Surface and Bulk Compositional Characterization of Plasma-Polymerized Fluorocarbons Prepared from Hexafluoroethane and Acetylene or Butadiene Reactant Gases

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Received 10 May 1996; accepted 24 July 1996

ABSTRACT: The surface tension and surface and bulk composition of plasma-polymerized fluorocarbon films (PPFCs) prepared from hexafluoroethane (HFE) and either acetylene or butadiene reactant gases were determined. Increasing the HFE reactant gas content from 0 to 100% gave an increase in the amount of fluorine incorporated in the films and a shift to incorporation of more highly fluorinated species at the film surface, according to X-ray photoelectron spectroscopy (XPS) data. Hydrogen levels in the films were determined by forward recoil spectrometry (FRS) and were shown to be inversely dependent on HFE concentration in the reactant gas feed and dependent on hydrocarbon co-reactant type. The compositional changes were mirrored by changes in the surface tension from 52 to 20 mN/m. XPS and surface tension results demonstrated that fluorine incorporation at the surface of the PPFCs is significantly reduced when butadiene, rather than acetylene, is used as a co-reactant gas with HFE. The differences are attributed to higher concentrations of hydrogen, which acts as a scavenger for reactive fluorine atoms and as an inhibitor in the $CF_x \rightarrow CF_{x+1}$ reaction, and of carbon, decreasing the F/C ratio, when butadiene is used as the hydrocarbon source. Furthermore, potential changes in surface composition due to energetic ion bombardment are discussed. Three factors were suggested as strongly influencing the composition and the properties of the PPFCs: 1) the energy input into the plasma polymerization reaction, 2) the amount and type of fluorine scavenging reagent introduced with the HFE, and 3) the elemental composition of the reactant gases. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 409–421, 1997

Key words: plasma polymerization; fluorocarbons; XPS; surface tension; RBS/FRS

INTRODUCTION

The surface characteristics of many materials can be tailored for specific applications through low-temperature plasma deposition of thin polymer films.[1] Reaction of monomers in the plasma gives formation of reactive ions, radicals, and excited molecules that react to form highly crosslinked films. The films do not possess the repeat structure characteristic of conventional polymers. The interaction of the energy input into the reactor and the gaseous monomers produces a product film whose structure and properties are highly process-dependent.[2–4] Because of the complexity of the process, much remains

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Journal of Applied Polymer Science, Vol. 66, 409–421 (1997)
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to be understood in the field of plasma polymerization.

Plasma polymerization of fluorocarbons can produce surface coatings with unique properties.[5] The use of plasma-polymerized fluorocarbon coatings (PPFCs) to produce low-surface-energy materials has led to their application as hydrophobic, protective,[6,7] and biocompatible[8,9] coatings. PPFCs are also useful in such diverse applications as coatings on gas permselective membranes.[10]

Initial work on PPFCs suggested that only cyclic or unsaturated monomers could be used to generate polymer films.[11] Numerous studies using hexafluoroethane (HFE) as the fluorocarbon monomer support the assertion.[12–15] However, it has been demonstrated that PPFCs can be produced using saturated monomers, such as HFE, if the substrate is capable of participating in the deposition process.[6,16]

The effect of substrate arises from the dual nature of fluorocarbon plasmas. Reaction of fluorocarbons in a plasma reactor represents a balance between etching by highly reactive fluorine atoms and polymerization.[2,13,17,18] For the case of HFE, Yasuda and Hsu suggested that the balance between the concentration of CF_2 and CF_3 radicals in the plasma controls the extent of film deposition on the substrates.[11] d'Agostino et al.[17] suggested an "activated growth model" in which specific surface sites are activated by energy transfer from the plasma to the surface site, typically by ion bombardment. Polymerization at the activated sites occurs by radical recombination. O'Keefe and Rigsbee[15] used transmission electron microscopy (TEM) to show that the initial phase in plasma polymerization of HFE with a graphite sputter target occurs through localized growth of islands of fluorocarbon on the substrate, supporting the activated growth model. Polymerization of HFE alone occurs on organic substrates because of detachment of hydrogen from the substrate, induced by energetic species in the plasma. The hydrogen acts as a scavenging reagent for fluorine etchant species, permitting the polymerization reaction to dominate over the etching reaction.

The addition of hydrogen (H_2) as a co-reactant gas with HFE in a plasma polymerization reaction has permitted deposition of fluorocarbon films on both reactive and non-reactive substrates.[14,17,19,20] Use of a graphite sputter target during plasma polymerization of HFE also has been effective in producing fluorocarbon coatings.[15] However, the use of a hydrocarbon co-reactant gas with HFE has not been explored.

In this article, the surface tension and surface and bulk composition of a series of PPFCs formed from HFE and acetylene or butadiene reactant gases on stainless steel substrates are analyzed. In order to overcome known problems of adhesion of PPFCs to their substrates,[21] an hydrogenated amorphous carbon (a-C : H) intermediate layer was deposited. Since adhesion of plasma-polymerized a-C : H films to metal substrates can be weak,[22] a thin silicon adhesion-promoting layer[23] was deposited first on the stainless steel substrate. The fluorocarbon films, prepared from reactant gas mixtures containing 0–100% hydrocarbon co-reactant, were deposited atop the a-C : H layer and characterized by contact angle, X-ray photoelectron spectroscopy (XPS), forward recoil spectrometry (FRS), and Rutherford backscattering spectrometry (RBS). Some variations in process parameters, as well as feed gas composition, were explored.

EXPERIMENTAL

Sample Preparation

A commercial parallel-plate plasma reactor (Plasma-Therm model 730) was used for deposition of all films. The deposition chamber consists of two 0.28-m outer diameter electrodes, a grounded upper electrode, and a powered lower electrode. The chamber walls are grounded, and the chamber is 0.38 m in diameter. Removal of heat from the electrodes is accomplished via a fluid jacket. The reactor volume is 0.006 m^3, and the active discharge volume is 0.0025 m^3. Four outlet ports (0.04 m^3), arranged 90° apart on a 0.33-m diameter circle on the lower wall of the reactor, lead the gases to a Roots blower backed by a mechanical pump. A capacitance manometer monitored the chamber pressure that was controlled by an exhaust valve and controller. The base pressure in the reactor is always < 1 mTorr. A 600-W generator delivers radio-frequency (RF) power at 13.56 MHz through an automatic matching network to the reactor. The reflected power was typically < 4 watts. The gases used in the deposition flowed radially outward from the perforated upper electrode in a shower head configuration in the chamber. Type 301 stainless steel substrate, 76.2 μm thick, was adhered to the lower, powered electrode for cleaning and sample deposition using double-stick tape. The substrate was coated nominally at room temperature.

The stainless steel substrate was cleaned prior

Table I Conditions for Deposition of Acetylene/Hexafluoroethane Films

Sample	Step	HFE Reactant Gas (%)	Gas Flow Rate (sccm)			RF Power (W)	Pressure (mTorr)	Negative Bias Voltage (V)	Duration (min)
			C_2H_2	Ar	HFE				
Ac/HFE-100	1	0	3.2	12.8	0	100	50	220	2
	2	67	3.2	12.8	6.4	100	100	135	1
	3	80	3.2	12.8	12.8	100	100	158	1
	4	86	3.2	12.8	19.2	100	100	158	1
	5	90	3.2	12.8	28.8	100	100	120	3
	6	100	0	0	28.8	100	100	70	2
Ac/HFE-90	1	0	3.2	12.8	0	100	50	225	2
	2	90	3.2	12.8	28.8	100	100	95	8
Ac/HFE-70	1	0	9.6	38.4	0	100	50	230	2
	2	70	9.6	38.4	22.4	100	100	128	8
Ac/HFE-50	1	0	16	64	0	100	50	230	2
	2	50	16	64	16	100	100	128	4
Ac/HFE-25	1	0	24	96	0	100	50	216	2
	2	25	24	96	8	100	100	127	4
Ac/HFE-0	1	0	32	116	0	100	100	155	6
Ac/HFE-90B	1	0	3.2	12.8	0	200	50	315	2
	2	90	3.2	12.8	28.8	200	50	305	8

to film deposition by exposing the surface to a pure argon plasma obtained using a flow rate of 50 sccm (std. cm^3), a pressure of 3.3 Pa, and an RF power of 150 W for 1 min. The silicon layer, ~ 10 nm thick, was deposited by exposing the cleaned substrate to a 2% silane gas in argon at a flow rate of 50 sccm, a pressure of 3.3 Pa, and an RF power of 150 W for 4 min. The a-C : H and fluorocarbon layers were deposited for each sample using the conditions listed in Tables I and II.

Samples were labeled according to the reactant feed gases used to produce the outermost layer. Samples prepared from acetylene (Ac) and hexafluoroethane (HFE) feed gases were labeled Ac/HFE-xx, where xx indicates the percentage of HFE present as reactive feed gas. A final letter at the end of a sample label is used to distinguish samples prepared from identical feed gas compositions but under different processing conditions. Note that the argon present in the feed gas is not used in calculation of the percentage of HFE. The flow rate of argon was always maintained at four times that of the hydrocarbon. Samples prepared from butadiene (Bu) are labeled similarly, except that the nomenclature begins with Bu/HFE.

Surface Tension Measurement

The contact angles of each sample with water and with diiodomethane were determined. An average of five measurements was used in each case. The surface tension was calculated using these data and the method described by Owens and Wendt.[24]

Table II Conditions for Deposition of Butadiene/Hexafluoroethane Films

Sample	Step	HFE Reactant Gas (%)	Gas Flow Rate (sccm)			RF Power (W)	Pressure (mTorr)	Negative Bias Voltage (V)	Duration (min)
			C_4H_6	Ar	HFE				
Bu/HFE-95	1	0	1.77	12.8	0	100	50	220	2
	2	95	1.77	12.8	28.8	100	100	100	8
Bu/HFE-70	1	0	9.6	38.4	0	100	50	220	2
	2	70	9.6	38.4	22.4	100	100	147	8
Bu/HFE-50	1	0	16	64	0	100	50	216	2
	2	50	16	64	16	100	100	145	4
Bu/HFE-0	1	0	23	92	0	150	100	250	2
	2	0	23	92	0	100	100	185	4

X-ray Photoelectron Spectroscopy

The X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Physical Electronics 5601 photoelectron spectrometer with monochromatic Al Kα X-rays (1486.6 eV). The X-ray source was operated with a 7-mm filament at 200 W. Charge neutralization for these insulating materials was accomplished by flooding the sample surface with low-energy electrons ($\leq$25 mA emission current, $\leq$0.5 eV bias voltage) from an electron gun mounted nearly perpendicular to the sample surface. The pressure in the spectrometer during analysis was typically below 6.5×10^{-8} Pa. For the high-resolution spectra, the analyzer operated at a pass energy of 11.75 eV. All spectra were referenced to the C 1s peak for neutral (aliphatic) carbon atoms, which was assigned a value of 284.6 eV. Peak-fitting to determine CF, CF_2, and CF_3 contents was done using a least-squares deconvolution routine employing line shapes with 90% Gaussian/10% Lorentzian character. Spectra were taken at a 45° electron takeoff angle (ETOA), which corresponds to an analysis depth of ~ 5 nm.

Forward Recoil Spectrometry and Rutherford Backscattering Spectrometry

Rutherford backscattering spectrometry (RBS) was used to measure the atomic concentrations of fluorine, carbon, and other elemental components as a function of depth. A probing beam of 2 MeV He^{2+} ions impinged at near normal incidence and backscattered particles were detected, at an angle of 171.5°, with a surface barrier detector having an energy resolution of 15 keV full width at half maximum.

Forward recoil spectrometry (FRS) was employed to determine the depth profile and concentration of hydrogen using a probing beam of 3-MeV He^{2+} ions. The sample was tilted 78° from normal incidence and a second surface barrier detector was positioned at a scattering angle of 24°. The acceptance angle of the detector was limited by a 1-mm-wide slit. A Mylar foil, 15.24 μm thick, was placed in front of the detector to stop forward-scattered He particles. This foil deteriorates the energy resolution of the detection electronics to ~ 50 keV full width at half maximum. RBS spectra were taken simultaneously with FRS spectra but were used only for normalization purposes. For each sample, the 2-MeV RBS and 3-MeV FRS data were modeled simultaneously, using the program RUMP,[25] to obtain the elemental composition as a function of depth.

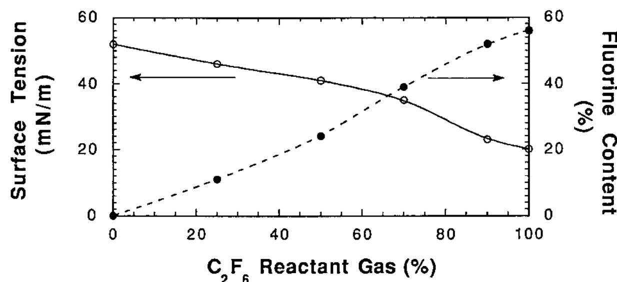

Figure 1 Influence of amount of HFE (C_2F_6) reactant gas in the feed stream on the surface tension and surface fluorine content of Ac/HFE films.

RESULTS AND DISCUSSION

Films Formed from Acetylene and Hexafluoroethane Reactant Gases

Fluorocarbon compounds are unique among organic compounds because they produce a high concentration of free radicals in plasma polymerization.[11] The only organic compounds producing a similar concentration are acetylene and ethylene.[11] Because of this unique property of acetylene, it was explored as the first co-reactant gas in combination with HFE.

A series of films were deposited on pre-coated stainless steel substrates using a variety of HFE-to-acetylene ratios in the feed gas. Contact angle data were used to calculate the surface tensions of the films, and the results are presented in Figure 1. The surface tensions of the films varied from a high value of 52 mN/m for the film prepared from the pure acetylene reactant gas (Ac/HFE-0) to 20 mN/m for the film prepared from the pure HFE reactant gas (Ac/HFE-100). The value for Ac/HFE-100 closely matches that determined for a film deposited from HFE reactant gas in an RF glow discharge reactor onto a polyethylene substrate, measured at 21 mN/m.[16] A gradual decrease in surface tension is seen as the HFE feed gas concentration is increased from zero to 70%; however, a significant drop in surface tension is seen as the concentration is increased further from 70% to 90% HFE reactant gas. In concert with the decrease in surface tension, the water contact angle measured for these films increased from 63° for the pure acetylene sample (Ac/HFE-0) to 83° for the sample prepared from 70% HFE (Ac/HFE-70), and then jumped to 101° for the film prepared from 90% HFE (Ac/HFE-90).

Sample Ac/HFE-90B, produced by increasing the power and lowering the pressure used during deposition compared to Ac/HFE-90, had a surface

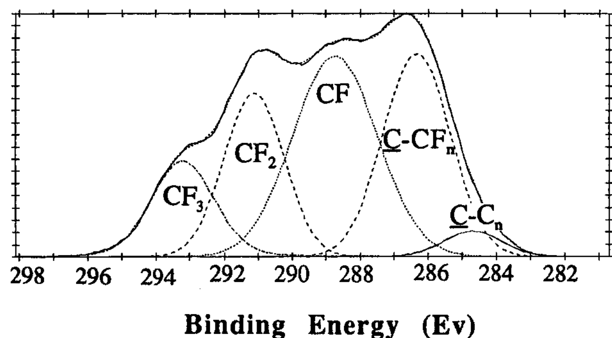

Figure 2 XPS C 1s spectrum for Ac/HFE-100.

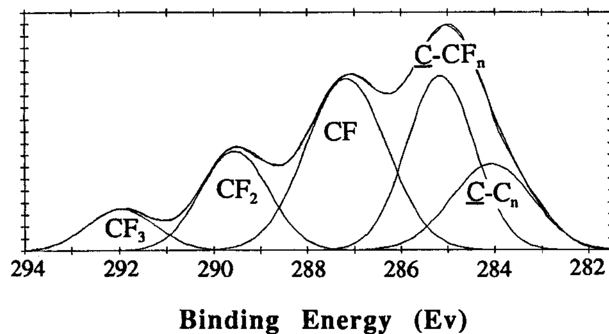

Figure 4 XPS C 1s spectrum for Ac/HFE-70.

tension of 31 mN/m and a water contact angle of 93°, in contrast to the surface tension of 22 mN/m and water contact angle of 101° measured for Ac/HFE-90. The increase in bias voltage associated with these process conditions results in significantly higher levels of ion bombardment at the surface during film growth, which leads to a significantly altered atomic distribution at the coating surface. A lower fluorine concentration at the film surface results, bringing a concomitant decrease in the water contact angle and an increase in the surface tension of the film.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition of the films. The C 1s spectra for films prepared from acetylene and HFE reactant gases are shown in Figures 2–8. The spectra were deconvoluted into five peaks, assigned in order of decreasing binding energy to CF_3, CF_2, CF, $\underline{C}$-CF_n, and $\underline{C}$-C_n, as described elsewhere.[26] The relative concentrations of the three fluorocarbon species are listed in Table III. The film formed from the pure HFE reactant gas shows a high concentration of fluorine in the film surface. Unlike plasma-polymerized films formed from an HFE reactant gas in combination with a graphite sputter target,[15] the predominant species in the C 1s spectra was not CF_2, suggesting that difluorocarbene was not the predominant reactive species in the plasma. Indeed, for the Ac/HFE-100 film, the amounts of CF, CF_2, and CF_3 detected were nearly equal, suggesting an HFE decomposition mechanism similar to that proposed by d'Agostino[14] was followed. In the presence of a hydrogen source, the mechanism provides for decomposition of HFE into $2CF_3$, which can further decompose into CF_2 and CF radicals.

As the concentration of HFE reactant gas decreases, however, the fluorocarbon distribution shifts to favor the less highly fluorinated species. The exception is the Ac/HFE-90 sample, in which the CF_3 concentration has increased, while the CF_2 and CF concentrations remain unchanged. Masuoka and Yasuda,[19] in their studies of films formed from HFE and H_2 reactant gases, noted an optimal concentration of non-fluorinated reactant gas that permits maximum CF_3 incorporation in the films. A similar phenomenon is detected here when the co-reactant gas is acetylene. The ratio of CF_3 groups to CF groups detected in the films increases from 1.14 for Ac/HFE-100 to 1.42 for Ac/HFE-90, then drops to 0.6 for Ac/HFE-70, and

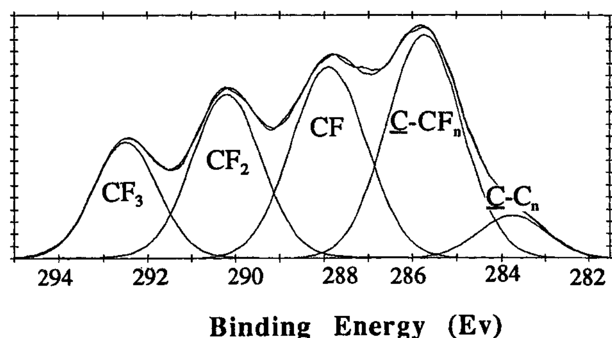

Figure 3 XPS C 1s spectrum for Ac/HFE-90.

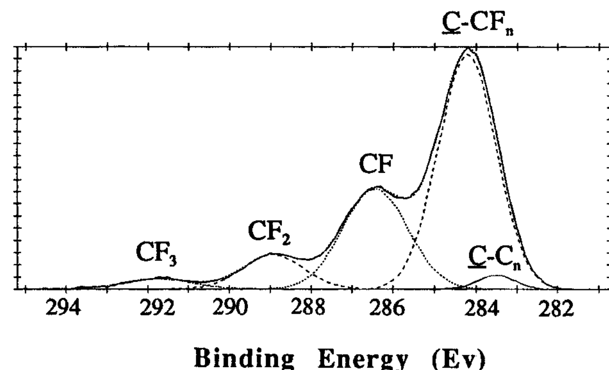

Figure 5 XPS C 1s spectrum for Ac/HFE-50.

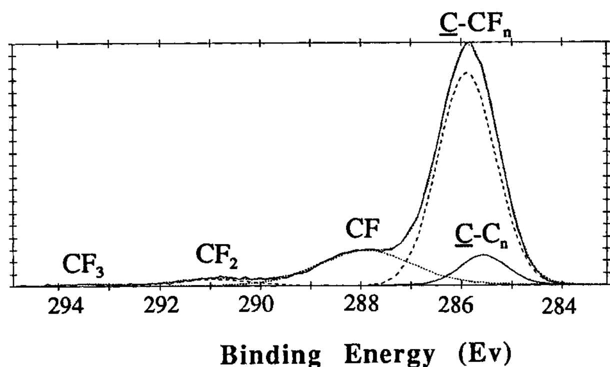

Figure 6 XPS C 1s spectrum for Ac/HFE-25.

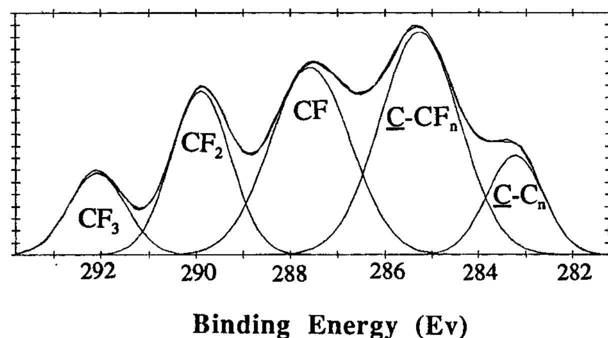

Figure 8 XPS C 1s spectrum for Ac/HFE-90B.

still further to 0.37 and 0.13 for Ac/HFE-50 and Ac/HFE-25, respectively. The initial increase may be attributed to the presence of hydrogen in the acetylene gas that can act as a scavenging reagent for reactive fluorine species in the plasma, favoring polymerization over etching.[17] The decrease may arise from two sources. First, as the hydrocarbon concentration is increased, the greater hydrogen concentration further inhibits the recombination processes of F atoms with CF_x, which leads to CF_{x+1}, resulting in a decrease in the concentration of the more highly fluorinated species. Changes in the concentration of radicals and the distribution of fluorinated species with feed gas ratios also has been seen in HFE/H_2 system.[20] Second, a higher level of ion bombardment of the growing surface with increasing hydrocarbon reactant feed gas concentration may cause a shift in the distribution of fluorinated species that are ultimately deposited in the film to the less fluorinated species.

An increase in the crosslinking or branching structures in the film (C—C species) also is seen with decreasing HFE reactant gas concentration. This is consistent with both a change in the radical distribution produced from the HFE and with incorporation of species generated from decomposition or reaction with the acetylene feed gas.

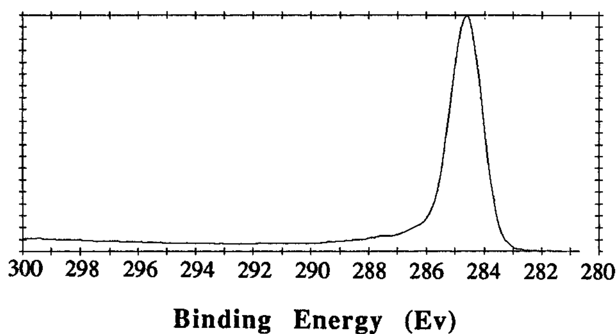

Figure 7 XPS C 1s spectrum for Ac/HFE-0.

The C 1s spectra for the Ac/HFE-0 sample shows evidence of species other than pure hydrocarbon on the film surface. Small peaks in the 286–288 eV binding energy range are evidence of carbon–oxygen bonds on the film surface. Although these could result from the presence of contaminant oxygen gas in the feed, it is more likely that they arise from reaction of atmospheric oxygen with residual reactive species (e.g., long-lived radicals) on the film surface when the samples are removed from the reactor.[16]

The effect of increasing the power during film deposition is seen by comparing the results for Ac/HFE-90B (Fig. 8) with those for Ac/HFE-90 (Fig. 3). Increasing the deposition power favors the appearance of less-fluorinated species in the film. The CF_3/CF ratio decreases from 1.42 for Ac/HFE-90 to 1.08 for Ac/HFE-90B, and the CF_2/CF ratio increases slightly from 1.19 to 1.29. Again, a higher level of ion bombardment may account for the observed differences, or higher levels of C—F bond cleavage in reactive species in the plasma may have occurred because of the higher power supplied to the reactor. Both cases result in the appearance of less highly fluorinated species in the film. A similar effect of energy input on fluorocarbon species distribution in the film has been observed for HFE/H_2 systems.[19]

The elemental composition of the film surfaces was determined by peak fitting of an XPS survey spectra. Integration of the area under the curves was followed by multiplication by the appropriate sensitivity factor for each element to provide the elemental compositions reported in Table III. The variation of fluorine content with reactant gas composition is shown in Figure 1. A nearly linear increase in fluorine content with increasing HFE reactant gas is observed. The large change in slope of the surface energy versus HFE concentra-

Table III XPS Results for Samples Prepared from Acetylene/Hexafluoroethane Reactant Feed Gases

Sample	Carbon (%)	Fluorine (%)	Oxygen (%)	Other (%)	Carbon Distribution		
					CF (%)	CF_2 (%)	CF_3 (%)
Ac/HFE-100	41.9	56.0	1.6	0.5	14.7	17.1	16.6
Ac/HFE-90	45.4	51.6	2.4	0.5	14.5	17.3	20.6
Ac/HFE-70	53.1	40.7	5.5	0.7	17.5	16.9	10.5
Ac/HFE-50	68.2	24.3	7.2	0.4	19.0	11.4	7.0
Ac/HFE-25	81.9	10.8	6.7	0.5	16.3	5.0	2.1
Ac/HFE-0	90.0	0.2	9.6	0.3	—	—	—
Ac/HFE-90B	50.0	44.8	4.3	0.7	14.2	18.3	13.2

[a] The amount of hexafluoroethane in feed gas relative to the sum of acetylene and hexafluoroethane.

tion is not mirrored in the fluorine content curve, providing further evidence for a change in the types of fluorocarbon species present in the film with changing reactant gas composition. Surface energy is determined not by the fluorine content of the film alone but also by the distribution of fluorine atoms in the fluorocarbon species.

As expected, the carbon concentration in the films increases as the HFE reactant gas concentration decreases. Interestingly, there is also an increase in the oxygen content of the film surfaces with decreasing HFE reactant gas. The presence of long-lived radicals on the surface of the films allows reaction of the film with atmospheric oxygen when the film is removed from the reaction chamber. The increase in oxygen concentration with increasing acetylene reactant gas suggests that these films have greater numbers of long-lived radicals on the surface.[16] This is further evidence for a change in the concentration and distribution of reactive species in the plasma with changing reactant gas composition.

When the HFE reactant gas concentration is held constant but the deposition power is increased, significant changes in the film surface composition are observed. Ac/HFE-90B has higher carbon and oxygen and lower fluorine concentrations than Ac/HFE-90. The higher energy input into the plasma, the lower pressure, and the increased ion bombardment at the growing film surface account for the observed differences. Ion bombardment may change the distribution of both fluorinated and radical species at the film surface, favoring lower fluorine contents and higher levels of long-lived radicals present on the final film surface. Thus, the final fluorine content in the film is less, and more reactive sites for atmospheric oxygen incorporation are left on the film surface.

The hydrogen content and depth composition of the samples were characterized by FRS and RBS. Typical RBS and FRS spectra for coatings are in Figures 9 and 10, where the data for Ac/HFE-90 are presented. Fitting of the experimental data gave the smooth curves shown in the figures, and the results of the curve fitting for all the Ac/HFE samples are included in Table IV. For samples in which silicon was detected, the data were fit to three layers, a silicon layer with hydrocarbon incorporation (layer 1), an a-C : H layer (layer 2), and a fluorinated layer on the outer surface (layer 3).

The data for the first layers show significant incorporation of hydrocarbon in the silicon layer. The porosity of the silicon may be partially responsible for the high levels of hydrocarbon incorporation, as it would permit intermixing of the layers. Failure to detect a silicon layer for Ac/HFE-25 is suggestive of very efficient intermixing of the silicon and a-C : H layers such that the

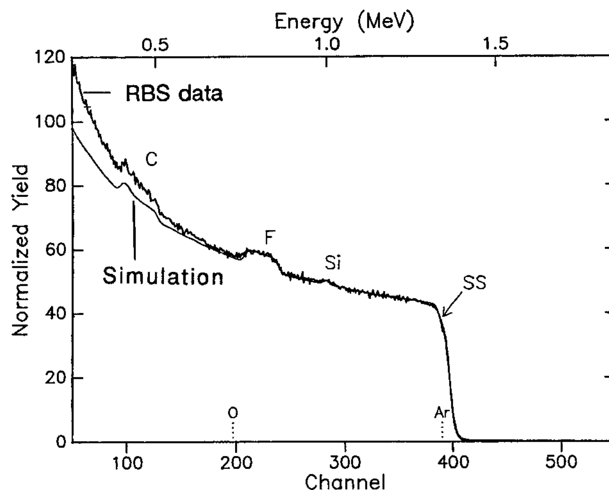

Figure 9 RBS spectrum and model fit for Ac/HFE-70.

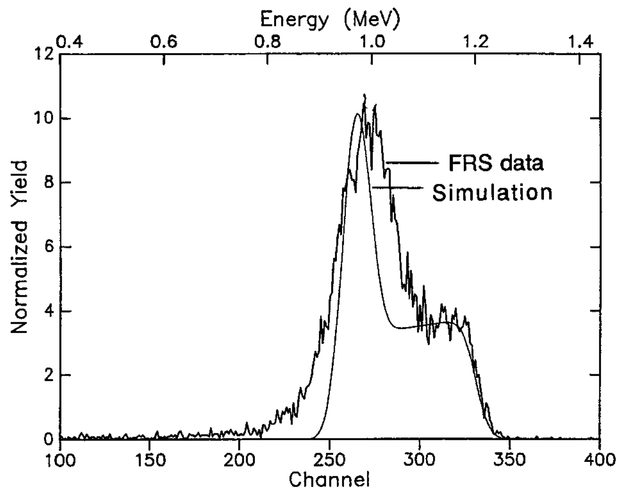

Figure 10 FRS spectrum and model fit for Ac/HFE-70.

silicon layer alone could not be detected by the RBS technique and model fitting. Significant interpenetration of the silicon and a-C : H layers would account for the strong adhesion of the layers observed here and elsewhere.[23]

Some variation in the carbon-to-hydrogen ratio for the second layer is observed. There is a correlation between the C/H ratio and the total gas flow rate, with higher flow rates resulting in lower C/H ratios. A dependence on process parameters, such as gas flow rate, is well known in the realm of plasma-polymerized hydrocarbons.

The fluorine concentration in the outermost layer follows the trend observed in the XPS results. Differences in absolute concentrations measured by XPS and by RBS may result from the differences in sampling areas. XPS samples the elements in the first ~ 5 nm of the sample surface, whereas RBS gives the average composition over the entire layer. The failure to detect fluorine in Ac/HFE-25 may indicate that the fluorine detected by the XPS is concentrated on the surface of the film and is below the detection limit of the RBS technique when the average over a greater depth is performed. Elemental concentrations much less than 10% cannot be detected reliably by RBS.

The variation of hydrogen concentration with feed gas composition in the outermost layer is shown in Figure 11. For the Ac/HFE films, the hydrogen concentration slowly decreases with increasing HFE reactant gas until 70% HFE concentration. At 70% and greater HFE concentrations, the hydrogen content drops to 5% or less, suggesting that most of the hydrogen present in these feed gases is involved in scavenging of reactive fluorine species or is lost in the exhaust gas stream.

Process parameters other than feed gas composition also influence the composition of the outermost layer. The higher power used during the deposition of the outermost layer of Ac/HFE-90B

Table IV RBS and FRS Results for Acetylene/Hexafluoroethane Samples

Sample	Layer	F (%)	C (%)	H (%)	Si (%)	Other
Ac/HFE-100	1	0	78	12	10	0
	2	0	88	12	0	0
	3	40	58	2	0	0
Ac/HFE-90	1	0	0	0	100	0
	2	0	83	17	0	0
	3	45	54	1	0	0
Ac/HFE-70	1	0	80	0	20	0
	2	0	84	16	0	0
	3	37	58	5	0	0
Ac/HFE-50	1	0	75	20	5	0
	2	0	75	25	0	0
	3	10	70	20	0	0
Ac/HFE-25	1	N.D.[a]	N.D.	N.D.	N.D.	N.D.
	2	0	68	32	0	0
Ac/HFE-0	1	0	60	35	5	0
	2	0	63	37	0	0
Ac/HFE-90B	1	0	30	0	70	0
	2	0	79	18	0	3 (Ar)
	3	40	53	7	0	0

[a] N.D., not detected.

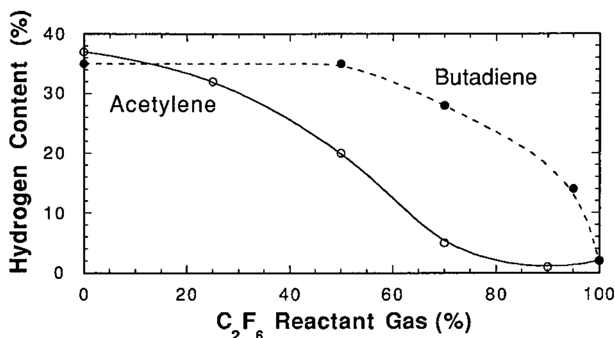

Figure 11 Influence of amount of HFE (C_2F_6) reactant gas in the feed stream on the hydrogen content of the outermost layer of films formed with acetylene and butadiene co-reactant gases.

results in a greater concentration of hydrogen in the fluorocarbon layer than that seen for Ac/HFE-90. Further, as shown by the XPS data, less fluorine is present in the outermost layer when the higher deposition power is used.

Films Formed from Butadiene and Hexafluoroethane Reactant Gases

Changing the hydrocarbon reactant gas from acetylene to butadiene significantly affects the composition and properties of the films. The surface tensions of films formed from the combination of butadiene and HFE reactant gases are reported in Figure 12. A decrease in surface tension with increasing HFE in the feed gas is evident; however, the decrease in surface tension, from 44 mN/m for the pure butadiene coating (Bu/HFE-0) to 33 mN/m for the 95% HFE coating (Bu/HFE-95), is significantly less than that seen for the acetylene co-reactant gas. Indeed, a significant decrease in surface tension from that measured for the pure hydrocarbon film (Bu/HFE-0) is not detected until the HFE constitutes 70% of the reactant feed gas.

Production of lower surface energy, higher fluorine content films through the use of acetylene rather than butadiene co-reactant gas has been observed in the plasma-polymerization of carbon tetrafluoride (CF_4). Inagaki, Tasaka, and Mori[27] produced plasma-polymerized thin films from CF_4 and acetylene co-reactant gases with surface energies as low as 21 mJ/m^2. The F/C ratio they observed for their low surface energy film was 1.8, and they showed XPS data that indicated the presence of CF, CF_2, and CF_3 species at the film surface. Sah et al.[28] saw similar results for films prepared from benzene and CF_4. In contrast, Seth and Babu[29] produced films using butadiene and CF_4 feed gas mixtures and saw no change in water contact angle as the CF_4 feed gas content was varied from 10% to 90%. Also, their infrared spectroscopy results showed evidence only of CF in the film; no CF_2 or CF_3 was detected. Similar differences in fluorine content, in the distribution of fluorinated species, and in surface tension of the films were seen by Visser et al.[30] in films prepared from hexafluoroacetone and acetylene or butadiene reactant gases.

The differences in surface tensions for films prepared from butadiene and acetylene co-reactants with HFE may arise partially from the greater amounts of hydrogen and carbon introduced with the butadiene feed gas. The higher hydrogen levels increase scavenging of reactive fluorine species and inhibit the $CF_x \rightarrow CF_{x+1}$ reaction that produces more highly fluorinated species for incorporation into the film. Furthermore, the higher carbon level decreases the F/C ratio in the feed gas, favoring formation of films with lower fluorine content.

Surface tension differences between films prepared from butadiene and acetylene co-reactants with HFE also may arise from a change in the distribution of reactive species types in the two plasmas. Changes in the reactive species produced from decomposition and recombination reactions involving HFE and the hydrocarbons will result in differences in the composition and bonding of the plasma-polymerized films. Thus, the changes in elemental composition of the films, when changing from acetylene to butadiene reactant feed gases, will not be directly proportional to the elemental stoichiometry of the reactant feed gases. This is consistent with the XPS results for the Bu/HFE samples, discussed below, which show that the carbon content increases with the change from acetylene to butadiene reactant feed gases, but the increase is not in direct proportion

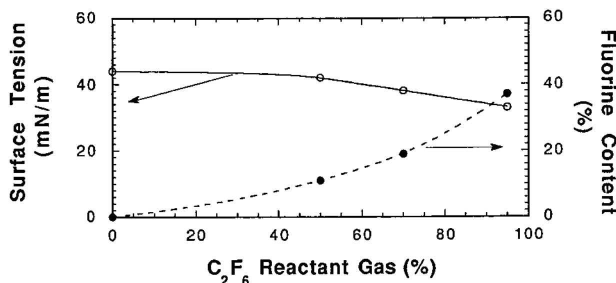

Figure 12 Influence of amount of HFE (C_2F_6) reactant gas in the feed stream on the surface tension and surface fluorine content of Bu/HFE films.

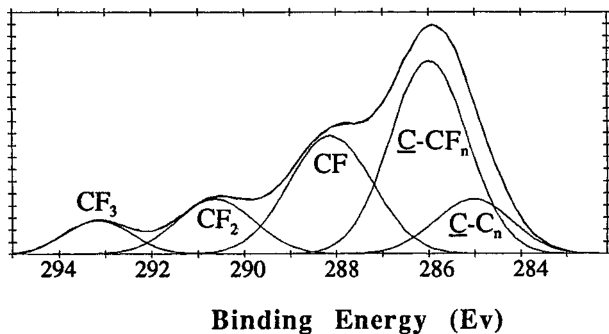

Figure 13 XPS C 1s spectrum for Bu/HFE-95.

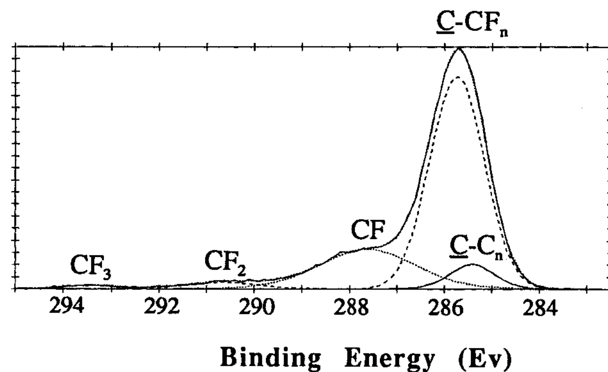

Figure 15 XPS C 1s spectrum for Bu/HFE-50.

to the twofold stoichiometric increase in carbon content of butadiene compared to acetylene.

The XPS data for the Bu/HFE samples, shown in Figures 13–16 and Table V, support the contention that the distribution of reactive species in the plasma may be changing when the hydrocarbon co-reactant gas is changed. The most highly fluorinated film of the series, Bu/HFE-95, has a lower fluorine content and a higher amount of crosslinking or branching (C—C) carbons than either Ac/HFE-100 or Ac/HFE-90. Comparing the butadiene and acetylene samples at 70% and 50% HFE reactant gas concentrations reveals the same trends.

The distribution of fluorinated species in the butadiene samples also favors the less highly fluorinated species. The CF_3/CF ratio for Bu/HFE-95 is 0.69, compared to 1.14 for Ac/HFE-100 and 1.42 for Ac/HFE-90. Note that the other process parameters were held constant as the feed gas was changed from butadiene to acetylene, indicating that the differences in film composition result solely from feed gas type. The CF_3 concentration in the films decreases with increasing butadiene concentration in the feed gas, as observed in general for the samples prepared with acetylene and HFE.

The carbon content of the films follows the trend of the carbon content of the reactant gases in the butadiene/HFE samples. Carbon content increases with increasing butadiene concentration in the reactant gas, and the amount of carbon incorporated into the films prepared with butadiene is significantly higher than that of films prepared with equal amounts of acetylene.

Another unique characteristic of the films prepared from butadiene is the higher levels of oxygen incorporation. Evidence of carbon—oxygen bonds in the Bu/HFE-0 sample is seen in its XPS C 1s spectrum (Fig. 16). Analysis of the elemental compositions of the film surfaces reveals oxygen incorporation at significant levels in all the films prepared from butadiene. The C/O ratio for the Bu/HFE-95 sample is 10.4, compared to 18.9 for the Ac/HFE-90 sample, and the C/O ratios for the pure hydrocarbon films are 6.3 and 9.3 for Bu/HFE-0 and Ac/HFE-0, respectively. Apparently, the presence of residual reactive sites (e.g., long-lived radicals) that can react with atmospheric oxygen is related directly to the amount of hydrocarbon in the film; fluorocarbon species apparently do not leave residual reactive sites on the surface. Differences in oxygen concentrations between the Bu/HFE and the Ac/HFE samples also suggest that variations occur in the distribution

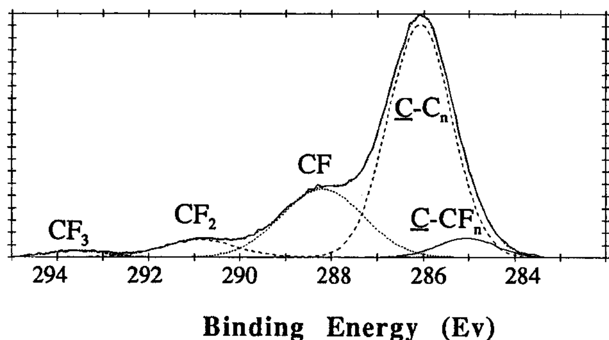

Figure 14 XPS C 1s spectrum for Bu/HFE-70.

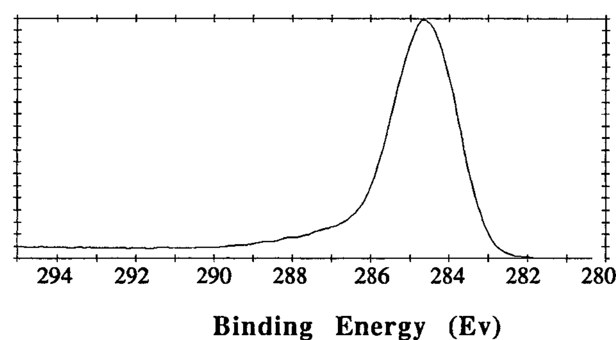

Figure 16 XPS C 1s spectrum for Bu/HFE-0.

Table V XPS Results for Butadiene/Hexafluoroethane Samples

Sample	Carbon (%)	Fluorine (%)	Oxygen (%)	Other (%)	Carbon Distribution CF (%)	CF_2 (%)	CF_3 (%)
Bu/HFE-95	57.1	37.0	5.5	0.4	15.8	13.7	10.9
Bu/HFE-70	72.5	18.9	8.1	0.4	17.4	8.7	3.6
Bu/HFE-50	79.0	10.7	10.1	0.1	18.4	5.1	2.9
Bu/HFE-0	86.1	0	13.6	0.2	—	—	—

of species that are present in the plasma and are incorporated into the films as a result of changing the type of hydrocarbon co-reactant gas.

The results of the RBS and FRS analysis of the Bu/HFE samples are shown in Table VI. Some incorporation of hydrogen and carbon into the silicon adhesion-promoting layer is observed in those samples in which the layer could be detected. Failure to detect a silicon layer in most of the samples is suggestive of a very high degree of intermixing of the silicon and a-C : H layers, so that a silicon layer is left that is too thin to be detected by the RBS technique and subsequent data modeling. Very efficient intermixing is consistent with the high levels of adhesion observed between the two layers. This is also consistent with the high level of intermixing between the silicon and a-C : H layers observed for the samples prepared with acetylene. As with the acetylene/HFE samples, the second, a-C : H layer shows an increase in hydrogen incorporation with increasing gas flow rate. The levels of hydrogen incorporation in this layer are greater when the reactant gas is butadiene, reflecting the higher hydrogen content of this molecule, as well as possible changes in reactive species distribution in the plasma.

Fluorine was detected in the outermost layer of only one Bu/HFE sample, Bu/HFE-95. The fluorine content measured is less than that reported by XPS, probably because of the differences in sampling depth discussed above.

The level of hydrogen present in the outermost layer of Bu/HFE-95 is significantly greater than that seen in a sample prepared from acetylene that has a similar fluorine concentration (Ac/HFE-70), indicating yet again that hydrogen content in the feed gas has an impact on hydrogen content in the films.

The surface and depth compositional analysis data provided by XPS, RBS, and FRS are consistent with the hypothesis offered to explain the surface tension results. A change in the radical distribution in the plasma and in the elemental composition of the films arises when the hydrocarbon coreactant is changed from acetylene to butadiene.

CONCLUSIONS

Films resulting from plasma polymerization of hexafluoroethane (HFE) with acetylene or buta-

Table VI RBS and FRS Results for Butadiene/Hexafluoroethane Samples

Sample	Layer	F (%)	C (%)	H (%)	Si (%)	Other
Bu/HFE-95	1	N.D.[a]	N.D.	N.D.	N.D.	N.D.
	2	0	90	10	0	0
	3	31	55	14	0	0
Bu/HFE-70	1	N.D.	N.D.	N.D.	N.D.	N.D.
	2	0	72	28	0	0
	3	N.D.	N.D.	N.D.	N.D.	N.D.
Bu/HFE-50	1	0	60	35	5	0
	2	0	65	35	0	0
	3	N.D.	N.D.	N.D.	N.D.	N.D.
Bu/HFE-0	1	0	60	35	5	0
	2	0	57	43	0	0
	3	N.D.	N.D.	N.D.	N.D.	N.D.

[a] N.D., not detected.

diene co-reactant gases have been prepared. Their surface tension and bulk and surface compositions were characterized. The results demonstrated that the combination of HFE and hydrocarbon reactant gases gave polymerized thin films with surface energies that varied from 20 to 50 mN/m, depending on feed gas composition and processing parameters.

Variation of the HFE/hydrocarbon ratio in the feed gas changed the amount of fluorine incorporated into the films and the distribution of fluorinated species in the films. Higher fluorine content in the films and lower surface tensions were observed when the HFE content of the feed gas was higher. An optimal ratio of HFE-to-acetylene was identified for maximizing incorporation of CF_3 species in the film. The level of hydrogen incorporation in the films was inversely related to the amount of fluorine in the films and directly related to the hydrogen content of the feed gases.

In contrast to the films prepared with acetylene, the films prepared with butadiene as the coreactant gas with HFE showed less fluorine incorporation and higher surface tensions at equal HFE reactant gas concentrations. Correlations between feed gas composition and surface tension and distribution of fluorinated species in the films were observed.

The data presented here for plasma polymerization of HFE with a hydrocarbon co-reactant gas are consistent with the mechanism proposed by d'Agostino[14] for decomposition of HFE in a plasma. Decomposition of HFE through this mechanism can follow two paths, one involving decomposition of HFE (C_2F_6) into two CF_3 radicals that decompose further into CF_2 and CF reactive species, and a second involving decomposition of C_2F_6 into CF_2 and CF_4. Further decomposition of CF_4 gives the three CF_x radicals and F atoms. While the CF_x species participate in polymerization reactions, the F atoms act as etchants.

Introduction of a fluorine scavenger into the system with the HFE feed gas changes the balance of the two decomposition pathways. Both acetylene and butadiene acted effectively as fluorine scavengers in the materials studied here, permitting polymerization of HFE into fluorocarbon films.

The distribution of fluorinated species and the fluorine content of films prepared from HFE and acetylene or butadiene differed between the two types of hydrocarbons. The presence of hydrogen in the hydrocarbons permitted both to act as F atom scavengers, decreasing the etching character of the HFE plasma. However, the higher concentration of hydrogen in the butadiene on a molar basis resulted in not only a decrease in the concentration of etchant species, but also an increase in the concentration of less highly fluorinated radicals in the plasma. With reference to d'Agostino's mechanism, removal of reactive F atoms from the plasma increases the concentration driving force for the second decomposition pathway, favoring formation of less highly fluorinated radicals. Further, the higher carbon content of butadiene compared to acetylene also favors deposition of films with lower F/C ratios.

A dependence of fluorocarbon film composition on plasma reactor power also was observed. The greater power input favors further decomposition of fluorinated species in the plasma to less fluorinated species, resulting in lower fluorine content and less incorporation of highly fluorinated species in the film. It also results in bombardment of the film surface by energetic ions that may alter the surface composition.

Thus, three factors contributed to the composition and properties of the films examined in this study: 1) the energy input into the plasma polymerization reaction, 2) the amount and type of fluorine scavenging reagent introduced with the HFE, and 3) the elemental composition of the reactant gases. Knowledge of the effect of these parameters on the decomposition of HFE and its radical distribution in the plasma permits design of materials with controlled composition and surface tension.

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