 seconds, while all of the co-hydrolyzed sol-gel solutions were spun at approximately 4.8 rpm for 20 seconds. This same process was repeated after the coating solutions had aged for 6 days. The percent transmittance of each sol-gel coated substrate approximately one day after spin deposition was measured using a Perkin Elmer Lambda 900 UV-VIS-NIR spectrophotometer. An uncoated substrate was placed in the reference beam of the spectrophotometer to subtract the absorbance characteristics of the substrate from the data. The samples were scanned over a wavelength range between 300 nm and 1500 nm. The wavelength of maximum AR efficiency of the coating was taken as the point of highest transmission on the transmission vs. wavelength curves. After 5 days exposure to laboratory air, the transmittance of each sample was measured again and compared to the original data. Table 1 summarizes these results.

Sol-Gel Composition	Amount prepared (ml)	Spin Speed (rpm)	Spin Time (sec)	% Transmittance @AR λ_{max}		Δ %T ($\Delta\lambda$)
				1 day exposure*	5 days exposure*	
TEOS stock soln.	250	4000	40	95% (533 nm)	94.1% (567 nm)	0.9% (34 nm)
MTES 10%	100	4800	20	94.8% (592 nm)	94.6% (627 nm)	0.2% (35 nm)
DDS 10%	100	4800	20	94.2% (573 nm)	94.2% (667 nm)	0.0% (94 nm)
MTES 20%	100	4800	20	94.8% (613nm)	93.3% (601 nm)	1.5% (12 nm)
DDS 20%	100	4800	20	94.7% (607 nm)	93.5% (670 nm)	1.2% (63 nm)
MTES 30%	100	4800	20	92.4% (530 nm)	94.3% (493 nm)	1.9% (37 nm)
DDS 30%	100	4800	20	91% (540 nm)	91.3% (601 nm)	0.3% (61 nm)

*Same sample evaluated 1 day after spin-coating and 5 days after exposure to laboratory air

Table 1: *Summary of sol-gel spin coating and transmittance data. λ_{max} = maximum AR wavelength; Δ%T=change in transmission between samples 1 and 2; (Δλ) = change in wavelength between samples1 and2*

Six different substrates each containing a standard TEOS-based sol-gel layer were exposed to decahydronaphthalene, isooctane, hexane, machine oil, deionized water, and ethanol in sealed containers at room temperature (as shown in Fig. 2) for 24 hours to produce a saturate environment of the contaminant. The change in the transmission characteristics of the coatings before and after exposure was determined. The same test procedure was followed for the co-hydrolyzed sol-gel samples employing MTES and DDS.
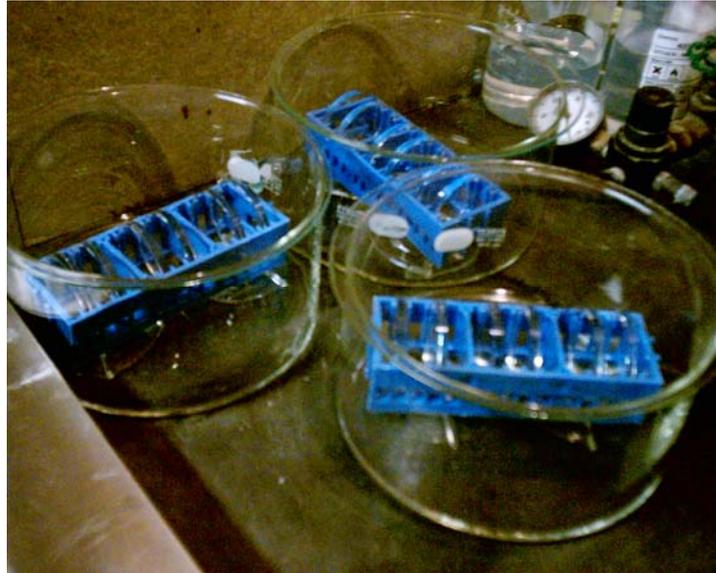
Figure 2: *Sealed containers where various coated substrates were exposed to contaminants.*

A majority of the results are shown in Fig. 3, and the general trend indicates that solutions with a higher percentage of DDS or MTES were more contaminant resistant. It is unclear why some samples had an *increase* in transmittance after exposure. More testing will be conducted to determine whether these results are valid.

Sol-gel Contaminated with Isooctane

Top line: non-contaminated sample
Bottom line: contaminated sample

Sol-gel + MTES 30% solution contaminated with Isooctane

Top line: non-contaminated sample
Bottom line: contaminated sample
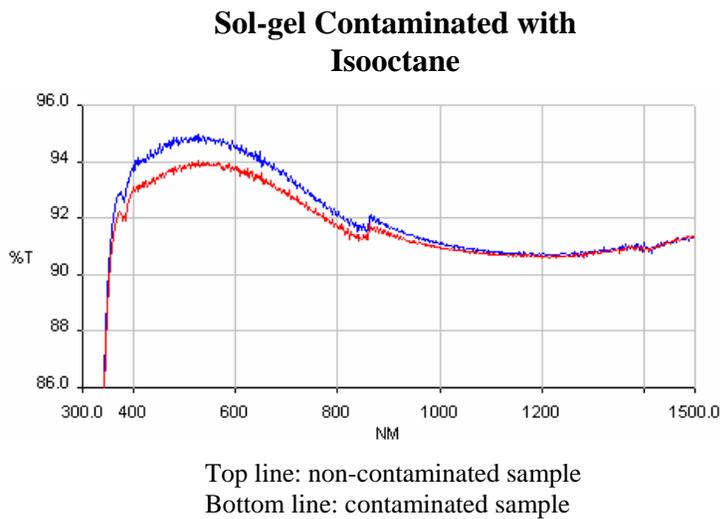
type	change in transmittance
Isooctane	
DDS10	no change
MTES20	<0.1% decrease
MTES30	0.1% decrease
MTES10	0.3% decrease
DDS30	0.5% decrease
DDS20	0.5% decrease
sol-gel	1% decrease
Ethanol	
DDS20	0.5% increase
DDS30	0.2% increase
MTES30	0.1% increase
sol-gel	0.1% increase
MTES20	<0.1% increase
MTES10	0.1% decrease
DDS10	.04% decrease
Decahyronaphthalene	
MTES30	0.4% increase
DDS20	<0.1% increase
MTES10	no change
MTES20	0.1% decrease
sol-gel	0.1% decrease
DDS10	0.1% decrease
DDS30	0.7% decrease
Hexane	
DDS30	0.5% increase
sol-gel	shift right ~50nm
MTES30	0.6% decrease
DDS20	1% decrease
MTES20	1.2% decrease
MTES10	1.5% decrease
DDS10	2% decrease
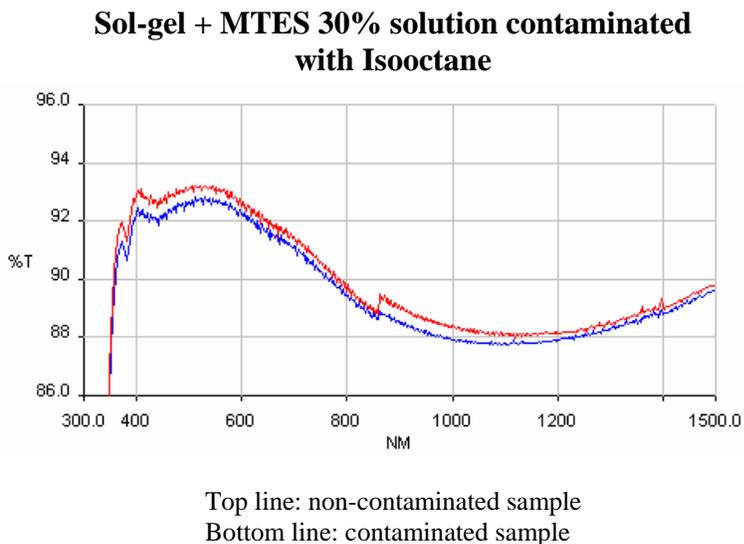
Error: $\pm$ 0.05% T

Figure 3: Contamination test results and corresponding visible-near IR spectra.

Because the samples coated with the DDS 30% and MTES 30% sol-gel solutions gave the best overall results in these experiment, these two compositions were selected for further testing in the Optical Maufactuing (OMAN) facility. The MTES 30% and

DDS 30% sol-gels were dip coated rather than spin coated onto the next set of test substrates because dip coating produces a more even and accurately coated sol-gel AR layer. A third set of susbstrates were dip-coated with the standard sol-gel stock solution as a control. The transmission profile was measured for each coated substrate. Because of coating adhesion problems encountered in the experiments, all three of the sol-gel solutions were diluted in a 1:1 ratio with ethanol and then filtered through a 0.2 μm membrane filter to eliminate particulate contamination.

More samples were dip coated with the newly filtered solutions. The MTES 30% coating showed slight spottiness, while the DDS 30% coating uniformity was good in the center of the substrate but poor around the edges. This was concluded to be a substrate-cleaning problem, so the substrates used in further experiments were cleaned very thoroughly. These samples were then used for contamination testing and were compared to the contamination test results from optics coated with sol-gel created by OMAN staff. The results were very similar in that the sol-gel coated optics with MTES or DDS in it were more contaminant resistant than those coated with the standard sol-gel.

Each of the three sol-gel solutions (standard TEOS-based, DDS 30%, and MTES 30%) were coated on 2" fused silica substrates. These samples were subjected to a 1-on-1 laser induced damage test. In this test the optic is irradiated at separate sites with increasing energy. The results are shown below in Table 2.

Sample	%T	%R	%T + %R	Laser Damage Threshold (J/cm^2, 1-on-1)
DDS 30*	99.91	0.03	99.94	18.97 $\pm$ 0.66
MTES 30*	99.33	0.58	99.91	19.93 $\pm$ 0.46
Std. Sol-Gel	99.65	0.31	99.96	19.43 $\pm$ 1.16

* Used as is- no purification

Table 2: Laser induced damage results on co-hydrolyzed sol-gel coatings (351 nm, 0.5 ns pulse).

There was very little discrepancy between the results of the three samples. The original sol-gel showed maximum Transmittance + Reflectance at 99.96%, yet the MTES and DDS samples were less than 0.05% away from that of the sol-gel. The MTES and DDS co-hydrolyzed sol-gels show equivalent damage thresholds to the standard TEOS-based sol gel even though the MTES and DDS were used as-supplied from the vendor with no special additional purification. Even higher damage thresholds may be possible if the MTES and DDS went through additional purification.

4. Conclusion

Test results showed that overall, MTES 30% and DDS 30% fared just as well or better in contamination tests and laser damage testing as the original sol-gel. Further research may be conducted to develop a coating that would provide a universal protection against any contaminants in the laser bay. Over time, the contaminants in the laser bay may change, so complete protection against all contaminants is more beneficial than protection against a select few. Different concentrations of MTES and DDS will be experimented with, along with purification techniques of these two chemicals before they are added to the sol-gel solution. If this experiment continues to be successful, it will

ultimately reduce or eliminate the need for frequent changing of the laser systems optics to achieve maximum system performance.

Acknowledgements:

References:

(1)   Y. Xu *et a*l 1, L. Zhang, D. Wu, Y. H. Sun, Z. X. Huang, X. D. Jiang, X. F. Wei, Z. H. Li, B. Z. Dong, and Z. H. Wu, "Durable Sol-Gel Antireflective Films with High Laser–Induced Damage Thresholds for Inertial Confinement Fusion", J. Opt. Soc. Am. B, Vol. 22, No. 4, April 2005, pp. 905-912.