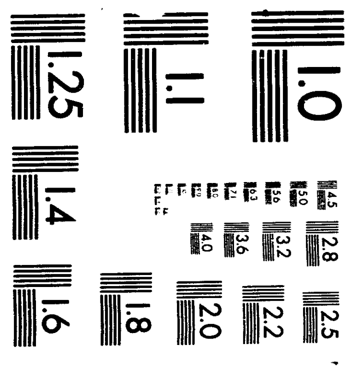

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High Damage Threshold Anti-Reflectors by Physical Vapor Deposited Amorphous Fluoropolymer

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High damage threshold anti-reflectors by physical vapor deposited amorphous fluoropolymer

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ABSTRACT

High laser-resistant anti-reflective coatings were made from an amorphous fluoropolymer (Teflon AF2400) material by physical vapor deposition.

Single layers of Teflon AF2400 were thermally deposited in a vacuum chamber. The refractive index and adhesion of the coatings were determined as a function of deposition rate (2 to 20 Å/s), substrate temperature (20 to 200°C), and glow-discharge bias potential (-1500 to 1500 V).

An anti-reflective coating of an amorphous fluoropolymer (Teflon AF2400) had a laser resistance of > 47 J/cm^2 (1.06 μm, 3-ns pulselength) and is transparent from 200 nm to 1600 nm. The majority of the coatings had a 1.30 refractive index, similar to that of the bulk material. Scanning electron microscopy and preliminary 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. Scotch tape with 12.6 gr/mm tension was sufficient to pull off every coating from fused silica substrates.

1. INTRODUCTION

There is a very small selection of coating materials available for high-performance optical multilayered coatings. The coating materials used for the ultra-violet through the near infrared regime are typically fluorides or oxides. Fluoride coatings have wide spectral transmission bands but are mechanically weak. On the other hand, oxide coatings are mechanically and environmentally rugged but absorb more in the ultra-violet. Another important consideration is that a material has either a very high or very low refractive index. High and low refractive index compounds are alternately layered together to make passive devices such as high and anti-reflectors, spectral filters, and polarizers. Increasing the refractive index difference between materials used in a multilayer decreases the number of layers required for a given optical performance, and increases the spectral bandwidth. We studied the suitability of an unconventional material, a polymer, as a high-performance anti-reflector.

The unconventional coating material belongs to a class of perfluorinated amorphous polymers (PAP). These PAPs are co-polymers consisting of one or more of the following monomers: tetrafluoroethylene (generically known as Teflon), 2,2-bistrifluoromethyl-4,5-difluoro-1,3-

dioxole, perfluoroallyl vinyl ether, and perfluorobutenyl vinyl ether. We limited our study on the PAP manufactured by DuPont under the trade name Teflon AF2400.

The polymer, Teflon AF2400, is an attractive candidate for an anti-reflective coating. The bulk properties of this particular PAP show a high transmittance range from 200 nm to 1600 nm and a low refractive index. In fact, the bulk refractive index of AF2400 is 1.29, lower than any fluoride or oxide compound currently used. Recent work on this material has shown that this material can be thermally evaporated[1] to make corrosion barriers for extra-terrestrial equipment[2] and as a possible insulator for submicron electronic devices.[3] Single layer optical coatings can also be deposited by spinning-on AF2400 dissolved in an expensive fluorinated solvent.[4,5] Another motivation for examining this material was the preliminary work at Lawrence Livermore National Laboratory (LLNL) with solution deposited AF2400. Anti-reflective (AR) coatings produced by this deposition method had the highest laser damage thresholds ever recorded at 1.06 μm. If the physical vapor deposition 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.

A major reason for determining the viability of physical vapor deposited (PVD) PAP coatings is that the PVD process is established throughout the optical coatings industry. If these coatings deposited by PVD have attractive optical properties, the material should find relative easy acceptance in this economic arena.

2. EXPERIMENTAL SET-UP

Teflon AF2400 is a co-polymer of tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole. The chemical make-up of AF2400 is given in Figure 1.

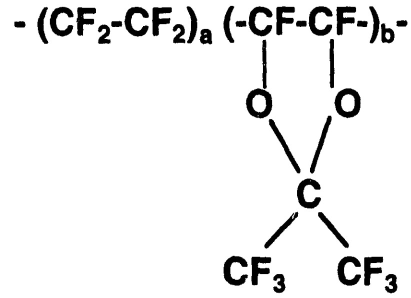

Fig. 1. Chemical make-up of Teflon AF2400. Teflon AF2400 is a co-polymer of tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole. The approximate ratio of b:a is 4:1.

Teflon AF has been thermally evaporated in other studies.[1,2,6] We used a simple resistance heater in a stainless steel bell jar. The chamber was diffusion pumped, had a liquid nitrogen trap between the high-vacuum valve and the pump, and the diffusion pump was backed by a mechanical pump. The single layers of ≈ 1500 Å thick were evaporated with a resistance-heated (0.1" diameter) W filament inserted into an open-mouth quartz crucible. Our initial use of a porcelain-glazed alumina crucible produced highly absorbing coatings. There may have been some chemical leeching of the glaze constituents by the PAP which subsequently evaporated onto the coating. The PAP in the quartz crucible never turned black as it did in the glazed crucible. All crucibles and filaments were cleaned by outgassing at temperatures higher than the evaporation temperature prior to the initial evaporation. The throw distance between the crucible and the platen was 14".

The substrates were heated with quartz-halogen lamps, monitored with a Type J thermocouple, and regulated manually with a 120 VAC variable transformer. The lamps were turned off during a glow discharge operation.

A glow-discharge plasma was made between an Al ring and the substrate platen. Oxygen was injected into the chamber to a pressure of 0.66 Pa (5 μm of Hg), and then the bias applied to the Al ring, generating the plasma. The bias was applied for five minutes.

A Box-Behnkem experimental strategy[7] 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 1). A quadratic interpolation was obtained between the response of the coating to the process variables. The model also included synergistic combinations (cross terms) between two process variables as well as the effects of the square of each process variable. The deposition rates were set at 2, 11, and 20 Å/s. The substrate temperatures were set at 20, 110, and 200°C. The substrate platen was biased at -1500, zero or +1500 V in a pre-coating glow discharge procedure. Replicates were also made at specific process parameters to obtain an estimate of the error of the coating properties.

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

Table 1: Process conditions for the minimum number of runs. Thirteen process conditions were established and samples generated in random order. The process conditions were established as the extreme/mid-points of the process range.

The adhesion, refractive index, and transmittance were the responses of interest. The transmittances (200 nm to 1200 nm) were measured on coated fused silica substrates using a Cary spectrophotometer. The refractive index (at 632.8 nm) and thickness were determined on coated Si wafers using a Rudolf Research AutoEl II-NIR-3 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-reflectors deposited onto superpolished fused silica substrates was obtained at the LLNL Damage facility.[8]

A laser conditioning procedure was used to increase the damage thresholds of these coatings. The procedure consisted of starting the laser damage test at a sub-damage fluence level, ramping up the laser fluence over a series of 400 shots at a given site, and sustaining the final fluence level for another 200 shots. The test site was exposed to the laser beam for one minute. If the test site did not damage, another site was selected for testing to a higher fluence level. The damage threshold was the average of the maximum laser fluence which did not cause damage and the minimum laser fluence which did cause damage. Damage was defined as any morphological change of the coating as observed with an optical microscope.

3. RESULTS

3.1. Adhesion

The coatings adhered to fused silica substrates and Si wafers under normal laboratory conditions but can be rubbed off these substrates. There appeared to be a stronger correlation between adhesion and the substrate temperature than to the glow discharge bias. The runs made at varying glow discharge values were folded into a two-variable regression analysis of adhesion to the deposition rate and substrate temperature. Figure 1 gives the surface contour lines of Teflon AF2400 adhesion on Si wafers as a function of substrate temperature and deposition rate. The adhesion (see Fig. 2) was defined as the amount of coating remaining on the substrate after a scotch-tape test. Adhesion increased with substrate temperature, and at high temperatures the adhesion decreased with deposition rate. Numerically, the adhesion, A (%), left on the substrate after the scotch-tape adhesion test was

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

where T is the substrate temperature in °C and R is the deposition rate as indicated by the quartz crystal monitor in Å/s. The degree of fit was 96%, and there was a 95% confidence level that the adhesion value was within ± 6 %.

3.2. Refractive Index

The Teflon AF2400 coatings have refractive indices that can be intentionally modified by the substrate temperature and/or the deposition rate. Normalized linear regression analysis revealed that the glow discharge, and the interaction between the temperature and rate terms had no significant effect on the refractive index. As in above, the responses from the glow discharge runs were folded into the final linear regression analysis between the refractive index and the process variables, substrate temperature and deposition rate. The surface contours of the refractive index are given as a function of deposition rate and substrate temperature in Fig. 3. For this series of coatings, the refractive index, N, depended on temperature and rate as

$$N = 1.23 - 5.5 \times 10^{-3} R + 1.5 \times 10^{-3} T + 3.2 \times 10^{5} RT + 2.1 \times 10^{-5} R^2 - 6 \times 10^{-6} T^2. \qquad \text{eqn. [2]}$$

The degree of fit of the Eqn. [2] was 96.2%, and there was a 95% confidence level that the refractive index was within ±0.034.

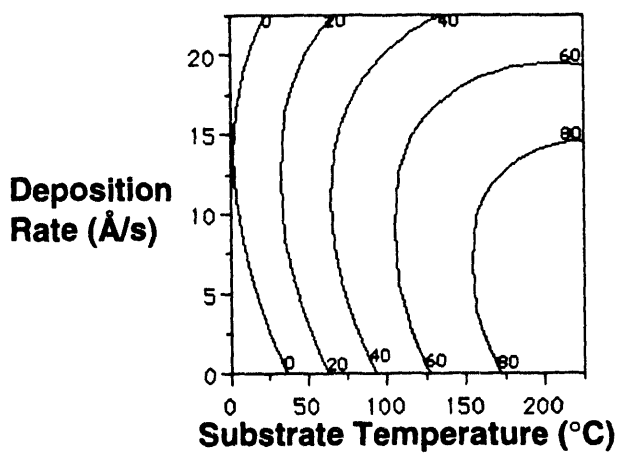

Fig. 2. Adhesion enhanced at higher substrate temperatures. Surface contour lines showed the remaining Teflon AF2400 coating on a Si wafer after a scotch-tape test. The best adhesion was observed on coatings deposited at a low rate and high substrate temperature. Glow discharge was observed to have an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

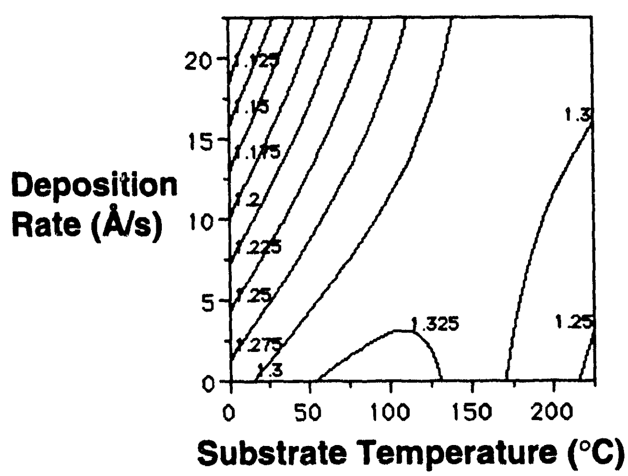

Fig. 3. Intentionally varied refractive index. The refractive index of the Teflon AF2400 was easily controlled by the substrate temperature and the deposition rate. The glow discharge, and temperature-rate interaction terms were determined to be insignificant contributors to the refractive index of these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

All the single layers maintained the high transmittance and low absorption of the bulk material. We could not observe any major differences in transmittance as the single layers of AF2400 was deposited within the parameter space defined by substrate temperature, deposition rate, and glow discharge. Figure 4 is a scan of the 1.064-µm anti-reflective AF2400 coating made at the optimal deposition parameters, a substrate temperature of 200°C and a deposition rate of 3.5 Å/s.

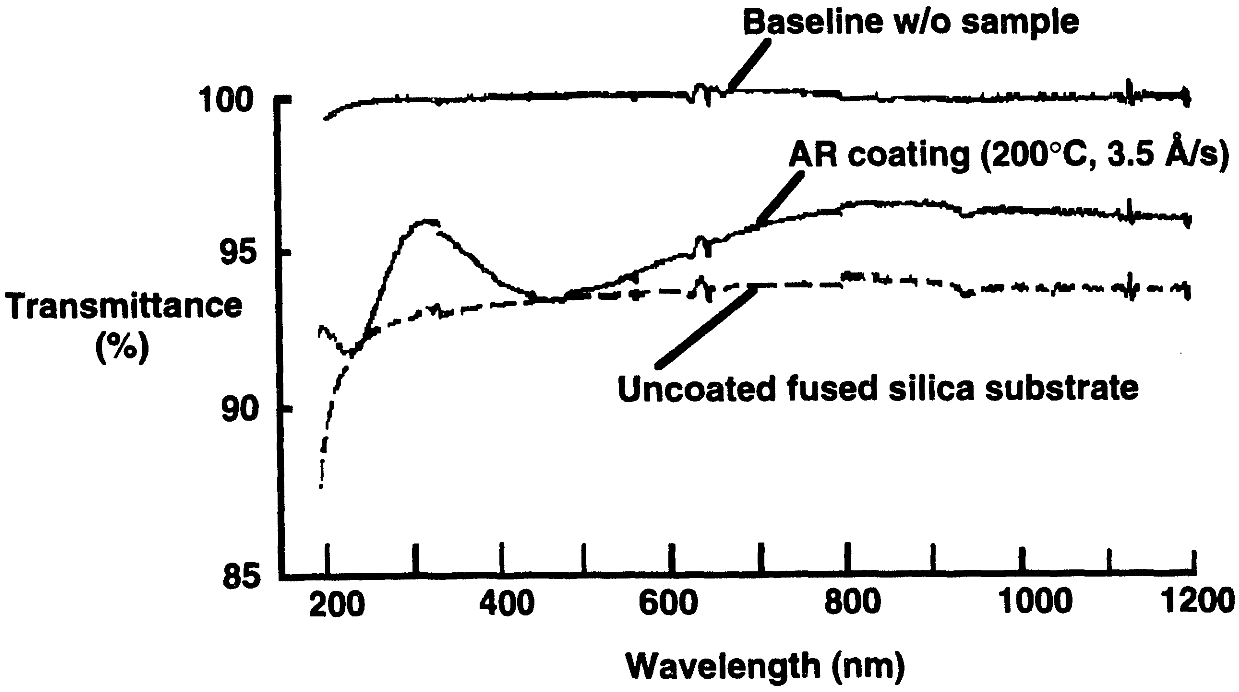

Fig. 4. Typical high transmittance of Teflon AF2400 coating. The solid line in the middle was the 1.064 µm anti-reflective coating deposited onto a single surface of a fused silica substrate. The top scan was the 100% transmittance line, performed without a sample in the optical spectrophotometer beam path. The dashed scan was the transmittance of the uncoated substrate.

The adhesion and refractive index variations as a function of substrate temperature and deposition rate, eqns. [1] and [2], respectively, were specific to the coating chamber set-up in which the samples were generated. However, the general trends shown by Figs. 2 and 3 provide insight into where the most appropriate coatings may be made. In the case of maximum adhesion, one would coat at the lower deposition rates and the higher substrate temperatures.

4. DISCUSSION

We considered that the variation in refractive index could be caused by changes in the coating composition, density and/or phase.

The composition of the coating was identical to that of the as-received material comparing nuclear magnetic resonance scans (Fig. 5). The coating and the as-received Teflon material was dissolved in hexafluorobenzene to less than 1 wt. %. Commercial preparations of hexafluorobenzene contain ^{19}F impurities at or about the same level as the solubility of AF2400, but none exhibit resonances at -78 to -79 ppm where the CF_3 group of AF2400 appeared. Actually, two CF_3 resonances are apparent in this region, one at -78.61 and the other at -78.23 with relative peak heights of 1.54. No peaks were discernible for the AF2400 CF_2 and CF backbone groups. This was not unexpected, as the rigid polymer structure (see Fig. 1) causes these peaks to be overly broad and lost in the noisy baseline, whereas free rotation of the CF_3 groups yielded fairly narrow lines. Thus the diagnostic region for AF2400 in hexafluorobenzene is at -78 to -79 ppm with respect to the single hexafluorobenzene solvent peak.

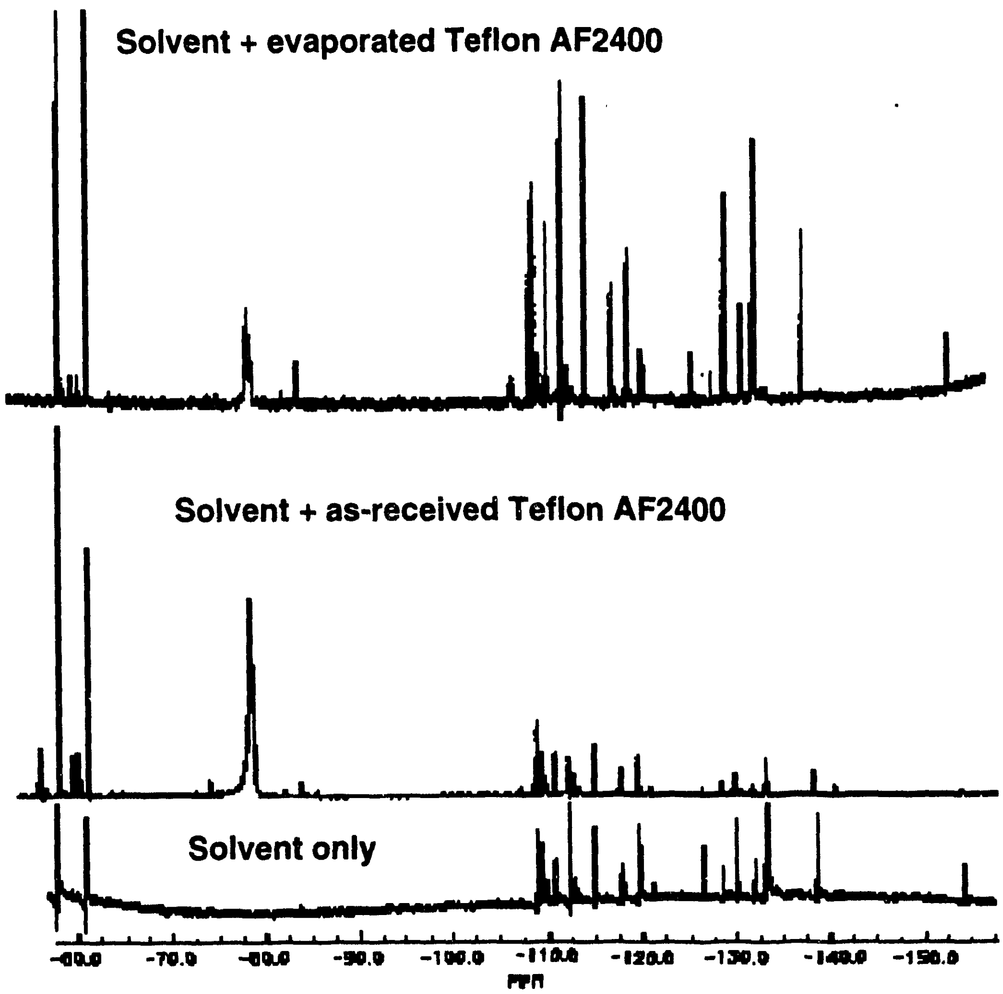

Fig. 5. Equivalent composition environment between the coated and the as-received material. Nuclear magnetic resonance scans of the evaporated and as-received Teflon dissolved in hexafluorobenzene (liquid) showed identical resonances and peak ratios for the CF_3 group in AF2400.

There appeared to be a density variation in the AF2400 coatings as observed by scanning electron microscopy. Four coatings, deposited at the extreme process conditions of temperature and rate, are shown in Fig. 6. Coatings deposited at 20°C had a columnar structure. At the high deposition rates, the columns and the voids between them were larger. Coatings deposited at 200°C appear planarized over the substrate yet still have voids. But in this high temperature case, the lower deposition rates appear to have more void volume than the coating at high rate. Assuming the voids to be filled with air, with a refractive index of 1.0, the observed density change is the most likely reason for the change in refractive index.

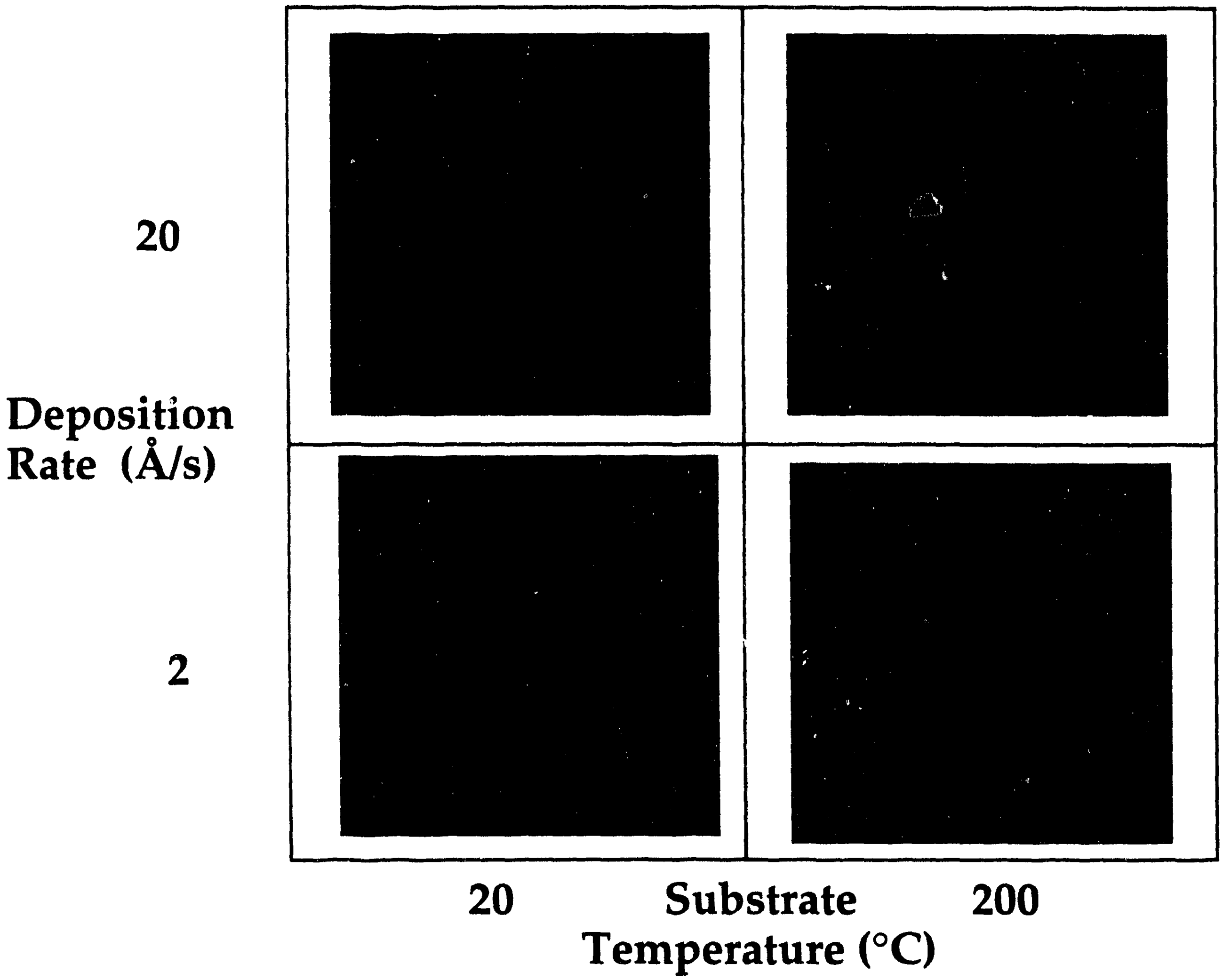

Fig. 6. Microstructure variation of Teflon AF2400 coatings. A columnar structure is obtained at the low substrate temperature, with larger columns and voids at the high deposition rate. The microstructure planarized when deposited at the higher substrate temperature, but voids are still apparent.

X-ray diffraction of the as-received AF2400 material showed two broad peaks at 20 and 40 degrees 2-Θ. However, no broad or narrow diffraction peaks from the coatings were observed, probably because the layers were 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 substrate temperature and the lowest deposition rate. An explanation for the increased adhesion may be that the high substrate temperature increases the surface mobility of the molecules to move into strong inter-molecular bonding configurations; the low rate allows adequate time for the molecules to diffuse into these positions before another incoming effluent molecule arrives onto the coating surface and buries the underlying molecule in a non-optimal bonding configuration.

5. APPLICATIONS

There was sufficient information from Figs. 2 and 3 to make an anti-reflector for laser damage threshold testing. A perfect AR coating has a refractive index equal to the square root of the substrate's refractive index. If the substrate is fused silica with a 1.45 refractive index, the anti-reflective coating should have a refractive index as close as possible to 1.2 (the square root of 1.45). There were two process conditions that fulfilled the refractive index criteria. One was at a high substrate temperature and a low deposition rate, where the coating was most robust mechanically. The other process condition was at a low substrate temperature and high deposition rate, where the adhesion was not as favorable. An AR coating for 1.064 µm was made at both process conditions. Figure 4 is a transmittance scan of a single surface AR coated fused silica substrate. This AR coating was deposited using the optimal process condition for adhesion.

Both AR coatings had high conditioned laser damage thresholds at 1.06 µm. Figure 7 shows the range of AR damage thresholds made from: (i) the two AR coatings made from this study, physical vapor deposited AF2400, (ii) AR coatings made from solution deposited AF2400, and (iii) a conventional process and materials, the PVD of oxides. These coatings were amenable to laser conditioning. The conditioned laser damage thresholds of the AR coating by PVD AF2400 were the highest ever recorded for PVD of any oxides (Fig. 7a). 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. The thresholds were on the same order as the AR coatings made by solution deposited AF2400. Damage thresholds at 355 nm were also made on these anti-reflector coatings although they did not transmit well at 355 nm. Figure 7b shows that the 355-nm thresholds were still high compared to ARs made by PVD of oxides. These two damage threshold measurements complement the fact that these coatings were still transparent and low absorbing, like the as-received material.

Other applications of single layer coatings might be to fabricate a graded AR coating which has a high refractive index at the substrate and grades down to a low refractive index at the coating/air interface. This is easily accomplished by coating at room temperature and increasing the deposition rate to the maximum possible.

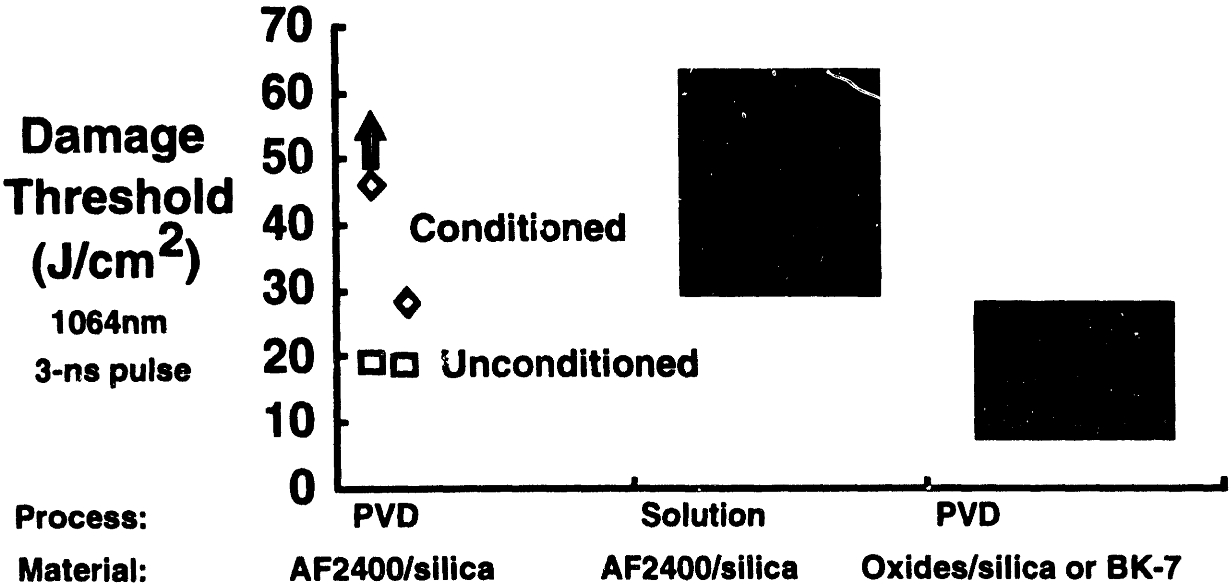

Fig. 7a. High laser damage thresholds at 1.06 µm. The damage thresholds were compared to the threshold ranges of other AR coatings made by solution dipped AF2400 and PVD of conventional oxides. The arrow means that the AR coating has a laser damage threshold greater than the 47 J/cm² value.

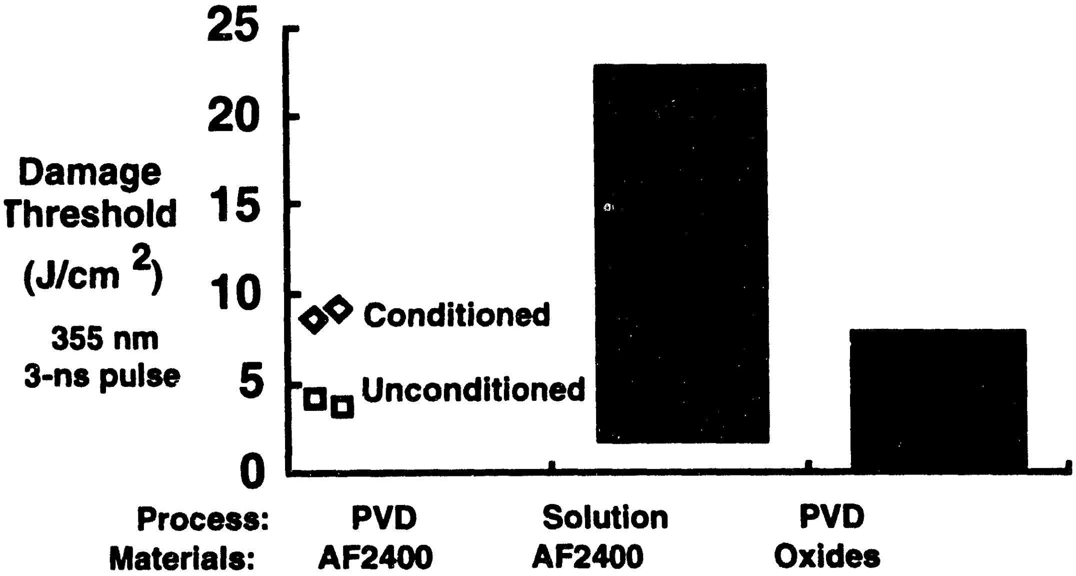

Fig. 7b. High laser damage thresholds at 355 nm. The damage thresholds were relatively high since these were the AR coatings made for operation at 1.064 µm but damage tested at 355 nm.

6. CONCLUSIONS

A physical vapor deposited perfluorinated amorphous polymer, Teflon AF2400, was used as an optical coating material for high performance anti-reflectors. 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 deposition rate or the substrate temperature changed. There was no indication that the composition or the crystallinity of the PVD PAP changed during the coating process. The coatings maintained the high transmittance property of the bulk materials from 200 nm to 1600 nm.

7. AUSPICES

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