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XPS and ^{19}F NMR Study of the Photodegradation at 157 nm of Photolithographic-Grade Teflon AF Thin Films

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Recently, a series of partially fluorinated polymers were synthesized, which had extremely high transparency.[1] Unfortunately, these polymers have been shown to deteriorate very rapidly when exposed to 157 nm light[1−3] despite their high transparency. In fact, perfluorinated polymers such as TAF and Cytop, which have much lower transparency at 157 nm, have been demonstrated to be significantly more photostable at 157 nm. For 157 nm lithography to become a commercially viable process, suitable pellicle materials are required that are both transparent and photostable. Although TAF polymers do not fulfill these criteria, they are currently one of the best performing materials in terms of transparency and photostability. For this reason we are studying photodegradation of TAF polymers at 157 nm so that the fundamental photodegradation mechanisms can be established. Equipped with this information, it is hoped that these families of polymers can be reformulated or redesigned to meet the needs of the semiconductor industry at 157 nm lithography.

This communication describes our initial efforts at characterizing the photodegradation of TAF 1600 at 157 nm. We present the results of X-ray photoelectron spectroscopy (XPS), ^{19}F solution-state nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy analyses of polymers irradiated with a 157 nm laser.

TAF1600 is a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole (PDD), 65%, and tetrafluoroethylene (TFE), 35% (see Figure 1). TAF 1600 thin films were prepared by spin-coating 3% solutions of photolithographic-grade TAF 1600 copolymer (Dupont) in Fluorinert 75 (Aldrich) onto VUV grade CaF_2 windows (Dupont). A spin program of 1000 rpm for 10 s followed by 3000 rpm for 25 s was used. The windows were irradiated with a 157 nm F_2 excimer laser (Lambda Physik, Optex) with a dry nitrogen purge. The concentration of oxygen in the reaction chamber was maintained at a maximum of 2 ppm. Films were irradiated at a dose of 0.1 mJ cm^{-2} per pulse, at a pulse rate of 200 Hz, to a range of total doses between 5 and 50 J. These settings were chosen because it was the closest approximation for the settings used in a commercial 157 nm photolithography tool.

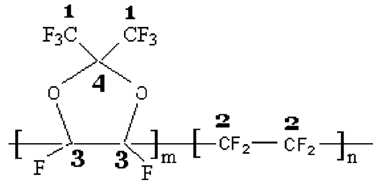

Figure 1. Structure of Teflon AF copolymers. The numbers refer to chemically different carbons referred to in the discussion of the XPS analyses.

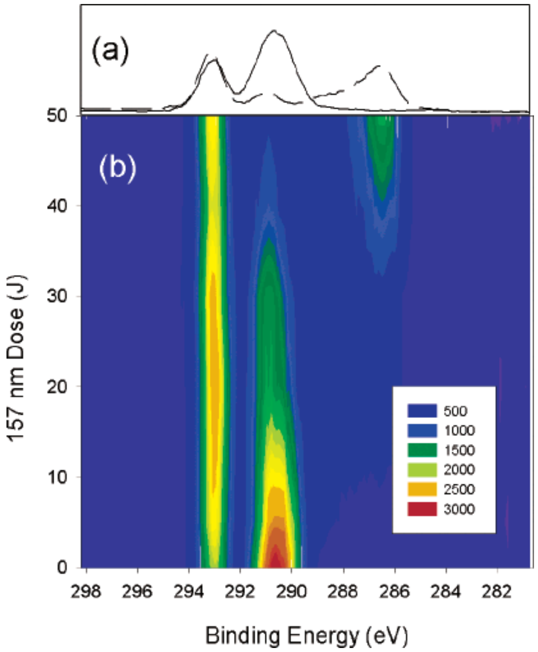

Figure 2. (a) C 1s XPS spectra of Teflon AF 1600 after exposure to 157 nm laser at doses of 0 J (solid line) and 50 J (dashed line). (b) Contour map created from C 1s XPS spectra of Teflon AF that had been exposed to total doses of 0, 5, 20, 30, 40, and 50 J of 157 nm radiation.

The changes in the chemical structure of the approximately top 6 nm of the polymer films were examined using XPS. Figure 2a shows the high-resolution C 1s XPS spectra of TAF 1600 prior to exposure (solid line) and after exposure to a total dose of 50 J (dashed line) of 157 nm laser radiation. In Figure 2b, a contour plot is presented that was constructed from high-resolution C 1s XPS spectra of TAF 1600 samples that have been irradiated with a 157 nm laser to total doses of 0, 5, 20, 30, 40, and 50 J. The contour plot shows most clearly the changes in intensity of exposure. The C 1s spectrum of the unexposed film exhibits two peaks at 293 and 290.5 eV. The peak at 293 eV is assigned to $-CF_3$ groups[4] (carbon 1, Figure 1). The broader peak at 290.5 eV is assigned to $-CF_2-$, $-CF\langle$, and $[-O_2-\mathit{C}-(CF_3)_2]$ (carbons 2, 3, and 4, Figure 1) consistent with previous assignments.[4] Deconvolution of the spectrum into two peaks gave relative peak areas consistent with the structure in Figure 1. Upon exposure to 157 nm radiation the peak at 290.5 eV was observed to decrease with increasing dose. Concurrently, a broad peak with a maximum at 286 eV can be observed to increase with

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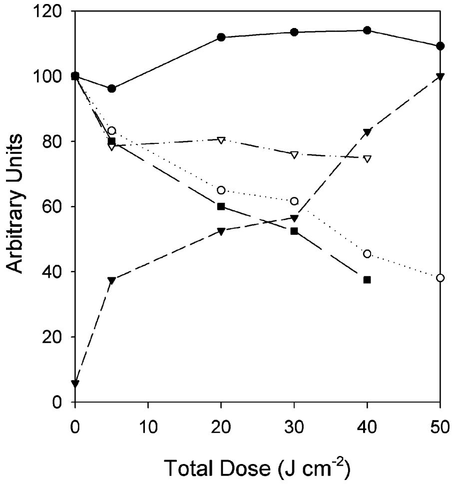


Figure 3. Relative contributions to the XPS spectra of TAF polymers that have been irradiated at 157 nm. The peak at 293 eV (filled circles) corresponds to CF_3 groups, the peak at 290.5 eV (open circles) corresponds to $-CF_2-$, $[-O_2-C-(CF_3)_2]$, and $\rangle CF-$ groups, the peak at 286 eV (filled inverted triangles) corresponds to defluorinated degradation products, and F/C (open triangles) and O/C (filled squares) represent the fluorine−carbon and fluorine−oxygen ratios, respectively. The error in these values is estimated to be ±5%.

increasing dose, which is consistent with structures formed by defluorination of the polymer and also changes to the PDD ring structure, such as oxygen loss. In contrast to this, the peak at 293 eV does not change significantly on exposure.

Figure 3 shows the relative areas obtained by fitting of the XPS spectra to a series of peaks at 293, 290.5, and 286 eV at various doses of 157 nm exposure for TAF 1600. The changes in fluorine−carbon and oxygen−carbon ratios are also shown. For ease of comparison, the values are normalized to an initial value of 100, apart from the area of the peak at 286 eV which is normalized to the area in the spectrum of the materials exposed to 50 J cm^{-2}. To summarize, it was found that on exposure to 157 nm light there was no significant change to the concentration of the fluorinated methyl groups (293 eV); however, there was a significant decrease in the intensity of the peak at 290.5 eV. There was also a continual accumulation of photodegradation products evidenced by the broad peak at 286 eV. Overall, both the O/C and F/C ratios were seen to decrease.

Details of the mechanism of degradation can be discerned from these XPS results. It has been found that the normalized area of the 290.5 eV peak is directly proportional to the O/C ratio at each exposure dose (Figure 4). This indicates that loss of carbons adjacent to oxygen, i.e., $-CF\langle$ and $[-O_2-C-(CF_3)]$, is primarily responsible for the decrease in the peak at 290.5 eV. Further evidence for this is the increase in binding energy of the 290.5 eV peak to a slightly higher binding energy, which is consistent with a greater proportion of $-CF_2-$ groups remaining in the copolymer after irradiation. The decrease in the O/C ratio indicates that oxygen-containing small molecules, or residues, are being generated and lost during irradiation. Forsythe et al.[5] have postulated the loss of hexafluoroacetone during the γ irradiation of TAF 1600. Oxygen-containing small molecules, such as carbonyl difluoride and carbon monoxide, have also been observed to form during the degradation of other oxygen-containing fluoropolymers such as perfluoropolyethers.[6]

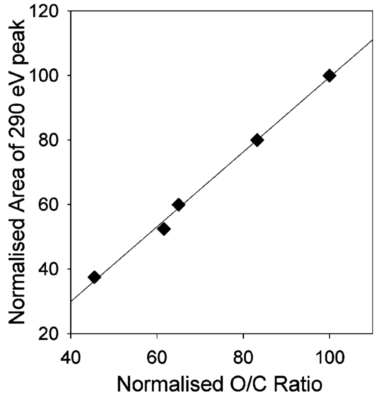


Figure 4. Plot of the change in normalized area of the peak at 290.5 eV vs the normalized O/C ratio for TAF 1600 after exposure to 157 nm radiation at 0, 5, 20, 30, and 40 J. The solid line is the linear regression fit that has an r^2 equal to 0.99.

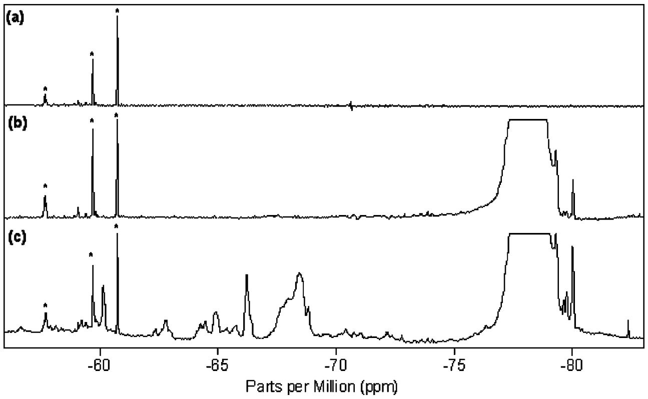
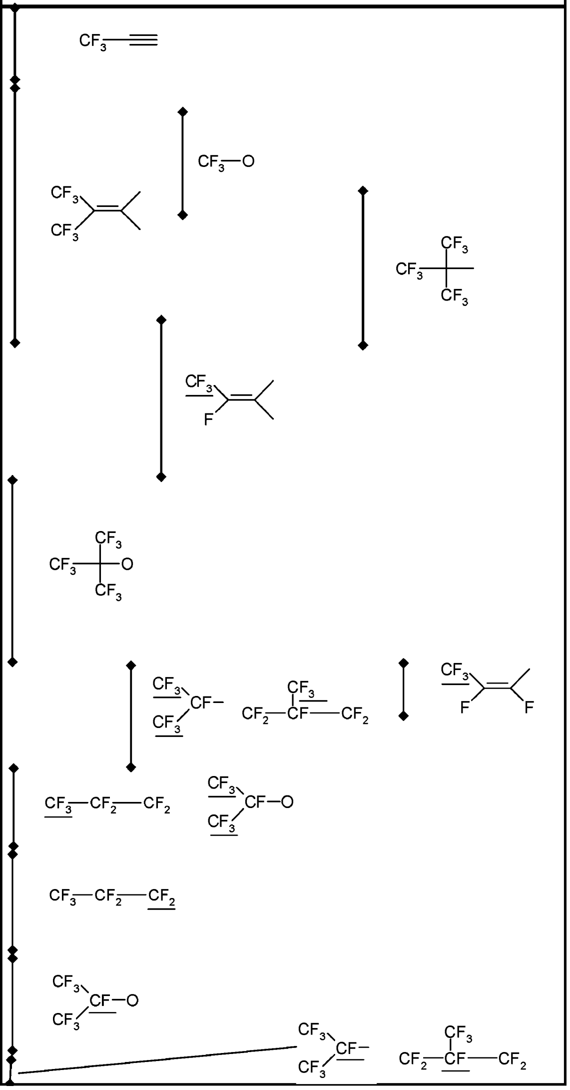


Figure 5. ^{19}F solution-state NMR of (a) hexafluorobenzene (HFB), (b) TAF1600 in HFB, and (c) TAF1600 irradiated to a total dose of 20 J in HFB. For the sake of clarity not all peaks were labeled.

The decrease in the O/C ratio and the contribution from $[-O_2-C-(CF_3)]$ groups in the XPS spectra of exposed polymer with increasing dose seems to be in conflict with the observation of a relatively unchanged $-CF_3$ concentration because loss of oxygen and $O_2-C-(CF_3)$ groups would be expected to lead to overall loss of CF_3 groups. Therefore, it must be concluded that $-CF_3$ chain ends or similar structures are being formed at a similar rate to the rate of breakdown of the PDD ring.

To test this hypothesis, ^{19}F solution-state NMR of the photodegraded samples was performed. To generate sufficient sample for the NMR spectra, approximately 20 thin films (4 cm^2 area, $\sim 1\ \mu m$ thick) were each irradiated to a dose of 20 J. Following irradiation the films were soaked in hexafluorobenzene (HFB) to remove them from the substrate. The entire sample was soluble; a cross-linked fraction was not observed. Unfortunately, the entire film could not be irradiated, and hence resonances from the virgin polymer still contribute to the spectra. Nonetheless, a large number of new resonances are observed in the ^{19}F NMR spectrum of TAF 1600 after 157 nm irradiation, particularly in the −50 to −85 ppm region of the spectrum. Figure 5 shows the ^{19}F solution-state NMR spectra in the −50 to −85 ppm region of (a) HFB, (b) virgin TAF 1600, and (c) TAF 1600 irradiated with a 157 nm laser to a dose of 20 J. In this region the HFB solvent has three impurity peaks which have been marked with asterisks. The virgin

Table 1. Peak Assignments to the ^{19}F Solution-State NMR Spectra of 157 nm Degraded Teflon AF 1600[18−23]

Peak Position (ppm)	Peak Assignments
54.4	
56.7	
57.9	
58.2	
58.4	
58.9	
59.3	
59.4	
60.2	
60.5	
62.4	
62.6	
62.8	
64.3	
64.5	
64.9	
65.4	
65.8	
66.2	
67.7	
68	
68.5	
68.8	
68.5	
68.8	
70.5	
72.1	
75.9	
76.3	
79.7	
79.8	
82.3	
121.5	
121.8	
122.2	
122.5	
142.5	
142.9	
143.3	
143.6	
184.2	

polymer has major peaks at −78.1 and −78.6 ppm that can be assigned to the $-CF_3$ groups in the PDD ring.[7] Note that in Figure 5 the spectrum has been expanded so that the splitting into individual peaks cannot be seen. Small peaks at −80 and −79.5 ppm are also present, which are due to $-CF_3$ end groups in the virgin polymer. In contrast to these simple spectra, the spectrum of the exposed material shows a large number of new resonances, which can be attributed to $-CF_3$ groups in various structures, which is consistent with the XPS results described above. The appearance of $-CF_3$-containing structures is not unexpected because they have also been observed in γ-irradiated poly(tetrafluorethylene-*co*-perfluorovinyl ethers),[8,9] poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP),[10] poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA),[11] and poly(tetrafluoroethylene) (PTFE).[12,13] Furthermore, $-CF_3$-containing structures are observed to be formed in other high-energy processes involving fluorinated polymers, such as electron-beam-irradiated vinylidene fluoride−TFE copolymers,[14] PTFE oligomers prepared by reaction with F_2 gas at high temperatures,[15] and plasma-polymerized fluorocarbon films.[16,17] However, it is difficult to make definite assignments of the degradation products for 157 nm degraded TAF 1600 due to the large number of overlapping peaks and the poor resolution resulting from the limited mobility of the polymer chains in solution. Attempts to confirm assignments of these peaks using 2D COSY ^{19}F NMR were unsuccessful, primarily due to the broad line widths obtained from the polymer solutions and the low concentrations of degradation products in the sample. However, to support the assignments and to indicate the types of structures likely to be formed on 157 nm irradiation, we have listed the ^{19}F chemical shifts of a number of structures reported in the literature (Table 1).

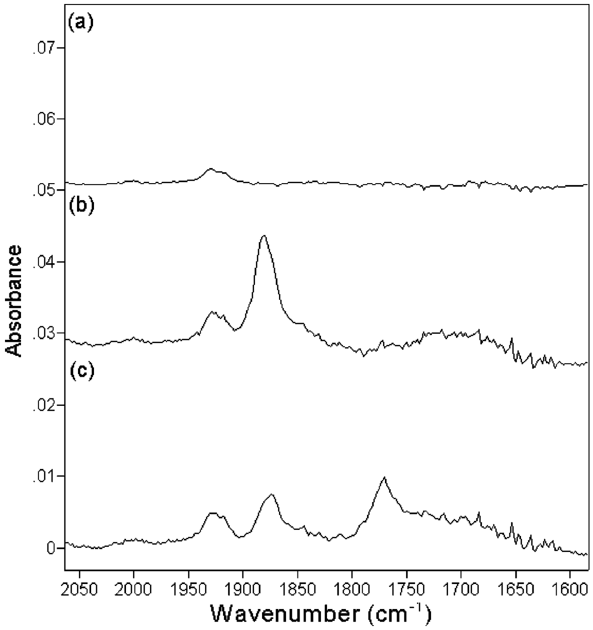


Figure 6. Transmission FTIR spectra of TAF 1600 (a) unirradiated, (b) after 157 nm irradiation to a total dose of 20 J, and (c) after 157 nm irradiation to a total dose of 20 J and the postirradiation exposure to the atmosphere for 16 h.

A comparison of chemical shifts of the peaks in the ^{19}F NMR spectra of irradiated TAF 1600 with literature assignments indicates that a large number of the new resonances may be due to end groups that contain $-CF_3$ groups. The significance of the formation of a large number of chain-end structures is that extensive chain scission must be occurring. This is also consistent with the high solubility of the exposed material and also the observation that the film becomes thinner on exposure. Table 1 indicates that unsaturated groups may also be forming, which again is consistent with the extensive defluorination of the surface observed by XPS.

FTIR transmission spectroscopy of thin films irradiated to a dose of 20 J was also performed. Figure 6 shows the 1600−2050 cm^{-1} region of the FTIR spectra of (a) the virgin polymer, (b) TAF irradiated with 157 nm to a total dose of 20 J, and (c) TAF irradiated with 157 nm to a total dose of 20 J and subsequently exposed to the atmosphere for 16 h. In this region the spectrum of the virgin polymer has a small peak at 1925 cm^{-1}, which is assigned to an overtone peak. Upon irradiation a peak at 1881 cm^{-1} appears, which has been assigned to an acid fluoride on a perfluorinated chain.[5] Further confirmation of this assignment is the conversion of the acid halide to a carboxylic acid (1770 cm^{-1}) via hydrolysis on exposure to the atmosphere.[5] Acid fluorides are also chain end structures, and their formation in TAF

1600 that has been irradiated in the absence of oxygen is indicative of chain scission at the PDD ring.

XPS and ^{19}F solution-state NMR of 157 nm degraded TAF 1600 have demonstrated that significant photochemical processes are occurring during irradiation. XPS results indicate that attack is primarily occurring at the PDD ring, resulting in loss of oxygen-containing small molecules and defluorination of the copolymer. The ^{19}F NMR results indicate that there is extensive chain scission resulting in the formation of $-CF_3$ end groups, which were also observed in the XPS results. FTIR results indicated that acid halides are forming, which probably result from chain scission at the PDD ring. Further experiments are currently underway involving Raman and ESR analysis of degraded TAF 1600. As well as this, mass spectrometry of the volatile products is also planned. These results, and the results of studies on TAF 1200 and 2400 copolymers, will be reported in the future.

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