Plasma Synthesis of a Novel CF_3-Dominated Fluorocarbon Film

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Previously, we have reported on film chemistry control during pulsed plasma synthesis of fluorocarbon films.[1,2] In these studies, relatively large scale progressive changes in film compositions were observed with sequential changes in the rf duty cycle employed during plasma polymerization of several perfluorocarbon monomers, all other plasma variables being held constant.[1,2] These fluorocarbon films exhibited a steady increase in $-CF_2-$ functional content as the plasma cycle was reduced, resulting in unusually low surface energy films at the lowest duty cycles employed. This trend toward higher $-CF_2-$ film incorporation was demonstrated both with monomers containing high initial $-CF_2-$ content (e.g., perfluoro-2-butyltetrahydrofuran) as well as with monomers having less abundant $-CF_2-$ groups (e.g., perfluoropropylene and hexafluoropropylene oxide).

In this report, we provide the first evidence for the controlled plasma synthesis of perfluorocarbon films dominated by $-CF_3$ groups. These exceptionally hydrophobic films were produced by plasma polymerization of a mixture of $-CF_3$ substituted perfluorohexenes [trimer of C_9F_{18} compounds]. This starting isomeric mixture is dominated by $-CF_3$ groups functionalities which account for 55% of the carbons present in these molecules. Additionally, these molecules contain a carbon−carbon double bond which we hoped would be useful in promoting polymerization, particularly under low-energy plasma conditions. The reaction system employed in the present work has been described previously.[2,3] The C_9F_{18} was obtained from PCR, Inc. (Gainesville, FL) and consisted of a mixture of three perfluoro compounds: 2,3,5-trimethyl-3-hexene; 2,3,5-trimethyl-2-hexene; and 2,4,5-trimethyl-2-hexene. This mixture was subjected to thorough degassing via freeze−thaw cycles but was not subjected to any further purification. All plasma runs were carried out at a C_9F_{18} pressure of 50 ± 2 mtorr and a flow rate of 5.05 $\pm$ 0.05 cm^3/min (at STP). The plasma-generated thin films were deposited on polished silicon substrates, and they were subsequently characterized by XPS analysis. The film thicknesses employed (as determined by profilometry) ranged from 600 to 2000 Å. No Si was detected in any of the XPS analyses. These films were also evaluated using the sessile drop water contact angle approach (Rame′-Hart type goniometer) and atomic force microscopy (AFM).

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Table 1. Relative F, C, and $-CF_3$ Content of Plasma-Polymerized C_9F_{18} Monomers Computed from the Resolved C (1s) XPS Peaks

on time/off time (ms)	peak power (W)	equivalent power (W)	% F	% C	% O	F/C	% CF3
		Pulsed Runs					
10/30	200	50	53.6	45.3	1.1	1.18	15
10/300	200	6.5	57.9	41.5	0.6	1.39	24
0.1/3	100	3.2	62.9	36.6	0.5	1.72	40
		Cw Runs					
		50	57.8	42.8	0.4	1.35	19
		5	60.8	38.4	0.8	1.58	34

Samples were prepared using both pulsed plasma and continuous-wave (cw) plasma operation. The pulsed plasma depositions involved rf duty cycles (i.e., ratio of plasma on to plasma off times, in milliseconds) of 10/30 and 10/300 at 200 W peak power and 0.1/3 at 100 W. The cw runs were carried out at 50 and 5 W. In terms of equivalent wattages, the pulsed runs approximate the total power of the cw runs when averaged with respect to total elapsed times. For example, the pulsed deposition at 10/30 and 200 W corresponds to an equivalent (or average) power of 50 W (i.e., $10/40 \times 200$).

XPS spectra were obtained using a Perkin-Elmer PSI 5000 series instrument equipped with an X-ray source monochromator. The XPS instrumental details have been provided previously.[2] Initial survey analyses were carried out using takeoff angles varying from 20 to 70°. Only very small variations in the carbon−fluorine functionalities were detected, with a slight (~1%) increase in $-CF_3$ group densities and F/C ratio with decreasing takeoff angle (i.e., the least penetrating X-rays) relative to the 70° results. In light of this observation, the data presented (Table 1) are for analyses carried out using a standard 45° takeoff angle. An electron flood gun was employed to neutralize charge buildup on the nonconductive films examined in this work. The electron flood gun was operated under conditions which provided optimum resolution of the C (1s) peaks. The C (1s) binding energies were established by centering the $-CF_3$ peak at 294 eV.[4]

The XPS film analyses are summarized in Table 1 and Figures 1 (pulsed runs) and 2 (cw runs). The C (1s) XPS peak assignment shown are based on the accepted peak identities for fluorocarbon films.[4] As shown in Table 1, the F/C atom ratio in the films increases with a decrease in average power under both pulsed and cw conditions. The atom ratios shown in Table 1 were computed from the resolved high-resolution C (1s) XPS peaks as opposed to the directly measured F to C values provided by integration of the respective F (1s) and C (1s) peaks. These latter values show the same trends in F to C ratios as reported in Table 1. However, they provide values as high as 2.26. Others have observed comparable results in contrasting the F to C ratios from resolution of C (1s) XPS peaks with the values obtained from the separate F (1s) and C (1s) signals.[4] These latter values are unrealistically high, reflecting a probably error in instrument sensitivity values. For example, our XPS analysis of a standard poly(tetrafluoroethylene) sample yielded a F/C value of 2.33 using integration of the F (1s) and C (1s) peaks. Assuming

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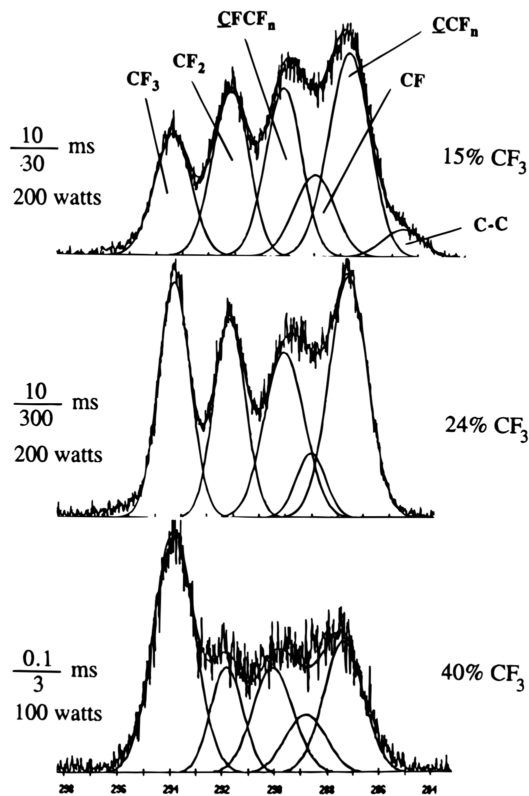

Figure 1. High-resolution C (1s) XPS spectra of pulsed plasma polymerized films of the C_9F_{18} monomers. Rf duty cycles and peak power employed are shown for each film.

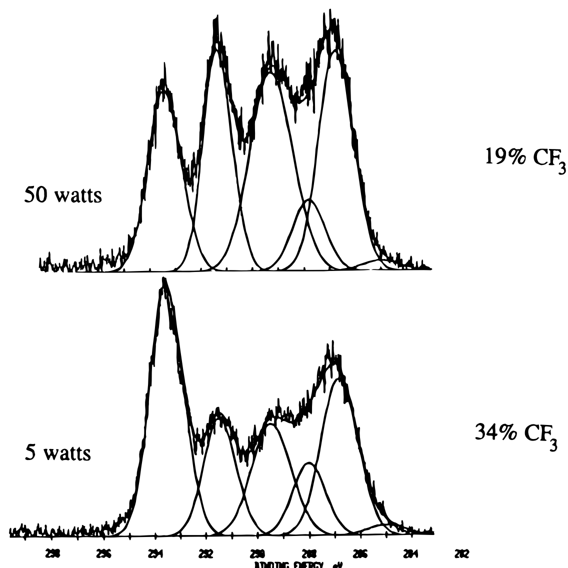

Figure 2. High-resolution C (1s) XPS of polymerized C_9F_{18} films obtained under cw plasma conditions of 50 and 5 W, as shown.

an actual F/C value of 2.00 for the C_2F_4 polymer results in an interpolated value for F/C of 1.94 for the highest F content films of the present work. This interpolated value is higher than the 1.72 calculated from the C (1s) peaks. Although there is only fair agreement between these two values, it is important to emphasize that the trend towards increasing fluorine content and, particularly $-CF_3$ groups with decreasing rf power, is clearly documented by the XPS results. As shown in Table 1 and as is evident in Figures 1 and 2, there is a notable increase in $-CF_3$ film content with decreasing average rf power during the deposition. The $-CF_3$ incorporation

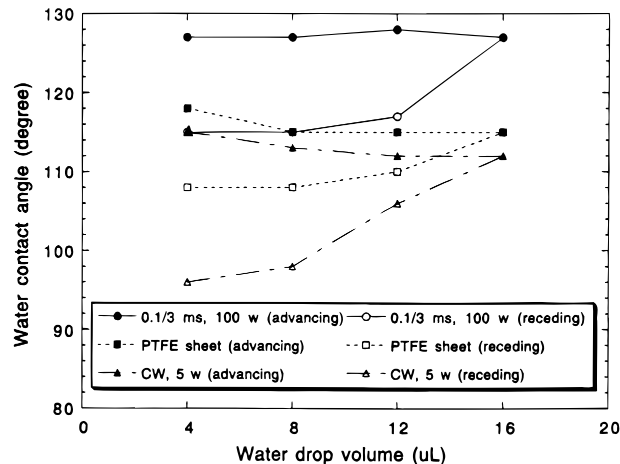

Figure 3. Comparison of advancing and receding water contact angles for low power pulsed and cw plasma synthesized films relative to a polytetrafluoroethylene standard.

in the film synthesized at a 0.1/3 duty cycle and 100 W represents 40% of the total carbon content of the film. This compares to the theoretical maximum of 55% present in the starting monomer mixture.

The hydrophobicities of these unusual fluorocarbon films were evaluated via both advancing (θ_a) and receding (θ_r) water contact angle measurements. In the advancing angle measurements, values were recorded after addition of each 4 μL water droplet. The receding angle measurements were made after removal of each 4 μL aliquot from the surface pool. Examples of the results obtained are shown in Figure 3, in which θ values from two of the $-CF_3$ dominated films are contrasted with values from a standard poly(tetrafluoroethylene) sample. The 5 W cw synthesized film exhibited θ_a values which were slightly less than those of the poly(tetrafluoroethylene) sample.

The contact angle differences noted in this study could arise from surface chemical composition effects and/or variations in the surface roughness of the plasma-deposited films. In general, it has been observed that increased surface roughness results in higher contact angles, all other variables being constant. Therefore, AFM studies of the plasma films were carried out to examine surface roughness as a function of the rf power and duty cycle employed during deposition. These measurements were made using a Nanoscope III (Digital Corp.) AFM unit operated in the tapping mode. The mean roughness of each film was determined quantitatively as measured by surface vertical height variations relative to the geometric center plane of the AFM image. To obtain statistically meaningful mean roughnesses, 20 randomly selected locations on each polymer film sample (using triplicate samples for each rf duty cycle) were imaged and analyzed. The results obtained are summarized in Table 2. The roughness measurements have a calculated precision of ± 0.01 nm. There is clearly a decrease in mean roughness of each film as the equivalent power employed during the deposition is decreased. Table 2 also shows the advancing and receding contact angles for each film. The values shown are for the initial (θ_a) and final (θ_r) measurement for each film.

The results obtained (Table 2) show that the unusually high water contact angle obtained with the highest $-CF_3$ content films do not result from surface roughness

Table 2. Surface Roughness and Water Contact Angles of the Films as Functions of the Rf Power Employed during Plasma Deposition

on time/off time (ms)	equivalent power (W)	mean roughness (nm)	contact Angles (deg)	
			θ_A	θ_R
		Pulsed Runs		
10/30	50	1.71	103	85
10/300	6.5	0.58	112	97
0.1/3	6.5	0.45	119	108
0.1/3	3.2	0.38	127	115
		Cw Runs		
	50	1.09	109	94
	5	*a*	115	96

[a] Not measured.

effects, as we observe a clear *increase* in contact angles with a *decrease* in surface roughness. Thus, the increasing water contact angles of the films with decreasing equivalent power during plasma deposition can be attributed unequivocally to the progressively changing surface chemical compositions and, particularly, to the increased presence of surface $-CF_3$ groups.

The high hydrophobicity of surfaces with high $-CF_3$ content has also been observed by others. The classical studies of Zisman and co-workers with monolayers constructed from fluorinated and nonfluorinated long-chain caroxylic acids revealed significantly lower critical surface tensions for monolayers terminated in $-CF_3$ groups compared to partially fluorinated or nonfluorinated surface structures.[5] Johnson and Dettre have provided a recent detailed review and analysis of the wettability of low-energy surfaces, including explicit discussion of fluorinated films.[6] The high hydrophobicity of $-CF_3$-terminated films is concluded to arise more from an increased surface density of such groups and not an increase in the force fields around the groups.[6] The present study confirms the exceptionally high hydrophobicity of high surface density $-CF_3$ surface films.

Plasma polymerization of perfluorocarbon films have been the subject of investigations in many other laboratories.[7−19] There is a general consensus among these reports that the exact structures of the fluorocarbon films obtained are strongly dependent on plasma deposition conditions, particularly the power and the location of substrates relative to the discharge zone. In general, lower power results in less highly cross-linked films. The results of the present study are certainly in accord with those of previous workers. In the present case, an enhanced retention of monomer $-CF_3$ functionality is observed in the plasma films as the equivalent power is reduced, thus providing less highly cross-linked films. The unique aspect of the present study is the unusually high $-CF_3$ surface density and thus high hydrophobicity of the surfaces produced at these low power densities.

The lowest duty cycle 100 W pulsed plasma generated films have slightly higher $-CF_3$ content and are more hydrophobic than the lowest wattage cw prepared films. Attempts to generate films at even less energetic conditions, under both pulsed and cw conditions, resulted in relatively unstable plasmas and/or exeptionally low deposition rates. Conceivably, lower energetic condtions, when coupled with other monomer processes and flow rates, might provide slight enhancements in $-CF_3$ fim content. However, the high retention of the monomers' $-CF_3$ groups obtained in the present study indicates there is probably little room for generation of even more hydrophobic films using this particular monomer mixture.

The plasma deposition process described in this work represents a convenient route to synthesis of ultralow energy surfaces. For example, these surfaces provide an ideal opportunity to compare and contrast adsorption and permeation properties of $-CF_3$-dominated surfaces with those of the much studied $-CF_2-$ and more highly cross-linked fluorocarbon surfaces. Such studies are currently underway in our laboratory.

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