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Sol-gel Coatings for High Power Laser Optics-Past, Present and Future

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ABSTRACT

An investigation into the preparation of sol-gel coatings for high power lasers was started at LLNL in 1983 and AR coatings were successfully developed for use in the Nova laser in 1984. Several other large lasers now use these coatings. Subsequent work on HR coatings resulted in AlOOH/SiO_2 and later ZrO_2 or $\text{HfO}_2/\text{SiO}_2$ systems of good optical performance. The use of organic polymer binders gave increased damage threshold and enhanced optical performance. We are in the process of scaling up HR fabrication for substrates approximately 38 cm square. Concurrently we are developing sol-gel random phase plates for laser beam smoothing. These have a patterned surface design of silica which induces phase shifts in the beam by variation in the optical path length. Plates of this type on 80 cm diameter substrates have been used successfully on the Nova.

1. INTRODUCTION

The sol-gel process has been known for many years and can be used to prepare a variety of products ranging from coatings to dense monolithic bodies. In general, the procedure involves the preparation of a solution of one or more precursor materials (the SOL) and conversion of this solution to useful products usually through a gelation (the GEL) stage. These precursor materials are compounds that are readily converted to the product which is usually an oxide. They must be soluble and may have other desirable properties such as volatility which allows purification by distillation. Metal alkoxides are common precursors and are easily converted to oxides by hydrolysis. Many alkoxides are volatile liquids and Table 1 lists several which are particularly useful.

TABLE 1

<u>Alkoxide</u>	<u>Boiling Point</u>	<u>Oxide Product</u>
$\text{Si}(\text{OCH}_3)_4$	121°C	SiO_2
$\text{Si}(\text{OC}_2\text{H}_5)_4$	167°C	SiO_2
$\text{Ge}(\text{OC}_2\text{H}_5)_4$	86°C/12mm	GeO_2
$\text{Al}(\text{OC}_4\text{H}_9^{\text{sec}})_3$	100°C/0.1mm	Al_2O_3
$\text{B}(\text{OCH}_3)_3$	67°C	B_2O_3
$\text{Ti}(\text{OC}_3\text{H}_7^{\text{iso}})_4$	50°C/0.1mm	TiO_2
$\text{Zr}(\text{OC}_4\text{H}_9^{\text{tert}})_4$	50°C/0.1mm	ZrO_2
$\text{Ta}(\text{OC}_2\text{H}_5)_5$	80°C/0.1mm	Ta_2O_5

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After the solution is prepared, it may be converted to a number of different products as illustrated in Fig. 1.

For the preparation of coatings, two methods can be used. In the first, the solution is applied directly to a suitable substrate, by any of the usual wet coating methods, and the precursor then converter to oxide by hydrolysis and/or heat. This method gives dense hard coatings but they are stressed because removal of organic material from the precursor while on the substrate causes shrinkage. In the second method the conversion to oxide is carried out prior to application of the solution to the substrate. No further hydrolysis or heat is necessary and the coatings are free of stress. They are however porous and of low abrasion resistance.

Many papers have been published on coating preparation and almost all of these describe work using the first method above. There have however been very few publications directed towards the preparation of coatings specifically for laser optics. The first of these was by Sokolova and colleagues in 1967 and there followed a series of at least a dozen papers describing work up to about 1980 at which time publications abruptly stopped.² Multilayer AR, HR, polarizer and beam splitting coatings on substrates up to 70 cm in diameter were prepared. These involved heat treatments up to 900° C giving stressed products which were in many cases crazed and had low laser damage threshold. Other coatings for laser application were described by McCollister and Boling³ and by Mukherjee and Lowdermilk.⁴ Both papers describe the preparation of graded index AR coatings by the application of a phase separable glass layer followed by extraction of one phase to leave a porous, variable index residue. Yoldas and Partlow⁵ prepared a similar graded index AR coating by making porous silica coatings and enlarging the surface pores with HF to give a graded index. All of these methods required a heat treatment to at least 400° and laser damage thresholds were relatively low.

An extensive investigation of laser sol-gel coatings was started at LLNL in 1983 primarily directed towards the preparation of coatings for the Nova laser being built at that time. The initial work was concentrated on the preparation of quarterwave AR coatings and this was soon followed by multilayer HR high-low index stacks. Both processes used colloidal suspensions of oxides (method two). This was particularly suitable for large optics and gave stress-free coatings of high laser damage threshold. More recently binary phase plates for laser beam smoothing have been prepared. These were made from dense silica coatings put down from solution (method one) but with room temperature processing.

2. QUARTERWAVE POROUS SILICA AR COATINGS

Initial efforts were directed towards the preparation of AR coatings for all the Nova transmissive optics. At that time no coatings of any type were available capable of handling the laser fluences that the laser was designed to produce.

We found that a porous silica quarterwave coating was readily prepared from a collidal suspension of silica in ethanol.⁶ The suspension was prepared by the base catalysed hydrolysis of high purity tetraethyl silicate in ethanol as shown in Fig. 2.

Application of the suspension by dip or spin to a suitable substrate at room temperature deposited a random layer of silica particles after evaporation of the ethanol. The particle size was about 20 nm and the refractive index of the coating was about 1.22. This gave typical quarterwave AR performance as shown in Fig. 3. This also shows that the coating can be stacked which allowed the thickness to be varied according to the required wavelength. Thickness could also be varied by changing the concentration of silica in the suspension or by changing the withdrawal rate or spin-speed during coating.

Of particular significance was the capability of coating KDP harmonic conversion crystals. The sensitivity of this substrate to water and heat was of no consequence because the silica suspension is anhydrous and applied at room temperature.

The laser damage threshold under a variety of conditions on fused silica substrates are shown in Table 2. These are at least twice as large as the thresholds of any other coatings prepared by other methods and easily within the performance range required for the Nova lasers.

TABLE 2

<u>Wavelength</u>	<u>Pulse width</u>	<u>Damage Threshold</u>
1064 nm	10 ns	>70 J/cm ²
	3 ns	50 J/cm ²
355 nm	10 ns	23 J/cm ²
	3 ns	20 J/cm ²

The loose stacking of silica particles results in low abrasion resistance and the coating is readily removed without upsetting the surface profile of the underlying substrate. Substrate are therefore easily recoated when used under environmentally severe conditions, such as the Nova target chamber. If required, there are two methods which can be used to increase abrasion resistance to a small extent. Both involve processes which cement or "glue" particles together by chemical reaction. In one the coating is exposed to ammonia-water vapor for a minimum of 16 hours.⁷ This causes a reaction illustrated in Fig. 4. in which particles are connected by siloxane bonds. The second method involves the incorporation of a soluble silicate binder in the suspension prior to application to the substrate. This process is illustrated in Fig. 5. In both cases particles are only connected by narrow necks and the coating remains porous. Abrasion resistance is increased but remains low compared to a dense coating. One advantage of these binding processes is that there is an apparent increase in laser damage threshold probably because of an overall increase in coating strength.

3. POROUS MULTILAYER HR COATINGS

We also found that multilayer HR coatings could be prepared using the colloidal silica suspension described earlier for the low index component and colloidal suspensions of other oxides for the high index components. It was possible to prepare suitable

suspensions of TiO_2 ,⁸ AlOOH ,⁹ ZrO_2 and HfO_2 and alternating layers of one of these with silica could be readily stacked using a spin or meniscus coater at room temperature and allowing a few minutes drying time between coats. Reflectivities of 99+% could be obtained in all cases but the number of layers required varied according to the refractive index of the high index component. This is illustrated in Table 3 which also list the laser damage thresholds at 1064 nm/3ns/10Hz.

TABLE 3

Oxide	Index	Layer for 99% reflect	Damage
TiO_2	1.75	16	2 J/cm ²
AlOOH	1.44	36	20 J/cm ²
ZrO_2	1.55	24	8 J/cm ²
HfO_2	1.55	24	5 J/cm ²

The single shot damage threshold of the TiO_2 system was much higher than 2 J/cm². The cumulative effect of multishots gave rapid deterioration. This was not observed with the others.

Further investigation showed that the damage thresholds of ZrO_2 and HfO_2 systems could be significantly improved by incorporation of a binder.¹⁰ This appears to be the same effect that was observed for silica alone in which the binder increases the strength of the coating. Binders investigated includes polyvinyl alcohol (PVA) and polyvinyl pyrrolidinone (PVP) both of which gave significant damage threshold increase. PVP was preferred because this could be used in organic solution, rather than one containing water, as was required for PVA. Water is not a good coating solvent because of its high surface tension. Increases in damage thresholds up to approximately 15-18 J/cm² could be obtained for ZrO_2 and HfO_2 HR's with silica. TiO_2 and AlOOH remained unaffected with binders.

One other advantage of the use of binders is that they increase the refractive index of the oxide coating by filling in some of the voids. The index can be raised to about 1.7 which means that 99% reflection can be obtained with only 20 total layers. A typical transmission spectrum of a $[\text{SiO}_2 - \text{ZrO}_2]$ -¹⁰ mirror containing PVP is shown in Fig. 6.

Investigation into methods of preparation of sol-gel HR coatings continues. A large number of mirrors are required for the proposed NIF facility and there is a potential economic advantage using the sol-gel process rather than others.

4. RANDOM PHASE PLATES

Phase plates are required for removing aberrations from laser beams caused by inhomogeneities, surface figure errors and thermal non-uniformities in the optical components of the laser. In their simplest form these plates consist of a random array of hexagonal or square pixels on a silica substrate, the pixel thickness being such that light

passing through is half a wave out of phase with light that enters the substrate directly.¹¹ This is illustrated in Fig. 7.

We found that the pixel pattern required for a phase plate could be fabricated from a sol-gel silicate solution as follows:

- a. The silica substrate was dip coated in a solution of acid catalysed hydrolysed ethyl silicate solution. After air drying, the silicate coating was converted to substantially dense silica by exposure to ammonia-water vapor for 16 hours.
- b. Photoresist was then spun coated over one side of the silica coated substrate and then exposed through a suitable mask in the usual manner.
- c. After development, the unprotected (by resist) areas of the silica coated substrate were etched off using HF. Removal of the remaining resist then left the pixel patterned substrate.

The whole process is illustrated in Fig. 8 and a typical pixel pattern (mask) is shown in Fig. 9. High laser damage phase plates on substrates up to 80 cm in diameter have been prepared in this manner and have performed very well on the Nova laser.

5. CONCLUSIONS

5.1 Antireflective coatings

The porous silica AR coating has performed very well for 9 years on the Nova and other high power lasers. It has the following desirable properties:

- a. low cost
- b. excellent optical performance
- c. high lasers damage threshold
- d. easily applied at room temperature on large substrates
- e. easily stripped off and removed

The process is now optimised and it is difficult to see how any significant improvement can be made in the future. It is likely that use will therefore continue until something better comes along.

5.2 Reflective Coatings

The research effort on the development of multilayer HR coatings continues. The significant points in these systems are as follows:

- a. easily applied at room temperature
- b. optical performance no better than coatings prepared by other methods
- c. probably no cost advantage for small samples but definite advantage for large ones.
- d. laser damage threshold lower than the best PVD samples

The future of these coatings will probably depend entirely on improvement of the damage threshold. Even so the application will only be for large substrates.

5.3 Random phase plates

The patterned silica binary phase plates have performed well on the Nova and other lasers. The significant points here are:

- a. low cost
- b. excellent performance
- c. high laser damage threshold
- d. applicable to large substrates

The demand for laser beam smoothing using phase plates is increasing and this demand is not restricted to high power lasers. Binary phase plates are easily prepared but not as efficient as the recently developed kinoform plates. Successful preparation of the latter (by a non sol-gel process) will probably obsolete the binary plates.

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Figure 1 Conversion of sol-gel solutions

Figure 2 Preparation of AR coating

Figure 3 Transmission spectra of AR coated fused silica substrates

Figure 4 Reaction between silica particles on exposure to $\text{NH}_3/\text{H}_2\text{O}$

Figure 5 Reaction between silica particles and silicate binder

Figure 6 Transmission spectrum of [SiO₂-ZrO₂]¹⁰ mirror on silica substrate

Optical path difference = path length through element
 (must be $\lambda/2$) - path length through air
 $= n \cdot t - t$
 $= t(n - 1)$

Where t = physical thickness of element
 n = refractive index of element

For $\lambda = 1064 \text{ nm}$	$t = 1209 \text{ nm}$
532 nm	604 nm
355 nm	403 nm

Figure 7 Optical path difference due to silica pixel

Figure 8 Process for preparation of pixel pattern

Figure 9 Section of typical pixel pattern mask used for phase plates

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