Preparation and Properties of Plasma-Deposited Films with Surface Energies Varying Over a Wide Range

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Synopsis

Polymer surfaces have been modified by chemical reaction or thin film deposition using a capacitatively coupled plasma RF-discharge system. This has allowed the production of a graded, reproducible series of surfaces with surface energies ranging from low to high. Three gases, hexafluoroethane (C_2F_6), perfluoropropane (C_3F_8), and hexafluoropropene ($CF_3CF{=}CF_2$), were used to prepare the low-energy surfaces. Ethylene oxide (C_2H_4O) was used to prepare the higher energy surfaces. Intermediate values of surface energy were obtained by using gas mixtures of perfluoropropane and ethylene oxide. The plasma-deposited films were characterized by ESCA and contact-angle studies. In the low-energy range, the critical surface tension (γ_c) values of the films prepared were found to be lower than those for Teflon. For the higher energy surfaces, values up to about 45 dyn/cm were obtained. Addition of oxygen to the plasma permitted the production of films with still higher γ_c values. ESCA studies indicate that, under the reaction conditions used, C_3F_8 and $CF_3CF{=}CF_2$ form a fluoropolymer deposit on glass that is at least 100 Å thick. For the same reaction parameters, C_2F_6 resulted in more etching and deposition of a much thinner film.

INTRODUCTION

Plasma polymerization is a useful technique for modifying surfaces and depositing thin films. Plasma-generated films have been suggested as corrosion protective coatings, photoconductive films, semipermeable membranes, and electrically insulating films, to name a few of the potential applications. In this study, the RF-plasma deposition process was utilized to prepare and modify surfaces that will be used to explore the interactions between biologic systems and synthetic materials. A detailed rationale for such model studies has been presented.[1] The information gained from these model studies might be used to improve the blood and tissue compatibility characteristics of biomaterials.

There are a number of advantages to utilizing plasma polymerization for the preparation of new materials for biologic and medical applications. The plasma reaction produces polymer films that adhere tenaciously to the substrate. Because of the pinhole-free nature of these films, their relatively high density, and their freedom from discontinuities on the molecular level, diffusing molecules cannot readily penetrate through these films. This is especially desirable since this prevents the extraction from the substrate material of low-molecular-weight leachables that may be cytotoxic. Another advantage of surface modification by plasma polymerization is that the treatment can be confined to the surface layers (50–100 Å) without affecting

the bulk properties of the substrate. Finally, many unique chemistries, often otherwise unobtainable, can be synthesized on a surface. These chemistries can result in large changes in the wettability and biologic reactivity of the surface. Biomedical applications for plasma-deposited films have been reviewed.[2]

Under appropriate conditions, a fluorinated gas plasma will introduce —CF_3, —CF_2—, and —C—F chemical groups on the surface, resulting in low surface energies. Studies of plasma polymerization of fluorocarbon gases indicate that the F/C ratio of the monomer gas plays an important role in determining whether etching or polymerization will dominate.[3] Gases with a high F/C ratio, such as CF_4 ($F/C = 4$), result in efficient etching, whereas a lower F/C ratio gas, such as C_2F_4 ($F/C = 2$), polymerizes easily. Since C_3F_8 has an intermediate F/C (= 2.67) ratio, glow discharge treatment with this gas should give rise to both etching and polymerization. Three perfluorocarbons were chosen for these experiments to study which gas yielded surfaces richest in CF_3 and CF_2 groups and lowest in surface energy. Carbonyl, carboxylate, and related oxygen-containing groups, on the other hand, would make the surface more polar and consequently result in a higher surface energy. Glow discharge polymerization in the presence of ethylene oxide introduces these oxygen functionalities into the polymer surface structure. A mixture of C_2H_4O and C_3F_8 will give a combination of these polar and apolar groups on the surface, rendering it an intermediate value of surface energy, depending on the relative concentrations of the two gases introduced into the reaction chamber.

EXPERIMENTAL

Apparatus

The RF plasma system used in these experiments consists of a reaction vessel capacitatively coupled to an RF generator. One end of the reactor is connected to the vacuum system. Through the other end, a gas-mixing system introduces the desired monomer gases into the system. The plasma system is illustrated schematically in Fig. 1. A Sargent Welch model 1405 rotary pump, with a pumping speed of 60 L/min, evacuates the system to pressures as low as 0.02 torr. A backstream filter and two cold traps between the pump and the reactor inhibit backstreaming of pump oil or other contaminants. Any desired pressure can be achieved in the reactor by bleeding in different amounts of the monomer gases.

The reaction vessel consists of a Pyrex tube about 60 cm long and 7.5 cm in diameter. The total length is comprised of two parts sealed with a Viton o-ring. Stainless steel bellows at the two ends simplify disassembly for the insertion of the samples into the reactor. A vibrating quartz crystal deposition monitor (Inficon XTM) allows the rate of deposition and the thickness of deposit to be studied. RF power, up to 300 W, can be applied to the reactor through an inductor-capacitor (LC) matching network.

To prepare plasma-deposited surfaces containing both fluorocarbon and oxygen functionalities, gases mixed in different ratios are required. A Linde FM4590 mass flow-controlled gas blender allows the mixing of the gases in any desired ratio. The C_3F_8 gas is considered the major component gas, and C_2H_4O can be introduced as some ratio of this major component.
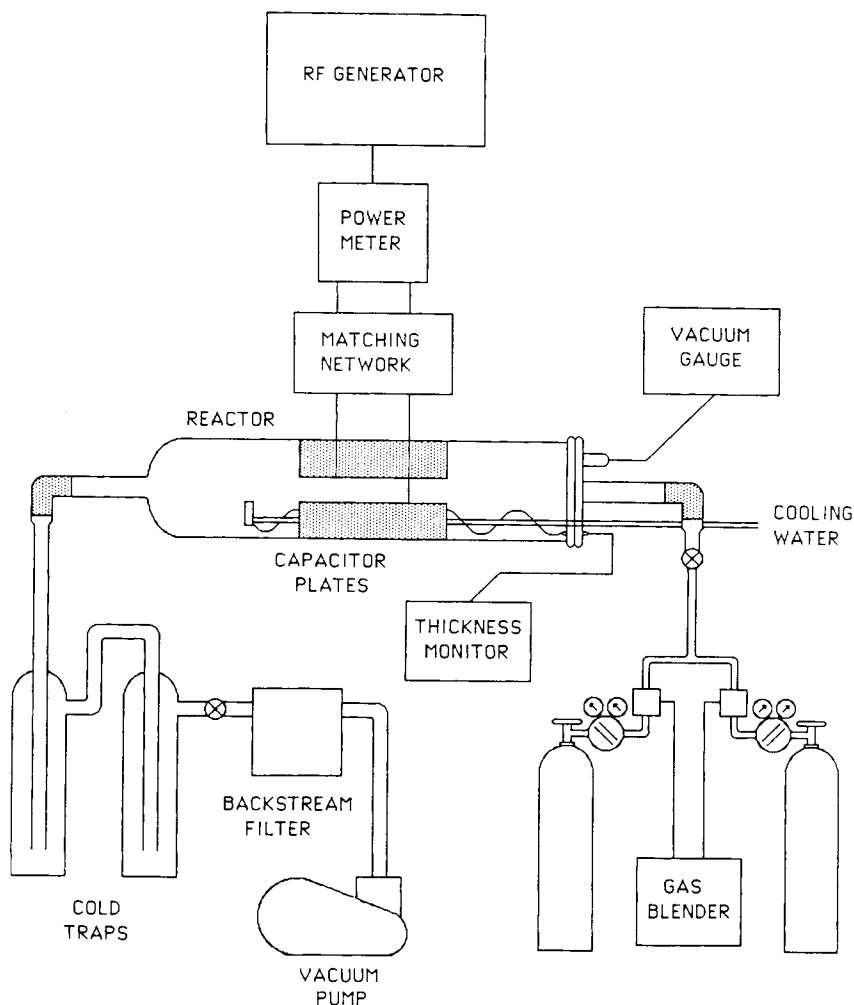
Fig. 1. RF plasma deposition system.

PROCEDURE

Glass coverslips are washed in 1.5% Isopanasol solution (C. R. Callen Corporation) and then rinsed with deionized water in an ultrasonic cleaner. The coverslips are dried overnight and then placed at different locations within the reactor (upstream end of the reactor is the end through which the monomer gas enters, center is defined as the location immediately below the capacitor plates, and the downstream position is the end through which the gas exits the reactor tube). The glass coverslips are further cleaned in the reactor by etching with an argon plasma initiated for 5 min at 50 W. After the system has been pumped down again, one or a combination of gases are introduced into the reactor through the gas mixer and the system is allowed to equilibrate at the desired pressure. The plasma is then ignited at the required power for a fixed time interval. After the completion of the plasma treatment, the samples are taken out of the reactor and kept either

in a dust-free laminar flow hood or in a vacuum desiccator until surface characterization is performed.

ESCA ANALYSIS

The surface analyses of the deposited polymer films are done primarily by electron spectroscopy for chemical analysis (ESCA) and by contact-angle measurements. ESCA involves the measurement of binding energies of electrons ejected from the surface region ($\sim$50–100 Å) upon interaction with a monoenergetic beam of x-rays. The information it provides can be related to the electronic structure of a molecule.[4] ESCA is particularly well suited for studying fluoropolymer surfaces.[5] ESCA analysis of the C_{1s} and F_{1s} regions indicates the degree of fluorination and the percentage concentration of the various fluorocarbon groups (i.e., CF_3, CF_2, and CF) in the surface region. The contributions due to the various chemical groups in the C_{1s} spectra are obtained by resolving the peak envelope into its constituent peaks by fitting a series of gaussian peaks at known binding energies using a computer program simulating an analog curve resolver. The full-width half-maxima of the peaks are predetermined from a specimen with a well-defined single fluorocarbon peak, for example, polytetrafluoroethylene. If the deposition takes place on glass, then additional scans for the silicon and oxygen signals are appropriate to assess if the glass substrate can be detected. The presence of these signals indicates that the deposition is less than $\sim$100 Å or that the deposition is patchy or pinholed. Also, the presence of an oxygen signal when no silicon signal is present may be indicative of trapped radicals in the deposited films, which subsequently react with the oxygen of the atmosphere once the samples are taken out of the reactor.

ESCA analysis was performed using a monochromatized Hewlett Packard 5950B spectrometer at an x-ray source power of 800 W. A low-energy electron flood gun was used to control charging on the nonconductive specimen surfaces. Peak positions were corrected for charge-induced shifts by referencing to literature values for the —CF_3 C_{1s} peak or for the F_{1s} peak for the ethylene oxide-perfluoropropane mixed gas films.

CONTACT-ANGLE ANALYSIS

Wettability was assessed by the contact-angle technique. Zisman introduced the concept of a critical surface tension γ_c as a parameter for expressing the wettability of a surface.[6] The static contact angles made by a series of liquids on the sample surface are measured by viewing the profile of a sessile drop of liquid, using a Ramé-Hart contact-angle goniometer. From a plot of the cosine of the contact angle θ versus the surface tension of the series of liquids, γ_c is found by extrapolating the points to $\cos \theta = 1$.

MATERIALS

The monomer gases perfluoropropane (C_3F_8) and ethylene oxide (C_2H_4O) were supplied by Matheson (California) with a purity of 99.00 and 99.70%, respectively, and used as received. PCR Research Chemicals Inc. (Florida)

provided the hexafluoropropene ($CF_3CF=CF_2$). Hexafluoroethane (C_2F_6) with a minimum purity of 99.60% was obtained from the Linde Division of Union Carbide Corporation (New York).

RESULTS AND DISCUSSION

Results of the ESCA analysis of the films show similar ESCA signal characteristics for plasma polymerization of the three fluorinated gases. Figure 2 shows the C_{1s} spectra observed for these samples after 10 min deposition time. These spectra, resolved into gaussian subpeaks, can be used to estimate the relative concentrations of carbons in different bonding environments (see Fig. 3, for example). These subpeaks may be assigned to —CF_3 (294.0 eV binding energy), —CF_2 (292.0 eV), —$\underline{C}F$—CF_n (291.5 eV),
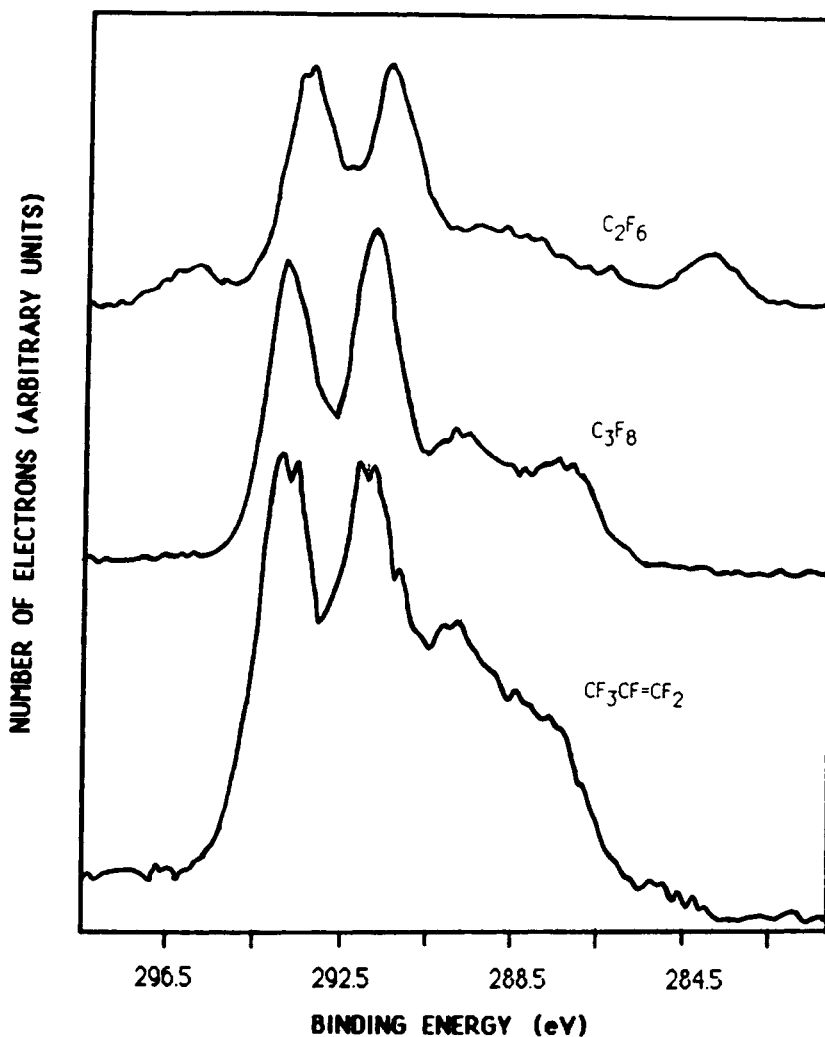

Fig. 2. C_{1s} spectra of fluorinated surfaces obtained with the different monomer gases at pressure 0.25 torr and RF power 30 W for reaction time 10 min.
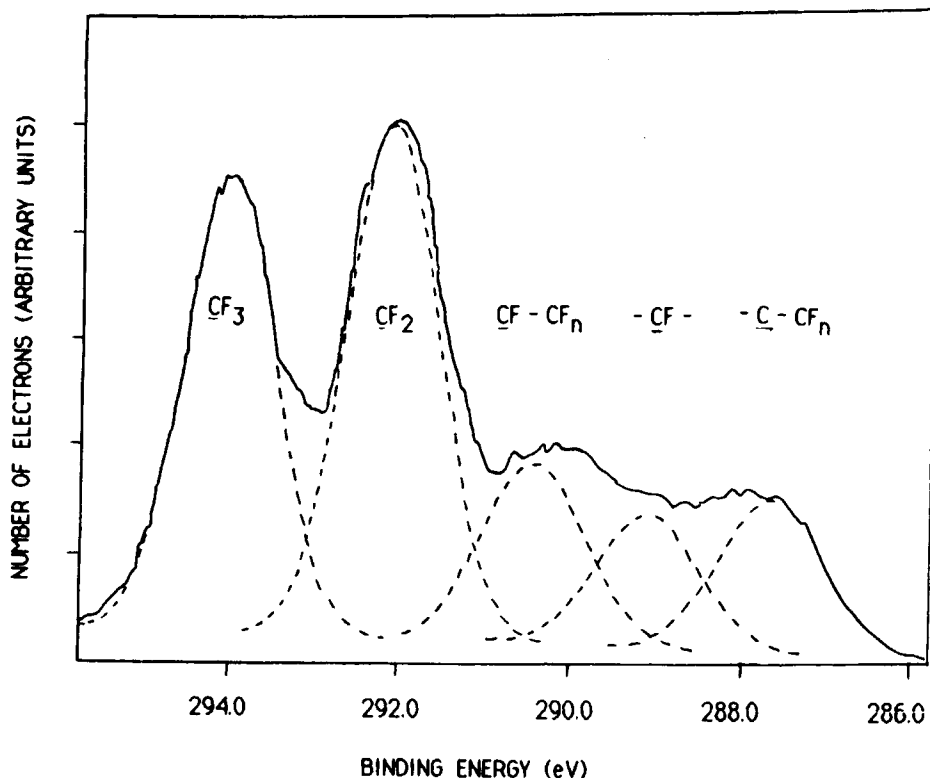
Fig. 3.   Resolved C_{1s} spectra for fluorinated surfaces obtained with C_3F_8 gas.

—CF— (289.0 eV), and —$\underline{C}$—CF_n (287.5 eV).[3,7] All the samples also showed strong F_{1s} and weak O_{1s} signals. The weak oxygen signals may arise because of trapped free radicals reacting with oxygen in the air[8,9] or glass showing through a thin plasma film. Pinholes in thin areas in the film seem an unlikely possibility since no potassium was noted in the ESCA spectra. Since only small amounts of oxygen were detected, the contributions to the C_{1s} spectra from carbon bonded to oxygen was considered to be negligible.

Of the three fluorinated gases tried, C_3F_8 and $CF_3CF{=}CF_2$ are found to have higher deposition rates than C_2F_6, consistent with previous reports in the literature.[10] This is evident since the glass surface is completely covered at 10 min by the polymer deposit using the former two gases compared to the surface treated with C_2F_6. For the C_2F_6 (Fig. 2), the higher binding energy peak (~296.7 eV) visible in the spectrum is attributed to potassium $K_{2p_{1/2}}$ arising from the glass substrate, suggesting a thinner coating. Also on this spectrum, the peak at 285.0 eV is presumed to be related to the hydrocarbon contamination present on the glass surface.

The fluorine-carbon ratio of the surfaces obtained with the different gases can be used to estimate the degree of fluorination of the polymer deposit. Table I gives the F/C ratios at the three different locations within the re-actor. The fluoropolymer obtained with C_2F_6 generally shows lower F/C ratios. This is not unexpected, since C_2F_6 monomer gas, with the highest

TABLE I
Atomic Percentages and Ratios of RF-Plasma-Treated Glass at Different
Locations Within the Reactor[a]

Gas	F/C (Theory)	Si	C	O	F	F/C	C/O
Upstream							
C_2F_6	3.0	10.38	30.87	20.80	37.95	1.18	1.48
C_3F_8	2.6	1.72	33.88	—[b]	65.70	1.64	—
$CF_3CF{=}CF_2$	2.0	0.0	41.72	1.12	57.16	1.47	37.25
Center							
C_2F_6	3.0	7.98	47.93	—[b]	44.08	1.04	—
C_3F_8	2.6	0.0	24.84	—[b]	75.16	1.63	—
$CF_3CF{=}CF_2$	2.0	0.0	40.39	1.37	58.24	1.44	29.48
Downstream							
C_2F_6	3.0	6.38	37.16	—[b]	56.46	1.52	—
C_3F_8	2.6	0.0	37.60	0.10	62.10	1.70	376.00
$CF_3CF{=}CF_2$	2.0	0.0	40.13	0.99	58.88	1.37	40.54

[a] At 0.25 torr, 30 W, 10 min.
[b] Measurement not taken.

F/C (= 3) ratio, results in more etching than polymerization, that is, poor film deposition. Also, surfaces with the lowest oxygen contents consistently have the highest F/C ratios. This suggests either hydrocarbon contamination on bare glass areas that occurs after removal from the reactor or an effect of oxygen on the chemistry of fluoropolymer films.

The data obtained from the resolution of the C_{1s} spectra, presented in Table II, show variations in the proportions of the various chemical groups present on the surface at three locations in the reactor. Table II demonstrates that C_2F_6 would not be a good choice as a monomer gas to prepare surfaces rich in —CF_3 and —CF_2— groups, at these reaction conditions.

Etching and polymerization both occur to varying degrees during the reaction, depending upon precise discharge conditions in the reactor. A high-energy input would result in a higher abstraction of F_2 leading to an en-

TABLE II
Contribution (%) of Carbon Functionalities to Total C_{1s} ESCA Signal on RF-Plasma-
Deposited Fluorinated Surfaces[a]

Location	Gas	% CF_3	% CF_2	% CF—CF_n	% CF	% —C—CF_n
Upstream	C_2F_6	12.86	22.62	8.53	10.00	7.54
	C_3F_8	29.72	38.24	12.62	9.30	10.13
	$CF_3CF{=}CF_2$	30.17	26.94	10.04	17.84	15.02
Center	C_2F_6	12.39	12.63	5.87	10.00	7.54
	C_3F_8	27.89	35.02	12.63	11.21	13.25
	$CF_3CF{=}CF_2$	29.02	26.86	17.42	14.13	12.57
Downstream	C_2F_6	19.97	31.31	11.57	8.40	5.96
	C_3F_8	30.99	34.72	13.06	9.62	11.62
	$CF_3CF{-}CF_2$	28.72	29.60	15.03	14.35	12.29

[a] At 0.25 torr, 30 W, 10 min.

hancement in etching compared with polymerization.[11] The data obtained in this study show that the polymer deposition on the downstream end of the reactor is always higher compared with the upstream and center locations. Studies on the deposition rates that occur in a C_3F_8 plasma indicate that the reactive species in the plasma deposit only after they have traveled a certain distance in the reactor and have an energy appropriate for deposition. These studies were done by placing aluminum foils at different locations within the reactor and striking a C_3F_8 plasma at different powers for a given (0.25 torr) pressure. The deposition rate was determined by weighing the foils. The results are shown in Fig. 4. As is evident from the figure, the location of the deposition maxima shifts toward the downstream end of the reactor as the RF power is increased. This suggests that the maxima occurs at a particular electron energy, and as the RF power is increased, that particular energy is attained further downstream. A future publication will address this issue in a more quantitative fashion.

As has been mentioned earlier, ethylene oxide was used to prepare the higher energy surfaces. Figure 5 shows C_{1s} spectra of the ethylene oxide plasma film deposited at three different pressures (0.05, 0.1, and 0.50 torr). A comparison of the three spectra shows complete coverage of the glass substrate at 0.1 torr pressure since the potassium peaks are absent here. A resolution of a C_{1s} spectrum (0.1 torr, Fig. 6) suggests at least four distinct types of carbon functionalities. The primary peak at ~285.0 eV has been
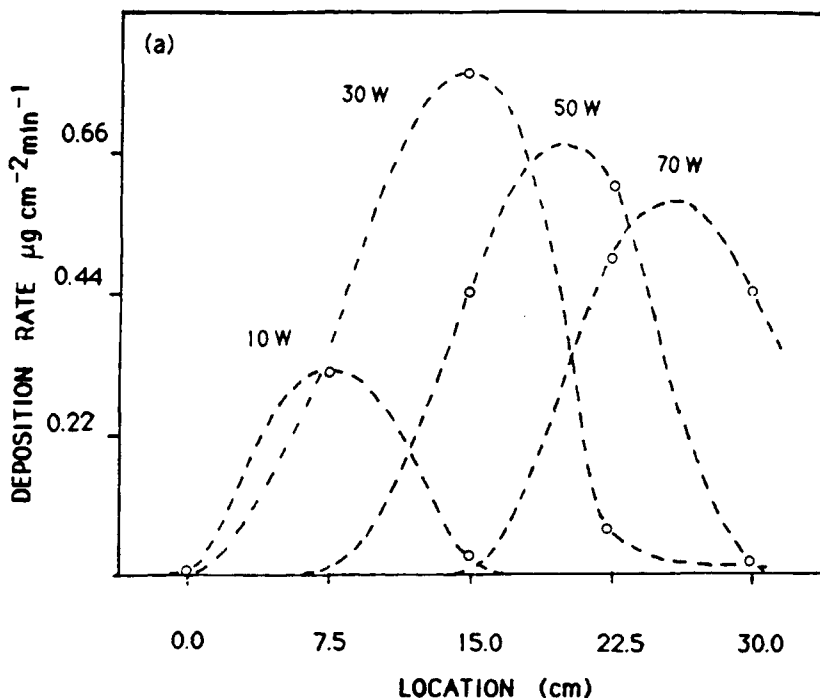

Fig. 4. The deposition rate in a C_3F_8 plasma as a function of location for different RF powers.
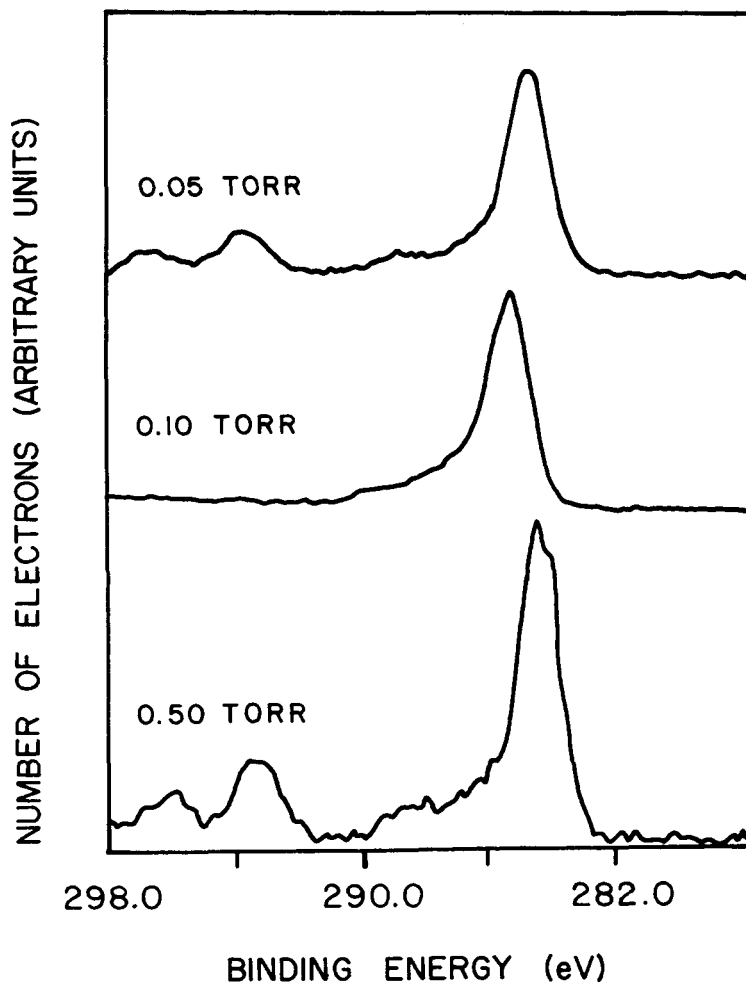
Fig. 5. C_{1s} spectra of surfaces prepared with C_2H_4O at three different pressures at RF power 30 W for reaction time 10 min.

assigned to carbons in a hydrocarbonlike environment based upon experiments with thin (<50 Å) C_2H_4O depositions on polytetrafluoroethylene film. The —CF_2— peak, observed through the C_2H_4O deposition, could then be used for binding energy referencing. These binding energy referencing experiments will be described in detail in a later publication. The "tail" in Fig. 6 extending to the higher binding energies can be assigned to a variety of oxygen-containing species. The component at 286.5 eV can be due to carbon singly bonded to oxygen (probably hydroxyl or ether carbons). Peaks at 287.8 and 283.9 eV can belong to such groups as ketones or aldehydes and carboxylic acids or carboxylic esters, respectively.[12,13]

When C_3F_8 is mixed with C_2H_4O in different ratios, changes in chemistry are revealed by ESCA. Figure 7 shows the C_{1s} spectra of a series of C_3F_8—C_2H_4O surfaces. As the ethylene oxide fraction is increased, the fluor-
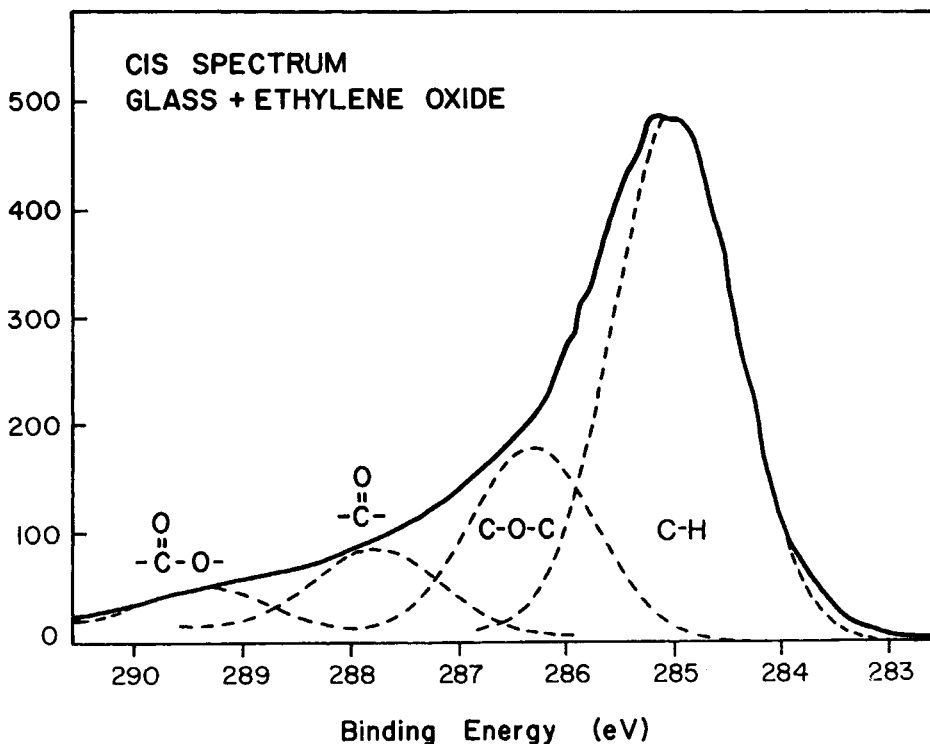
Fig. 6. Resolved C_{1s} spectrum of surface obtained with C_2H_4O plasma.

inated groups on the surface diminish in intensity while the hydrocarbon and carbon-oxygen type functional groups become more pronounced. At a 50:50 ratio of C_3F_8 to C_2H_4O, only trace amounts of fluorine can be detected in the film. C_2H_4O shows a higher propensity toward incorporation than C_3F_8. This may be due to the C—O bond having a lower bond energy (84.0 kcal/mol) and, therefore, breaking more easily compared with a C—F bond with a bond energy of 102 kcal/mol.

A series of chemically nonhomologous liquids with a range of surface tensions were used for contact-angle measurements on these surfaces. The critical surface tension γ_c, an approximation to the surface free energy of the surfaces, was then obtained by using the Zisman method. The γ_c values of the films prepared using C_3F_8 and C_2H_4O are listed in Table III. A wide range of γ_c values was obtained.

The extremely low γ_c values obtained for the C_3F_8 films, as shown in Fig. 8, may reflect inherent limitations in the contact-angle method attributable to the use of liquids exhibiting substantial polar character on extremely nonpolar surfaces.[14] However, since PTFE sheets under the same critical surface tension measurement conditions gave values of 18–19 dyn/cm, this strongly suggests that these plasma-deposited fluorinated surfaces are less wettable than Teflon. Blending of additional oxygen with the C_2H_4O or pre-etching with oxygen can result in films with higher γ_c than those obtained with the pure C_2H_4O gas.
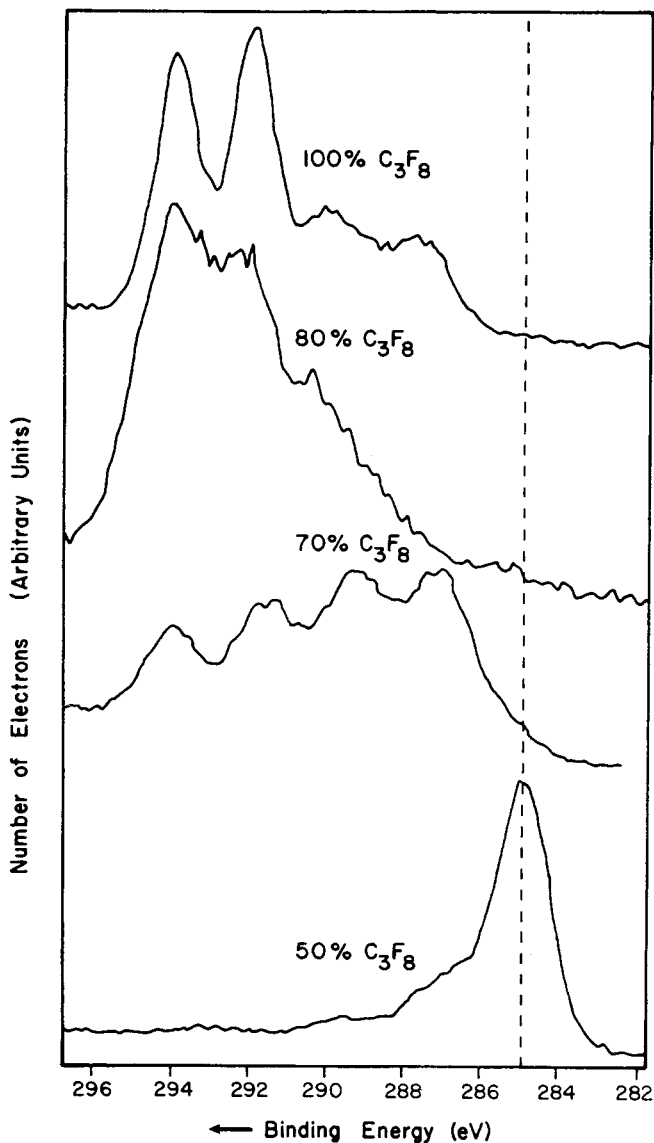
Fig. 7. C_{1s} spectra of surfaces prepared by using mixtures of C_3F_8 and C_2H_4O at pressure 0.25 torr and power 30 W for reaction time 10 min.

TABLE III
γ_c for RF plasma films

C_3F_8	C_2H_4O	O_2	γ_c (erg/cm^2)
100	—	—	1 ± 4
50	50	—	22 ± 7
—	100	—	$40^a \pm 4$
—	100	—	$43^b \pm 6$
—	80^c	20^c	45 ± 9

[a] Glass pre-etched with argon plasma.
[b] Glass pre-etched with oxygen plasma.
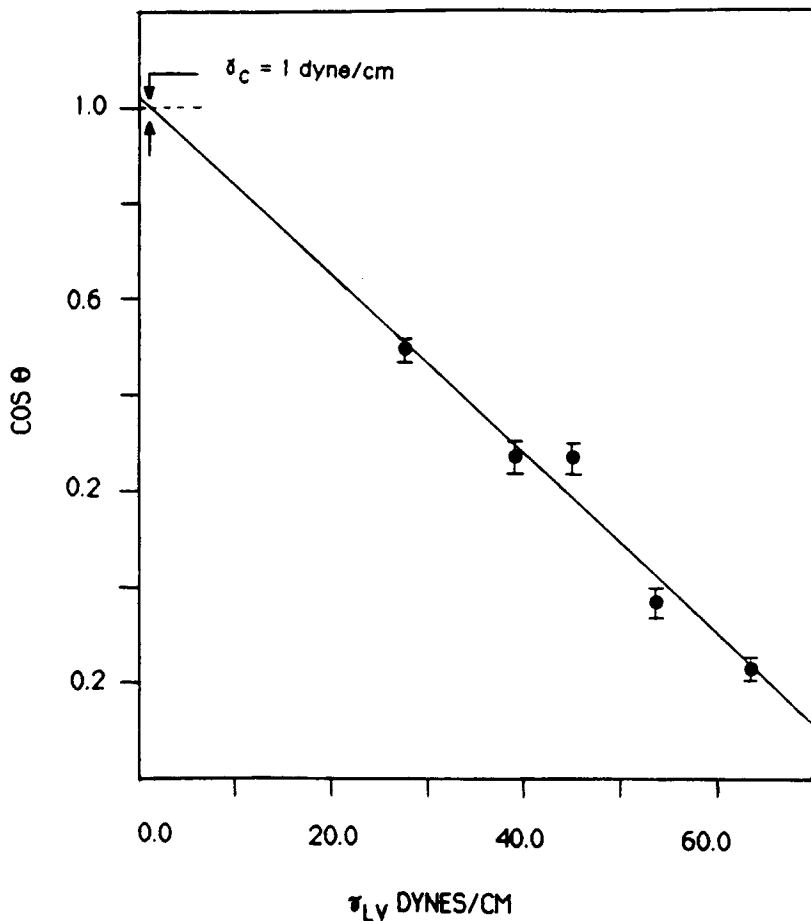[c] Approximate values.

Fig. 8.   Determination of γ_c from a Zisman plot for a surface treated with perfluoropropane plasma.

CONCLUSIONS

In this work, we have demonstrated that C_3F_8 and C_2H_4O gases can be used to tailor-make plasma polymers of varying surface energies. By varying the inlet gas ratios, a graded series of surfaces with a wide range of γ_c values is possible. Also C_2F_6, which is considered to be mainly an etching gas, can be polymerized under certain sets of reaction conditions. Experiments are underway to study the organization and nature of protein films adsorbed on these surfaces and the nature of biologic interactions with these films.

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