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Surface modification of fluoropolymers for the improvement of adhesion: O2-CF4-Ar radio frequency plasma modification of poly (tetrafluoroethylene)

Kan Lu

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SURFACE MODIFICATION OF FLUOROPOLYMERS FOR THE IMPROVEMENT OF ADHESION: O_2- CF_4- Ar RADIO FREQUENCY PLASMA MODIFICATION OF POLY (TETRAFLUOROETHYLENE)

KAN P. LU

JUNE, 1994

THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR DEGREE OF MASTER OF SCIENCE

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MATERIALS SCIENCE AND ENGINEERING

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PERMISSION GRANTED

Title of thesis Surface Modification of Fluoropolymers for The Improvement of Adhesion: O_2-CF_4-Ar Radio Frequency Plasma Modification of Poly(Tetrafluoroethylene)

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FIGURE CAPTIONS

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I. INTRODUCTION

Polymers with low dielectric constant have definite advantages in electronic component manufacture as etch masking materials and for electrical insulation between levels of circuitization. Among these polymers, poly (tetrafluoroethylene), PTFE or Teflon, has the lowest dielectric constant, and has potential application for computers, communications, and radar as circuit frequencies rise. Because its excellent thermal stabilities and chemical inertness, PTFE could be a perfect substrate of depositing copper circuit to lead smaller chips and higher frequencies(1-5). It seems more and more important to find a better way to improve the adhesion between copper and PTFE.

Plasma treatment is an efficient method for etching and surface modification of polymers, thereby changing such properties as wettability (6,7) and adhesion(8). In particular, O_2/CF_4 plasma are being more frequently used for enhancing those properties by radio frequency (RF, 13.56 MHZ), or microwave power, or even mixed frequency(9). In order to obtain a thorough characterization of polymer surfaces, plasma treated and untreated surfaces, it is usually necessary to combine analytical techniques to determine the chemical and physical nature of these surfaces, i.e., the elemental composition, surface energetics, heteromorphy, and roughness.

Contact angle measurements have been employed as a useful technique to determine the surface energy, wettability, and roughness. Under the different conditions of roughness given by Wenzel's law(10), wettable surfaces (contact angle $\theta<90^o$) will become more wettable surfaces ($\theta<<90^o$) when roughened; and nonwettable surfaces ($\theta>90^o$) become more nonwettable when toughened. PTFE is a highly nonwettable polymer with contact angle of 108^o (11). The contact angles of TFE deposited by a RF plasma process have extremely high values between 165^o and 170^o(12).

Surfaces are usually not ideally smooth and chemically homogeneous. As a result, different contact angles might be obtained depending on whether a water drop is advanced or receded on the surface, then contact angles are defined as advancing and receding angles, respectively.

G.A. Takacs et al. (13) reported results for exposed PTFE exposed to vacuum ultraviolet (VUV) radiation from low current (3-7.A), high pressure (6.7×10^4 Pa) inert gas are plasmas. It was found that receding contact angle measurements were found to be more sensitive to surface modification than advancing contact angles. Similar receding contact angle results for exposed PTFE and polyethylene (PE) to radiation downstream from a He microwave plasma were obtained by Egitto and Matienzo (14).

The difference between the advancing contact angle and receding contact angle affected by surface morphological changes or chemical heterogeneity is well known as the contact angle hysteresis. The detailed study of contact angle hysteresis has been provided by Johnson and Dettre(15, 16). Many authors considered contact angle hysteresis as a remarkable method to analyze the behavior of rough and heterogeneous surfaces. It is very interesting that this relatively simple model of contact angle measurements can provide important information on surfaces which often complements information obtained with other techniques, e.g. measured by X-ray photoelectron spectroscopy (XPS). For example, composite thin films have been deposited by simultaneous plasma polymerization of the feed gas mixture, 80% C_2F_6 and 13% H_2, and sputtering of Au onto PTFE targets at a powered electrode in an RF glow discharge (17, 18). It was reported that the dependence of advancing and receding appears to be the key parameter in controlling the wettability and film composition and their surface macroscopic properties. When the F/C ratio increases on the surface, hysteresis decreases, in fact, receding angle diminishes whenever a hydrophilic portion of the surface is introduced. On the other hand, advancing contact angle remains high until only a small portion of the hydrophobic part is maintained, but it suddenly drops when the surface is almost completely wettable.

In a series of investigations of PTFE and other polymers in O_2/CF_4 plasmas (1, 19-22), XPS has been selected to look at the surface chemical composition and structural change, as well as to better understand etch mechanism. Etching rates were found to be dependent upon feeding gas composition, ion bombardment, polymer structure, and etching system. As one might expect, etching behavior is a function of feed gas concentration, but as mentioned above, the elemental compositions and their ratios provide some clues to the etching mechanisms more clearly. For example, Egitto et al have suggested that the ratio of [O]/[F] is most significant in the etching of polyimide and an oxirane-based copolymer by O_2/CF_4 in a diode reactor at around 350M Torr. The concentration of CF_4 for which maximum rate is achieved is not a function of O atom or F atom concentrations alone, but the ratio of these two concentrations. Substituting SF_6 for CF_4 provides similar surface composition(23, 24).

The mechanism of reactive ion etching (RIE) is different from that of downstream of a microwave (MW) plasma with neutrals, or vacuum ultraviolet (VUV) radiation with energetic photons. Reactive ion etching of PTFE is thought to be initiated by ion bombardment induced radical generation. The substrate electrode in RIE is powered, and the ion energies may reach several hundred electron volts (1, 25).

Oxygen and fluorine atoms have different surface affinities to the polymer structure (20,26). According to molecular orbital calculations, saturated polymers have a large energy gap between the highest occupied molecular orbital and its lowest unoccupied counterpart, whereas the gap decreases with increasing degree of unsaturation. Since the surface affinity of unsaturated polymers for atomic fluorine is greater than that for saturated polymers, more fluorine would be required in the feed gas (more % of CF_4 in O_2) to achieve the maximum etching rate for saturated polymers than for unsaturated polymers. The etching rates of polyethylene, cyclized polysoprene and polyimide have been reported, and their surfaces have been examined using XPS technique. The composition at the maximum etching rate becomes more oxygen-rich with increasing degree of unsaturation. The etch susceptibility of a given polymer correlates strongly with the degree of unsaturation in the polymer's structure. But, it must be noticed that even though two polymers have a high degree of saturation, they might have a significant different composition at maximum etching rate because of their bond strength, elemental composition, and other factors. For example, both polyethylene and PTFE have saturated polymer structure (-CH_2- and CF_2- groups), but their mechanisms for etching are substantially different. Abstraction of an H atom by O or F atoms are thought to be the initiating steps in the etching of polyethylene. Initiating of PTFE etching is probably not due to abstraction of fluorine atoms from PTFE by O and F atoms. Since these reactions are highly endothermic and hence energetically unfavorable, etching of PTFE is mainly dependent on ion bombardment.

Interest in adhesion between polymer and metal has been increasing in recent years. To improve these kinds of adhesion, roughening polymer surfaces (sometimes presputter) and metal deposition by sputtering or evaporation are mainly used.

The stress, morphology, and resistivity of copper sputtered onto polyimide film (2500 Å thick) has been studied at various pressures and deposition rate (27). For a fixed Cu deposition rate of 2Å/sec., the stress of the film makes an abrupt transition from initial compression to tension at 2.5 m Torr, and a maximum stress between Cu and PI of 0.30GPA was obtained at an Ar pressure of 3.3m Torr. The stress decreases to zero at higher pressure.

Several composite metal polymer films have been prepared by plasma polymerization. A planar magnetron target was employed for copper, gold and aluminum incorporation(individually) into films growing in an RF discharge operated in CF_4 or CF_4/Ar mixture. (28) This arrangement enabled a very wide range of metal concentrations to be attained. In transmitted light, coatings were orange in the case of copper, from red to blue as gold content increased, but no colors appeared for aluminum incorporation. Composite fluorocarbon polymer/ gold films in the similar arrangement using a planar magnetron with gold or composite /PTFE target has been studied also (29, 30). Metal-doped polymers films can also be prepared by other methods, and were suggested for use as insulating layers on microelectronic devices, as protective coatings and as intermediate adhesive layers.

The chemical interactions between polymer surface and metal atoms from the vapor phase may play an important role in interfacial metal-polymer adhesion. C.A. Kovac and his co-workers reported that the evaporation of copper metal directly onto the polymer surface results in films with relatively poor adhesion. But, if a thin film of chromium is deposited first, adhesion is dramatically increased (31). Another paper described the effect of oxygen reactive ion-beam etching of a polyimide film to enhance its adhesion to a deposited copper film (32). The adhesion strength of metal to polymer, such as copper to polyimide is somewhat due to mechanical interlocking, which in turn depends on the structure of the metal/polymer interface. To improve the adhesion between copper and polymer one of the simple ways is to roughen one surface or the other. Copper films were deposited on the etched polyimide films. Peel testing (at 90^{o}) was performed to measure the peel strength at the copper-polyimide interface. The adhesion strength of the copper film to the polyimied could be increased by as much as a factor of 25 as a result of the etching.

The adhesion of copper to PTFE with and without a presputtering prior to the copper deposition has been investigated (33, 34). The polished Teflon was still showing an appreciable roughness as viewed by SEM. All alcohol cleaned samples were dried, then loaded to the evaporator for Cu deposition either presputtered with 500 eV Ar^+ ions, or without presputtering. The peel test by Scotch tape showed the poor Cu-Teflon adhesion without presputtering with a peel strength below 1 g/mm, and the strong Cu-Teflon adhesion with a peel strength 50 g/mm (after 30 seconds of treatment). 10 second sputtering can rapidly increase the adhesion. The peel strength slightly decreases with more than 60 second sputtering, and then remains almost constant with longer presputtering. Presputtering treatment might be the dominant factor for the enhanced adhesion, because 1 week air exposure following presputtering doesn't effect the Cu-Teflon adhesion. The explanation for this improvement would be considered as the effects of sputtering which include chemical and mechanical factors, as well as changing surface morphology and creating radicals to lead to crosslinks of polymer chains. A simple geometric model was used to analyze the contribution from the morphology changes to the observed peel strength: the peel strength depends on the contact area of Cu and Teflon, if interface bonding force is constant for selected materials in unit area.

The objective of this thesis is to determine the effects of exposed PTFE to a radio frequency plasma containing various O_2-CF_4-Ar mixtures on the adhesion between PTFE and deposited copper. Relatively little work has been previously reported on enhanced adhesion of Cu-Teflon by O_2/CF_4 RF plasma treatment. It would not be surprising that etching behavior of PTFE might be pronouncedly different from other polymers, either unsaturated or the saturated, because of its polymer structure and selected modification conditions. The surfaces of PTFE with or without exposure from RF plasma were investigated by XPS, contact angle measurements, and SEM. Peel tests were performed to evaluate the interface bonding strength.

II. EXPERIMENTAL

2.1 Apparatus

The present plasma etching studies were performed using a planar diode etching system, which is shown schematically in Fig. 2-1(23,35). Samples were placed on the RF water cooled electrode (cathode) with 8.2 cm diameter of this reactive ion etching system. The stainless steel chamber is grounded. The chamber consists of a 50.8 cm diameter X 44.5 cm deep stainless steel and aluminum cylinder, evacuated to 10^{-5} Torr monitored by an ion gauge at high vacuum. The pressure of exposure is set at 0.3 Torr. Aluminum is an excellent material for use in CF_4 plasma chamber because an inert nonvolatile aluminum fluoride layer is quickly established which passivates the surface and discourages the recombination of fluorine atoms. The relative low pressure would avoid the presence of water vapor which can result in scavenging of F atoms by H atoms formed from fragmentation of H_2O molecules, as well as $F+H_2O \rightarrow HF+OH$. The O_2-CF_4-Ar gas mixture was supplied to the chamber through a hole on the cover plate above the electrode. A capacitance manometer is used at higher pressures for etching. The flow rate of those gases at a total flow rate of 50 SCCM (standard cm^3/ min) were controlled by three Tylan FC-260 mass flow controls. The pressure in the chamber was established by a mechanical pump and diffusion pump system, and was monitored with a Baratron 170M-27 digital readout (10^{-4} -1.0 Torr).

The power supplied from an RF (13.56 MHZ) generator (RF Plasma Products) through a matching unit divided into two parts (AM -5 Matching Network and AMNPS -2A Controller) using a variable capacitor, supplied a pure, stable power source from 0 to 500 watts. In my studies, a constant power of 50 watts was used for all samples.

Measurements of contact angles, either advancing or receding, of distilled water were made using an NRL -CA Goniometer Model 100 -10 -115. Fig 2 -2 shows the assembled instrument (36). A standard microscope supplied with the instrument is equipped with a 2.3X objective lens and a 10X Ramsden type eyepiece to produce

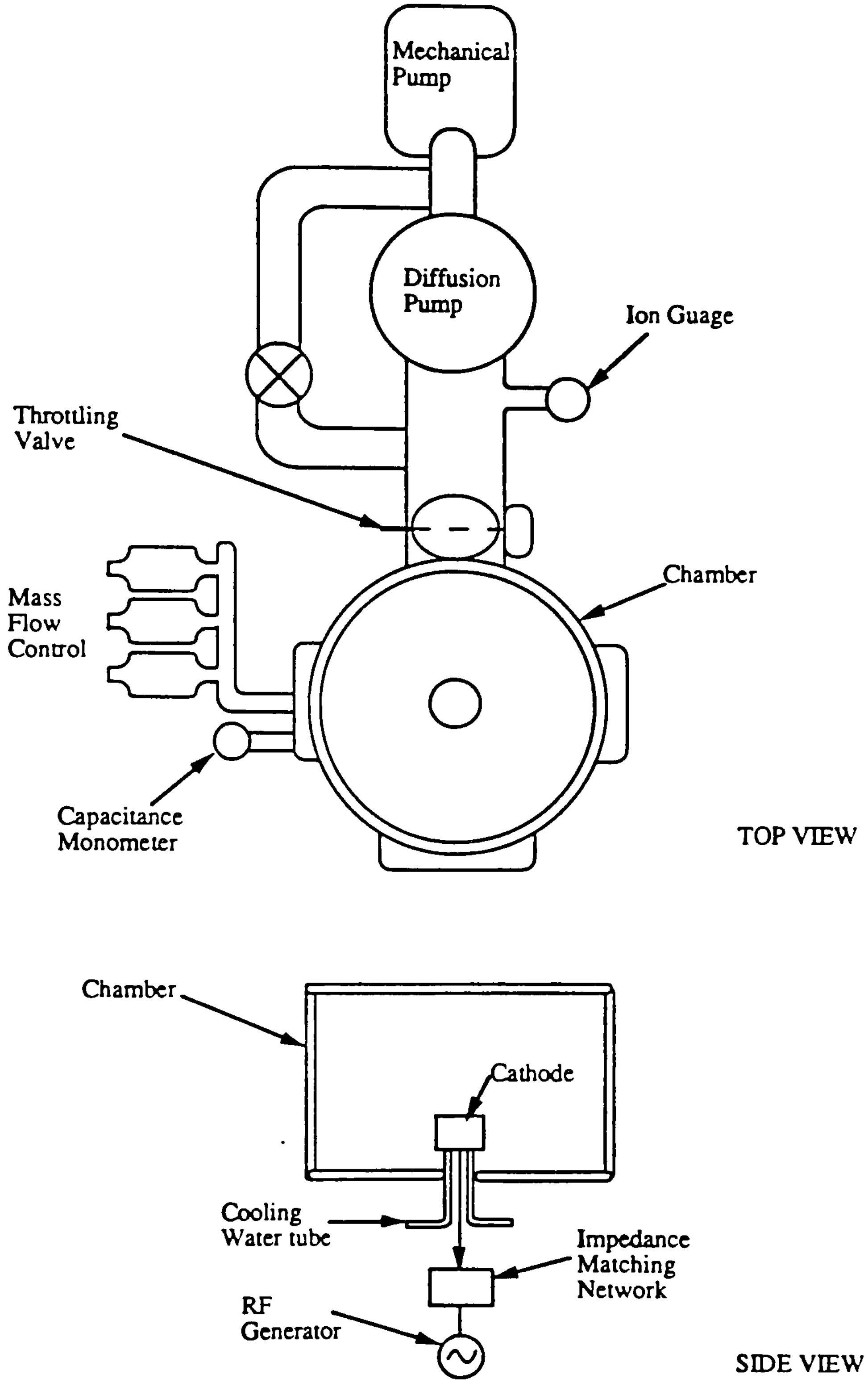


Fig. 2-1 Schematic diagram of planar diode etching system

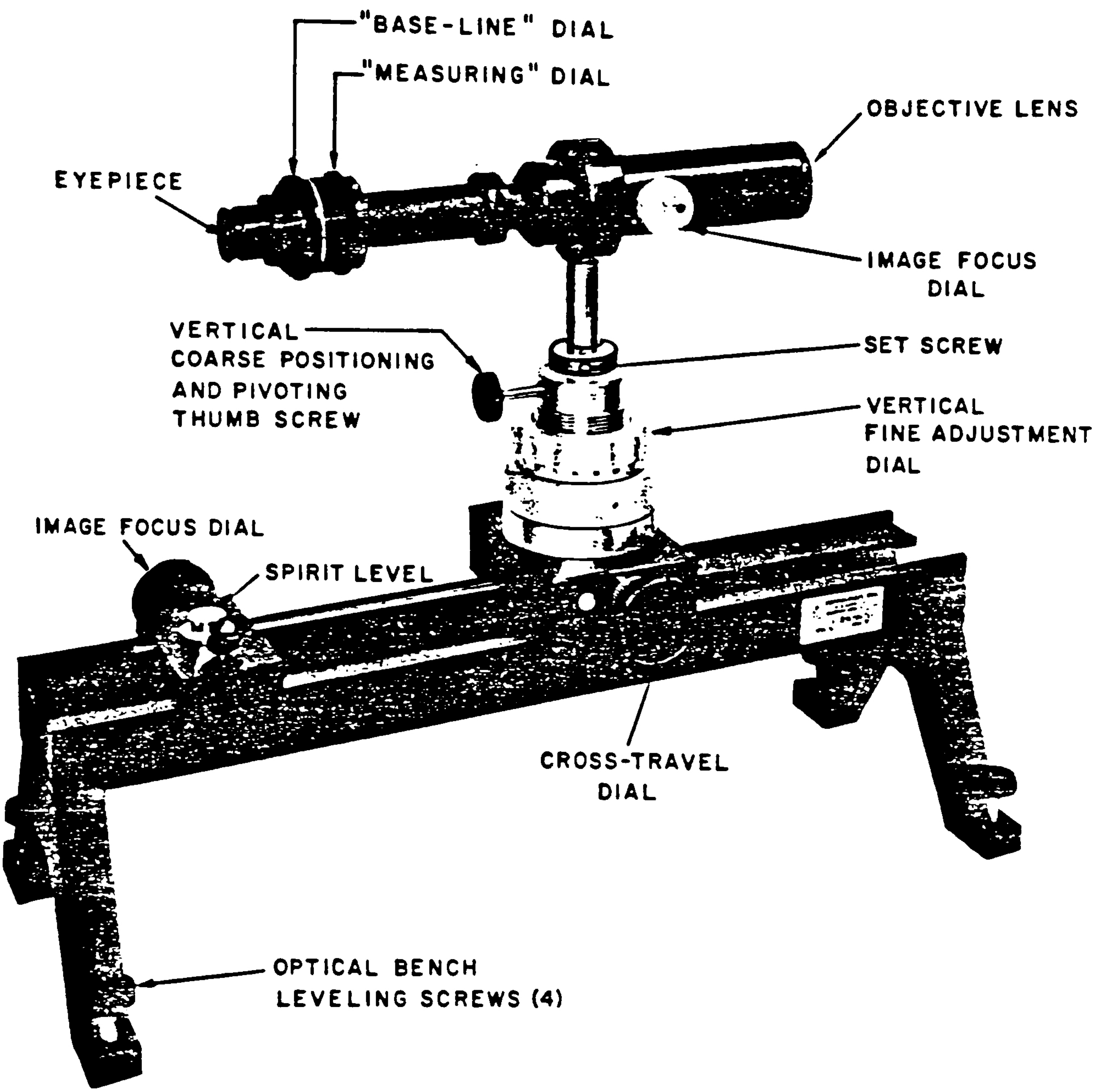


Fig. 2-2 Contact Angle Telegonimeter Model 100-00 (Ref. 36)

an overall system magnification of 23X. At this magnification, the approximate working distance from the extreme end of the objective lens housing to the Specimen is 57mm. An object viewed through the microscope is inverted. Located within the Microscope optical tube, at the focal plane of the Objective Lens, are two glass reticles which have crosslines and a protractor scale. One reticle contains the "base-line", or horizontal reference line, which is aligned with the top surface of the substrate. The other reticle contains the "measuring" cross-line which is aligned tangent to the drop profile at its base line (Contact Angle). The Contact Angle, or its complement angle (if over 105 degrees), is read directly on the "measuring" reticle at the six o'clock position. Rotation of the reticles is by means of the external knurled dials as indicated in Fig 2-2. By slowly rotating and simultaneously sliding the Eyepiece, in or out, the reticle lines are brought into sharp focus. The image focus is adjusted by means of the knurled knob located on the left of the Microscope Base Plate.

A DC planar magnetron sputtering system (U.S.-Gun Inc.) was used to deposit Cu films on the PTFE surfaces. The schematic of sputtering chamber and holder are shown in Fig. 2-3 (37). In the evacuated chamber (50 liter), the copper is made into a sputtering target (2 inch diameter by 3/8 inch thick) which becomes the cathode of an electrical circuit, and a high negative voltage V (dc) applied to it. A circulation water system is to keep cooling the cathode, Cu target. The samples to be coated are placed on an electrically grounded anode 7.5" away. Argon gas is introduced through a mass flow controller at a rate of 7.5 SCCM into the chamber at $2x10^{-3}$ Torr ($8x10^{-6}$ Torr base pressure) evacuated with a liquid nitrogen trapped diffusion pump and a rotary pump. An electric field accelerates the electrons which in turn collide with argon atoms, breaking some of them up into argon ions, and more electrons to produce the glow discharge. Thus, the electrons are tending towards the anode (deposited films), and the ions toward the cathode(Cu target) which in turn strike the Cu target. The sputtering Cu atoms from the target fly off in random directions, and some of them land on the anode (substrate) to deposit a thin film. The magnetic field is used in planar diode glow discharge for the purpose of increasing the path length of the electrons before they are collected by the anode, and for keeping electrons away from the vacuum chamber walls to hence reduce

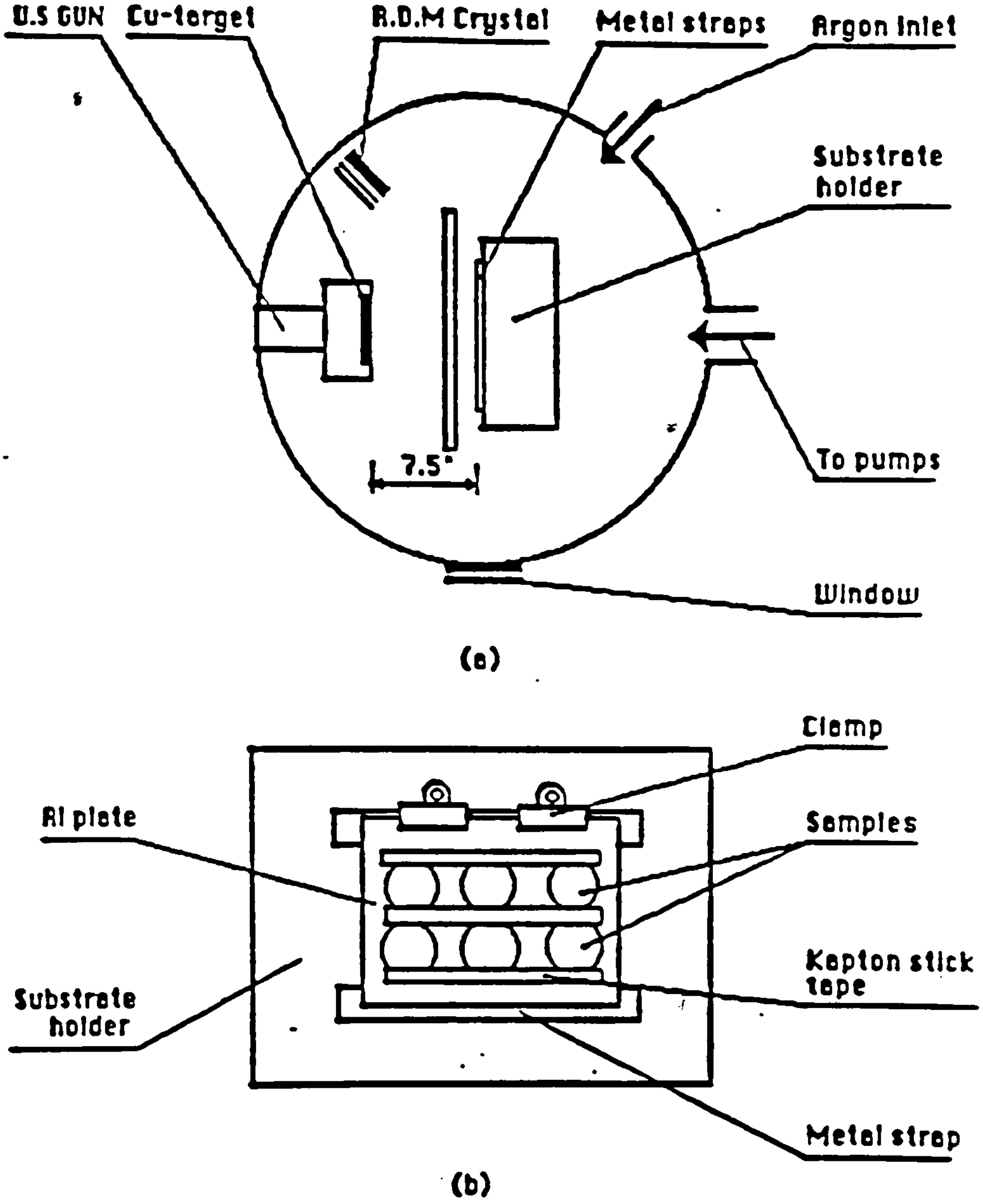
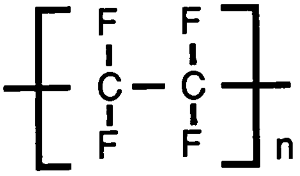


Fig. 2-3. Schematic diagram of the DC planar magnetron sputtering chamber and holder



$$\left[-\mathrm{CF_2}-\mathrm{CF_2}- \right]_n$$

Fig. 2-4 PTFE structure

recombination. Hence the sputtering rate is at a constant pressure. The working pressure was maintained at a near constant value of 2×10^{-3} Torr for all deposited samples. The deposition rate and film thickness were read on an Inficon quartz-crystal rate deposition monitor which was calibrated with a Dektak surface profilometer.

2.2 Materials and Procedure

The material used in this study is poly(tetrafluoethylene). PTFE, trade name Teflon, obtained from Du Pont Inc. The structure repeat unit is shown in Fig. 2-4.

Circular films, 2.5" in diameter, were washed using commercial detergent with water at 100°C for couple minutes to purge away oil and tiny impurities from the surfaces. The oil and impurities are usually obtained from the manufacturing processes. Then, samples were washed with water and distilled water. After air drying, the surfaces were cleaned in vapor acetone for 2 minutes, dried in the air again. As the surfaces were dried almost immediately, it is necessary to place samples into the etching chamber as soon as possible to avoid any second pollution. For the same reason, the chamber pressure has to be roughed using mechanical pump first, then evacuated to a base pressure using diffusion pump. The chamber was isolated from the pump system, when samples are replaced, or feed gases are refilled. Working pressure is set at 300 m Torr by manually adjusting the position of the throttling value. The mixture of oxygen (O_2), tetrafluoromethane (CF_4), and Argon (Ar) was used as the etching feed gas. The volume percentage of the total flow of CF_4 was varied from a condition of pure O_2 to a condition of 95% CF_4. The treated and untreated samples were examined with advancing and receding angle measurements immediately. Advancing contact angles were determined on a 50 µl water droplet placed on the PTFE film surface, and were reported as the average values of the angles measured on the right and left hand sides of the droplet for four or five droplets placed at different locations on the film surface. Similarly, receding contact angles were reported as the average values determined on the right and left hand sides of water droplets of 10, 20, 30, 40, and 50 µl resulting from the sequential removal of water in 10 µl increments from the 50 µl droplet initially placed on surface.

Copper depositions on the PTFE surfaces were performed with a dc magnetron planar sputtering system at deposition rate of 2A°/second. The thickness of Cu film was 2,000 A°. In order to avoid any kind of interferences, two different samples at same etching condition were used for contact angle measurements and copper coating separately. Then, the samples were used for 90°-peel test with scotch tape to determine the adhesion at the interface of the treated PTFE. The pressing of transparent tape onto the surface of the sputtered copper and slowly (manually) peeling the tape was performed. The fraction of the copper remaining on the PTFE film was approximated and the relative strength of the interfacial adhesion was considered to be directly related to the percentage of copper remaining on the film; more copper remaining on the PTFE film indicated stronger interfacial adhesion between copper and PTFE film, and less copper remaining on the PTFE film showed weaker adhesion.

X-ray photoelectron spectroscopy (XPS) analysis of one half of samples was carried out in a JEOL Model JSM-T200 microscope. The other half of samples was used for scanning electron microscopy (SEM) analysis. This method makes it possible to compare the results of analytical techniques at exactly same conditions.

The XPS data was provided by IBM Technology Products, Endicott, NY.

A thin silver film was coated onto samples to conduct electrons, but still thin enough to ensure high resolution before SEM analysis. This conductive layer is used on all polymers in SEM, including PTFE. The Model ISI-40, Intentional Scientific Instruments, and the Model SEM Coating Unit E 5100, Polaron Instruments, Inc., were employed for the performance of SEM.

III. RESULTS

3.1 Elemental Composition on Surfaces by XPS

The elemental composition of Teflon films as determined by XPS are shown in Table 3-1. Atomic oxygen on treated surfaces varies from 0.37 to 4.68% for all gas feed composition with O_2. Atomic carbon has values around 32 to 34%. Fluorine has values around 62 to 67%. The first item listed is for an untreated sample. After carefully analyzing these data, it has been found that the ratio of O/F increases with % O_2 increasing in feeding gas mixture for longer etching time (45 minutes) except 85% CF_4 in O_2 (5% Ar) gas feed condition. No similar tendency appears for shorter etching time (5 minutes). The ratio of two elements from etching conditions in high % oxygen, or 95% CF_4 + 5% Ar show some differences, but the ratio from the pure Argon etching condition shows extreme differences for both long and short etching time. Table 3-1 also shows the values of the O/F elemental ratio. There is no significant change of carbon element composition, except 100% Ar plasma treated samples for either 45 or 5 minutes.

Table 3-1. X-Ray Photoelectron Spectroscopic Analysis of Poly(tetrafluoroethylene) Films Exposed to Radiofrequency Plasma* as a Function of the Time of Exposure and the Composition of the Plasma Gas Feed.

Exposure Time (min)	Plasma Gas Feed Composition, %			Element			Element Ratio	Sample No.**
	Ar	O_2	CF_4	C1s	O1s	F1s	O/F	
0	-	-	-	33.93	0.22	65.85	0.003	8
5	5	95	0	33.93	2.66	63.40	0.042	12
5	5	50	45	33.42	0.96	66.62	0.014	10
5	5	10	85	32.70	1.14	66.16	0.017	9
5	5	0	95	33.41	2.04	64.55	0.032	14
5	0	100	0	33.37	2.66	63.96	0.042	13
5	100	0	0	37.00	5.58	57.42	0.097	15
45	5	95	0	32.72	5.54	61.74	0.090	4
45	5	90	5	32.37	2.72	64.91	0.042	3
45	5	50	45	31.76	2.73	65.50	0.042	2
45	5	10	85	32.93	0.37	66.70	0.006	1
45	5	0	95	33.31	0.72	65.97	0.011	6
45	0	100	0	33.81	4.68	61.51	0.076	5
45	100	0	0	37.68	9.44	52.88	0.179	7

* RF plasma (13.56 MHz), RF power 50W, total gas flow rate 50 SCCM, total pressure 300 mTorr

** See Appendix 2 for actual XPS spectra

3.2 Contact Angles of Teflon

Table 3-2 provides the advancing contact angles for distilled water on RF plasma treated Teflon at different exposure times of 1, 5, 15, 30, 45 and 60 minutes, and plasma gas feed compositions of % CF_4 in O_2 (5% Ar), pure O_2, and pure Ar. The variation in the advancing contact angle on the PTFE surface as a function of the percent of CF_4 in the gas feed is shown in Figs. 3-1 to 3-3 for 5, 15, 45 minute exposure times. The O_2- CF_4- Ar Plasma treated PTFE films showed high advancing contact angle with distilled water. The results indicated that the contact angle for the RF plasma treated PTFE films under any of conditions containing 5% Ar used in the present study is increased from 108^o to somewhere in the range of 113^o to 158^o, depending upon the exact experimental conditions employed, e. g, plasma gas feed composition and exposure time. The contact angle reaches the maximum value at any given exposure time using 95% CF_4 + 5% Ar. Exposure of the PTFE film was also performed in pure O_2 containing no Ar, and in 100% Ar. For all 100% Ar RF treated films, the contact angle decreases from 108^o to 86^o.

Fig. 3- 4 to Fig. 3-10 are plots of advancing contact angles of water drops as a function of exposure time for a number of gas feed compositions. Most curves have similar shape. Rapid changes occur in the first 5 minutes of exposure, with little change takes place after 15 minutes.

Advancing Contact Angle on RF Plasma Treated PTFE at Different Exposure Times and Plasma Gas Feed Compositions

Gas Composition		Advancing Contact Angle, Degree						
		0 min	1 min	5 min	15 min	30 min	45 min	60 min
% CF_4 in O_2 (5% Ar)	0	108.0	-	121.6	132.3	139.3	145.0	-
	5	108.0	125.3	138.7	144.0	149.0	149.0	146.0
	45	108.0	131.3	139.3	147.4	-	150.3	-
	85	108.0	131.3	145.4	156.4	-	156.0	158.0
	95	108.0	-	147.6	157.5	-	156.6	-
100% O_2		108.0	-	108.0	113.8	-	140.2	134.3
100% Ar		108.0	-	90.0	86.0	-	86.0	-

Table 3-2 Advancing Contact Angle Results

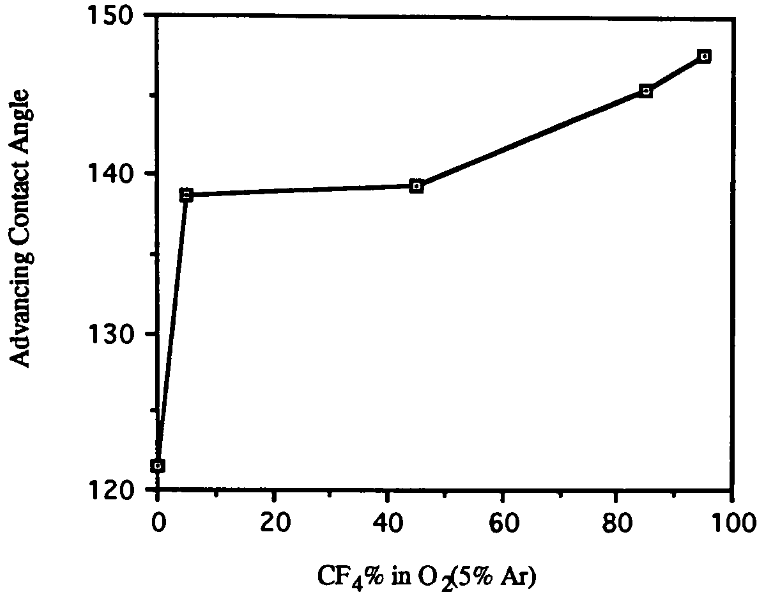


Fig. 3-1. Plot of the advancing contact angle of RF plasma treated (5 minutes) PTFE vs. % CF_4 in plasma gas feed

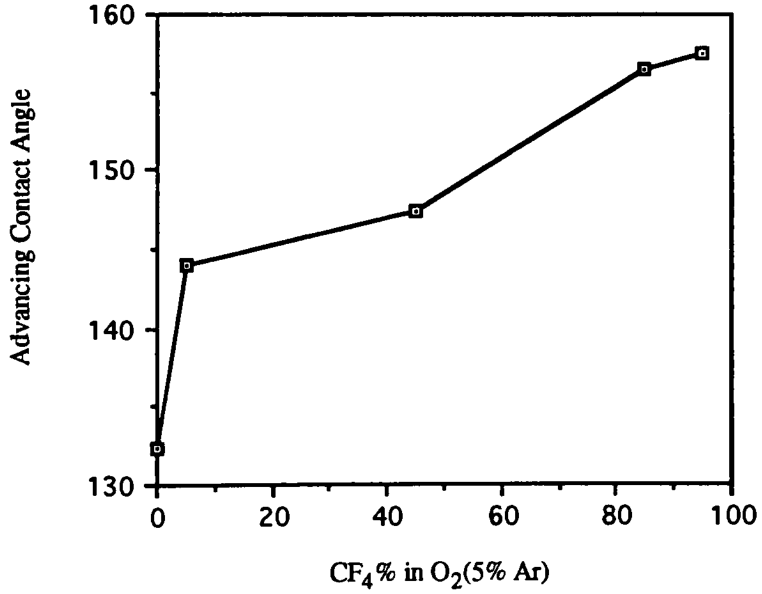


Fig. 3-2. Plot of the advancing contact angle of RF plasma treated (15 minutes) PTFE vs. % CF_4 in plasma gas feed

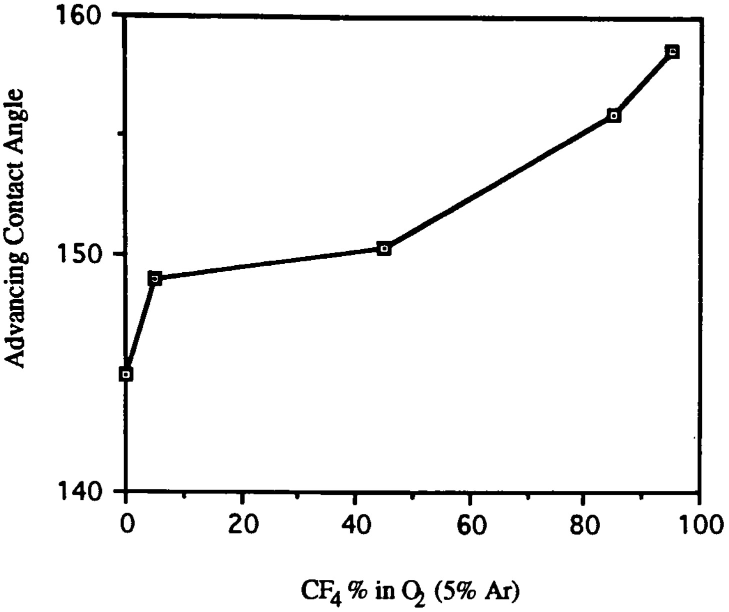


Fig. 3-3. Plot of the advancing contact angle of RF plasma treated (45 minutes) PTFE vs. % CF_4 in plasma gas feed

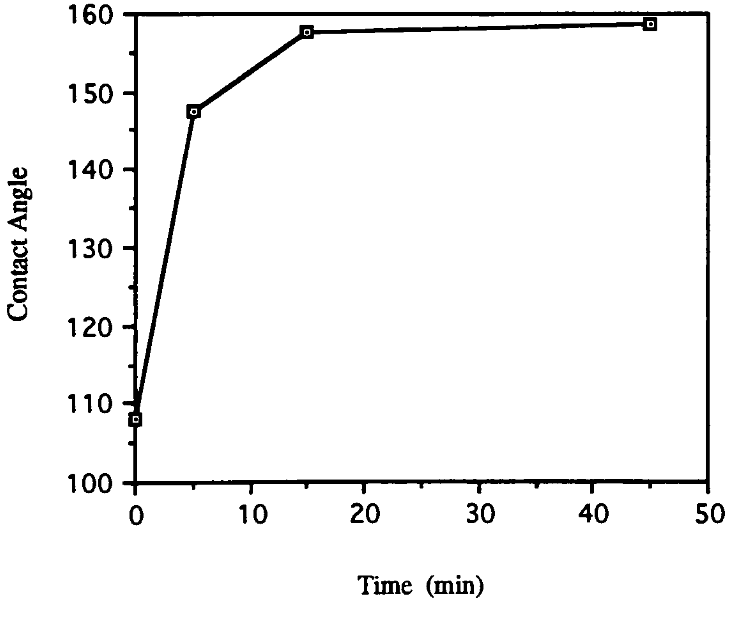


Fig. 3-4. Plot of contact angle vs. exposure to RF plasma time for 95% CF_4 +5%Ar

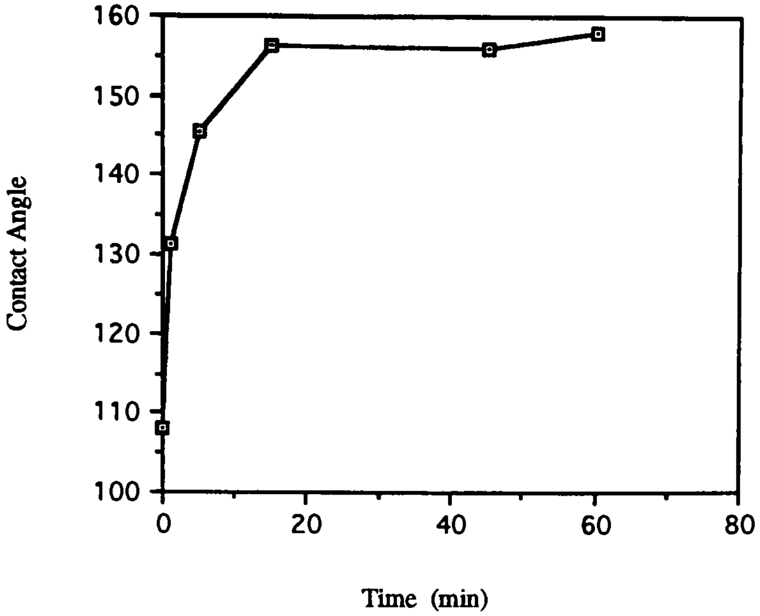


Fig. 3-5. Plot of contact angle vs. exposure to RF plasma time for 85% CF_4 in O_2 (5% Ar)

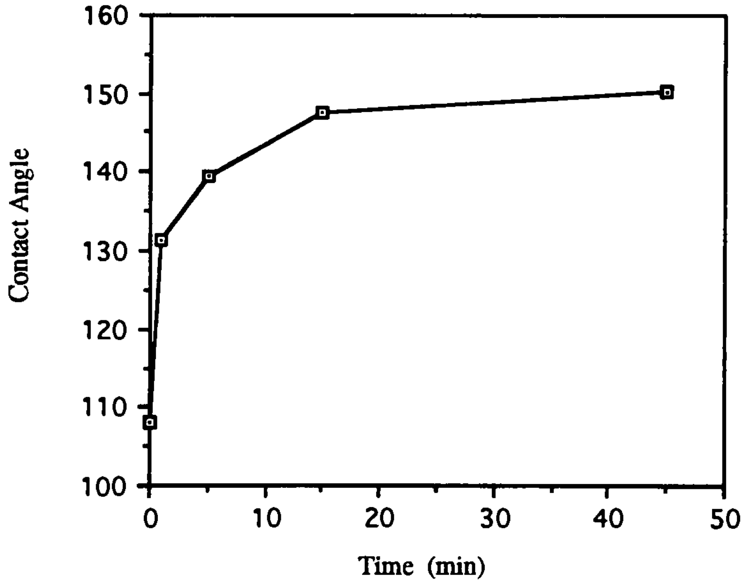


Fig. 3-6. Plot of contact angle vs. exposure to RF plasma time for 45% CF_4 in O_2 (5% Ar)

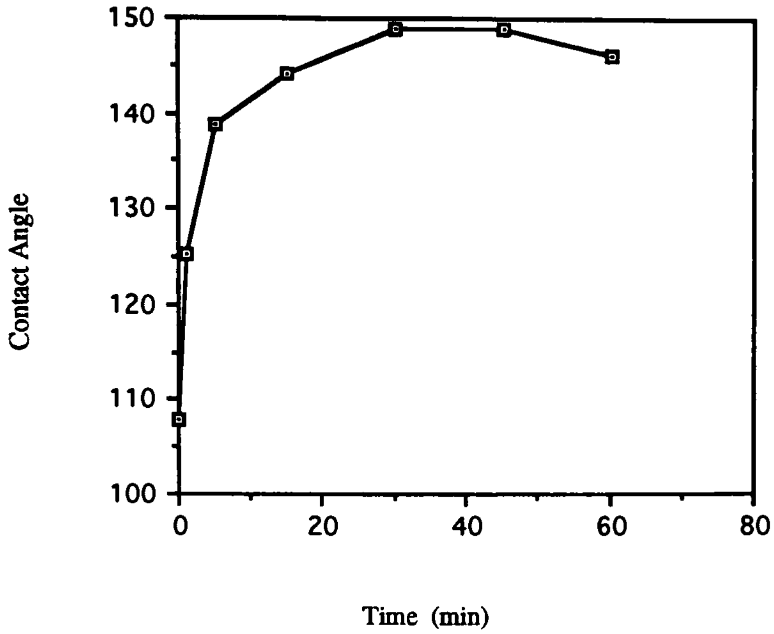


Fig. 3-7. Plot of contact angle vs. exposure to RF plasma time for 5% CF_4 in O_2 (5% Ar)

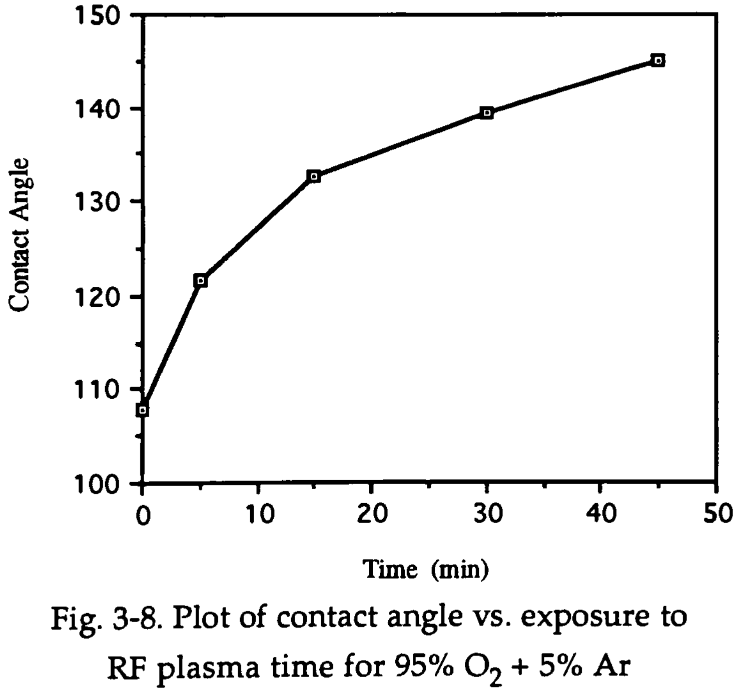


Fig. 3-8. Plot of contact angle vs. exposure to RF plasma time for 95% O_2 + 5% Ar

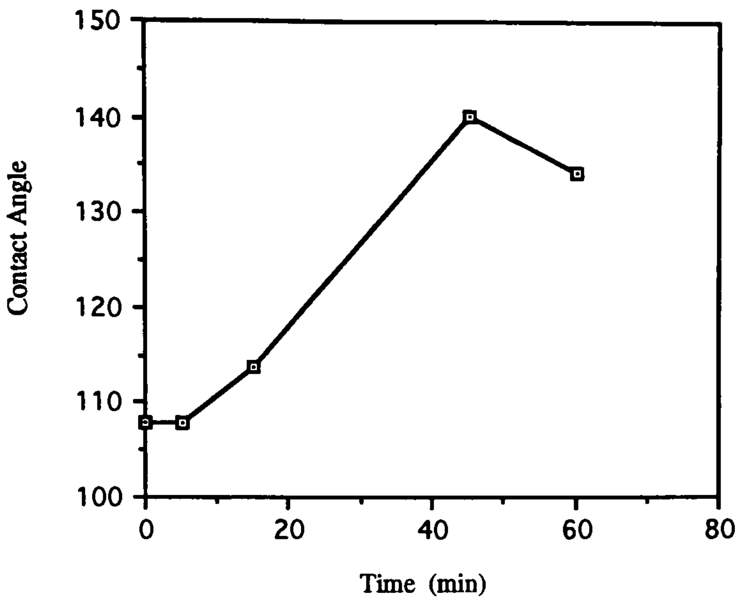


Fig. 3-9. Plot of contact angle vs. exposure to RF plasma time for 100% O_2

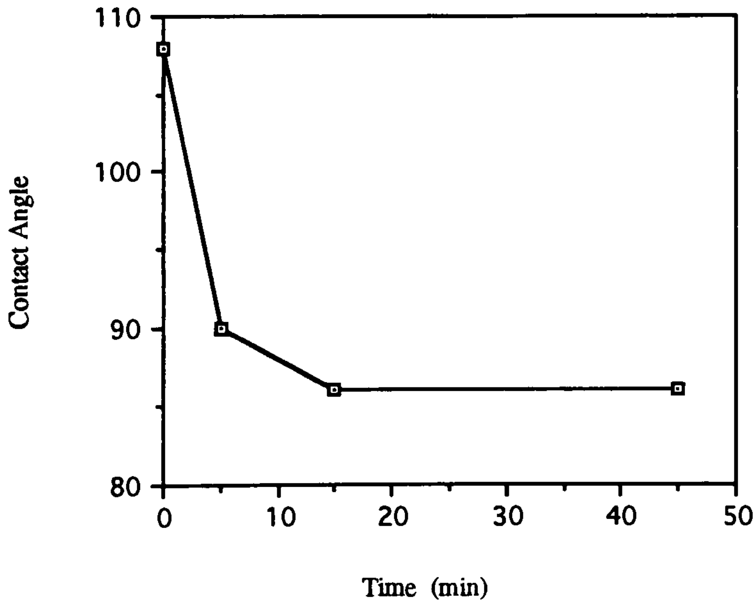


Fig. 3-10. Plot of contact angle vs. exposure to RF plasma time for 100% Ar

Figs. 3- 11 to 3-13 are plots of the receding contact angle versus drop size on PTFE films exposed for 5 minutes to RF plasma generated from a gas feed containing 85%, 45%, and 5% CF_4 in O_2 (5% Ar), respectively. In all cases, the variation of the contact angle with drop size had a linear dependence which decreased with decreasing drop size. The straight lines were analyzed using the method of least squares, where R^2 is the correctation coefficient. The fit of these experimental data to linearity is excellent. Table 3-3 shows the slope of receding contact angle vs. drop size on RF plasma treated PTFE. In general, the receding contact angle decreases as water is removed from the water drop.

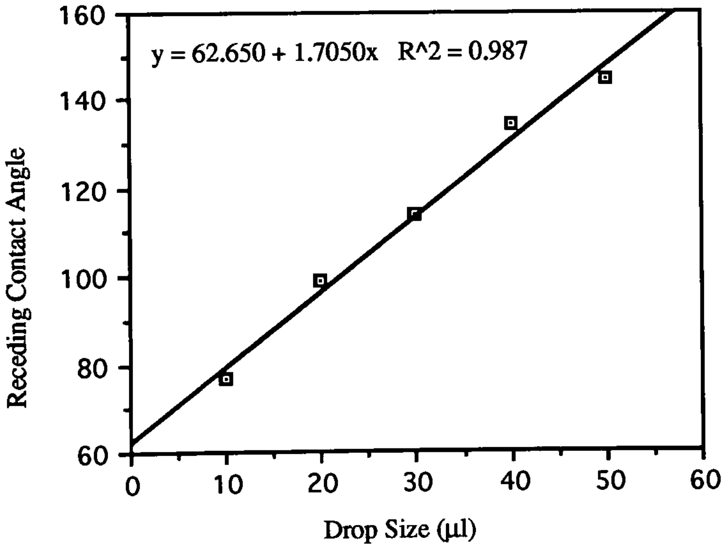


Fig. 3-11. Plot of receding contact angle against drop size ($85\%\ CF_4$, $10\%\ O_2$, 5% Ar, 5 minutes)

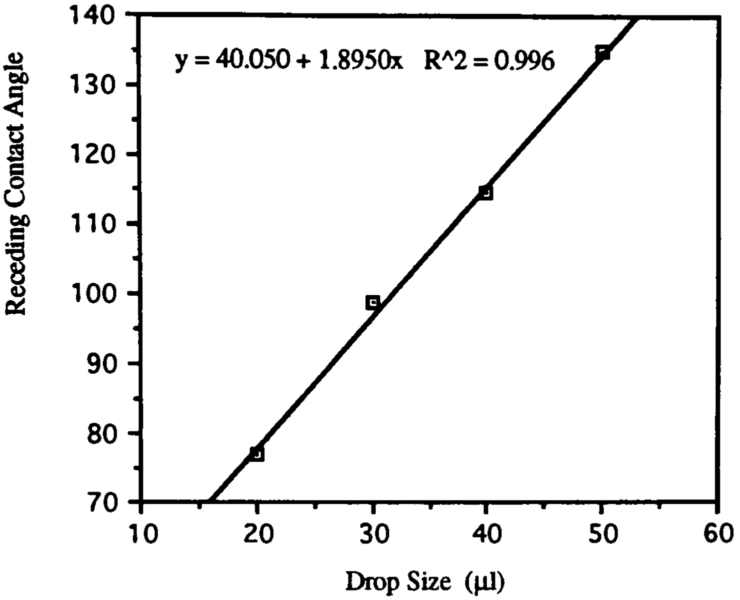


Fig. 3-12 . Plot of receding contact angle against drop size ($45\%\ CF_4$, $50\%\ O_2$, 5% Ar, 5 minutes)

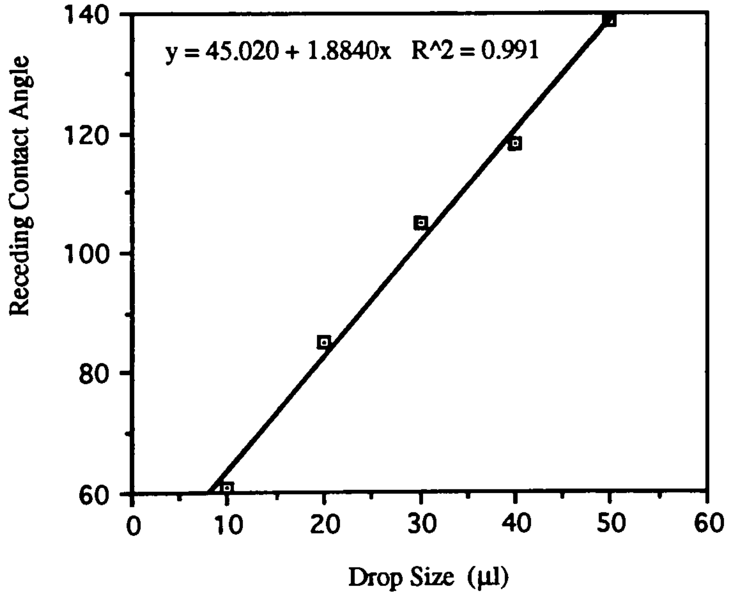


Fig. 3-13. Plot of receding contact angle against drop size ($5\%\ CF_4$, $90\%\ O_2$, 5%Ar, 5 minutes)

Table 3-3 Receding Contact Angle (Slope of Contact Angle vs. Drop Size) on RF Plasma Treated PTFE

% CF_4 in O_2 (5% Ar)	Slope of Contact Angle vs. Drop Size		
	t = 5 min	t = 15 min	t = 45 min
0	1.2	1.7	2.7
5	1.9	1.5	1.0
45	2.0	1.0	-
85	1.9	0.5	0.4
95	1.8	0.6	0.3

-: Not measured

3.3 Surface Features by SEM

Scanning electron microscopy was used to measure surface morphological changes of treated PTFE films. The untreated PTFE was very smooth (Fig. 3-14). Films treated in 80 % CF_4 + 10 % O_2 + 5 % Ar plasma for 5 and 45 minute exposures are still relative smooth. Some etch pits formation is shown in Fig. 3-15 at 5 minute exposure time. When the exposure time was increased to 45 minutes, the surface looks bloated, but not rough (Fig. 3-16).

Figs. 3-17 and 3-18 show the film surfaces with smaller pits for 5 minute 45 % CF_4 + 50 % O_2 + 5 % Ar treatment, and with much bigger pits for 45 minute 95% O_2 + 5 % Ar treatment. The pits shown in Fig. 3-17 are apparent smaller, and less than that in Fig. 3-15.

For 5 minute treatment, the 100% Ar exposed film surface (Fig. 3-19) is very similar to 100 % O_2 exposed film surface (Fig. 3-20). The Fig. 3-20 seems magnified from the Fig. 3-19, in fact, both of them are at same magnification.

Figs. 3-21, 3-22, and 3-23 show some intertwined structures for 45 minute plasma exposure which increase the size of the structure with increasing % of oxygen in gas feed composition. None of the pits shown on 5 minute treated samples exist on 45 minute treated film surface.

Pure Ar modified film (45 minutes) shown in Fig. 3-24 and pure O_2 modified film (45 minutes) shown in Fig. 3-25 have a totally different structure on their surfaces, one has tiny plate-like structure, and another one has intertwined structure which is more similar to other oxygen- rich plasma treated film surfaces.

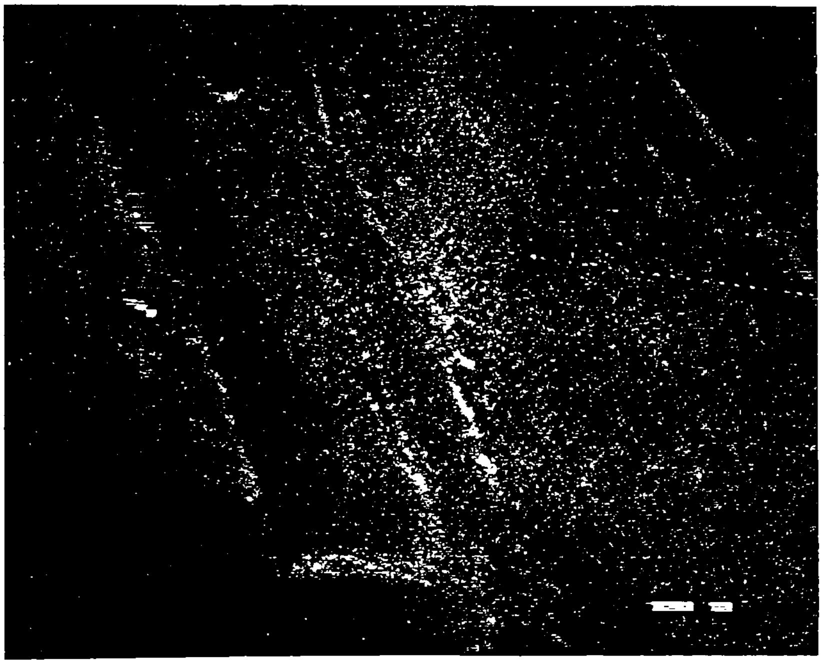


Fig. 3-14. SEM Micrograph of Untreated PTFE Surface 5,000X

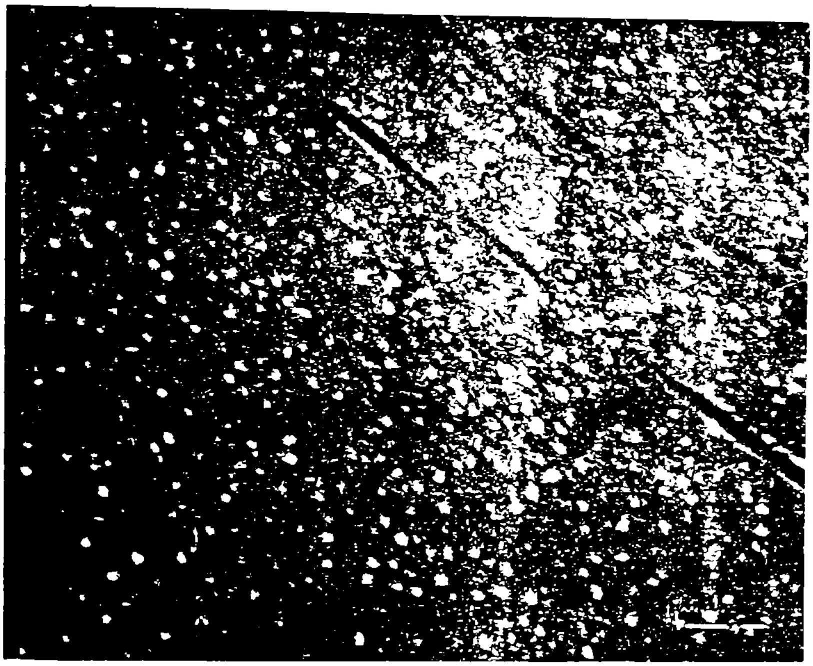


Fig. 3-15. SEM Micrograph of PTFE surface after treatment ($85\%\ CF_4$, $5\%\ O_2$, 5% Ar, 5 minutes) 5,000X

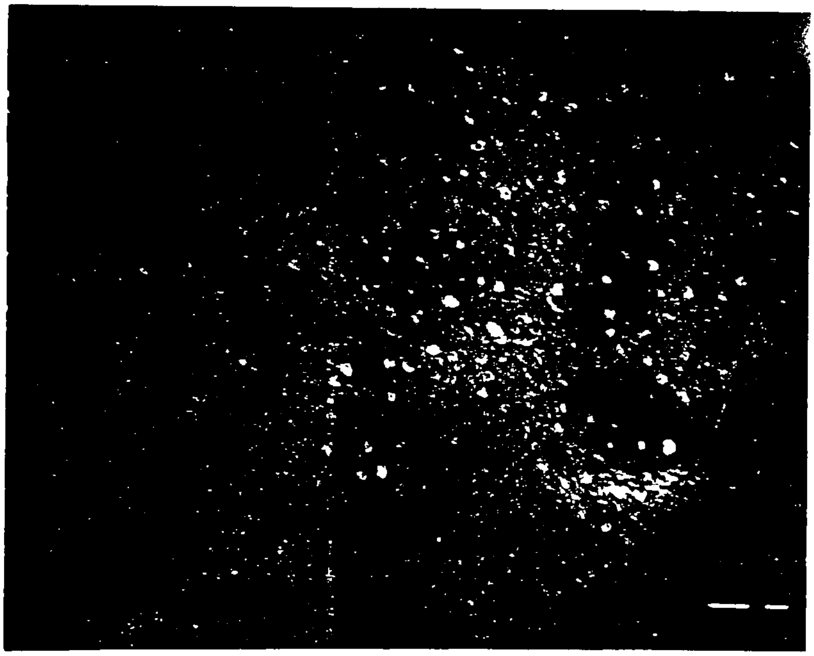


Fig. 3-16. SEM Micrograph of PTFE surface after treatment ($45\%\ CF_4$, $50\%\ O_2$, 5% Ar, 5 minutes) 5,000X

Fig. 3-17. SEM Micrograph of PTFE surface after treatment (0% CF_4, 95% O_2, 5% Ar, 5 minutes) 5,000X

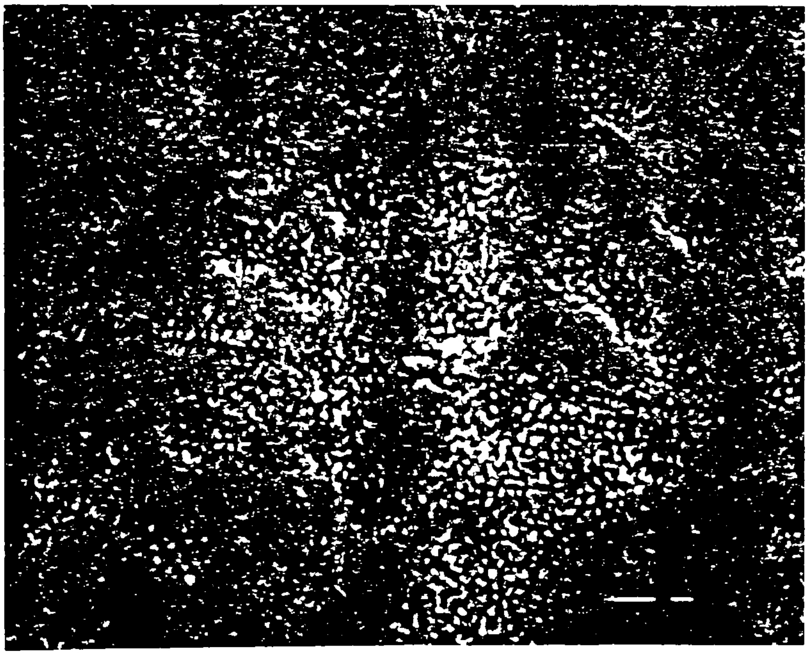


Fig. 3-18. SEM Micrograph of PTFE surface after treatment (100% Ar, 5 minutes) 5,000X

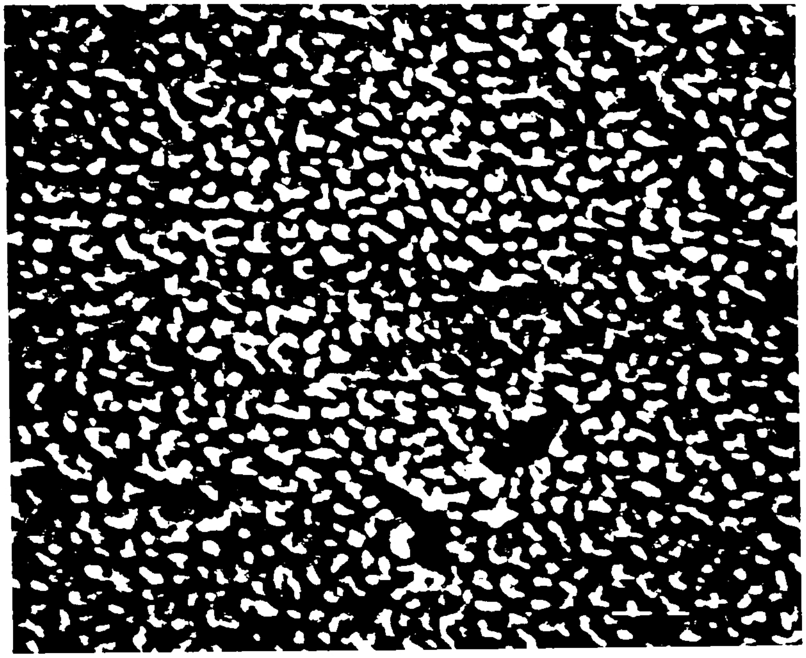


Fig. 3-19. SEM Micrograph of PTFE surface after treatment (100% O_2, 5 minutes) 5,000X

Fig. 3-20. SEM Micrograph of PTFE surface after treatment (85% CF_4, 10% O_2, 5% Ar, 45 minutes) 5,000X

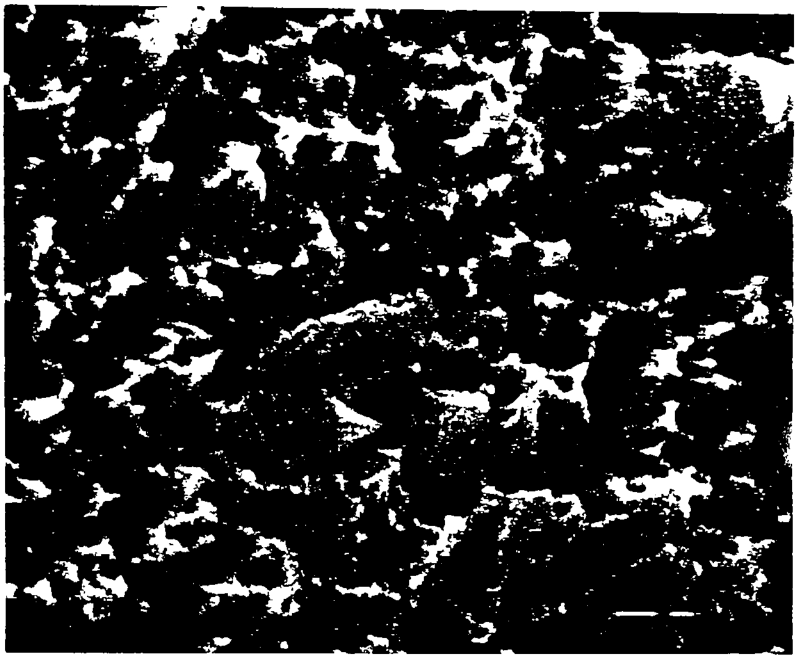


Fig. 3-21. SEM Micrograph of PTFE surface after treatment (45% CF_4, 50% O_2, 5% Ar, 45 minutes) 5,000X

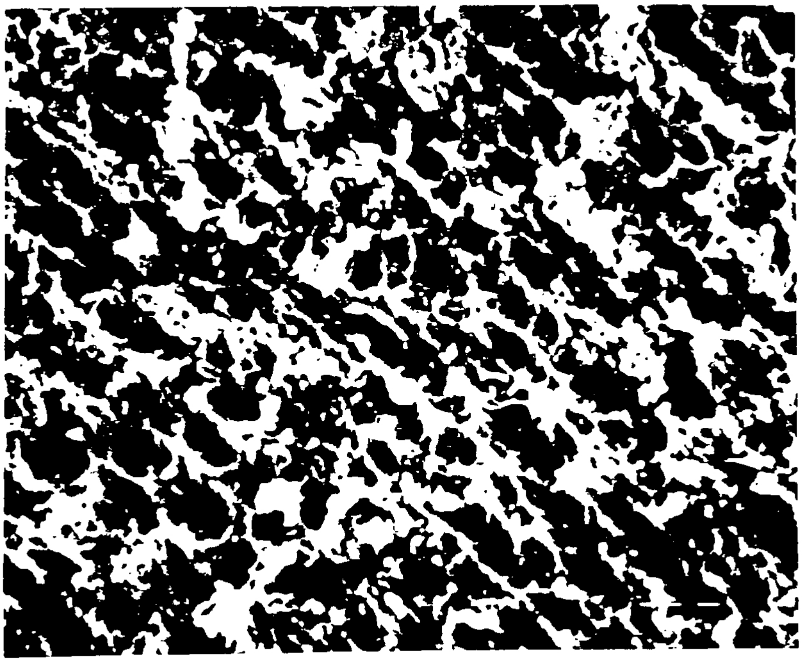


Fig. 3-22. SEM Micrograph of PTFE surface after treatment (5% CF_4, 90% O_2, 5% Ar, 45 minutes) 5,000X

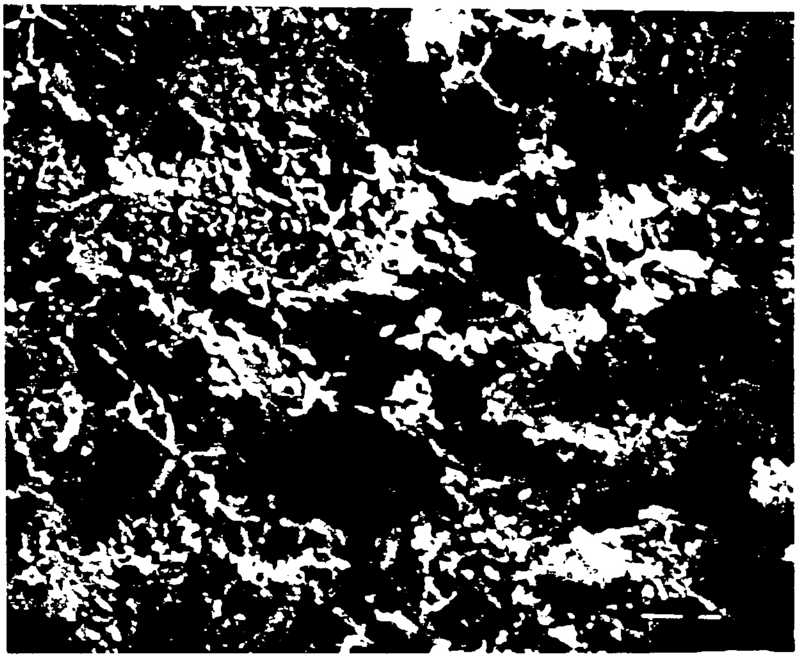


Fig. 3-23. SEM Micrograph of PTFE surface after treatment (0% CF_4, 95% O_2, 5% Ar, 45 minutes) 5,000X

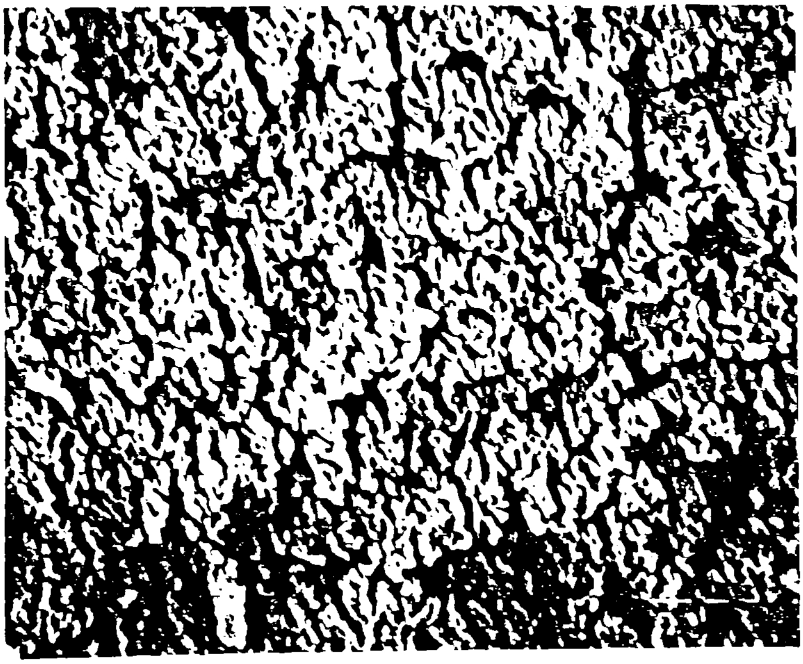


Fig. 3-24. SEM Micrograph of PTFE after treatment (100% Ar, 45 minutes) 5,000X

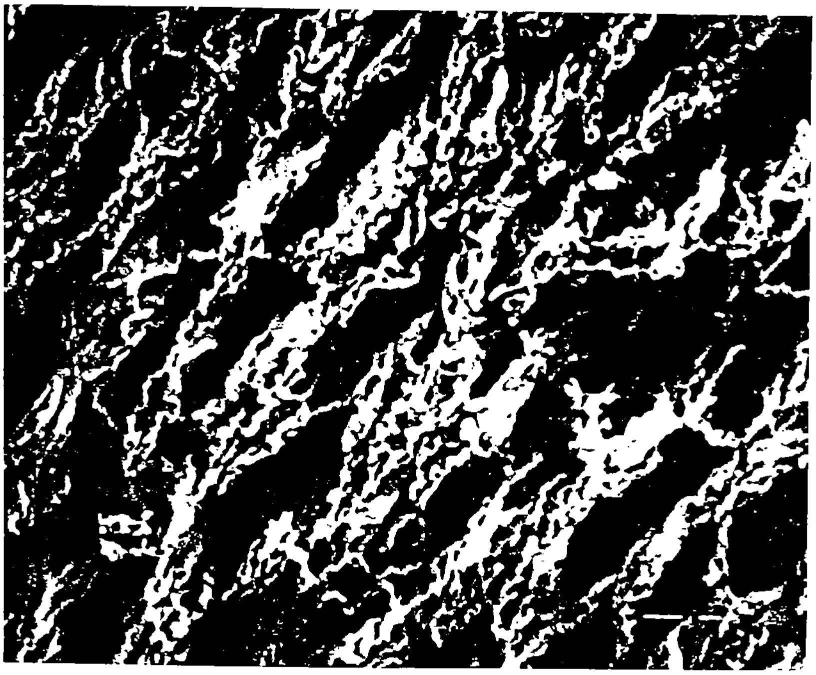


Fig. 3-25. SEM Micrograph of PTFE after treatment (100% O_2, 45 minutes) 5,000X

3.4 Adhesion Between Cu and Teflon

Table 3-4 shows the percentage of sputtered Cu remaining on RF plasma treated Teflon following peel test, and corresponding % CF_4 in O_2 (5% Ar) plasma. In general, the adhesion becomes stronger with decreasing % of CF_4 in the gas feed composition for a certain etching time. In other words, more CF_4 concentration treatment leads to weaker interface bonding force between deposited copper and RF plasma etched Teflon. For same gas feed condition, longer exposure time usually increases % of Cu remaining on the peeled film surface, especially for 100% O_2 treatment, and higher oxygen exposure. The longer exposure time decreases adhesion with the gas feed composition of more % CF_4 in O_2 (5% Ar). It was found that at the exposure times from 5 minutes to 45 minutes, the % of Cu remaining on the Teflon surface decreases from 75% to 0% after plasma etching at 85% CF_4 in O_2 (5% Ar) .

% Sputtered Cu Remaining on RF Plasma Treated PTFE Following Peel Test

% CF_4 in O_2 (5% Ar)	% Cu Remaining on PTFE		
	t = 5 min	t = 15 min	t = 45 min
0	90	95	100
5	85	90	100
45	80	85	60
85	75	70	0
95	65	60	50

Table 3-4. Peel Test Results

IV. DISCUSSION

This section will present a discussion of the results of the experiments with a focus on the following main issues as they relate to variations in the surface properties and adhesion of RIE plasma-modified PTFE surfaces to sputtered copper films:

1. a proposal of a mechanism for PTFE etching, especially for the initial step in the PTFE etching sequence, in the RIE environment used in this study;
2. an analysis of the two fundamental reaction processes occurring on the plasma-exposed PTFE surface from the chemical changes, as revealed by x-ray photoelectron spectroscopy (XPS) surface analysis, and from the physical changes as revealed by scanning electron microscopy (SEM); and
3. a presentation of surface contact angle results as a secondary indicator of adhesion at the plasma-modified PTFE - copper interface.

The key step in the initiation of PTFE RF plasma etching process has been suggested as the generation of a radical site created mainly by high energy ion bombardment.(1) Neither neutral atomic fluorine nor neutral atomic oxygen can abstract fluorine atoms from the polymer; the C-F bond (5 eV) is significantly stronger than either the O-F bond (2.3 eV) or the F-F bond (1.5 eV). Some radical generation by the ultraviolet photons produced by the plasma might occur, but it is probably relatively unimportant for PTFE in this system . It has been reported that exposure to the downstream effluent from a microwave discharge in O_2/CF_4 mixtures, where energetic ions are absent, is incapable of etching PTFE.(23)

A likely mechanism for the initiation of the surface processes on PTFE under these conditions involves the detachment of fluorine atoms by the impact of energetic ions. A recent investigation of the peak-to-peak RF voltage and the absorbed RF power strongly suggest the initiating step in PTFE etching, under conditions quite similar to those used in the present study, to involve ion bombardment-induced polymer radical generation. Thus, the etching of PTFE takes place in $CF_4/O_2/Ar$ plasmas at a rate which depends essentially on the RF power delivered to the plasma; hence on the number density of the ions in the cathode dark space, and only secondarily on their chemical identity.(1)

Ion bombardment and the consequent formation of radical sites on the exposed PTFE surface could involve any kind of energetic ions, including Ar, present in the plasma glow discharge. At the relatively low operating pressure of 0.3 Torr, the sheath collisions that diminish the ion kinetic energies are minimized. The important process of PTFE surface radical generation can be written as:

$$-CF_2-CF_2- + \text{Kinetic Energy} \rightarrow -CF_2-CF^{\bullet}- + F^{\bullet}$$

It is believed that these surface radical sites then interact with oxygen atoms, ions, or molecules. The subsequent steps in the PTFE etching are then not significantly different from those of etching of other polymers. In other words, radical formation in a physical reaction by high kinetic energy ion impact is a characteristic of the PTFE plasma etch process in the RIE environment used in this study. It appears that the creation of these radical sites by chemical reaction is not significant in the initiation of the etching of PTFE under these conditions. The results of plasma exposure of PTFE in 100% Ar feed gas, which suggest the formation of surface radical sites in this system, provide evidence to support this conclusion.

The XPS data (Table 3.1) show that in all samples the ratio of F(1s) to C(1s) remains close to its stoichiometrc value of 2. However, the O(1s) concentration varies considerably in this work, between 0.37 and 5.54% depending, but not linearly, on the O_2 concentration in the plasma feed gas. The lowest O(1s) concentration and the highest F(1s) concentration on the treated surface was measured at 85% CF_4, 10% O_2, 5% Ar gas feed composition. Egitto(1) reported obtaining one of the lowest O(1s) concentrations on PTFE at 85% CF_4, 12% O_2, 3% Ar gas feed composition in an RF plasma modification of PTFE under conditions very similar to those of the present study. In general, enhanced wettability can be correlated with decreasing F(1s) on the modified PTFE surface or with increasing O(1s), as can the improvement in adhesion to the sputtered copper film. Thus, all samples showing good adhesion (> 90% copper remaining on the PTFE film surface following the peel test) are found to have an increased O(1s)/F(1s) surface composition ratio (XPS, *cf.*, Table 3-1). Conversely, a lower O(1s)/F(1s) atom ratio on the treated PTFE surface leads to a poorer adhesion (Table 3-1 and 3-4). The poorest adhesion at the copper PTFE interface corresponded to the lowest O/F ratio following RF plasma treatment at 85% CF_4, 10% O_2, 5% Ar gas feed composition.

The XPS results, especially the broadening of the C(1s)signal (Appendix 2) also indicate that the O_2-rich plasma treated PTFE surfaces contain higher amounts of C-F, C-O, C-C, and C-H groups; conversely, CF_4-rich plasma treated surfaces contain only smaller amounts of these functional groups.

The incorporation of oxygen or fluorine on the PTFE surface may occur due to reaction between oxygen atoms with radical sites on the surface, or with fluorine atoms and surface radical sites, respectively. The surface O/F ratio, as determined by XPS, indicates which of these is the main reaction under the conditions of plasma exposure. It appears probable that the oxygen found by XPS on the 100% Ar exposed PTFE film results from surface reactive site reaction with atmospheric oxygen introduced when the sample is removed from the plasma reactor. This result suggests that some density of surface radical sites are sufficiently long-lived to survive until the reactor system vacuum is broken following the plasma treatment. The degree to which this post-plasma-treatment reaction impacts the surface composition, as determined by XPS, of the PTFE surfaces exposed to the CF_4, O_2, Ar RF plasma is presently unknown.

As all of the SEM micrographs were determined at the same magnification (5,000x), it is easy to see that increases in the % O_2 (decreases in the % CF_4) in the plasma gas feed and longer exposure times both lead to microstructural changes on the PTFE surface. The nature of these physical surface changes are somewhat different; increasing the percentage of oxygen in the plasma gas feed at shorter exposure times leads to increasingly larger, but separated, pits (Fig. 3-15 and 3-17), whereas increases in the exposure time leads to an interlocked structure (Fig. 3-16 and 3-21). This surface roughening provides an increased total contact area per nominal unit area of film surface for the Cu/polymer film bonding, as well as producing an interlocking "hill/valley" structure; both of these effects are expected to lead to improved metal-polymer interfacial adhesion. This conclusion is consistent with the experimental observation that for the plasma treated PTFE samples having approximately the same surface elemental composition, increased surface roughness, as determined by SEM, leads to improved adhesion to the sputtered copper films; *e.g.*, 45% CF_4, 50% O_2, 5% Ar; 45 min. (Fig. 3-21) and 5% CF_4, 90% O_2, 5% Ar; 45 min. (Fig. 3-22); *cf.*, Table 3-1 and Table 3-4.

At comparable exposure times, increasing the concentration of O_2 in the gas feed in the RIE plasma treatment of PTFE films generally results in both an increase in the oxygen atom concentration (XPS) and in an increase in the roughness (SEM) on the film surface. These two factors appear to contribute to the observed improvement in the adhesion of the sputtered copper films to the RIE modified PTFE films.

Contact angle determinations provide a measure of the net result of the chemical (atom percents) and physical (morphological microstructure) changes on the plasma exposed PTFE surface. The changes in the contact angle correlate well with the surface O/F atom ratio at longer exposure times when the surface appears to have reached a near steady state condition; e.g., at 45 min. exposure times, and with the surface roughness at the shorter exposure times; *e.g.*, at 5 min. exposure. Thus, the variation in the contact angle is then indicative of both chemical and physical changes on the PTFE surface and provide the basis of a simple method for estimation of adhesion between the plasma modified PTFE surface and the sputtered copper film.

As can be seen from the advancing contact angle results (Table 3-2) and peel test results (Table 3-4), as a general rule at a given exposure time, the plasma treated surfaces with higher contact angle show poorer adhesion and those with the lower value of the advancing contact angle show better interfacial adhesion. It should be noted, however, that surfaces exposed for extended times with very high contact angles show some variation from this tendency.

Variation in the wettability of the plasma treated PTFE surfaces resulting from either changes in the chemical composition or changes in the roughness of the surface, or both, was observed through the contact angle measurements. The wettability phenomenon could be interpreted from the elemental O/F ratio, as determined by XPS, and also from the surface microstructure, as determined by SEM. It is reasonable to assume that the etch process during the initial stages; *i.e.*, at very short exposure times (≤ 5 min.), is dominated by the physical reaction resulting from the impact of the energetic ions and that these physical changes on the surface are the main factors that cause the observed variations in the contact angle at short exposure times. Thus, the results of the SEM determinations are expected to provide more information regarding the changes in the surface properties of the plasma modified PTFE at the shorter exposure times. At the longer exposure times (≥ 45 min.), the elemental O/F atom ratio appears to become the dominant factor determining changes in the contact angle, and hence in the adhesion modifications. Therefore, surface chemical reactions seem to be the more important processes at these extended exposure times, and hence the XPS spectra contain more information under these exposure conditions. For the intermediate exposure times, both physical and the chemical processes are probably important contributors to the modifications of the PTFE surface. It is not possible from the data collected in this study to determine the relative importance of the chemical and physical processes at these intermediate exposure times and hence whether the XPS spectra or the SEM micrographs are better indicators of the variations in the contact angle and the interfacial adhesion to the plasma modified PTFE surface.

Analyses of the contact angle data collected in this investigation with the results of the peel test (adhesion) measurements show some differences in the sensitivity of the advancing and the receding contact angles to the plasma produced changes in the adhesion of the sputtered copper to the PTFE film surface, and these variations appear to be correlated with the extent of the PTFE surface modification. In particular, it appears that the advancing contact angle is more sensitive to variations in the interfacial adhesion on those modified PTFE surfaces with the higher O/F atom ratios (XPS) and the higher degree of surface roughness (SEM) and is less sensitive to such variations on smoother PTFE surfaces with a lower O/F atom ratio. At 45 minute exposure, it seems that the advancing contact angle decreases with increases in the O/F elemental ratio and the roughness of the surface of the plasma treated PTFE surfaces and that these surfaces show improved Cu/PTFE adhesion. As discussed previously, it appears that the changes in the chemical composition dominate the surface character at the longer exposure times and that the consequences of the physical reaction are more important for the shorter exposure times. After 45 minutes of RIE exposure, the advancing contact angle corresponds reasonably well to increases in the surface O/F atomic ratio and accompanying improvements in the adhesion to the sputtered copper film. On the other hand, for the 5 minute RIE treatments variation in the advancing contact angle correspond mainly to changes in the surface morphology rather than to the O/F atomic ratio. Adhesion improvement at this shorter exposure time is principally caused by the rougher surface which is accompanied by a lower advancing contact angle. Thus, while the advancing contact angle appears to be more reflective of the physical/morphological changes (surface roughness) at the shorter exposure times and more sensitive to the changes in the chemical composition of the surface (O/F atom ratio) on longer exposure in the RIE plasma environment, this contact angle measurement is a good indicator of the adhesion properties of the plasma treated PTFE surface toward the sputtered copper film. As a result, the adhesion to the polymer film surfaces displaying an advancing contact angle near 160°, for which adhesion to the sputtered copper film is usually very poor, may not be well characterized by this measurement. This disadvantage of the advancing contact angle may not severely limit its application as a predictor in these systems where surface adhesion is significant.

For the relatively long plasma exposure (45 minute), receding contact angle hysteresis seems to be principally sensitive only to changes in the chemical composition on the surface; that is, the chemical change. Quantitatively, a receding contact angle hysteresis of greater than a 40° correlates to better adhesion (more than 90% Cu remaining on the peeled PTFE surface); and a less than 20° change would correlate to poorer adhesion. However, this hysteresis appears not to correlate well with either the small changes in the O/F atom ratio or with the changes in surface roughness suggesting that the receding contact angle hysteresis is relatively insensitive to physical changes on the PTFE surface.

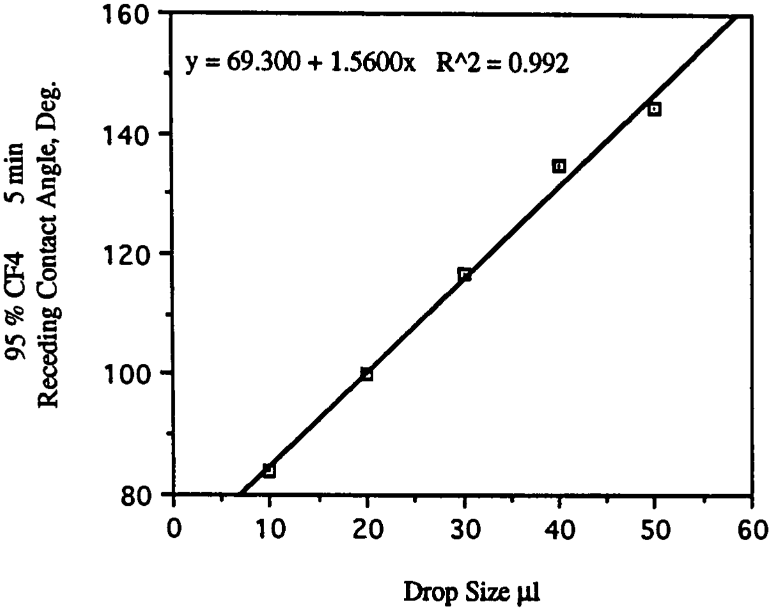
In general, the advancing contact angle provides an indication of the surface changes that are the net result of the chemical compositional changes (as determined by XPS analysis) and the physical/ morphological changes (as determined by SEM) on the treated PTFE surfaces and correlates well with the results of adhesion experiments (peel test) for both the short (5 minute) and the long (45 minute) RIE plasma exposures. It is expected that this advancing contact angle would also correlate well with the results of adhesion experiments at the intermediate exposure times. The receding contact angle appears to correlate best with the chemical changes on the plasma treated PTFE surface (O/F atom ratio) and therefore is most useful at the longer exposure times.

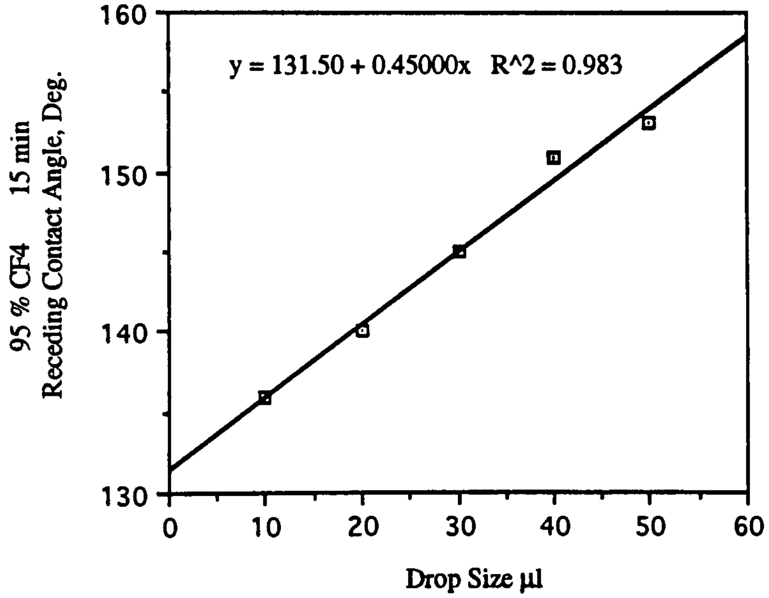
V. CONCLUSIONS

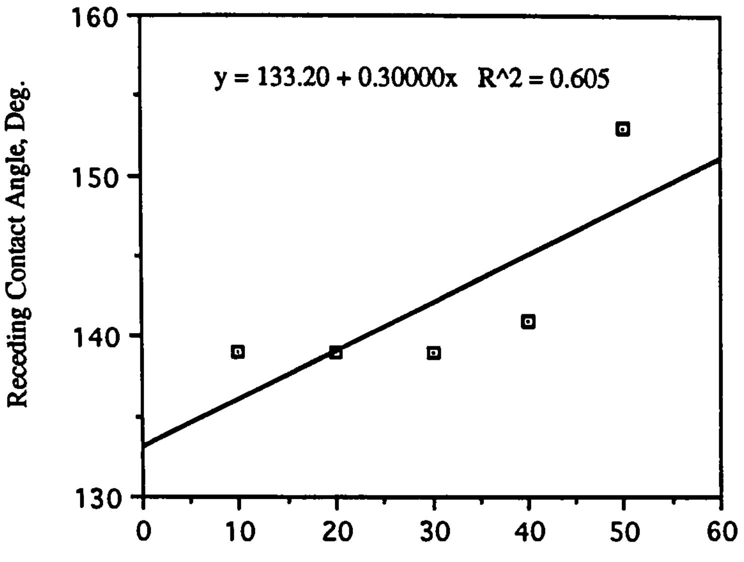
The contact angle is a good way to estimate the adhesion properties between PTFE exposed to an O_2, CF_4, Ar RF plasma in an RIE environment; high advancing contact angles are obtained from high % CF_4 in the gas feed and longer exposure times. The advancing contact angle increases rapidly during the first 15 minutes of exposure for all gas feed compositions except 100% Ar. The increase in the advancing contact angle in the RIE environment becomes larger as the percentage of CF_4 in the plasma gas feed is increased. Between the 15 minute and 45 minute exposures, the advancing contact angle increases more slowly than over the first 15 minutes, especially at the higher CF_4 feed gas compositions. After 45 minute exposure, the advancing contact angle becomes stable and shows no significant change. The receding contact angle decreased with droplet size for all exposures showing an approximately linear dependency.

The best Cu/PTFE adhesion is observed in the pure O_2 and pure Ar plasma exposures; SEM micrographs show increased surface roughness in both of these cases. Oxygen-rich plasma treated PTFE leads to improved adhesion between sputtered copper and Teflon; the higher the O/F atom ratio (XPS) on the surface, the more improved the adhesion.

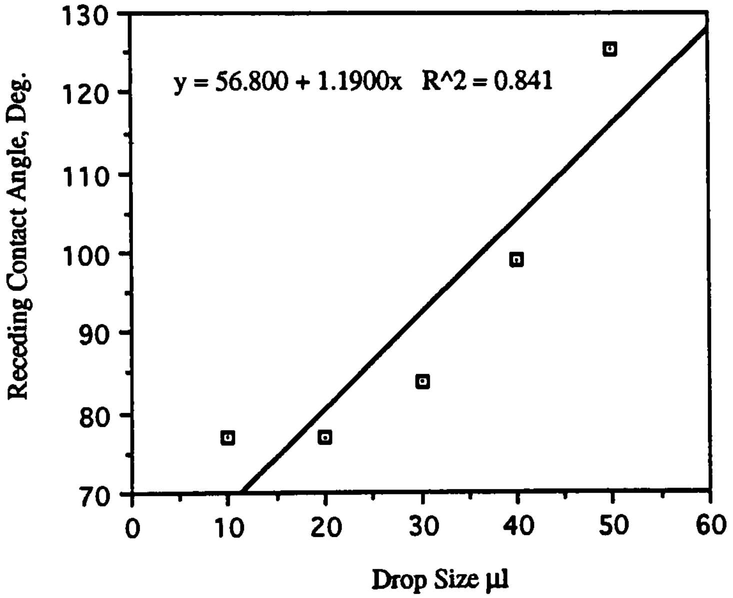
Appendix 1 Receding Contact Angle Results



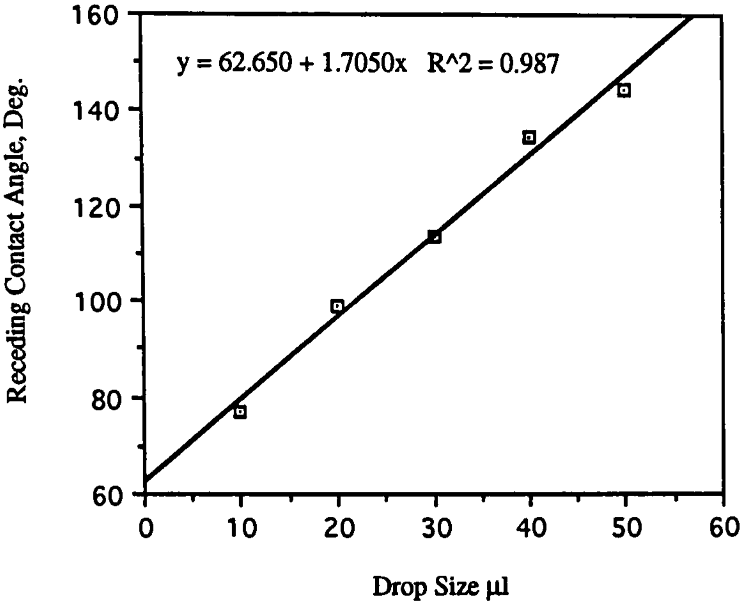




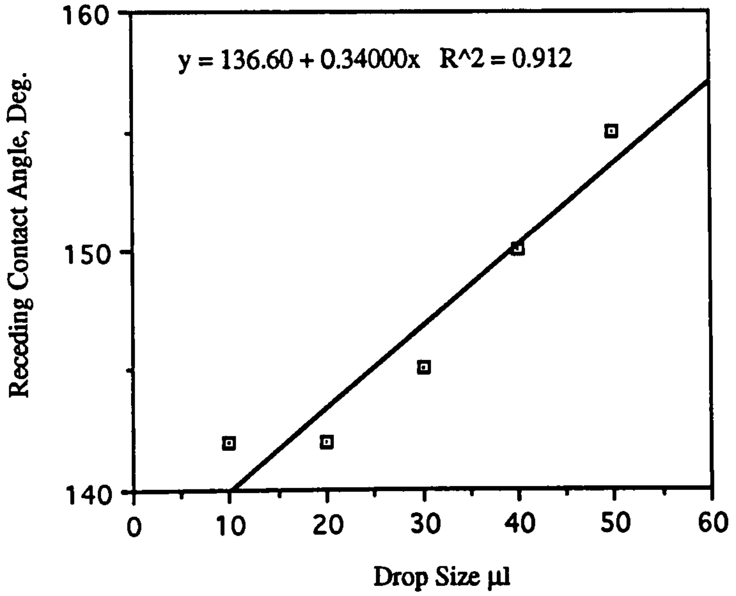
(95 % CF4 45 min)



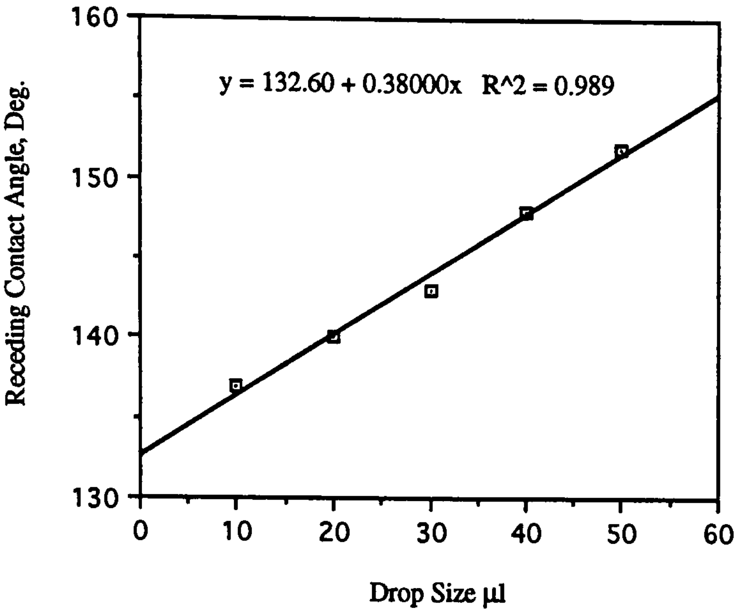
(85 % CF4 1 min)



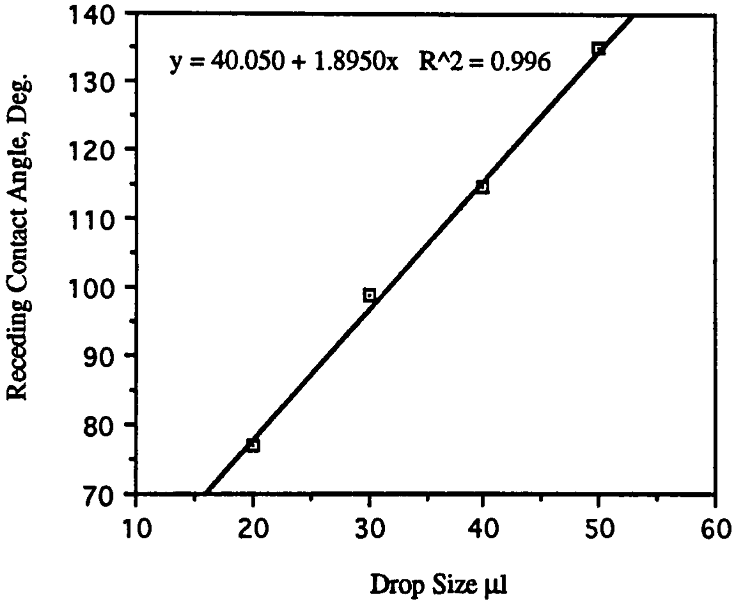
(85 % CF4 5 min)



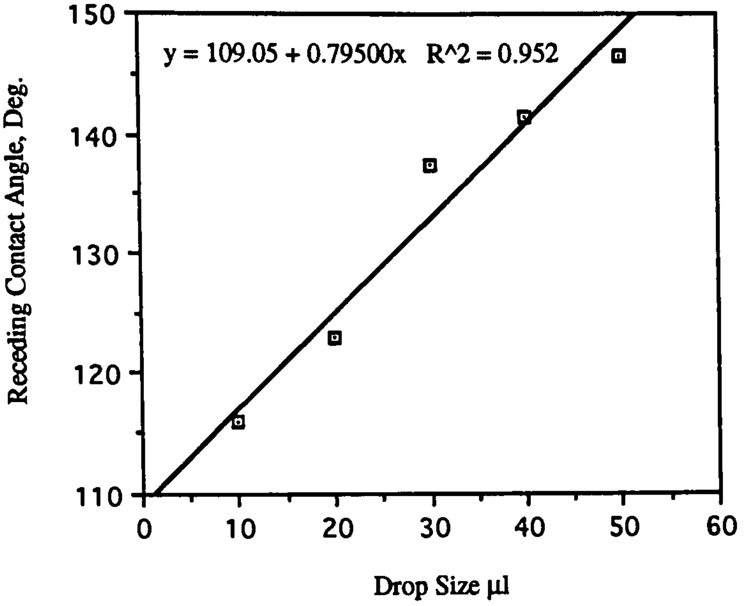
(85 % CF4 1 5 min)



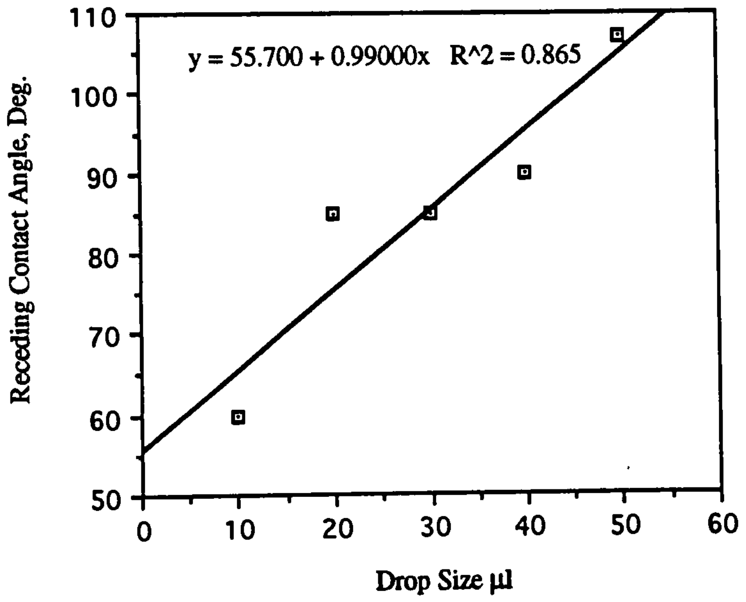
(85 % CF4 45 min)



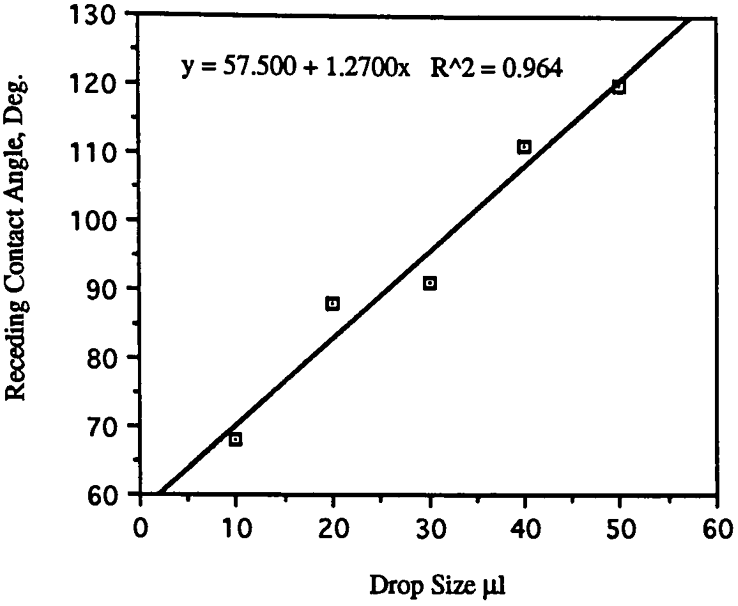
(45 % CF4 5 min)



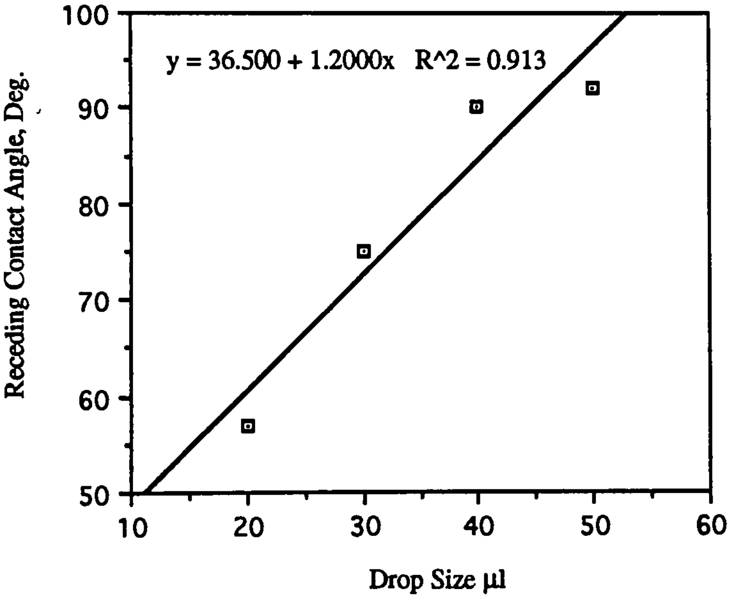
(45 % CF4 15 min)



(100% O2 5 min)



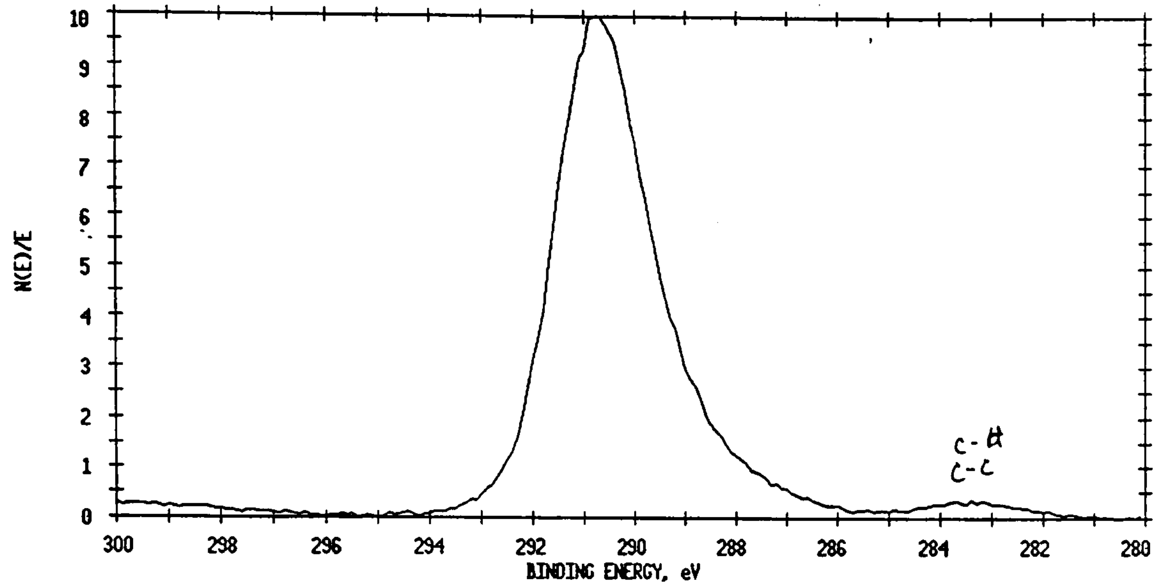
(100 % O2 45 min)



(100% Cr 5 min)

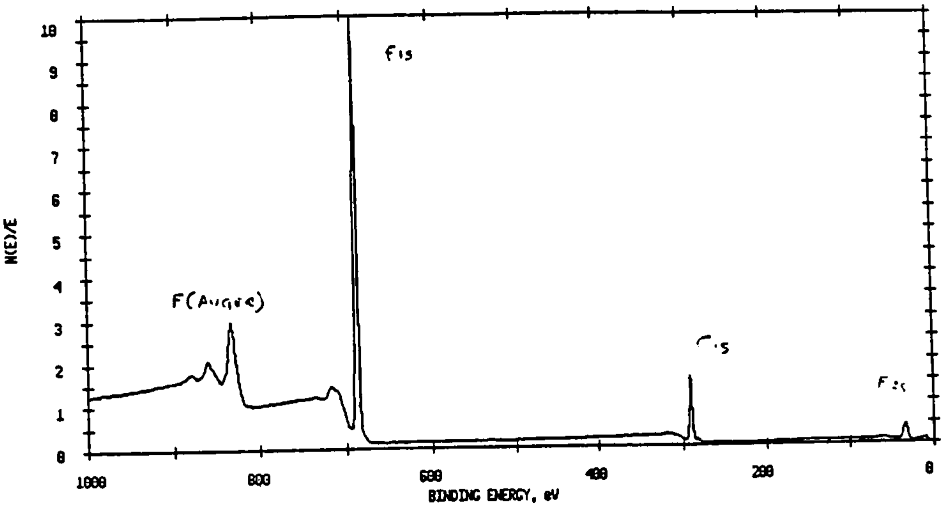
APPENDIX 2 XPS RESULTS

ESCA MULTIPLEX 9/6/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=8.00 min
FILE: 9_rit4 RIT sample #1 041791-1
SCALE FACTOR= 0.467 k c/s, OFFSET= 0.200 k c/s PASS ENERGY= 11.750 eV Al 400 W



SAMPLE 1

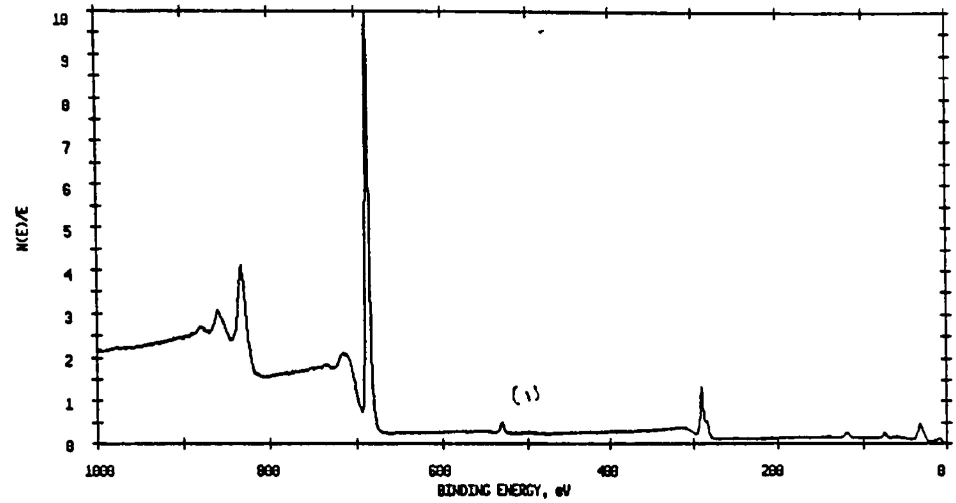
ESCA SURVEY 9/6/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit3 RIT sample #1 041791-1
SCALE FACTOR= 70.400 k c/s, OFFSET= 0.162 k c/s PASS ENERGY=187.850 eV Al 400 W



ESCA SURVEY 9/9/91 ANGLE= 65 deg ACQ TIME=5.00 min

FILE: 9_rit5 RIT sample #042291-4, 45 %CF4, 45 min

SCALE FACTOR= 38.285 k c/s, OFFSET= 0.587 k c/s PASS ENERGY=187.850 eV Al 400 W

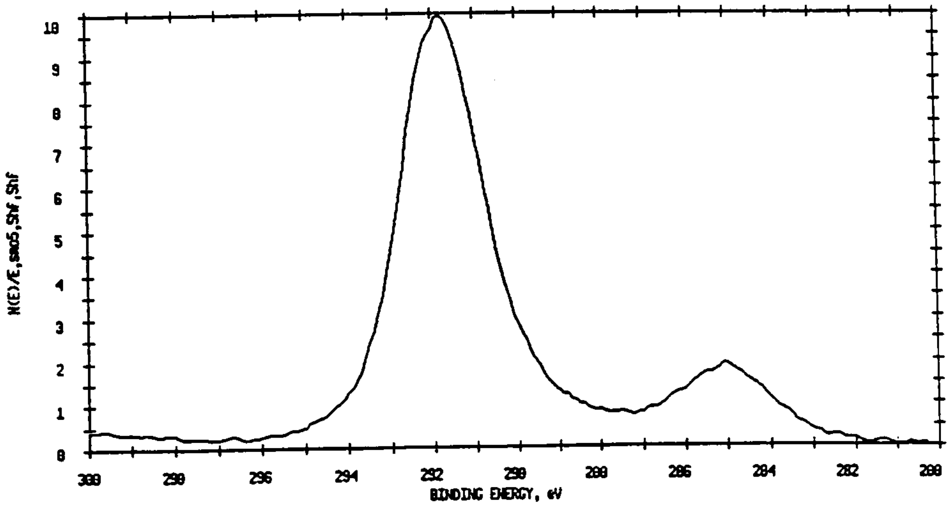


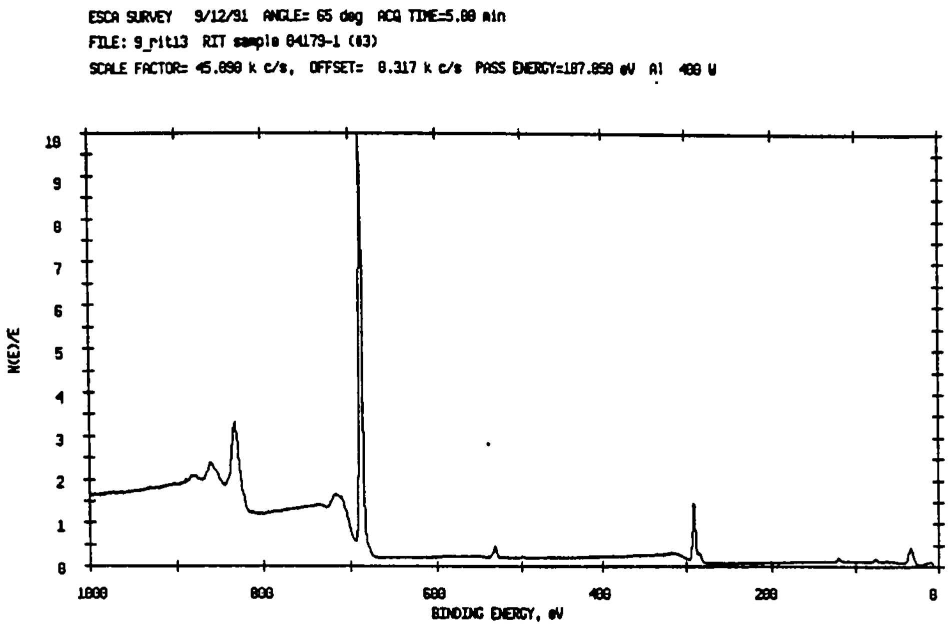
SAMPLE 2

ESCA MULTIPLEX 9/9/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=8.00 min

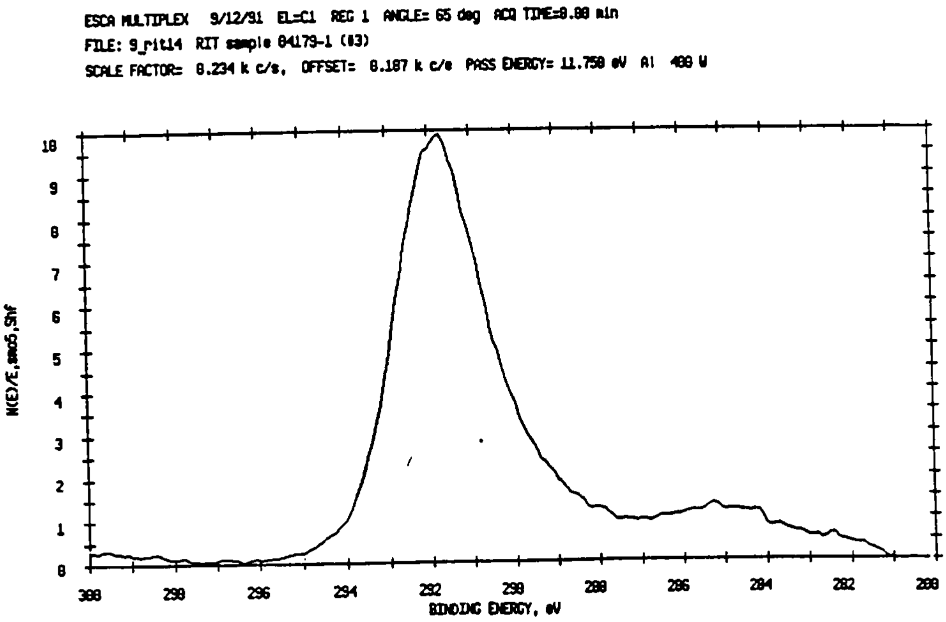
FILE: 9_rit6 RIT sample #042291-4, 45 %CF4, 45 min

SCALE FACTOR= 0.301 k c/s, OFFSET= 0.179 k c/s PASS ENERGY= 11.750 eV Al 400 W

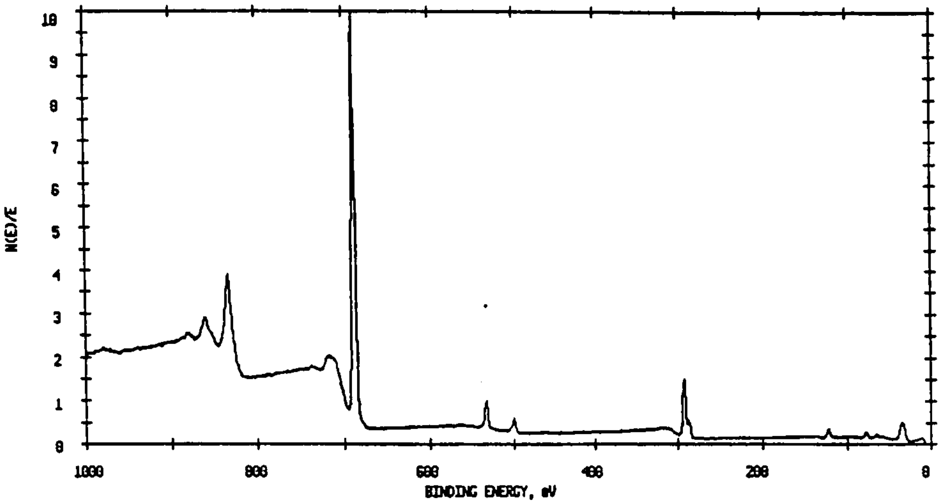



ESCA SURVEY 9/12/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit13 RIT sample 04179-1 (#3)
SCALE FACTOR= 45.090 k c/s, OFFSET= 0.317 k c/s PASS ENERGY=187.850 eV Al 400 W
N(E)/E
10
9
8
7
6
5
4
3
2
1
0
1000
800
600
400
200
0
BINDING ENERGY, eV

SAMPLE 3

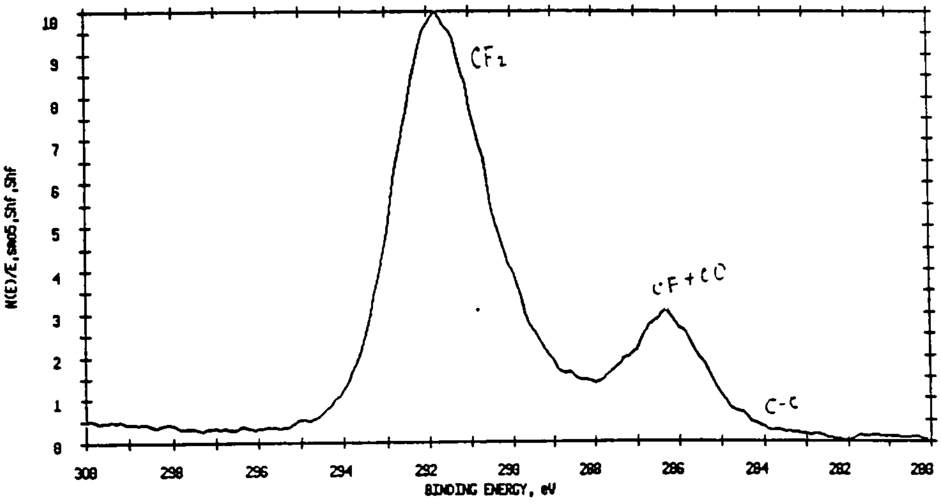

ESCA MULTIPLEX 9/12/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=8.00 min
FILE: 9_rit14 RIT sample 04179-1 (#3)
SCALE FACTOR= 0.234 k c/s, OFFSET= 0.187 k c/s PASS ENERGY= 11.750 eV Al 400 W
N(E)/E,smo5,Shf
10
9
8
7
6
5
4
3
2
1
0
300
298
296
294
292
290
288
286
284
282
280
BINDING ENERGY, eV

ESCA SURVEY 9/13/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit15 RIR 042291-3 (#4)
SCALE FACTOR= 31.621 k c/s, OFFSET= 0.104 k c/s PASS ENERGY=187.850 eV Al 400 W

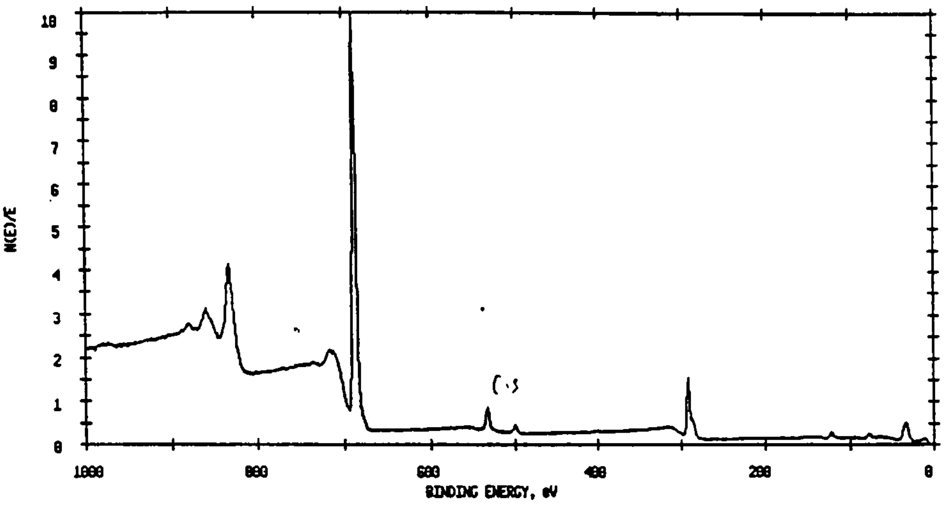


SAMPLE 4

ESCA MULTIPLEX 9/13/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=0.00 min
FILE: 9_rit16 RIR 042291-3 (#4)
SCALE FACTOR= 0.193 k c/s, OFFSET= 0.143 k c/s PASS ENERGY= 11.750 eV Al 400 W

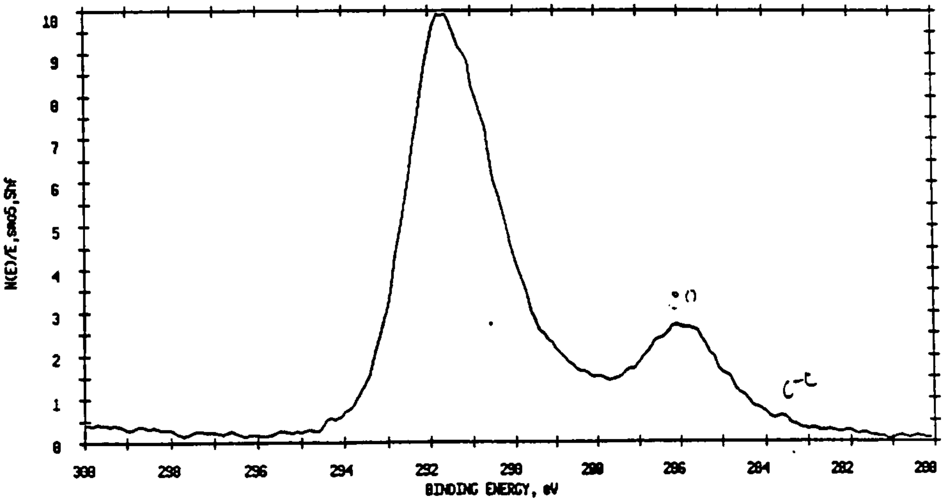


ESCA SURVEY 9/13/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit17 RIT 041191-3 (#5)
SCALE FACTOR= 30.936 k c/s, OFFSET= 0.242 k c/s PASS ENERGY=107.050 eV Al 400 W

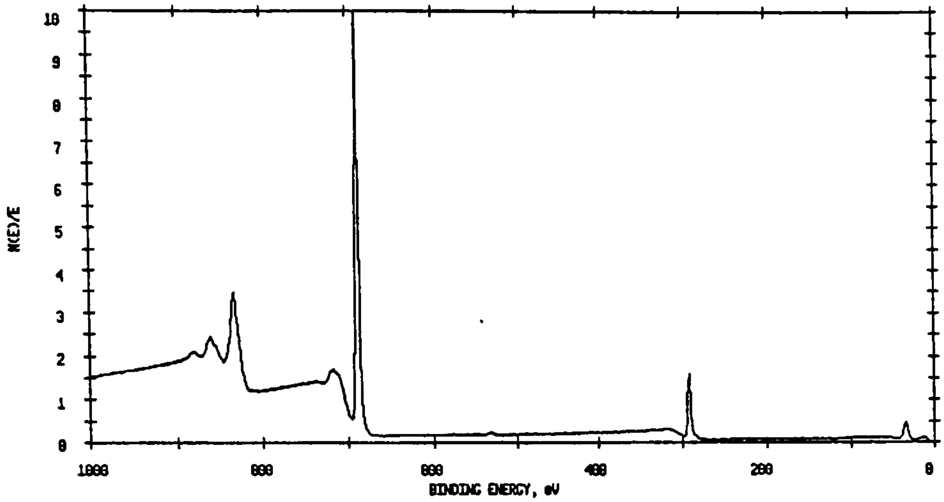


SAMPLE 5

ESCA MULTIPLEX 9/13/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=0.00 min
FILE: 9_rit18 RIT 041191-3 (#5)
SCALE FACTOR= 0.287 k c/s, OFFSET= 0.173 k c/s PASS ENERGY= 11.750 eV Al 400 W

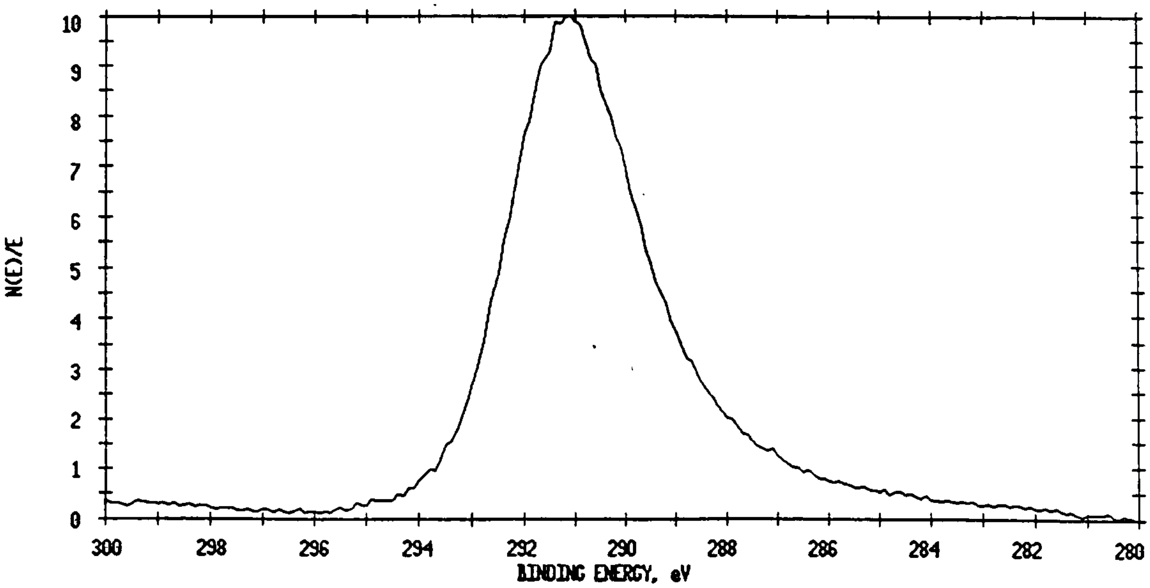


ESCA SURVEY 9/13/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit19 RIT 042091-4 (#6)
SCALE FACTOR= 57.714 k c/s, OFFSET= 0.221 k c/s PASS ENERGY=187.850 eV Al 400 W

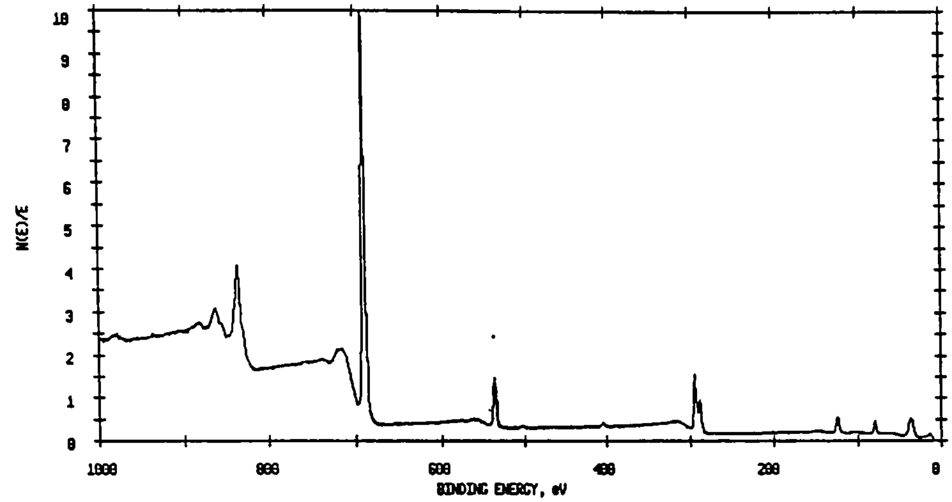


SAMPLE 6

ESCA MULTIPLEX 9/13/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=8.00 min
FILE: 9_rit20 RIT 042091-4 (#6)
SCALE FACTOR= 0.343 k c/s, OFFSET= 0.205 k c/s PASS ENERGY= 11.750 eV Al 400 W

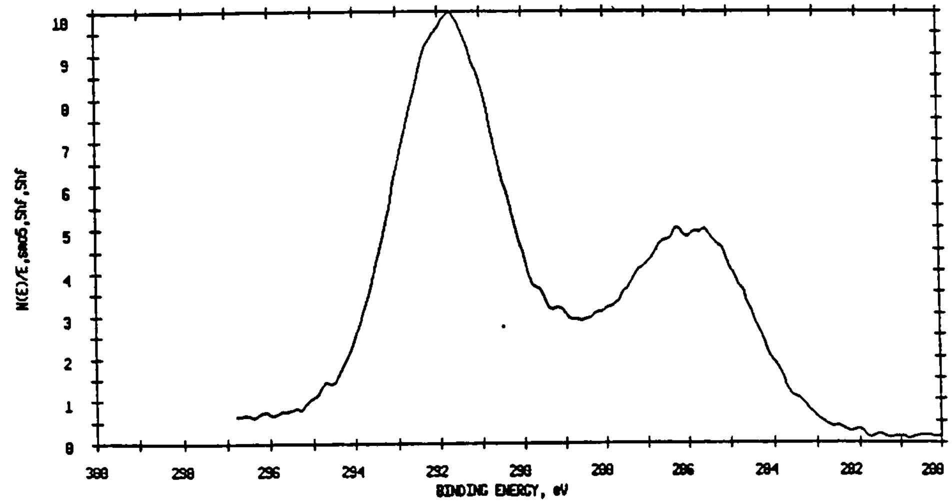


ESCA SURVEY 9/16/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit21 RIT 042291-1 (#7)
SCALE FACTOR= 35.331 k c/s, OFFSET= 0.063 k c/s PASS ENERGY=187.850 eV Al 400 W

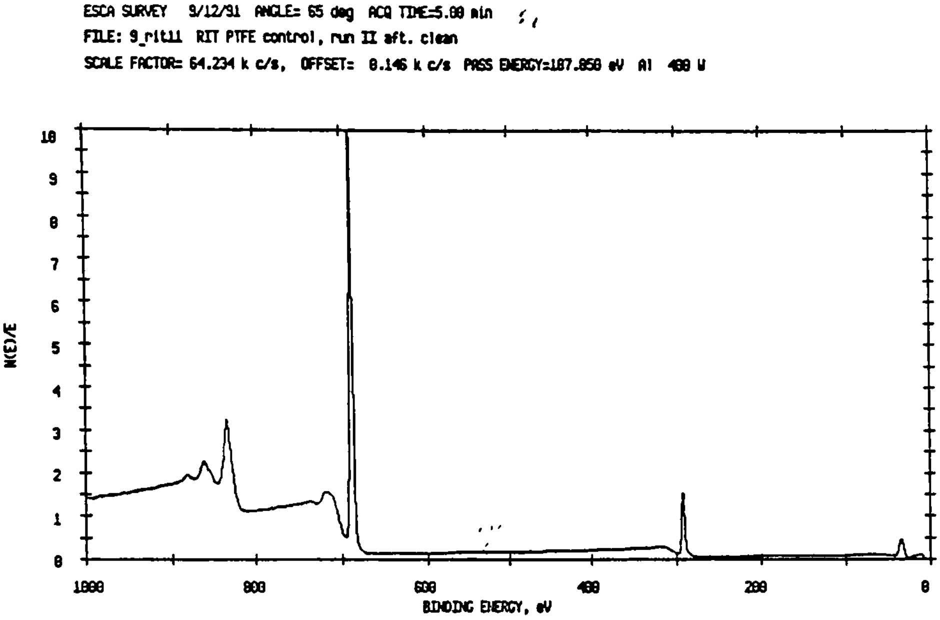


SAMPLE 7

ESCA MULTIPLEX 9/16/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=0.00 min
FILE: 9_rit22 RIT 042291-1 (#7)
SCALE FACTOR= 0.174 k c/s, OFFSET= 0.198 k c/s PASS ENERGY= 11.750 eV Al 400 W



-#-

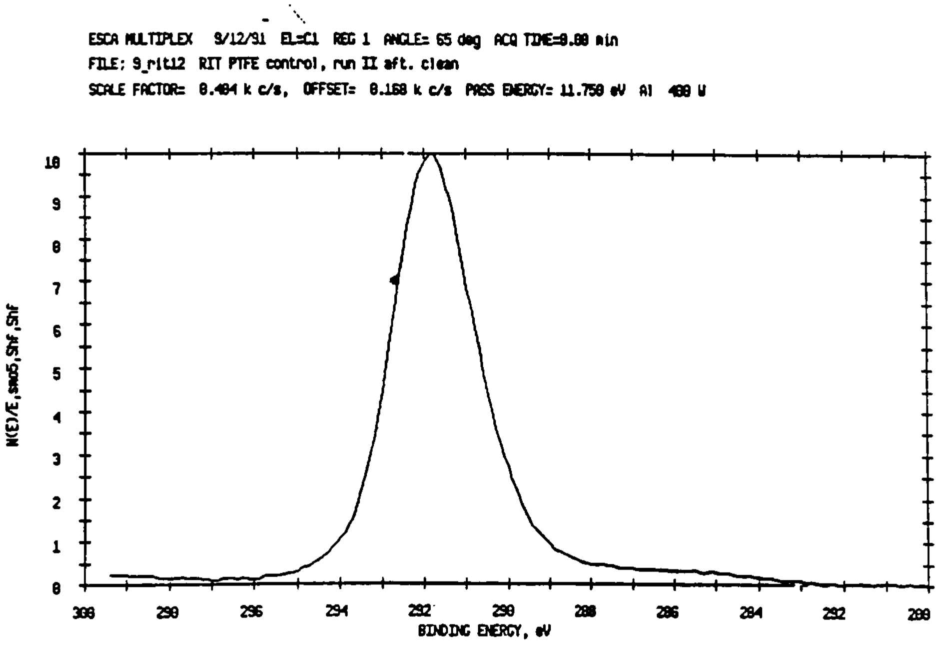


ESCA SURVEY 9/12/91 ANGLE= 65 deg ACQ TIME=5.00 min

FILE: 9_rit11 RIT PTFE control, run II aft. clean

SCALE FACTOR= 64.234 k c/s, OFFSET= 0.146 k c/s PASS ENERGY=187.850 eV Al 400 W

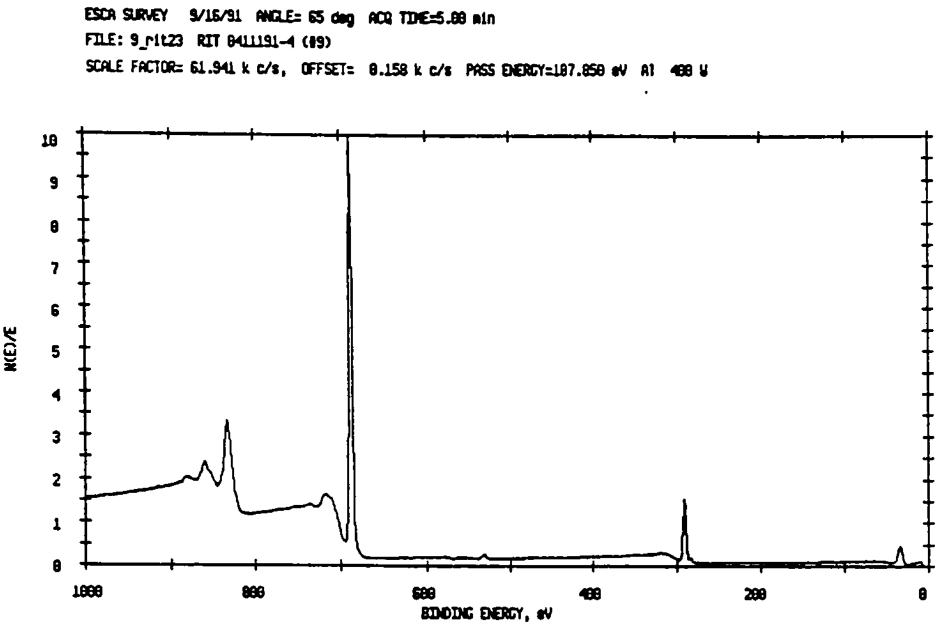
SAMPLE 8



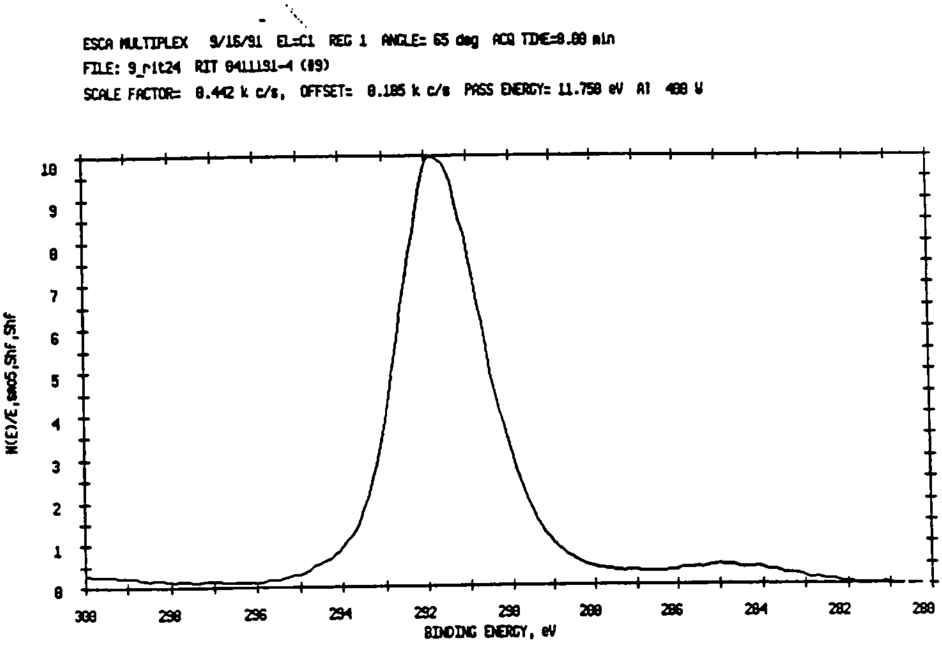
ESCA MULTIPLEX 9/12/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=9.00 min

FILE; 9_rit12 RIT PTFE control, run II aft. clean

SCALE FACTOR= 0.404 k c/s, OFFSET= 0.168 k c/s PASS ENERGY= 11.750 eV Al 400 W


ESCA SURVEY 9/16/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit23 RIT 0411191-4 (#9)
SCALE FACTOR= 61.941 k c/s, OFFSET= 0.158 k c/s PASS ENERGY=187.850 eV Al 400 W
N(E)/E
10
9
8
7
6
5
4
3
2
1
0
1000
800
600
400
200
0
BINDING ENERGY, eV

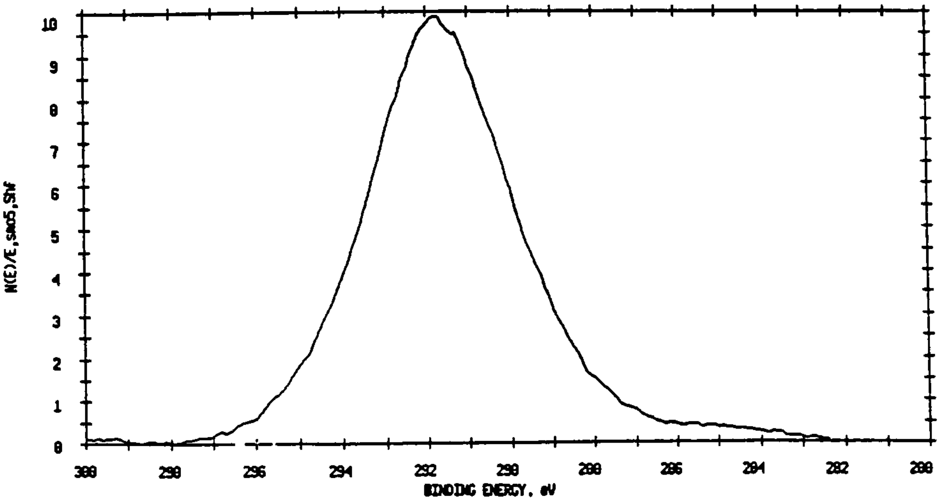
SAMPLE 9

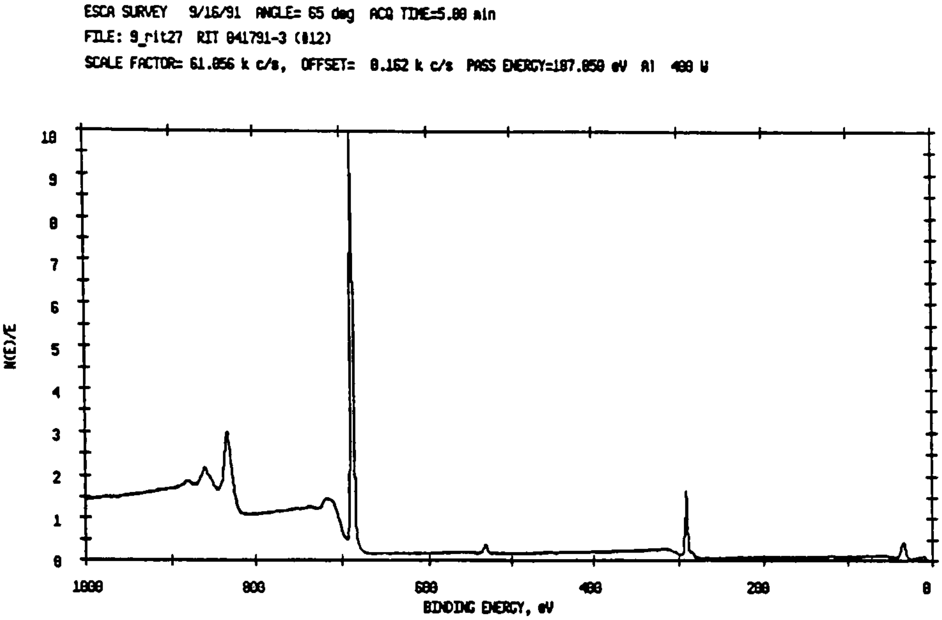

ESCA MULTIPLEX 9/16/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=0.00 min
FILE: 9_rit24 RIT 0411191-4 (#9)
SCALE FACTOR= 0.442 k c/s, OFFSET= 0.185 k c/s PASS ENERGY= 11.750 eV Al 400 W
N(E)/E,sm05,Shf,Shf
10
9
8
7
6
5
4
3
2
1
0
300
298
296
294
292
290
288
286
284
282
280
BINDING ENERGY, eV

ESCA SURVEY 9/16/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit25 RIT 0441191-5 (#10)
SCALE FACTOR= 45.531 k c/s, OFFSET= 0.350 k c/s PASS ENERGY=187.850 eV Al 400 W

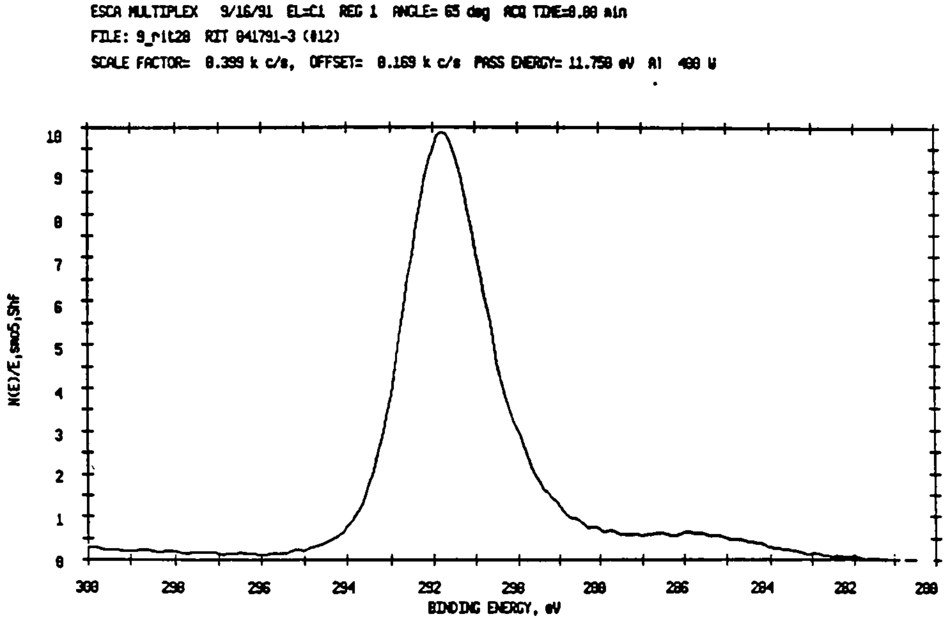
SAMPLE 10

ESCA MULTIPLEX 9/16/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=0.00 min
FILE: 9_rit26 RIT 0441191-5 (#10)
SCALE FACTOR= 0.255 k c/s, OFFSET= 0.272 k c/s PASS ENERGY= 11.750 eV Al 400 W




ESCA SURVEY 9/16/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit27 RIT 041791-3 (#12)
SCALE FACTOR= 61.056 k c/s, OFFSET= 0.162 k c/s PASS ENERGY=187.850 eV Al 400 W

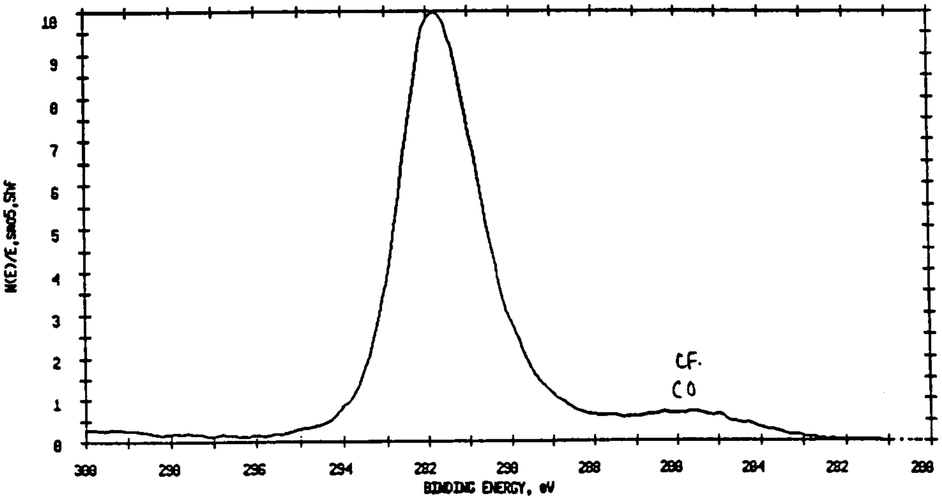
SAMPLE 12


ESCA MULTIPLEX 9/16/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=0.00 min
FILE: 9_rit28 RIT 041791-3 (#12)
SCALE FACTOR= 0.399 k c/s, OFFSET= 0.169 k c/s PASS ENERGY= 11.750 eV Al 400 W

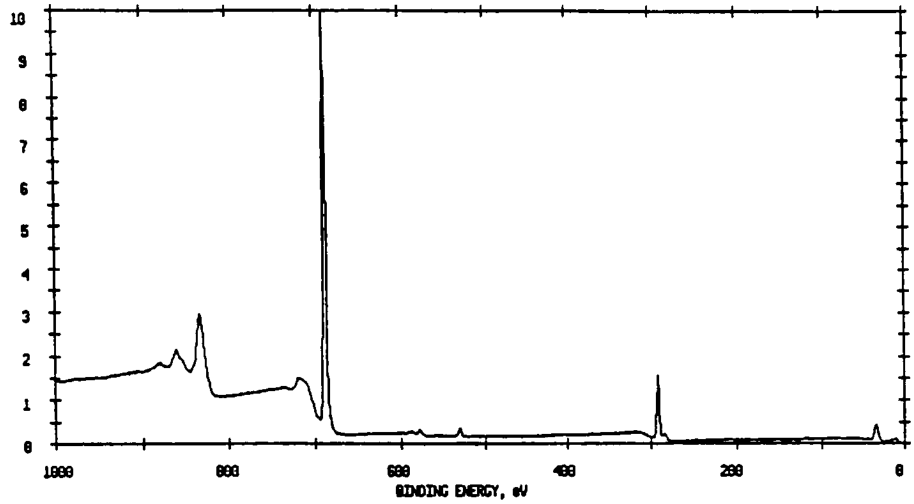
ESCA SURVEY 9/16/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit29 RIT 041191-2 (#13)
SCALE FACTOR= 63.090 k c/s, OFFSET= 0.167 k c/s PASS ENERGY=187.850 eV Al 400 W

SAMPLE 13

ESCA MULTIPLEX 9/16/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=8.00 min
FILE: 9_rit30 RIT 041191-2 (#13)
SCALE FACTOR= 0.423 k c/s, OFFSET= 0.170 k c/s PASS ENERGY= 11.750 eV Al 400 W

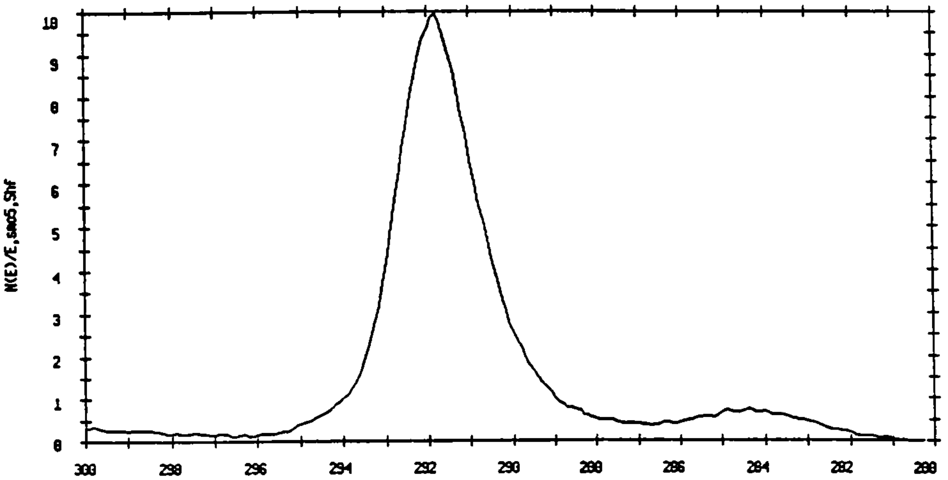


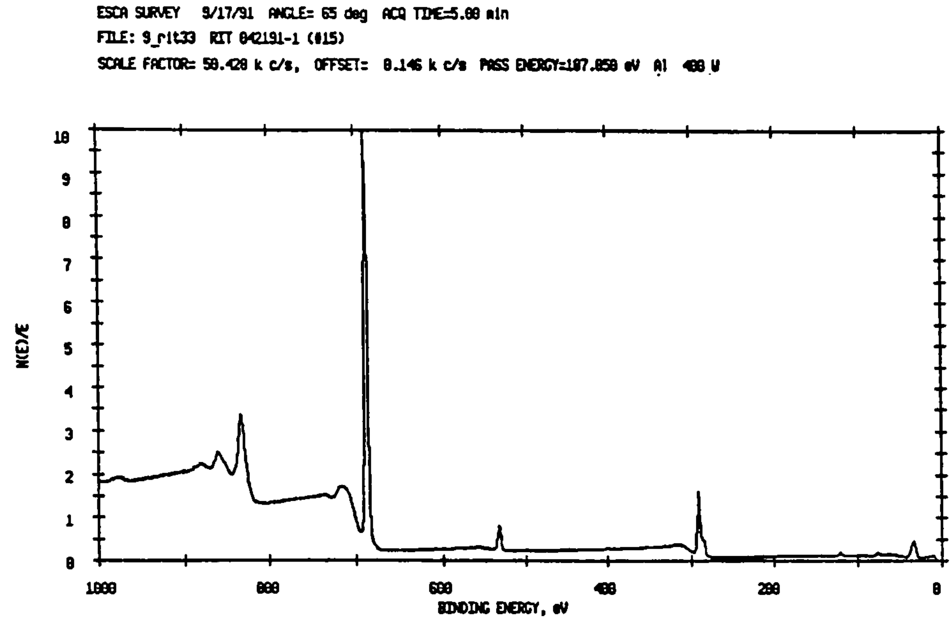
ESCA SURVEY 9/17/91 ANGLE= 65 deg ACQ TIME=5.00 min
FILE: 9_rit31 RIT 042891-2 (#14)
SCALE FACTOR= 63.466 k c/s, OFFSET= 0.213 k c/s PASS ENERGY=187.850 eV Al 400 W



SAMPLE 14

ESCA MULTIPLEX 9/17/91 EL=C1 REG 1 ANGLE= 65 deg ACQ TIME=0.00 min
FILE: 9_rit32 RIT 042891-2 (#14)
SCALE FACTOR= 0.371 k c/s, OFFSET= 0.164 k c/s PASS ENERGY= 11.750 eV Al 400 W





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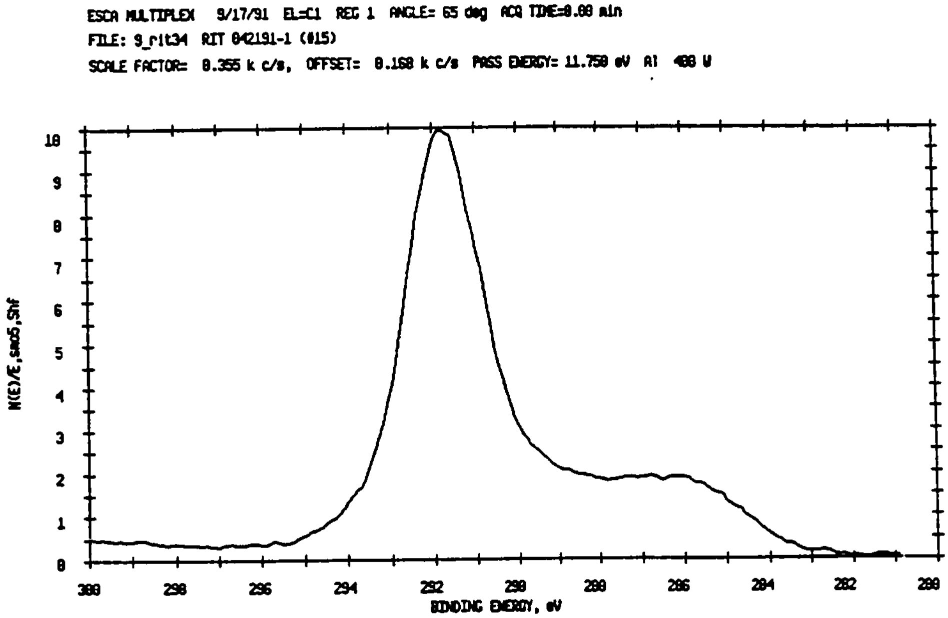
ESCA SURVEY   9/17/91  ANGLE= 65 deg  ACQ TIME=5.00 min
FILE: 9_rit33  RIT 042191-1 (#15)
SCALE FACTOR= 50.420 k c/s,  OFFSET=  0.146 k c/s  PASS ENERGY=107.050 eV  Al  400 W
```

SAMPLE 15



```
ESCA MULTIPLEX   9/17/91  EL=C1  REG 1  ANGLE= 65 deg  ACQ TIME=8.00 min
FILE: 9_rit34  RIT 042191-1 (#15)
SCALE FACTOR=  0.355 k c/s,  OFFSET=  0.168 k c/s  PASS ENERGY= 11.750 eV  Al  400 W
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REFERENCES

[1]. F. D. Egitto, L. J. Matienzo, and H. B. Schreyer, J. Vac. Sci. Technol., A10, 3060, (1992).

[2]. R. Dagani, Chem. and Eng. News, Jan. 6, (1992) 24.

[3]. H. Hiraoka, S. Lazare, T. J. Chuang, C. T. Rettner, and H. E. Hunziker, Microelec. Eng., 13, 429 (1991).

[4]. S. Stinson, Chem. and Eng. News, Apr. 30, (1990) 8.

[5]. S. J. Mumby, J. Elec. Mat'l., Vol. 18, No. 2, 241 (1989).

[6]. R. d'Agostino, F. Cramarossa, F. Francassi, E. Desimoni, L. Sabbatini, G. Zambonin, and G. Caporiccio, Thin Solid Films 143, 163 , (1986).

[7]. D. T. Clark and D. R. Hutten, J. Polym. Sci. A 25, 2643 (1987).

[8]. P. Ho, B. Silverman, R. Haight, R. White, P. Sanda, and A. Rossi, IBM J. Res. Develop., Vol. 32, No. 5, 658 (1988).

[9]. B. Lamontagne and M. R. Wertheimer, 9th Internat. Symp. on Plasma Chem. (ISPC-9), Pugnochiuso, Italy, P. 1045 (1989).

[10]. R. N. Wenzel, Ind. Eng. Chem., 28, 988 (1936).

[11]. W. A. Zisman, Record of Chemical Progress, 26, 13 (1968).

[12]. B. D. Washo, "Highly Nonwettable Surfaces Via Plasma Polymer Vapor Deposition", edited by H. V. Boenig, 1st Int. Conf. of Plasma Chem. and Tech., San Diego, Nov. 14-17 (1982).

[13]. G. A. Takacs, V. Vukanovic, F. D. Egitto, L. J. Msatienzo, F. Emmi, D. Tracy and J. X. Chen, "Modification of Organic Polymer Surfaces with Radiation from High Pressure Inert Gas Plasma Rotating in a Magnetic Field", 10th Int. Sym. Plasma Chem. (ISPC-10), Bochum, Germany, Aug. (1991); Polymer Degradation and Stability, 40 (1993) 73-81

[14]. F.D. Egitto and L. J. Matienzo, Polym. Degrad. and Stab., 30, 293 (1990).

[15]. R. E. Jognson and R. H. Dettre, Adv. Chem. Ser., 43, 112, 136 (1964).

[16]. F. E. Jognson and R. H. Dettre, J. Phys. Chem., 68, 1744 (1964).

[17]. R. d'Agostino, L. Martinu, and V. Pische, Plasma Chem. and Plasma Proc., Vol. 11, No.1, P. 1 (1991).

[18]. L. Martnu, V. Pische, and R. d'Agostino, 9th Int. Sym. Plasma Chem. (ISPC-9), Pugnochiuso, Italy, P. 1642 (1989).

[19]. V. Mugica, J. P. Kusior, E. Matuszak, R. Clark, G. A. Takacs, V. Vukanovic, F. D. Egitto, F. Emmi, and L. J. Matienzo, 9th Interant. Symp. on Plasma Chem. (ISPC-9), Pugnochiuso, Italy, P. 997 (1989).

[20]. A. M. Wrobel, B. Lamontagne, and M. R. Wertheimer, Plasma Chem. and Plasma Proc. Vol. 8, No. 3, P. 315 (1988).

[21]. S. J. Moss, Polymer Degrad. and Stab. 17, 205 (1987).

[22]. F. D. Egitto, V. Vukanovic, and G. N. Taylor, edited by R.d'Agostino, "plasma Deposition, Treatment, and Etching of Polymers", Academic Press, Inc., Boston, P. 321 (1990).

[23]. F. D. Egitto, F. Emmi, R. S. Horwath, and V. Vukanovic, J. Vac. Sci. Tech., B3, 3, 893 (1985).

[24]. F. Emmi, F. D. Egitto, R. S. Horwath, and V. Vukanovic, Proc. Electro. Chem. Soc., 85-1 (Plasma Process), 193 (1985).

[25]. Ch. Steinbruchel, B. J. Curtis, H. W. Lehmann, and R. Widmer, J. Vac. Sci. Technol., A4 (3), 1798 (1986).

[26]. S. R. Cain, F. D. Egitto, and F. Emmi, J. Vac. Sci. Technol., A5 (3), 1578 (1987).

[27]. A. Entenberg, V. Lindberg, L. Fendrock, Sang-Ki Hong, T. S. Chen, and R. S. Horwath, Metalized Plastics I, edited by K. L. Mittal and J. R. Susko, Plenum Publishing Corp., P. 103 (1989).

[28]. H. Biederman and L. Holland, Nucl. Instrum. Meth. 212, 497 (1983).

[29]. H. Biederman, Vacuum, 34, 405 (1984).

[30]. H. Biederman and L. Martinu, Plasma Chem. Technol. Applic., 1, 37 (1984).

[31]. C. A. Kovac, J. L. Jordan-Sweet, M. J. Boldberg, J. G. Clabes, A. Viehbeck, and R. A. Rollak, IBM J. Res. Develop. Vol.32, No. 5, 603 (1988).

[32]. A. L. Ruoff, E.J. Kramer, and C. Y. Li, IBM J. Res. Develop. Vol. ew, No.5, 628 (1988).

[33. C. A. Chang, J. E. E. Baglin, A. G. Schrott, and K. C. Lin, Appl. Phys. Lett. 51 (2), 13, 103 (1987).

[34]. C. A. Chang, Appl. Phys. Lett. 51 (16), 19, 1236 (1987).

[35]. J. G. Fagan, "Reaction Ion Etching of Polyamide Films Using a Radio Frequency Discharge", M. S. Thesis, Rochester Institute of Technology, 1987.

[36]. "Contact Angle Goniometers"--Instruction Manual, Rame-hart,Inc., Mountain Lakes, NJ.

[37]. A. Entenberg. V. Lindberg, K. Fletcher, A. Gatesman, and R. S. Horwath, J. Vac. Sci. Technol. A5 (6), 3373 (1987).