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CHARACTERIZATION OF PHYSICALLY VAPOR DEPOSITED AF2400 THIN FILMS

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ABSTRACT

Anti-reflective coatings made with Teflon AF2400 had the highest damage thresholds recorded for physical vapor deposited coatings at the Lawrence Livermore National Laboratory damage facility. Physical vapor deposited layers of Teflon AF2400, a perfluorinated amorphous polymer, maintained the bulk optical properties of a high transmittance from 200 nm to 1600 nm, and a low refractive index. In addition, the refractive index can be intentionally reduced by control of two common deposition parameters, deposition rate and 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. The coatings adhered to fused silica and silicon wafers under normal laboratory handling conditions.

INTRODUCTION

Teflon AF2400 is an attractive candidate for a high performance optical coating. 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 can be deposited by spinning onto or dipping substrates in solutions of AF2400 dissolved in an expensive fluorinated solvent.[1,2,3] Recent work on this material has shown that this material can be thermally evaporated[4,5] to make corrosion barriers for extra-terrestrial equipment[6] and as a possible insulator for submicron electronic devices.[7] If the viability of PVD AF2400 optical coatings can be demonstrated, the material should find easy acceptance in the optical coatings community. Also, anti-reflective coatings produced by the solution process had the highest damage thresholds ever recorded at 1.06 µm. If the physical vapor deposition (PVD) process does not increase the absorption of the material during evaporation, the resulting coatings should also retain the low absorption required for high laser damage thresholds.

EXPERIMENTAL SET-UP

Resistance heating was used to evaporate the Teflon AF2400 layers in a stainless steel vacuum chamber. The pump stack consisted of a diffusion pump, a liquid N_2 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 O_2 to 5 microns for a glow discharge cleaning. The discharge bias was applied between the Al ring and the substrate platen for five minutes. Figure 1 shows the chemical constituents of AF2400.

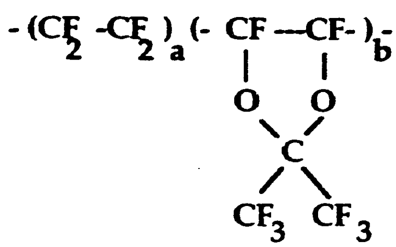

Fig. 1. Chemical make-up of Teflon AF2400. Teflon AF2400 is a co-polymer of tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole. The approximate ratio of a:b is 1:4.

A Box-Behnkem experimental strategy[8] was used to examine the relationship between the evaporation parameters and the material properties. Three process variables were used in a 13-run matrix (see Table I). Single layer samples of ≈ 1500Å were made under each process condition. The 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 specific process parameters to obtain an estimate of the error of the coating properties.

Table I: Process conditions for the minimum number of runs. Thirteen process conditions were established and samples generated in a randomized order. The process conditions were established as the extreme/mid-points of the process range.

Substrate Temperature (°C)	Deposition Rate (Å/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 n, transmittance, 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. Scotch tape with a 12.6 gr/mm tension (Scotch Magic tape) was applied firmly to the coatings, and then pulled off with the free end perpendicular to the surface. The laser damage resistance of the anti-reflective (AR) coatings deposited onto superpolished fused silica substrates was obtained at the LLNL damage facility. A laser conditioning procedure was used to increase the damage thresholds of these coatings.[9]

RESULTS

The coatings adhered to fused silica substrates and Si wafers under normal laboratory conditions but can be easily removed. 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 the deposition rate, R (Å/s), and substrate temperature, T (°C). 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 degree of fit was 96%, and there was a 95% confidence level that the long term adhesion average was within ± 6 %.

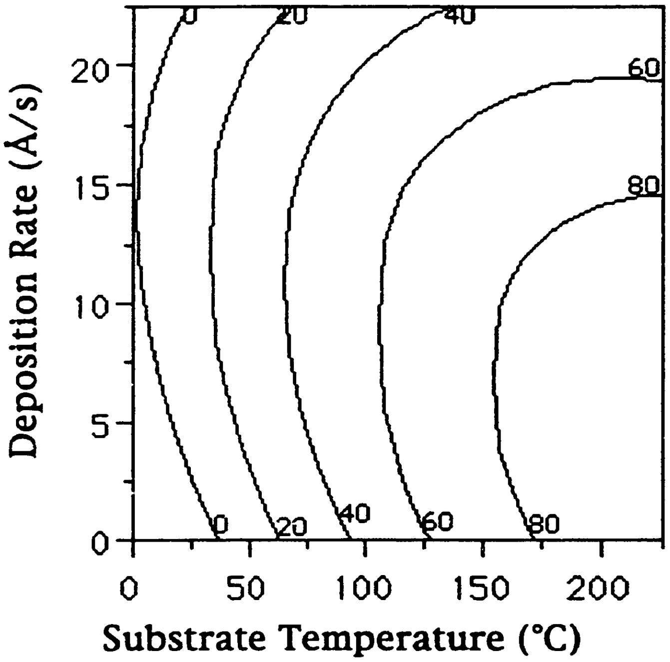

Fig. 2. Adhesion was enhanced at high substrate temperatures. Surface contour lines showing the amount of remaining Teflon AF2400 coating on a Si wafer after a scotch-tape test. The best adhesion was observed on coatings deposited at a low rate and high substrate temperature. Glow discharge was observed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

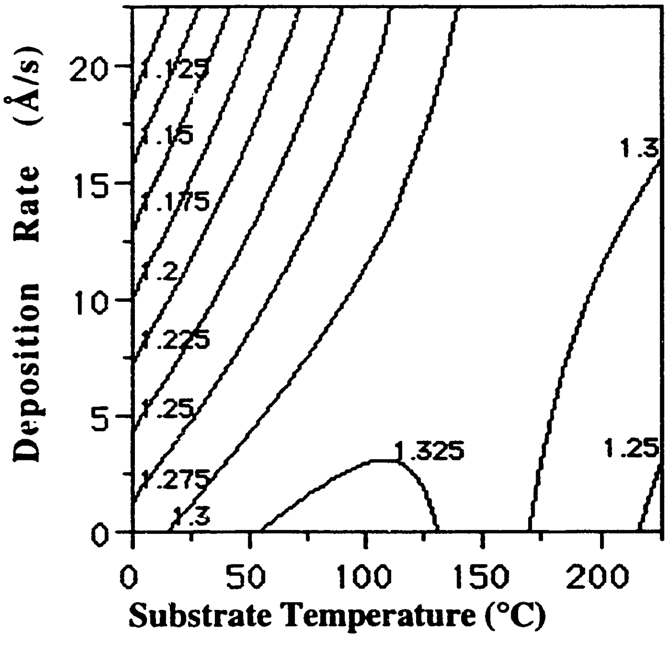

Fig. 3. The refractive index can be intentionally varied. The refractive index of the Teflon AF2400 was easily controlled by the substrate temperature and the deposition rate. The glow discharge and temperature-rate interaction terms were determined to be insignificant contributors to the refractive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

The AF2400 coatings have an n that can be modified intentionally via the T and/or R. Normalized linear regression analysis revealed that the glow discharge, and the cross-term R*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 degree of fit was 96.2%, and there was a 95% confidence level that the long term average of the n was within ±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 acheive 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.

DISCUSSION

^{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 radical 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.

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 had a columnar structure. 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 have voids. At the higher T, the lower R produced more voids in contrast to the coating at higher R. Assuming the voids to be filled with air, with an n = 1.0, the porosity changes were the most likely reason for the n variations.

X-ray diffraction of the bulk AF2400 material showed two broad peaks at 20° and 40° 2-Θ. However, no diffraction peaks from the coatings were observed to indicate any crystalline structure. The layers may have been too thin and the elemental composition too light to yield an adequate signal.

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 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.

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 ≈ 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 absorption 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 and conventionally, by PVD of oxides onto fused silica and BK-7 substrates. The laser damage thresholds of the AR coating by PVD AF2400 were the highest ever recorded for PVD of any oxides. The upper limit of the laser damage thresholds for the AR coating deposited for the optimal adhesion was above the capacity of the LLNL damage facility. Table II shows that the 355-nm thresholds were still high compared to ARs made by PVD of oxides even though our ARs were not designed to operate at 352 nm. The damage threshold measurements at the two wavelengths indicated the low absorption of these PVD coatings.

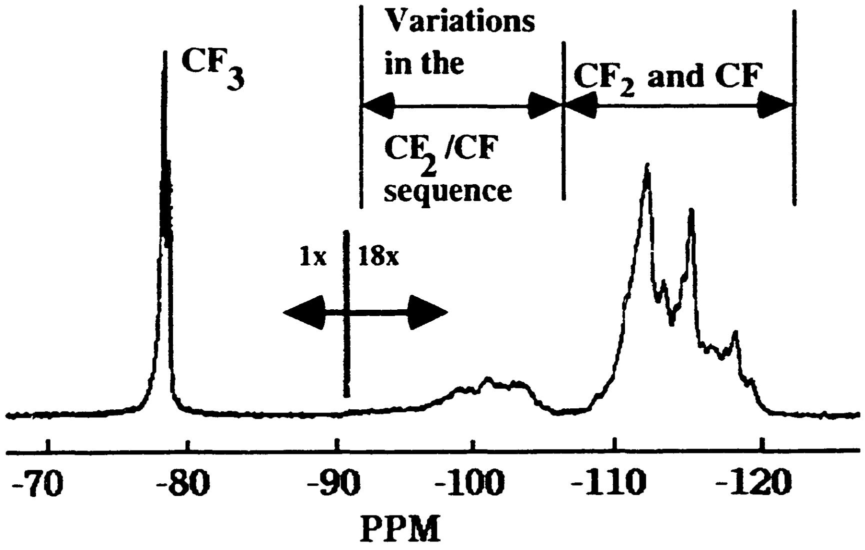

Fig. 5. Unchanged composition between the coated and the bulk AF2400 material. Liquid nuclear magnetic resonance scans of the evaporated and bulk AF2400 dissolved in hexafluorobenzene showed identical resonances and peak ratios at -78 to -79 ppm and -107.5 to -125 ppm.

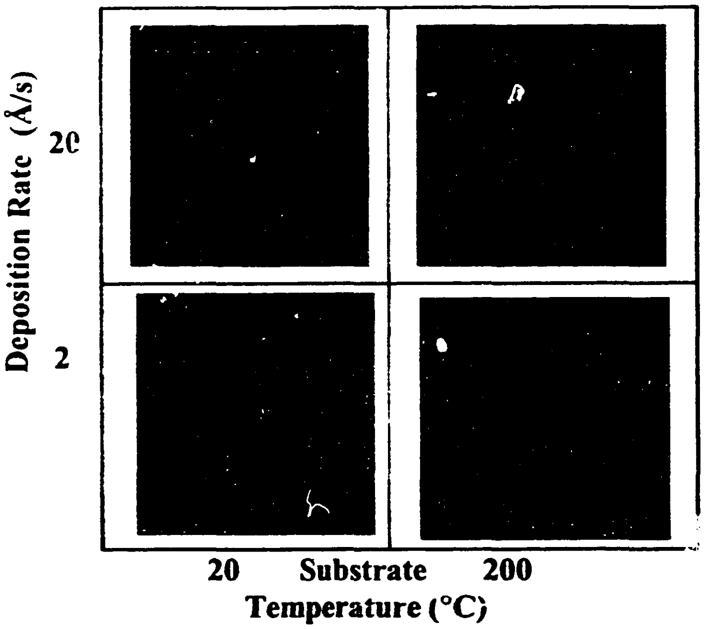

Fig. 6. Microstructure variation of Teflon AF2400 coatings. A columnar structure is obtained at the low substrate temperature, with larger columns and voids at the high deposition rate. The microstructure planarized when deposited at the higher substrate temperature, but voids are still apparent. Scale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

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.

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

CONCLUSIONS

A physical vapor deposited perfluorinated amorphous polymer, Teflon AF2400, was used as an optical coating material for high performance ARs. The refractive index was low and also could be intentionally varied to values as low as 1.16. The variation of the refractive index appeared to be related to the void density in the coating as the rate or the substrate temperature changed. There was no indication that the composition or the crystallinity of the coating changed during the deposition process. The coatings maintained the high transmittance property of the bulk materials from 200 nm to 1600 nm. The coatings had low absorption as indicated by the high damage thresholds of AR coatings tested at 1064 nm and 352 nm.

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