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Next Generation Optical Coating Candidate**

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An amorphous fluoropolymer: next generation optical coating candidate

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ABSTRACT

Anti-reflective (AR) and high reflector (HR) optical coatings were made by physical vapor deposition (PVD) of Teflon AF2400, a perfluorinated amorphous polymer. The AR had the highest laser damage thresholds recorded for PVD coatings at the Lawrence Livermore National Laboratory damage facility. The HR was a multilayer of ZnS and AF2400. The bandwidth was 550 nm, centered at 1064 nm. Single layers of Teflon AF2400 deposited by PVD were characterized optically. The refractive index could be intentionally reduced below the bulk value by varying either deposition rate or substrate temperature. Scanning electron microscopy and nuclear magnetic resonance observations indicated that morphological changes caused the variations in the refractive index rather than compositional changes.

1. INTRODUCTION

Teflon AF2400 is an attractive candidate for high performance optical coatings. The bulk properties of this particular perfluorinated amorphous polymer show a high transmittance range from 200 nm to 2000 nm, and a low refractive index, n . In fact, the bulk n of 1.29 for AF2400 is lower than any dielectric compound currently used for optical coatings. Single layer coatings are deposited using either a spin or dip solution technique. In these cases, a solution of AF2400 dissolved in an expensive (hundreds of U.S. \$ per gallon) fluorinated solvent are required.^{1,2,3} Recent work has shown that this material can be thermally evaporated^{4,5} as a corrosion barriers for extra-terrestrial equipment,⁶ and as a possible insulator for submicron electronic devices.⁷ If the viability of physical-vapor-deposition (PVD) of AF2400 optical coatings can be demonstrated, the material should have applications in the optical coatings community. Anti-reflective coatings produced by a solution process had very high laser damage thresholds at 1.06 μm .¹ In this paper, the compatibility of AF2400 in a PVD process and with other dielectric optical materials in PVD processes is described.

2. EXPERIMENTAL SET-UP

Figure 1 shows the chemical constituents of Teflon AF2400. A W-filament resistance heater was used to evaporate the Teflon AF2400 in a stainless steel vacuum chamber. The pump stack consisted of a diffusion pump, a liquid N₂ trap, and a mechanical roughing pump. The substrates were heated with quartz-halogen lamps controlled manually with a 120 VAC variable transformer. The chamber was backfilled with O₂ to 0.66 Pa (5×10^{-3} Torr) for a glow discharge cleaning. The discharge bias was applied between the Al ring and the substrate platen for five minutes.

Fig. 1. Chemical make-up of Teflon AF2400. Teflon AF2400 is a copolymer of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole. The approximate ratio of a:b is 1:4.

A Box-Behnken experimental strategy⁸ was used to examine the relationship between the evaporation parameters and the material properties. Three process variables, (i) substrate temperature, (ii) deposition rate, and (iii) glow discharge bias, were used in a 13-run matrix (see Table I). Single layer samples of $\approx 1500\text{\AA}$ thick were made under each process condition. The coating properties were measured and used in a linear regression analysis. The analysis determined the coefficients for the process variables, including cross-terms and square-terms of each process variable. The coating properties then could be expressed as a linear combination of the process variables. Replicates were also made at a specific process parameters to obtain an estimate of the error of the coating properties.

Table I: Process conditions for the Box-Behnken experimental strategy. Thirteen process conditions were established and samples generated in a randomized order. The process conditions were established as the extreme and mid-points of the process range.

Substrate Temperature ($^{\circ}\text{C}$)	Deposition Rate ($\text{\AA}/\text{sec}$)	Glow Discharge Bias (V)
20	2	0
20	11	-1500
20	11	1500
20	20	0
110	2	1500
110	2	1500
110	20	-1500
110	20	-1500
110	11	0
200	2	0
200	11	-1500
200	11	1500
200	20	0

The transmittance, n , and the adhesion were the measured coating properties. The transmittances (from 200 nm to 1200 nm) were measured on coated fused silica substrates using an optical spectrophotometer. The n (at 633 nm) and thickness were determined on coated Si wafers using an ellipsometer. Adhesion was measured with a Scotch-tape test. Scotch tape with a 12.6 gr/mm tension (Scotch Magic tape variety) was applied firmly to the coatings, and then pulled off with the free end perpendicular to the surface.

The anti-reflective (AR) coatings were deposited in the same chamber where the single layers were made. The high reflector (HR) was made in a similar chamber, except that the ZnS was deposited using either a resistance heater or an electron gun system. The samples for damage testing were deposited onto superpolished fused silica substrates.

The laser damage resistance of the AR and HR coatings was obtained at the LLNL damage facility. A laser conditioning procedure was used to increase the damage thresholds of these coatings.⁹ The conditioning consisted of exposing the test site initially with low (non-damaging) fluences and ramping up to fluences which eventually cause damage.

3. RESULTS

3.1 Single layers

The coatings adhered to fused silica substrates and Si wafers under normal laboratory conditions but were easily rubbed off. Unexpectedly, there was a stronger correlation between adhesion and the substrate temperature than to the glow discharge bias. The responses from the glow discharge variable were then folded into a two-variable regression analysis of adhesion to deposition rate, R , and substrate temperature, T . Figure 2 gives the iso-adhesion lines of Teflon AF2400 coatings on Si wafers as a function of T and R . The adhesion, A (%), was defined as the amount of coating remaining on the substrate after a scotch-tape test. Adhesion increased with T , and at high temperatures the adhesion decreased with increasing R . The adhesion, A (%), was modeled numerically as

$$A (\%) = -32.26 + 0.921 T + 4.34 R - 1.56 \times 10^{-3} T^2 - 1.39 \times 10^{-2} R \cdot T - 0.156 R^2, \quad \text{eqn. [1]}$$

where T is the substrate temperature in $^{\circ}\text{C}$ and R is the deposition rate as indicated by the quartz crystal monitor in $\text{\AA}/\text{s}$. The degree of fit was 96%. There was a 95% confidence level that the adhesion values were ± 6 % in eqn. [1].

The AF2400 coatings had an n that could be modified intentionally via the T and/or R . Normalized linear regression analysis revealed that the glow discharge, and the cross-term $R \cdot T$ had no significant effect on the n . As in the above adhesion analysis, the responses from the glow discharge runs were folded into the linear regression analysis between n and the process variables, T and R . The iso- n contours are given in Fig. 3. For this series of coatings, the refractive index, N , depended on T and R as

$$N = 1.23 - 5.5 \times 10^{-3} R + 1.5 \times 10^{-3} T + 2.1 \times 10^{-5} R^2 - 6 \times 10^{-6} T^2. \quad \text{eqn. [2]}$$

The degree of fit was 96.2%. There was a 95% confidence level that the long term average of the n was ± 0.034 .

The adhesion and n surface contours, Figs. 2 and 3, respectively, were determined from our specific chamber set-up. However, the general trends shown by Figs. 2 and 3 provide insight into where the most appropriate coatings may be made. For example, to achieve maximum adhesion, one would make a coating at the lower R and the higher T regime.

All the single layers maintained the high transmittance of the bulk material. We did not observe any major differences in optical absorption as the single layers of AF2400 were deposited within the parameter space defined by T , R and glow discharge bias.

Fig. 2. Adhesion was enhanced at high substrate temperatures. Surface contour lines showing the fraction, in (%), of remaining Teflon AF2400 coating on a Si wafer after a scotch-tape test. The best adhesion was observed on coatings deposited at a low rate and high substrate temperature. Glow discharge was observed to have an insignificant effect on adhesion.

Fig. 3. The refractive index can be intentionally varied. The refractive index (at 633 nm) of the Teflon AF2400 was easily controlled by the substrate temperature and the deposition rate. The glow discharge and temperature-rate interaction terms were determined to be insignificant contributors to the refractive index of these AF2400 single layers.

3.2 Optical coatings

The transmittance scans of the AR and HR are shown in Figures 4a and b, respectively. The AR was designed for 1.053- μm and made at near-optimal deposition parameters of substrate temperature =

200°C and deposition rate = 3.5 Å/s. The HR was designed for 1.053 μm. The substrate temperature started at room temperature and was 90°C by the end of the run; the deposition rates were 5 Å/s for both AF2400 and ZnS. The HR design was Substrate/ (ZnS AF2400)⁴ ZnS / Air, where quarter-wave optical thicknesses were used for all layers. Attempts to make HRs of AF2400 with either hafnia or silica ended prematurely due to crazing in the coating (see Figure 5a and b).

Fig. 4a. Typical high transmittance of Teflon AF2400 coating. The solid line in the middle was the 1.053 μm anti-reflective coating deposited onto a single surface of a fused silica substrate. The top scan was the 100% transmittance line, performed without a sample in the optical spectrophotometer beam path. The dashed scan was the transmittance of the uncoated substrate.

Fig. 4b ZnS with AF2400 in an HR. The top trace was the baseline performance of the spectrophotometer without a sample. The phantom trace was an HR design of BK-7 / (ZnS AF2400)⁴ ZnS / Air, where the refractive index of ZnS and AF2400 were 2.1 and 1.3, respectively. The solid trace is the transmittance of the real ZnS/AF2400 HR; it had a 99% reflectance and a bandwidth of 550 nm.

3.2. Laser damage thresholds

A perfect AR coating has a refractive index equal to the square root of the substrate's refractive index. According to Figs. 2 and 3, there were two acceptable process conditions for making an AR coating on fused silica substrate ($n = 1.45$), where the AR coating should have $n \approx 1.2$. One was at a high T and a low R, where the adhesion was optimal. The other process condition was at a low T and high R, where the adhesion was not as favorable. Coatings transmitting at 1064 nm were made at both process conditions and tested for laser damage at 1064 nm and 352 nm by a high peak power laser damage system.

Both AR coatings had high laser-damage thresholds at 1064 nm and 352 nm. Table II compares the maximum damage thresholds of AR coatings made in this study by PVD of oxides onto fused silica and BK-7 substrates. The 1064-nm laser damage thresholds of the AR coating by PVD of AF2400 were the highest ever recorded when compared to PVD of the oxides tested. The upper limit of the laser damage thresholds for the AR coating deposited for the optimal adhesion was above the capacity of the LLNL laser damage facility. Table II shows that the 352-nm thresholds were still high compared to ARs made by PVD of oxides although our ARs were not designed to operate at 352 nm. The 352-nm damage threshold should increase on an actual 352-nm AR since a thinner (therefore lower absorption) coating is required.

Table II. Maximum damage thresholds of PVD anti-reflective coatings. The damage threshold of AF2400 anti-reflective coatings deposited under the optimal and sub-optimal conditions are compared to the maximum thresholds obtained with oxides, the conventional coating material, deposited under their optimal conditions. The laser pulsewidth was 3 ns. *The data for this entry was obtained from the LLNL laser damage data base, which included coatings made from various vendors.

Coating Material	Coating conditions	Damage Thresholds (J/cm ²)	
		1064 nm	352 nm
AF2400	optimal	>47.4	9.6
AF2400	sub-optimal	28.9	8.2
Oxides *	optimal	30	9

The ZnS/AF2400 HR had 1.06- μ m damage thresholds of < 2.8 J/cm². The absorption from 4 layers of ZnS was comparable to 10 layers of hafnia.¹⁰ The defect density was $\approx 1/\mu\text{m}^2$ for defects > 5 μ m in length. The defect generation from the evaporation of AF2400 was well controlled, as indicated by the high AR damage thresholds. However, we could not prevent the ZnS from spitting during the e-gun evaporation. The high defect density may be the reason for the low damage thresholds.

4. DISCUSSION

4.2. Refractive index variation

^{19}F nuclear magnetic resonance (NMR) spectroscopy of material dissolved in hexafluorobenzene showed that the composition of the coating was identical to that of the bulk material (Fig. 5). The coating and bulk material were soluble in hexafluorobenzene to less than 1 wt. %. This low solubility required a solvent suppression NMR pulse sequence to reduce the solvent NMR peak intensity in order to detect the coating material. The AF2400 ^{19}F NMR spectrum consisted of two main regions: a doublet due to CF_3 groups with peak positions at -78.61 and -78.23 ppm, and a multi-component region due to CF_2 and CF groups which extends from -107.5 to -125 ppm. (The chemical shift reference was the solvent, C_6F_6 , -162.9 ppm, with CFCl_3 as 0.0 ppm). A minor region due to differences in the CF_2/CF sequence spanned the region -95 to -107.5 ppm. The analysis consisted in comparing area ratios for the peaks at -78 to -79 ppm and -107.5 to -125 ppm. Since no significant compositional differences were observed between the bulk and coatings, the changes in n probably did not arise from composition differences between the AF2400 coating.

Fig. 5. Unchanged composition between the coated and the bulk AF2400 material. Liquid nuclear magnetic resonance scans of the evaporated and bulk AF2400 dissolved in hexafluorobenzene showed identical resonances and peak ratios at -78 to -79 ppm and -107.5 to -125 ppm.

Scanning electron microscopy showed a microstructure variation in the AF2400 coatings. Four coatings, deposited at the extreme process conditions of T and R, are pictured in Fig. 6. Coatings deposited at 20°C were columnar and at the higher R, the columns and the voids were larger. Coatings deposited at 200°C were planarized but still had voids. At the higher T, the lower R produced more voids in contrast to the coating at higher R. Assuming the voids were filled with air (an $n = 1.0$), the porosity changes were the most likely reason for the n variations.

Fig. 6. Microstructure variation of Teflon AF2400 coatings. A columnar structure is obtained at the low substrate temperature, with larger columns and voids at the high deposition rate. The microstructure planarized when deposited at the higher substrate temperature, but voids are still apparent. The scale bar in the lower left hand corner is 328 nm.

4.2. Adhesion

The optimal adhesion occurred when the coating was deposited at the highest T and the lowest R. An explanation for the increased adhesion may be that the high T increased the surface mobility of the molecules, allowing them to move into strong inter-molecular bonding configurations; and the low R allowed adequate time for the molecules to diffuse into these positions before another incoming effluent molecule arrived at the surface and buried the underlying molecule in a non-optimal bonding configuration.

4.3. Multilayer compatibility

We found that neither a oxide stressed in tension, hafnia, or in compression, silica, were compatible materials for AF2400. The hafnia/AF2400 multilayer crazed after only 4 layers. A 19-layer reflector of silica/AF2400 came out of the vacuum system in tact but crazed after a couple days of atmospheric exposure. A possible driving force for crazing was the stress buildup from source heating. AF2400/oxide multilayers are susceptible to thermal induced stresses because of a large thermal expansion coefficient mismatch. AF2400 has a thermal expansion coefficient of 80 ppm/°K, 30x higher than that of a typical oxide.^{10,11} Also, the thermal mismatch may be aggravated because AF2400 is an organic polymer, and absorbs more infrared radiation than that of oxide layers.

An indirect proof that source heating initiated the failure mechanism was to compare the HR made of ZnS/AF2400, where ZnS was either evaporated resistively from a heated baffled boat or an electron-gun. The power required to operate the boat was over twice that required by the electron gun to evaporate ZnS, 95 W vs. 46 W. The multilayer using the resistively heated boat failed, we believe, to the thermal diffusion of the AF2400 and mixing into the ZnS layers as shown in Figure 7. The diameter of the "tube" features appeared to be on the order of 1.5 μm , and intertwined among each other to about 2 diameter

lengths. The multilayer was probably destroyed from the large amounts of mass transfer required to form these tubes. In contrast, no definitive structure could be resolved on the surface of the HR made with e-beam evaporated ZnS. An SEM cross-section in Figure 8 of this HR showed that the multilayer integrity was maintained using a source with a lower heat load.

Fig. 7. Alloying of the AF2400 and ZnS at high temperatures. This is an SEM picture of the top a ZnS/AF2400 multilayer. The large surface area of the boat containing ZnS may have heated the AF2400 layers in the coating past the softening temperature. The $3.0\text{ }\mu\text{m}$ scale bar is in the lower right hand corner.

Fig. 8. Multilayer integrity of a ZnS/AF2400 HR. The ZnS layers had the columnar structure. The AF2400 layers had the large pores. A ZnS layer is 123.7 nm and a AF2400 layer is 204.6 nm thick.

5. CONCLUSIONS

A physical vapor deposited perfluorinated amorphous polymer, Teflon AF2400, was used as an optical coating material for a laser-resistant AR coating and a wide band-width HR. The AR was a simple quarter-wave optically thick layer where the refractive index was could be intentionally varied to values between 1.31 to 1.16. The variation of the refractive index appeared to be related to the coating porosity as the rate or substrate temperature changed. The coatings maintained the high transmittance property of the bulk materials from 200 nm to 1200 nm . The HR was made with ZnS as the high refractive index

material. Observations indicate that the AF2400 compatibility with other dielectrics was limited by thermal loading of the AF2400 multilayer from the deposition sources.

6. AUSPICES AND REFERENCES

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