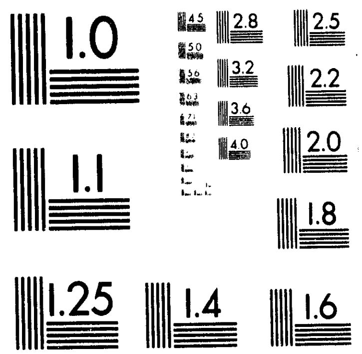
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Sol-gel metal oxide and metal oxide/polymer multilayers applied by meniscus coating

Jerald A. Britten and Ian M. Thomas

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Jerald A. Britten and Ian M. Thomas

Lawrence Livermore National Laboratory, Livermore, CA 94550

ABSTRACT

We are developing a meniscus coating process for manufacturing large-aperture dielectric multilayer high reflectors (HR's) at ambient conditions from liquid suspensions. Using a lab-scale coater capable of coating 150 mm. square substrates, we have produced several HR's which give 99%+ reflection with 24 layers and with edge effects confined to about 10 mm. In calendar 1993 we are taking delivery of an automated meniscus coating machine capable of coating substrates up to 400 mm wide and 600 mm long.

The laser-damage threshold and failure stress of sol-gel thin films can be substantially increased through the use of soluble polymers which act as binders for the metal oxide particles comprising the deposited film. Refractive index control of the film is also possible through varying the polymer/oxide ratio. Much of our present effort present is in optimizing oxide particle/binder/solvent formulations for the high-index material. Films from colloidal zirconia strengthened with polyvinylpyrollidone (PVP) have given the best results to date. An increase in the laser damage threshold (LDT) for single layers has been shown to significantly increase with increased polymer loading, but as yet the LDT for multilayer stacks remains low.

1. INTRODUCTION

The success of the next–generation fusion laser system will be determined as much by cost as by performance. For this reason several development efforts are underway at LLNL aimed at reducing the the cost of a variety of laser optics while still adhering to stringent performance and laser damage critera. One such effort is the extension of sol–gel coatings, which have had considerable success in antireflective applications[1,2] to multilayer high-reflective coatings. These coatings are applied at ambient temperature and pressure by relatively simple means, and thus can offer cost advantages with respect to e-beam evaporated coatings. In the last two years our group as well as others have characterized and determined the feasibility of meniscus coating as the process of choice to apply multilayers from colloidal suspensions[3–5]. The basic concept of meniscus coating is shown in Figure 1. Coating fluid is forced into the ends of a horizontal applicator tube to flow through a slot cut lengthwise out and over the outer surface of the tube. The substrate, with the side to be coated facing down, contacts the thin liquid film flowing over the tube when it is moved over it. A thin liquid film is entrained on the substrate as it moves. The fluid mechanics of this process have been shown to be virtually identical to the familiar dip–coating process[3]. The advantages of meniscus coating over dip coating for single-side coating applications include very small coating fluid inventories, minimal intercontamination of different coating fluids, and compactness. Advantages over spin-coating include straightforward scaleup, application to large, rectangular heavy parts, and insensitivity to non–Newtonian fluid flow effects which can lead to radial coating thickness variations on large spin–coated parts.[6].

The challenge of sol-gel HR's lies not in the coating process but in the formulation of the coating fluids, in particular the high-index material. Several previous studies have been devoted to the search for a suitable high-index coating suspension. Titanium dioxide has been rejected due to low LDT[7]. A general problem of other high-index layers from oxide sols, namely those of niobium and tantalum[8], and hafnium and zirconium, is insufficient strength due to the point contact of the weakly attracted particles comprising the coating. Severe crazing results after a few layers have been built up. An exception is coatings made from colloidal hydrated alumina sols, wherein hydrogen bonding between OH groups on the particle surfaces promotes excellent adhesion. Thomas[9] has demonstrated $SiO_2/AlOOH$ multilayers of up to 36 layers made by spin coating which give 99+% reflection and have n-on-1, 16 ns laser damage thresholds of 30-50 J/cm^2. This system was used in the original meniscus coating scoping studies[4]. A drawback of this system is the small index difference between SiO_2 layers (n=1.20) and AlOOH layers (n=1.44). Attempts to make stable, fine-particle gallium oxide sols, which exist in a hydrated phase analogous to AlOOH but with a higher index, have not been successful[10].

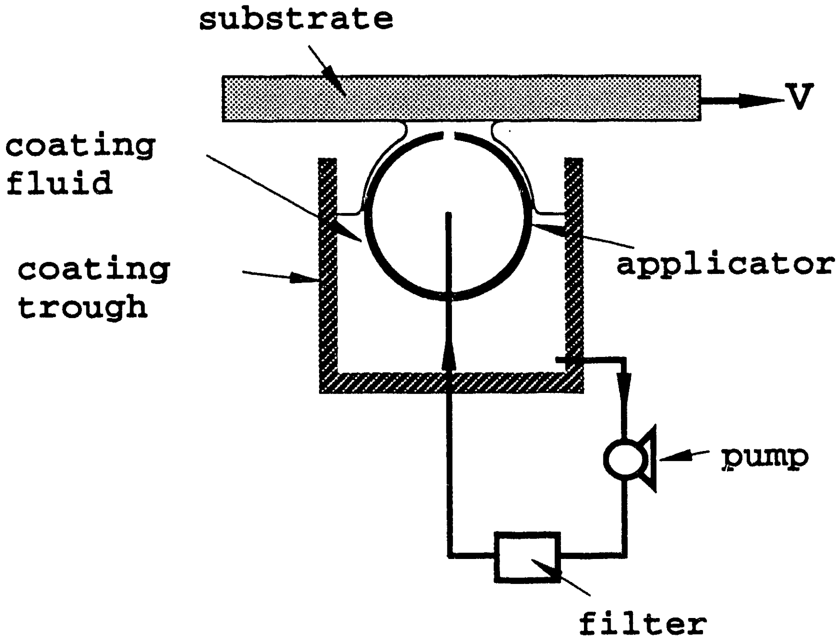

Figure 1. Schematic of meniscus coating process

Oxide coatings can be strengthened by use of a polymeric binder in the sol. This binder can, under ideal circumstances, add tensile strength and elastic properties to the coating and also increase the index of the layer by filling in open porosity. The binder must not destabilize the colloid and cause aggregation, and must not readily redissolve upon subsequent applications in a multilayer coating. Binders made by adding unhydrolyzed precursors of oxides to the particulate sol tend to shrink and age upon drying, inducing crazing[11]. Recently, Thomas[12] demonstrated multilayers made by spin coating with a high-index (n=1.7) layer of hafnia reinforced with the organic polymer polyvinyl alcohol (PVA). These coatings also exhibited laser damage thresholds of 25-28 J/cm^2 at 10 ns, 1.06 μ. Unfortunately, this formulation proved to be unsuitable for meniscus coating, due largely to the much longer drying times associated with meniscus coating (minutes) -vs- spin coating (seconds). PVA is soluble only in water, and water-based coatings on the low-energy silica layer tended to creep, forming large edge nonuniformities. When most of the water is replaced with methanol, phase separation of the PVA and HfO_2 occurred during drying.

We have recently been successful in using polyvinylpyrollidone (PVP) as a binder for zirconia in a single low-surface tension solvent. With this system, we have made SiO_2/ZrO_2-PVP multilayers of up to 30 total layers. These coatings have excellent optical properties and adequate laser damage thresholds to be useful to our laser fusion program requirements. This polymer can also be added in small amounts to the low-index SiO_2 sol to strengthen it without impacting its index. These coatings will be discussed below.

2. EXPERIMENTAL

2.1 Sol preparation

The low-index silica suspension was prepared as previously described[1] with the exception that methanol was used in place of ethanol as the reaction medium since it gives rise to smaller particle sizes. The PVP binder (a 10% solution of 360,000 MW PVP in methanol) was added either prior to or subsequent to the hydrolysis/condensation reactions which creates the silica particles. Three days was sufficient to allow this reaction to proceed to completion and after this time the sol was solvent–exchanged with sec-butanol.

The high-index zirconia sol was prepared by a method similar to that described elsewhere[13]. This involved neutralization of zirconyl chloride by urea in water followed by crystallization of the produced amorphous oxide gel at 220°C in a pressure reactor. The resulting crystalline particulate sol was redispersed by addition of a small amount of HCl and ultrasonfication. Ionic species were then removed from the sol by several days of dialysis. A solvent exchange to methoxyethanol was then performed, and the PVP binder (a 10% solution of 360,000 MW PVP in methoxyethanol) added to give a stable sol of a predetermined oxide/binder ratio.

2.2 Coating procedure

A lab-scale meniscus coater designed and built at LLNL was used to apply the multilayer coatings. Applicators consist of 175 mm long, 20 mm diameter stainless steel tubes with 1 mm slots cut lengthwise, contained in a trough. The recirculating coating flow loop is driven by small centrifugal pumps through a disposable 5μ cartridge filter. The entire liquid–filled volume is about 300 ml. Lids are emplaced over the applicator when not in use, but some solvent evaporation does occur, neccessitating that the suspension be topped off with fresh solvent before each run. The coating fluid itself remains viable for several weeks, however.

The coater is located in a laminar flow clean hood. The substrate to be coated is held inverted by vacuum in a carriage supported by two linear motion guideways. The applicator to be used is raised to a preset height, typically 0.25 mm down from the surface to be coated. The substrate is then moved over the applicator by a variable-speed dc motor with a cable drive. Typical speeds are 2.5-5 mm/s. Calibrations are made, and then the multilayer is applied with about a 10 min. wait between coatings to allow the previous layer to dry under ambient conditions. A fiber-optic spectrophotometer installed on the coater allows monitoring of a small area of the coating after each application, and based on this data minor adjustments to the translation rates can be made to optimize the peak reflectance wavelength.

3. RESULTS AND DISCUSSION

3.1 Low–index sol

Thin films applied by meniscus coating in early experiments[4] exhibited visible bands or stripes parallel to the applicator tube. These were attributed to vibrations or disturbances in the linear motion of the coating trough as the coating was being applied, and were always more prominent with the silica sol than with the high–index suspension. The root cause was traced to the linear motion system and selection of the proper linear motion guideways have minimized the problem, but it was also found that banding was exacerbated by freezing of locally thick regions by the rapid evaporation of the highly volatile ethanol suspending fluid. Replacement of this solvent with less–volatile sec-butanol allows for locally thick regions to planarize by lateral flow before the coating dries to immobility. This solvent exchange and properly engineered linear motion systems have virtually eliminated the banding problem.

It was also discovered that coating strength and appearance were enhanced by addition of binder to the silica suspension as well as the high-index suspension. A minimal amount of binder is necessary to acheive this effect since we want to maintain the refractive index of this layer as low as practicable. PVP in small amounts was added to the silica suspension after solvent exchange, films were spun onto silica and silicon substrates and evaluated. Refractive indices were measured by ellipsometry and the relative strengths of the films was evaluated by stacking films and observing the onset of crazing under 40x magnification. Results of these experiments are shown in Table 1. Addition of only 2% of polymer by weight with respect to the SiO_2 in the sol has a relatively large effect on the strength of the film without increasing n significantly. About 4% PVP was determined to be the optimum loading, since sols with 8-10% PVP were unstable to coagulation in less than 24 hours and sols typically showed some aging at even lower concentrations.

Table 1. Properties of SiO_2-PVP layers

wt. % PVP†	Index	# layers to crazing
0	1.18	4
1.9	1.18	6
3.8	1.18	7
5.6	1.19	10
9.0*	1.20	10

† with respect to SiO_2
* not stable

3.2 High–index sol

The laser damage and refractive index of the high-index layer is increased with the addition of the PVP binder up to at least 50 volume %, as is shown in Table 2. These single–layer coatings show no conditioning effect; s–on–1 damage values are the same as ramped fluence r–on–1 values. The majority of this data is for a hafnia-PVP system. Attempts to make multilayers with this system have proven unsuccessful, because application of a second hafnia coating redissolves the first. However, zirconia-PVP sols with volume ratios of up to 3:2 were found to stack without redissolution. The reason for this difference in behavior of the two oxides, which were prepared identically and have nominally identical chemistries, is not understood. It may be that the preparation method results in differing degrees of conversion from amorphous to crystalline phases of the oxide particulates, which could lead to differences in particle–particle and particle–polymer attractive forces.

Table 2. Properties of high-index oxide-PVP single layers. LDT at 1064 nm, 3ns, 10 Hz.

HfO_2–PVP

vol. % PVP	Index	LDT* (J/cm^2)
0	1.53	7-9
25	1.57	7-8
33	1.62	11-12
50	1.72	19-28
100	1.50	20

ZrO_2–PVP

vol. % PVP	Index	LDT* (J/cm^2)
0	1.53	7-9
40	1.63	14

* No conditioning effect

3.3 Multilayers

Multilayer stacks for reflection of 1 μ light at normal incidence were applied with suspensions of 2.5 % SiO_2, 0.1% PVP (by weight) in sec-butanol as the low-index layer, and 7% ZrO_2, 0.5% PVP in methoxyethanol as the high-index layer. Calibration coatings were applied onto clean 15 cm. square glass plates to determine the correct coating rate, and then multilayers were applied starting with the low-index layer. Ten minutes were typically allowed for air-drying between coats. Spectral transmittance was monitored with the fiber-optic spectrophotometer mounted on the apparatus. If a constant speed for each layer was used throughout the operation, the reflectance peak was observed to gradually shift to higher wavelengths. This was due to the slight concentration of the sol over the course of several hours by evaporation of the solvent. A gradual decrease in the coating rate (about a 10% decrease from first coat to last for the SiO_2 sol and about 5% for the ZrO_2, for a 12 layer-pair HR) was found to be sufficient to maintain the reflectance peak at the desired wavelength. About 5 hours were required to prepare a 24 layer HR, which gave 99.4% reflection at the measurement location. This compares well with theoretical reflectivities of 99.85% calculated using indices of 1.20 and 1.63.

The uniformity of one HR was measured by precision photometry at 225 locations and the values interpolated to give the iso-transmission contours shown in Figure 2. Approximately 85% of the 225 cm^2 surface is between 99.0 and 99.5% reflective at 1.064 μ. The largest edge effect on this sample was due to an adjustment problem which caused the liquid film to attach about 1 cm back from the leading edge during one application. Application of one or two more layer pairs would further diminish the edge roll-off, and since typical designs call for a 1 cm edge allowance for fixturing, we feel that reflection uniformity specifications can be straightforwardly achieved by meniscus coated optics.

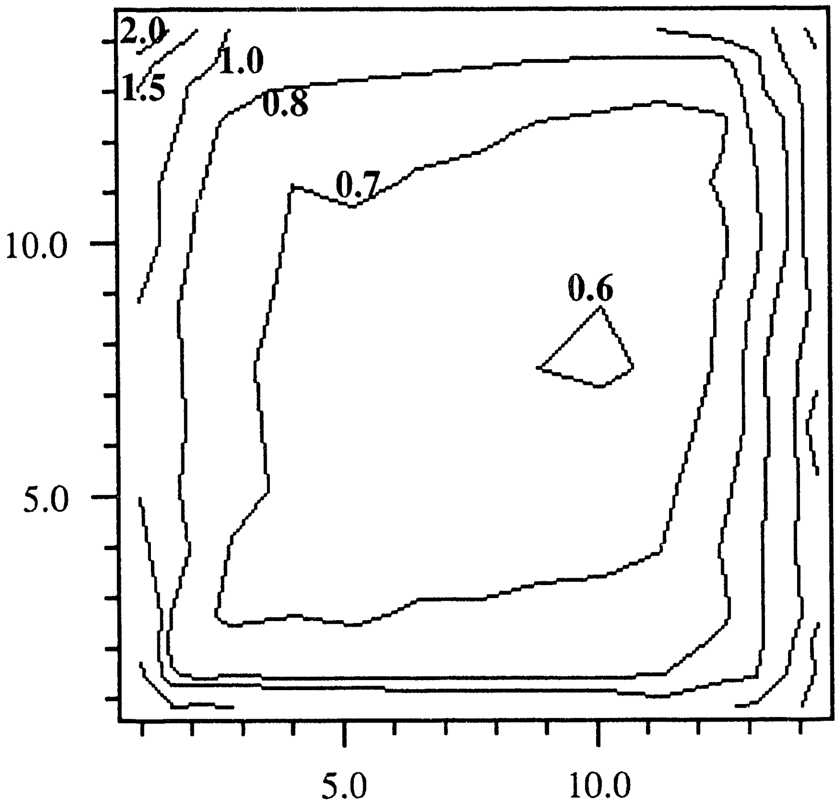

Figure 2. Contours of constant % transmission for a (SiO_2-PVP/ZrO_2-PVP)^{12} HR meniscus coated onto a 15 cm square substrate.

The laser damage characteristics of these silica-zirconia-PVP HR's has been to date disappointing, however. Unconditioned and conditioned LDT fluences for 1.064 μ, 3ns, 10 Hz laser pulses as measured for four typical HR's are shown in Table 3. Unconditioned fluences barely meet the specifications for one cavity mirror for the Beamlet laser under construction at LLNL. Conditioned LDT's are sufficient for both cavity mirrors, but one of the advantages touted for sol-gel coatings is that they require no conditioning. The damage appears to be due to a large number of pre-existing defects in the film. Cleanliness, and likely LDT's would improve if the coatings were carried out under clean–room conditions. We are also investigating the use of UV curable binders to further crosslink and strengthen the coatings, as well as hybrid multilayers using both zirconia/hafnia to provide index contrast and alumina to provide laser damage resistance.

Table 3. Laser damage thresholds for several SiO_2-PVP/ZrO_2-PVP HR's, measured at 1064 nm, 3 ns, 10 Hz.

# of layers	Unconditioned	Conditioned
24	3.5 ± 0.5	8.3 ± 1.3
24	3.4 ± 0.5	5.7 ± 0.9
24	2.3 ± 0.4	7.2 ± 1.1
30	1.4 ± 0.4	6.7 ± 1.0

In calendar 1993 we are taking delivery of a full-scale prototype meniscus coater capable of processing substrates up to 400x600x120 mm. This coater will be used to provide demonstration sol–gel mirrors for the Beamlet laser. Some of the features engineered in this coater are automated operation, three coating applicators, automated trailing edge bead cleaning, and in–line photometry. The coater is in itself a clean environment, with laminar flow air filtering and exhaust control. With this coater we hope to improve the laser damage performance of our sol–gel mirrors, and soon produce useful parts for large–aperture lasers.

4. CONCLUSIONS

Sol-gel/polymer multilayer reflectors of up to 30 layers have been made by meniscus coating on 150mm square substrates. These coatings exhibit >99% reflectivity, have excellent spatial uniformity and possess laser-damage thresholds sufficient to be useful as cavity mirrors for multipass laser geometries. The feasibility of the meniscus coating process has been demonstrated. Further improvements to laser damage thresholds through several methods are being explored.

5. ACKNOWLEDGEMENTS

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