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ABSTRACT

A new commercially available perfluorinated organic polymer has been used to prepare a combined quarterwave AR and protective coating for KDP and other optical materials. Coatings are applied from solution at room temperature by spin or dip, they are fully dense and have a refractive index of 1.29. The laser damage threshold at 1064 nm and 355 nm is the highest that we have ever measured for an AR coating material.

1. INTRODUCTION

The Nova Nd^{3+}:glass laser at LLNL has been in operation for over six years. During this time a porous silica antireflective (AR) coating has been used on the 1054-, 532- and 351- nm transmissive optical components in the high fluence areas of the beams.[1] This coating was chosen because of its very high laser damage threshold at multiple wavelengths and excellent optical performance. It has a refractive index of approximately 1.22 and thus is an ideal single-layer AR for common substrates with an index near 1.5. Other advantages include ease of preparation and ease of application.

Over the years of operation in the Nova laser, the porous silica AR performance has in general, been highly satisfactory. Only minor problems have arisen and these have usually been due to the high surface area associated with the porous nature of the coating. In a "dirty" high vaccum environment, such as the Nova target chamber, the coating can absorb undesirable contaminants. This can lead to a degradation in performance if these contaminants are not removed by washing at intervals of several weeks (after about fifty shots). This has not been necessary in clean vacuum or atmospheric pressure environments. There is no easy solution to this problem because it is the porosity of the coating that lowers the refractive index sufficiently to give good optical performance.

Dense non-porous coatings would be preferable if the other properties could be retained. Multilayer AR coatings are dense and have excellent optical performance but their laser damage threshold is low especially at the shorter wavelengths. Until recently only MgF_2 and Na_3AlF_6 had refractive indices low enough to be even considered as suitable for single layer AR coatings but these only gave moderate optical performance at best, as shown in Table 1.

Table 1. Comparison of three low index materials used to form single layer AR coatings

Coating Material	n_d	% reflection(single surface) SiO_2	BK-7
MgF_2	1.38	1.7	1.3
Na_3AlF_6	1.36	1.4	1.0
porous SiO_2	1.22	~ 0	~ 0

The DuPont Company has now made commercially available a new type of fluorocarbon polymer called Teflon® AF 2400.[2,3] This polymer has a very low refractive index (1.29), is transparent and can be fabricated into coatings. Although this index is higher than that required for a zero reflection coating on common substrates (e.g. fused silica), it is much lower than that of any other non-porous coating material. We therefore decided to investigate this as a dense quarterwave AR coating for optical components with indices in the 1.5 range. We were also particularly interested in its laser damage threshold as there was the possibility that it could replace our porous silica coating in applications where environmental protection is desirable.

2. TEFLON® AF 2400

Teflon® AF 2400 is a random copolymer of tetrafluorethylene (15 mole%) and 2,2 bis-trifluoromethyl, 4,5 difluoro, 1,3 dioxole (85 mole%) [hereafter abbreviated as 2,2-bis-T].[2] Its structure is shown in Fig. 1. Like other fluorocarbon polymers, for example poly-tetrafluoroethylene (poly TFE) or Teflon®, it is fully fluorinated and contains no hydrogen. Unlike other fluorocarbon polymers, it has some room temperature solubility in fluorine-containing solvents, is amorphous and non-absorbing down to 200 nm. It also has the lowest refractive index of any known solid material (1.29). Because of its solubility, coatings can readily be prepared from solutions by any of the usual methods. Furthermore, because the material is amorphous it has low scatter losses and excellent transmission over a broad range of wavelengths. If applied as a quarterwave AR coating, the theoretical reflections that could be expected for a range of substrate indices are shown in Fig. 2. The percent reflection at normal incidence was calculated using the well known expression:

$$R(\%) = \left[\frac{n_c^2 - n_o n_s}{n_c^2 + n_o n_s}\right]^2 \times 100\% \qquad (1)$$

where n_c, n_o and n_s are the refractive indices for the fluorocarbon coating (1.29), the incident media (air = 1.0) and the substrate, respectively. It is notable that these reflectivities are lower than could be obtained using MgF_2 or Na_3AlF_6 on substrates with indices below about 1.75. Therefore the AF 2400 should provide useful optical performance especially on substrates with a refractive index between about 1.5 and 1.75.

The low refractive index of the AF 2400 polymer compared to, for example, normal Teflon® (poly-TFE) is due largely to its abnormally low density. We have calculated the refractive index of the AF 2400 polymer from the well known Lorenz-Lorentz relationship assuming additivity of the functional group contributions to the molar refraction:

$$n = \left[\frac{1 + \left(\frac{2\rho R_T}{M}\right)}{1 - \left(\frac{\rho R_T}{M}\right)}\right]^{1/2} \qquad (2)$$

where ρ is the density (g/cm^3), M the molecular weight (g/mole) and R_T the molar refraction. R_T is the sum of the refraction contributions from various functional groups in the structure:

$$R_T = \sum_{i=1}^{n} R_i \qquad (3)$$

The function group contributions (R_i) we have used are the values compiled by Van Krevelen.[4] Using these data and the measured density of the AF 2400 polymer, we calculate a refractive index of 1.252 vs. the reported value of 1.29.[2,3] Surprisingly the total molar refraction (R_T) is affected little by the change in polymer structure from Teflon® (100% poly TFE) to AF 2400. Instead, what seems to be controlling the index change is the dramatic

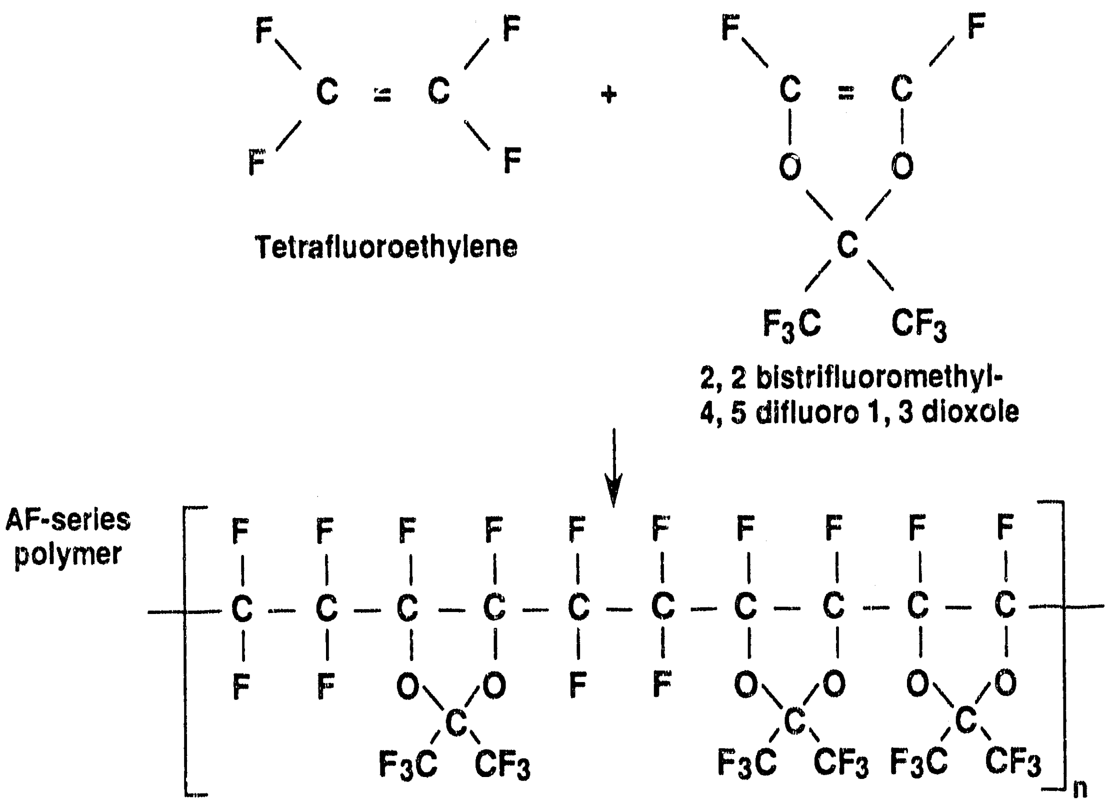


Fig. 1 Structure of the 2,2 bistrifluoromethyl 4,5 difluoro 1,3 dioxole monomer that is polymerized with tetrafluoroethylene to give the AF series copolymers.

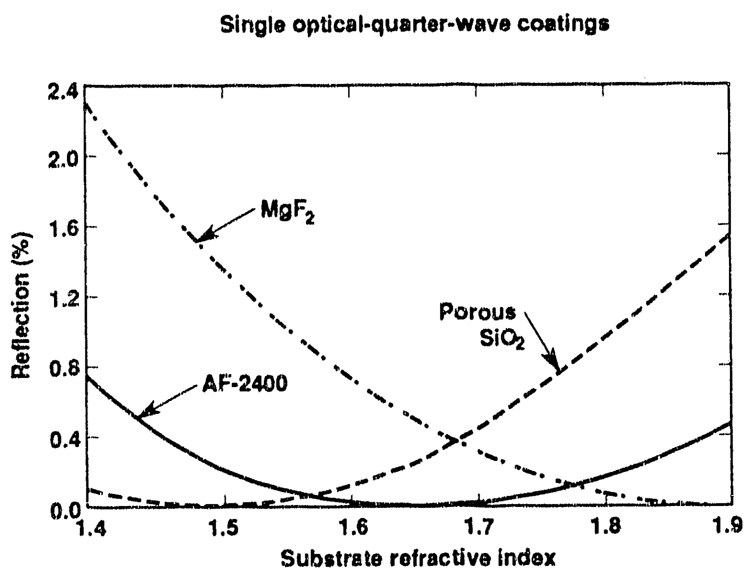


Fig. 2 Reflectivity (%) at normal incidence vs. substrate refractive index for porous silica, Teflon® AF-2400 and MgF_2 single quarterwave optical AR coatings.

reduction in density from about 2.2 g/cm² for 100% poly TFE to about 1.67 for AF 2400. This is shown in Fig. 3 where the reported density and refractive index are plotted vs. the mol% 2,2-bis-T in the structure. The values for poly TFE are from Van Krevelen[5] whereas the values for the AF series polymers are from Resnick[2] and the product data sheets distributed by the manufacturer.[3] Thus it seems clear that the 2,2-bis-T produces a much more open, less dense structure than exists in pure poly TFE.

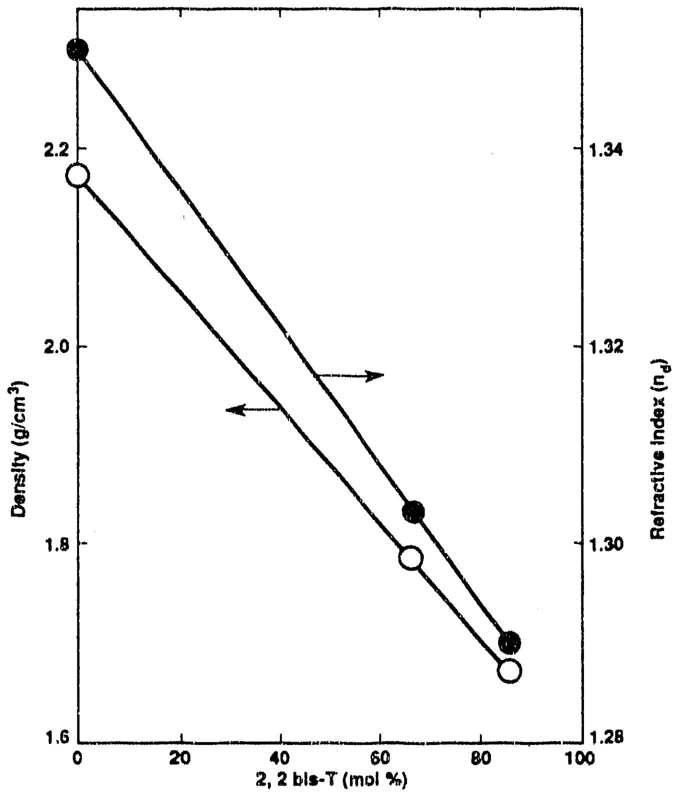


Fig. 3 Teflon® AF polymer density and refractive index vs. mole % 2,2 bistrifluoromethyl 4,5 difluoro 1,3 dioxole monomer (2,2-bis-T) in the structure.

3. EXPERIMENTAL

A 1.25% solution by weight of Teflon® AF 2400 in Fluorinert® FC-75 was prepared by stirring the powdered polymer in the solvent at room temperature. Fluorinert® FC-75 is a perfluorinated ether, b.p. 105°, manufactured by the 3M Company. Because of the high molecular weight of the polymer, complete dissolution took about 24 hours. The solution was filtered through a 1 µm glass fiber filter pad and it was significant that some insoluble material was retained on the filter.

Coatings were prepared on a variety of glass substrates plus single crystal potassium dihydrogen phosphate (KDP) and CaF_2 by dip coating from this solution in a clean environment. Thickness was adjusted by variation in the withdrawal rate and was arranged to be quarterwave at 1064 nm. This corresponded to a true thickness of 206 nm.

Table 2 gives the refractive index (n_d) and brief description of the various substrates used in this study.

Table 2. Summary of substrates used in this coating study

Sample	Material	n_d	$n_{1.0\,\mu m}$
CaF_2	melt grown, single crystal	1.434	1.429
SiO_2	CVD fused silica	1.459	1.450
potassium dihydrogen phosphate (KDP)	solution grown, single crystal	1.47-1.51	1.46-1.49
BK-7	borosilicate crown glass	1.517	1.507
SF-2	silicate; dense flint glass	1.648	1.628
SF-12	silicate; dense flint glass	1.648	1.628
SF-8	silicate; dense flint glass	1.689	1.666

4. OPTICAL PERFORMANCE

The transmission curves for various substrates coated on both sides with Teflon® AF-2400 are shown in Figures 4 and 5. The maximum transmissions, or lowest reflections, agree well with the calculated values as shown in Fig. 6. The values plotted in Fig. 6 are for single surface reflections whereas the measured sample reflections (Figs. 4-5) are for two surfaces. We have simply divided the measured values by two to obtain the points in Fig. 6. Note that SF-2, SF-12 and SF-8 substrate glasses give essentially zero reflection as was expected for glasses having an index near 1.66.

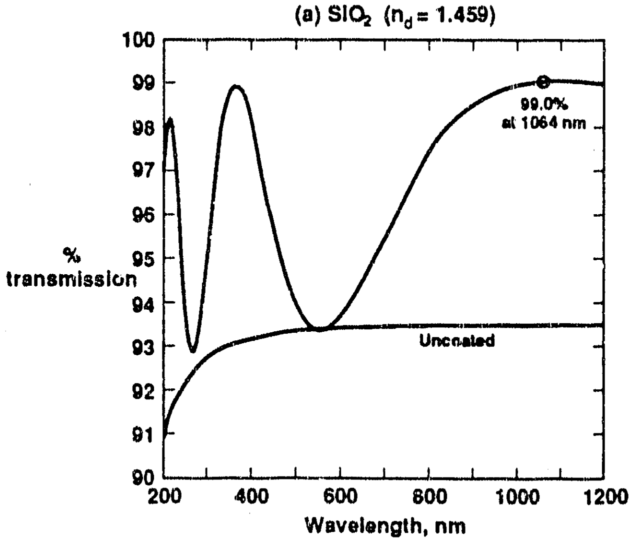
All transmission curves are near classic curves for uniform quarterwave coatings. With SiO_2, CaF_2 and KDP substrates there are maxima at the first, third and fifth harmonics and minima at the second and fourth harmonics (optical half waves). The only anomaly is that the transmission at the fourth harmonic should be the same as that of the base surface, as it is at the second harmonic. The reason for the slight increased transmission in all the samples is not known. This effect is not seen with SF-2 and SF-8 because of absorption by these substrates at shorter wavelengths.

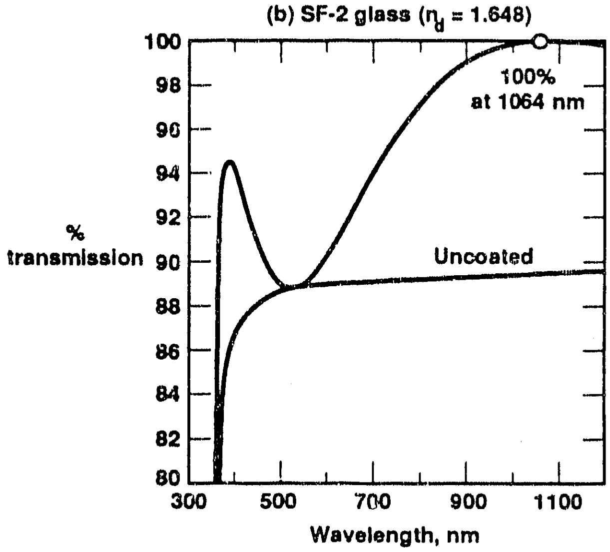
For comparison, the transmission curve for a free-standing film of teflon AF 2400 is shown in Fig. 7. This film was prepared using the method discribed in Section 6. The film has good transmission down to about 200 nm. The roll-off in transmission in this region is most likely due to scattering rather than absorption.

5. DAMAGE THRESHOLD MEASUREMENTS

5.1 Small area tests

The laser damage threshold of several different substrates coated with Teflon® AF 2400 were measured on our Nd:YAG Reptile facility[5] using a spot size of about 1-2 mm diameter (1/e). Measurements were carried out at two different wavelengths, 1064 nm and 355 nm, with a pulse length of 10 ns. Usually 600 shots were applied to a single spot at a repetition rate of 10 Hz. Unconditioned samples received all shots at one fluence at one site, if no damage was observed the fluence was increased and more shots applied to a new site. This was continued until damage was observed. Conditioned sites received shots with the fluence ramped from near zero to the desired maximum, if no damage was observed this was repeated on a fresh site to a higher maximum until damage was observed.





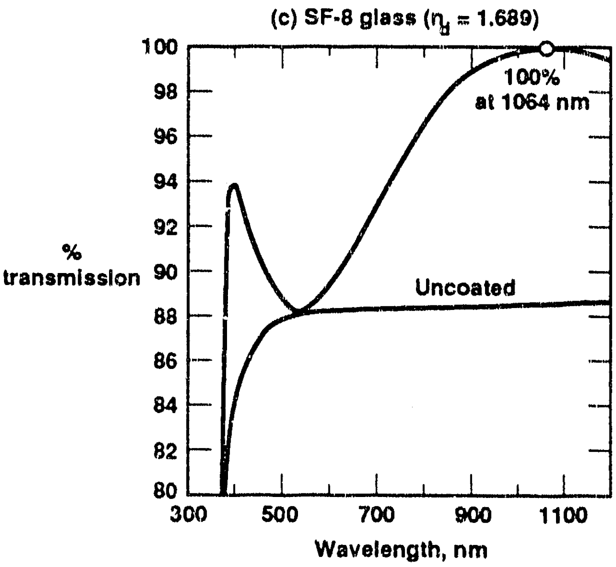
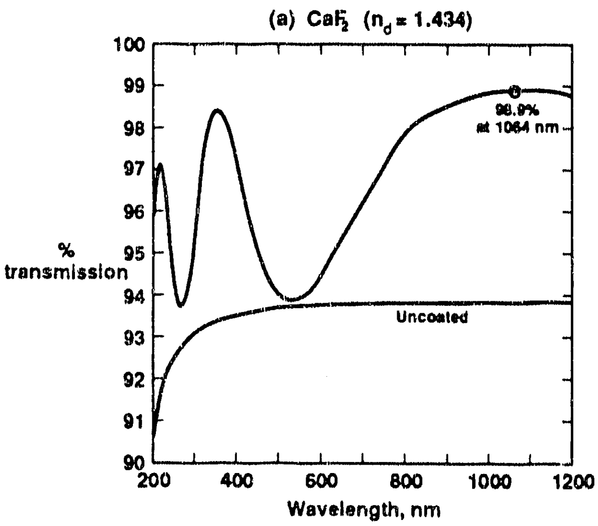
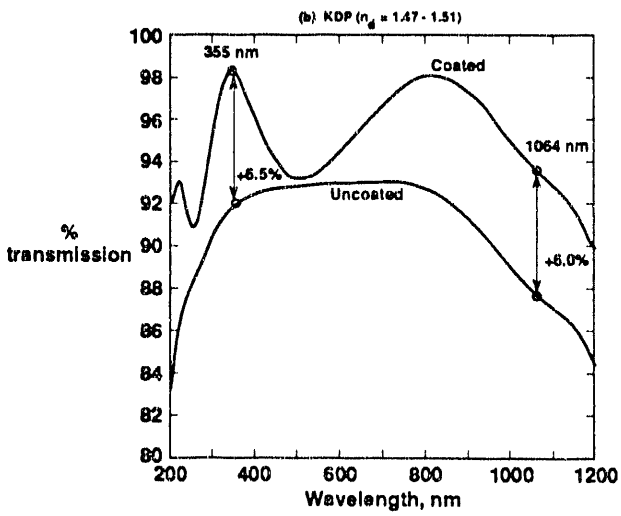


Fig. 4 Transmission (%) vs. wavelength for three silicate glass substrates coated with a single optical quarterwave layer of AF-2400 polymer (a) fused silica, (b) SF-2 and (c) SF-8.

Fig. 5 Transmission (%) vs. wavelength for single crystals of (a) CaF_2 and (b) KDP coated with a single optical quarterwave layer (at 1064 nm) of AF-2400 fluoropolymer.





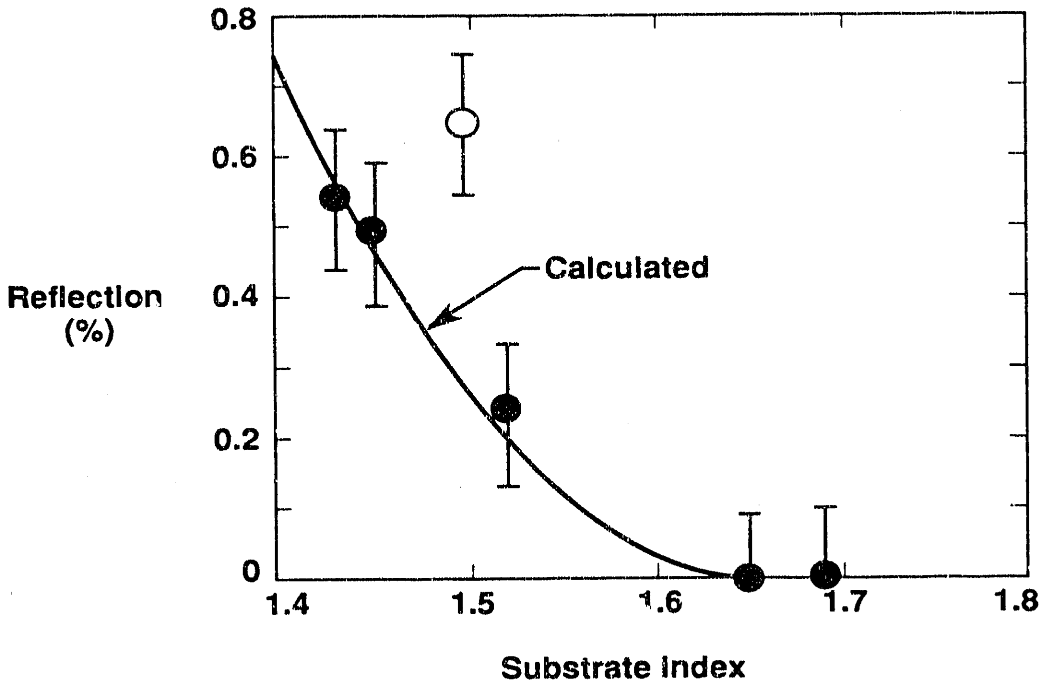


Fig. 6 Comparison of measured reflectivity (at 1064 nm and normal incidence) with that predicted from equation 1 for various substrates. The open circle is for KDP; absorption in the bulk crystal material make this measurement difficult.

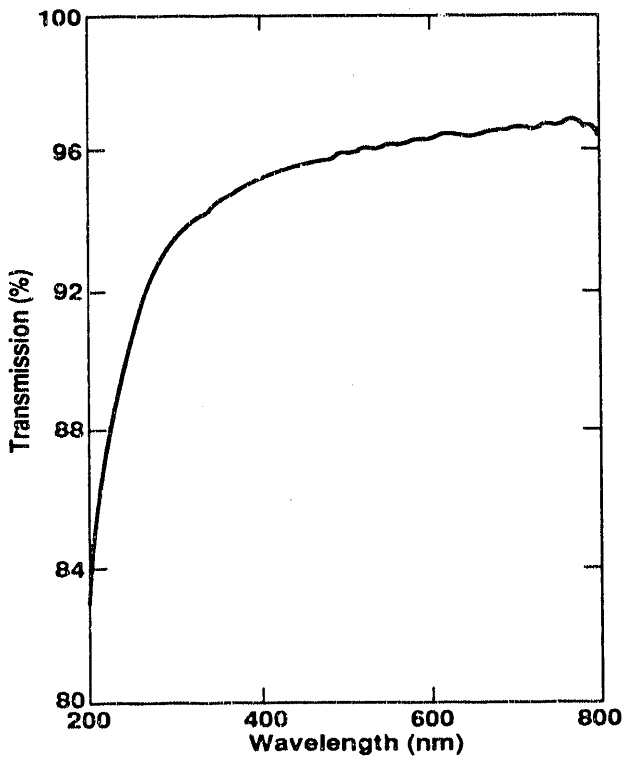


Fig. 7 Single film transmission for AF-2400 polymer vs. wavelength. The film was approximately 25 μm thick.

The results are shown in Table 3. For comparison, our porous silica AR coating has an unconditioned (S-on-1) damage threshold at 10-ns of 35-55 J/cm^2 at 1064 nm and 30-35 J/cm^2 at 350 nm. The Teflon coating compares very favorably, especially if conditioned. The lack of apparent conditioning on KDP at 350 nm is of note and is, so far, unexplained.

Table 3. Results from small area (~ 1-2 mm^2) laser damage tests of AR coatings of Dupont fluorocarbon (AF-2400)

	1064 nm, 10 ns		355 nm, 10 ns	
Substrate	Unconditioned (S-on-1) J/cm^2	Conditioned (R-on-1) J/cm^2	Unconditioned (S-on-1) J/cm^2	Conditioned (R-on-1) J/cm^2
SiO_2	45	> 55	11	> 35
CaF_2	—	72	—	28
BK-7	> 70	—	—	—
KDP	—	> 60	17	18
free film (~ 25 μm)	—	16	—	7

5.2 Large area tests

To be of practical use, the AF 2400 coating must have a high damage threshold over a large area. For example, the transmission optics in use on the Nova laser system are typically 1-meter in diameter. Therefore, before using new coating materials on our Nova laser we often verify the results from the small area damage tests with tests at large areas (typically several cm^2).

Figure 8 shows the experimental set-up on our Nova laser for large area tests. In this particular case we measured the damage threshold at 3ω by frequency converting the Nova beam using a type II/type II KDP frequency conversion array. The damage tests were carried out mid-way down the amplifier chain on a single Nova beamline. The highly collimated beam was apertured to about 3-cm diameter and the energy and intensity profile were determined by reflecting 8% of the incident beam to a calorimeter and photographic plate using a bare, fused silica beam splitter. Typically the peak-to-average intensity ratio on the test aperture was about 1.5-to-1. In all cases we used a temporally square pulse, 3-ns in width. Two samples were tested: KDP and fused silica. The KDP surface was diamond turned whereas the fused silica was finished with a standard optical "super-polish". Both were then coated with AF-2400 using a dip coating process.

The coatings were not "laser conditioned" by low fluence irradiations. Thus the damage thresholds are comparable to the unconditioned (S-on-1) small area tests. The measured 3ω damage threshold for the large area tests was about 6-7 J/cm^2 for AF 2400 on KDP and about 8-9 J/cm^2 for AF 2400 on SiO_2. The damage was characterized by a series of small (~ 5-10 μm) spots or pits. The somewhat lower damage threshold for the coating on KDP may be due to the fact that the bulk crystal was also damaging at this fluence. As expected, the bulk fused silica remained undamaged.

These results at 3-ns can be compared with the small area tests at 10-ns by assuming an approximate $t^{1/2}$ pulse length scaling. The large area damage tests scale to about 11 to 13 J/cm^2 and 14.5 to 16.5 J/cm^2 at 10-ns for KDP and SiO_2, respectively. This corresponds to values of 17 and 11 J/cm^2 at 10-ns for unconditioned, small area tests at 355 nm (see Table 3). Thus the values for the large and small area tests agree to within about 30%.

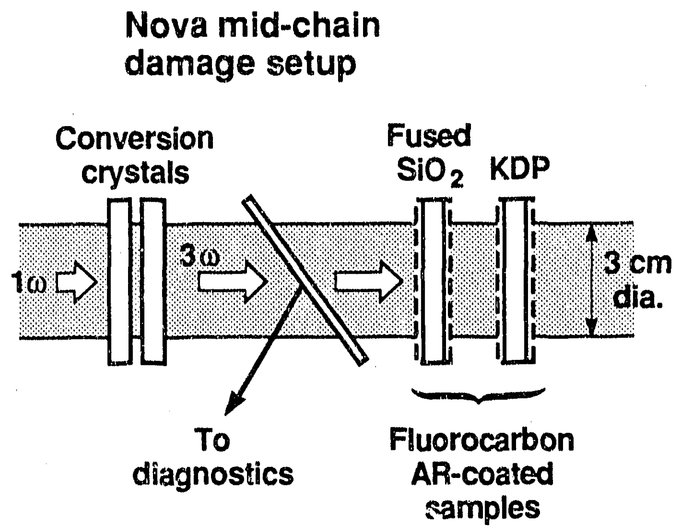


Fig. 8 Schematic of large area, 3ω damage test set-up at mid-chain on one of the 10 beamlines of the Nova laser.

6. ENVIRONMENTAL

The protective effect of a Teflon® AF 2400 coating on a sensitive substrate is hindered by the thinness of the coating necessitated by its optical requirement. A quarterwave coating for 1064 nm light, for example, has a thickness of only 206 nm. This is not thick enough to stop fairly rapid diffusion of vapors through the film which can still be detrimental to the substrate. The coating can be a liquid barrier however, and we found that a coated KDP sample (which is highly water soluble) could briefly be sprayed with a jet of water from a wash bottle with no effect; the water just beaded up and flowed off. Total immersion of the sample in water however caused the coating to soon peel.

The same effect was observed with a coated fused silica sample and this became a good method of preparing free films of the polymer. Adhesion and water resistance on silica was very much improved by the use of hexamethyldisilazane as a coupling agent. Pretreatment of the silica with this material prior to coating allowed water immersion for many days with no peeling.

7. CONCLUSION

Teflon® AF 2400 has been shown to be a good quarterwave AR coating material for optical substrates with refractive indices in the range 1.45-1.75. The measured residual reflection ranges from about 0.5% per surface for fused silica (index 1.46) to near zero for Schott SF-12 glass (index 1.65).

Coatings are easily applied from solution by dip coating at room temperature and can readily be removed. The laser damage thresholds at 350 nm and 1064 nm are among the highest that we have ever observed for AR coating materials.

There is a possibility that some environmental protection will also be obtained when the material is used on sensitive substrates such as KDP.

8. ACKNOWLEDGEMENTS

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