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Preparation and Characterization of Glow Discharge Fluorocarbon-Type Polymers

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ABSTRACT

Thin polymer films have been prepared by electrodeless glow discharge polymerization of tetrafluoroethylene monomer. Process conditions are described for the deposition of adherent, Freon-insoluble polymer films on smooth metal surfaces. The polymer deposition rate is strongly dependent on position in the system. At the operating pressure of 0.05 Torr, the deposition rate was not dependent on rf power over the range of 200 to 500 W. However, the rate did increase with an increase in pressure. The polymer films were characterized by x-ray photoelectron spectroscopy, IR absorption spectrum, and surface wettability. The film deposited in the main chamber had a uniform chemical composition which consists of CF_2 functional groups with a small fraction of CF_3. The film closer to the plasma zone had a more complex chemistry. The carbon 1s binding energies were compared to calculated values based upon group shifts and electrostatic potential models. The critical surface tension of the polymer film in the deposition chamber was lower than Teflon. The presence of CF_3 groups and the character of the glow discharge polymer may account for the lower surface energy.

INTRODUCTION

The present study was designed to investigate the deposition of thin films (<100 nm) of fluorocarbon-type polymers on metal surfaces. The films were deposited with an electrodeless rf source external to the polymer deposition system. Other investigators [1, 2] have used an electrodeless rf system for styrene polymerization. Fluorocarbon-type films have been deposited by glow discharge polymerization in an electrode-type system [3]; the films which were deposited on alkali halide crystals were pin-hole free, chemically resistant, and highly adherent. Electrodeless discharge carried out in a flow system is more suitable for polymer deposition onto a metal surface. The metal can be placed outside the rf field where inductive heating is avoided. Also, the substrates can be easily rotated to provide a uniform polymer film thickness. Our films were of interest as corrosion protective coatings for metals and as low friction surfaces. The films were characterized by x-ray photoelectron spectroscopy (XPS), contact angle measurements, and IR spectroscopy. XPS was important as a means to show how polymer composition changed in relation to the distance from the plasma.

EXPERIMENTAL

Figure 1 shows the thin polymer film deposition system. A 500-W, 13.56 MHz rf generator (LFE Corporation) was used to inductively couple to tetrafluoroethylene (TFE) monomer flowing through a fused silica tube. Substrates were placed immediately before the rf coil (A), inside the rf coil zone (B), immediately after the rf coil (C), in the deposition chamber (0.41 m diam × 0.21 m) (D), and at the exit of the deposition chamber (E). The system was evacuated to less than 0.001 Torr. The samples in the deposition chamber were rotated at 6 rpm to provide a uniform polymer coating. A Sloan quartz crystal thickness sensor and a laser deflection system [4] provided in situ information on the rate of polymer deposition. The latter system was synchronized with a rotating sample. The flow rate of the TFE monomer was calculated from the rate of pressure increase when the pump was disconnected from the deposition chamber. At a pressure of 0.04 Torr, the TFE flow rate was approximately 2.3 cm^3 (STP)/min.

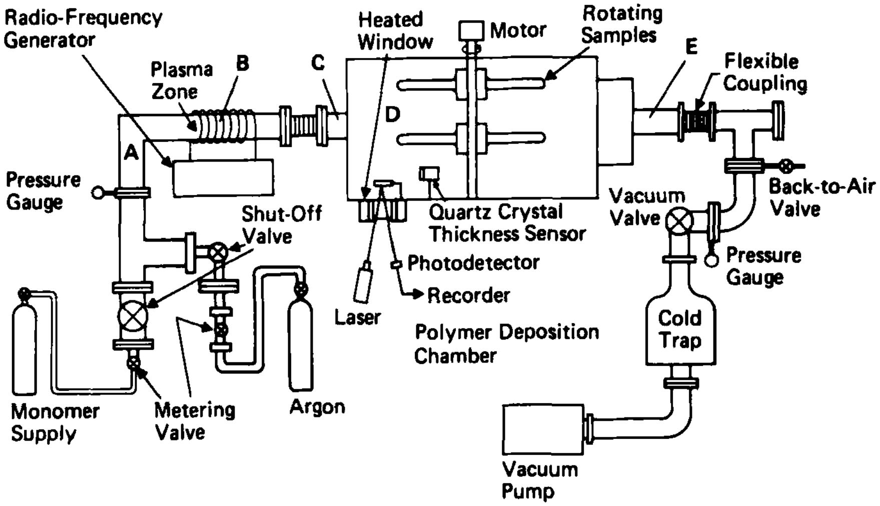


FIG. 1. Glow discharge thin polymer film deposition system.

The substrates were highly polished iron alloy surfaces and thin polycrystalline cobalt films (100 nm) on glass slides. All substrates were electrically grounded during the deposition process. The substrates were cleaned ultrasonically in hexane, acetone, and isopropanol before being loaded in the deposition system. The substrates were treated in situ with an argon plasma immediately before the polymer deposition. The argon plasma was shown [5] by Auger analysis to remove traces of carbon and sulfur which may influence the polymer adhesion. The TFE monomer with 1% α-terpinene was admitted to the deposition system and a plasma established. Depositions were made with the rf power between 200 and 500 W and with the TFE pressure between 0.02 and 0.18 Torr at the entry to the plasma zone.

The deposited films were examined microscopically for continuity. Furthermore, they were exposed to a simulated gaseous environment that accelerates indoor corrosion processes common to transition metal systems. The test environment is given in Table 1. This environment will "decorate" pores in the polymer film by corroding the metal substrate. Pore density, size, and surface roughness were measured as a function of time. Polymer film thickness was measured with a Gould Microtopographer which also indicated surface smoothness. Adhesion was measured by a Scotch tape test and a diamond probe scratch method. The scratch test indicated the degree of loading before film failure

TABLE 1. Corrosion Test Environment (temperature, 25.0°C; gas velocity, 10 cm/sec)[a]

Gas	Concentration ($\mu g/m^3$)	Rational	Analytic method
H_2O	70% RH	Known accelerator of galvanic corrosion and present at relatively large P/P_0	Dew point on cooled Au surface (continuous)
SO_2	810	Major pollutant—known to attack Fe, Ni, Co. Forms acid on metal surface	Flame photometric (continuous)
NO_2	940	Major pollutant—known to attack Ti, Co, Ni, Fe	Chemiluminescence (continuous)
O_3	334	Major pollutant—degrades polymers and accelerates oxidative decay of H_2S, NO_2, SO_2	Chemiluminescence (continuous)
H_2S	21	Stress corrosion accelerator	Pb acetate densitometry (periodic)
Cl_2	8.6	Destabilizes otherwise passive films by lattice impregnation and acid dissolution	o-Tolidine densitometry (periodic)

[a] Balance, purified dry air.

and the mode of failure (tearing or rupture). Coating solubility was evaluated using Freon TF.

The surface energies of the deposited films were evaluated using the concept of critical surface tension developed by Zisman [6]. Contact angles were measured with a Rame Hart Model A-100 goniometer using hexane, heptane, tetradecane, hexadecane, benzene, and 1-methylnaphthalene as reference fluids.

The IR spectrum of the polymer films deposited on KBr pellets was obtained with a Perkin-Elmer Model 457 Spectrophotometer. X-ray photoelectron spectrum were measured with a dispersion compensated monochromatized spectrometer using Al(Kα) radiation (Hewlett-Packard Model 5950 A). The fluorine 1s binding energy was used as a reference (689.85 eV) [7] with particular emphasis being given to the carbon 1s region of the spectrum. XPS is well suited to fluorocarbon analysis because of the long-lived final states (minimizes relaxation contributions) and large carbon 1s shifts due to fluorine bonding. The escape depth of the C(1s) photoelectron is approximately 3.0 nm [8] and its resolution 0.8 eV.

RESULTS

Polymer coatings were deposited uniformly on the rotating substrates in the deposition chamber (region D of Fig. 1). Film thickness ranged from 30 to 80 nm depending on the deposition time. Coatings in the plasma zone and immediately after the plasma (regions B and C in Fig. 1) were 100 to 1000 times thicker. Figure 2 shows the polymer deposition rate recorded on the quartz crystal rate monitor (region D) vs the pressure squared between

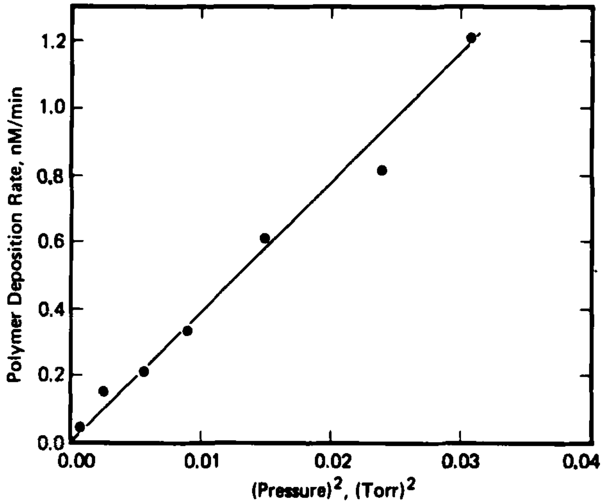


FIG. 2. Polymer deposition rate in region D of Fig. 1 vs pressure squared.

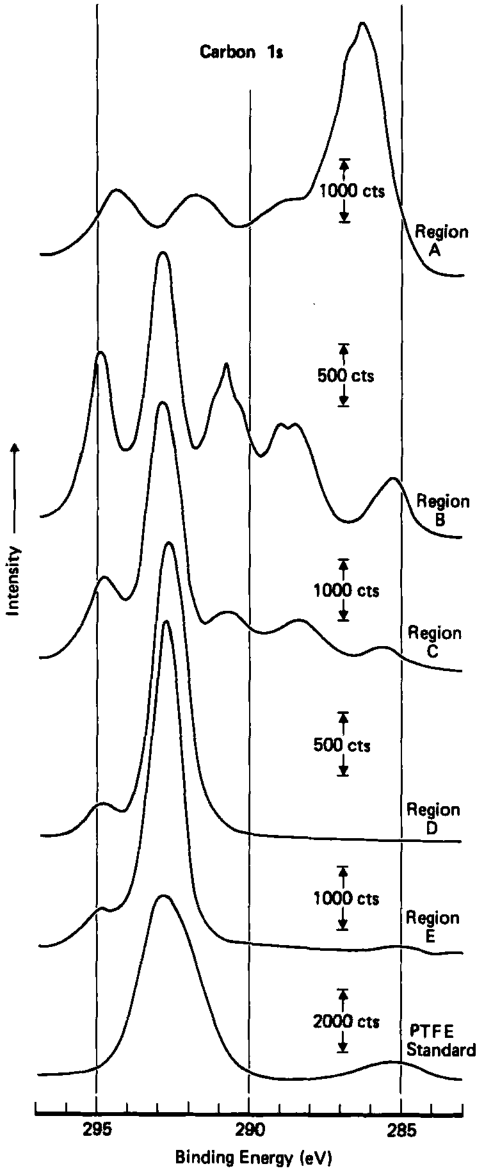


FIG. 3. Carbon 1s x-ray photoelectron spectra of plasma-deposited fluorocarbon polymer films from different regions of the plasma system.

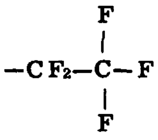
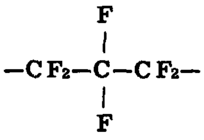
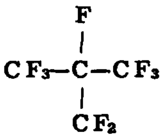
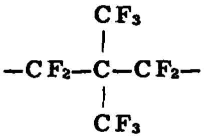
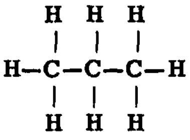
0.025 and 0.175 Torr. The deposition rate is directly proportional to the pressure squared. Above 0.175 Torr the deposition rate decreased. The best quality polymer films in region D were prepared at 0.05 Torr or less and 300 W power. These films were insoluble in Freon TF. Power levels of 200 to 500 W did not alter the deposition rate.

Figure 3 shows the carbon 1s region of the x-ray photoelectron spectra for representative films deposited in regions A → E of the plasma system (Fig. 1). The bonding of carbon is more complex in the films deposited in the plasma region (A → C) than in the deposition chamber (D → E). Furthermore, the carbon-to-fluorine intensity ratio shows enhanced carbon in the films deposited in the plasma region as compared to polytetrafluoroethylene. In fact, the stoichiometry is closer to that of CF than CF_2. Assignment of the carbon bonding can be made on the basis of group shifts and electrostatic potential models [9] coupled with experimental work done on bulk polymers [7]. Table 2 lists the binding energies for the carbon 1s region, the F(1s)/C(1s) intensity ratios, the shift in binding energy (ΔBE exp) compared to the low binding energy state, and the calculated shift in binding energy (ΔBE cal) based upon the group shift work of Gelius et al. [9]. In the plasma region (B), carbon is bonded in a minimum of seven forms ranging from $-CF_3$ to $-CH_2-$. In the deposition chamber only two forms are distinguishable: $-CF_3$ and $-CF_2-$, with the former present at levels approximately equal to 5%. Region A shows what is speculated to be preferrential deposition of a predominantly hydrocarbon-like polymer from the α-terpinene used as the inhibitor in TFE. The peaks due to fluorinated carbon are shifted to lower binding energy because of the reduced fluorine density in the polymer.

The 1800 to 400 cm^{-1} IR absorption spectrum for our glow discharge fluorocarbon-type film is shown in Fig. 4. This film was taken from the deposition chamber (D). The major absorption peaks are near 1215 and 1160 cm^{-1}. No other major absorptions were observed from 4000 to 200 cm^{-1}. The spectrum is very similar to that reported for PTFE [10, 11]. The major peaks in PTFE at 1207 and 1152 cm^{-1} have been assigned to $-CF_2-$ stretching modes. Small quantities of $-CF$ and $-CF_3$ are not precluded by the IR spectrum. The small peak at 980 cm^{-1} in Fig. 4 is not present in PTFE, but has been attributed to the C—F group in the tetrafluoroethylene-hexafluoropropene copolymer. The symmetric stretching of the CF_3 group is expected at 1166 cm^{-1} and cannot be distinguished from the CF_2 band at 1152 cm^{-1}.

The polymer films were not removed by the Scotch tape test. Also, a diamond probe scratch test [12] indicated good adhesion of the polymer film to a highly polished metal surface (CLA = 8.9 nm, RMS = 13.5 nm) and a smooth evaporated metal surface (CLA = 4.5 nm, RMS = 8.3 nm). Surface roughness of the substrates is

TABLE 2. Carbon 1s XPS Results for Plasma Deposited Fluorocarbon-type Films

Deposition region	Carbon 1s binding energy (eV)					$\frac{I_F\,(1s)}{I_C\,(1s)}$
B	294.8	292.8	290.3 290.8	288.4 289.0	285.4	4.82
C	294.8	292.8	290.7	288.3	285.5	5.79
D	294.7	292.7	-	-	-	10.9
E	294.7	292.8	-	-	285.3	10.8
$\overline{BE}$ (eV)	294.8	292.8	290.6	288.6	285.4	-
ΔBE (exp)	9.4	7.4	5.2	3.2	0	-
ΔBE (cal) [9]	9.4	7.0	4.6	2.6	0	-
Bond structure	$-CF_3$	$-CF_2-$	$-\overset{\vert}{\underset{\vert}{C}}-F$	$-\overset{\vert}{\underset{\vert}{C}}-$	$-CH_2-$	-
Model groups	 $-CF_2-\overset{F}{\underset{F}{C}}-F$	 $-CF_2-\overset{F}{\underset{F}{C}}-CF_2-$	 $CF_3-\overset{F}{\underset{CF_2}{C}}-CF_3$	 $-CF_2-\overset{CF_3}{\underset{CF_3}{C}}-CF_2-$	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	-

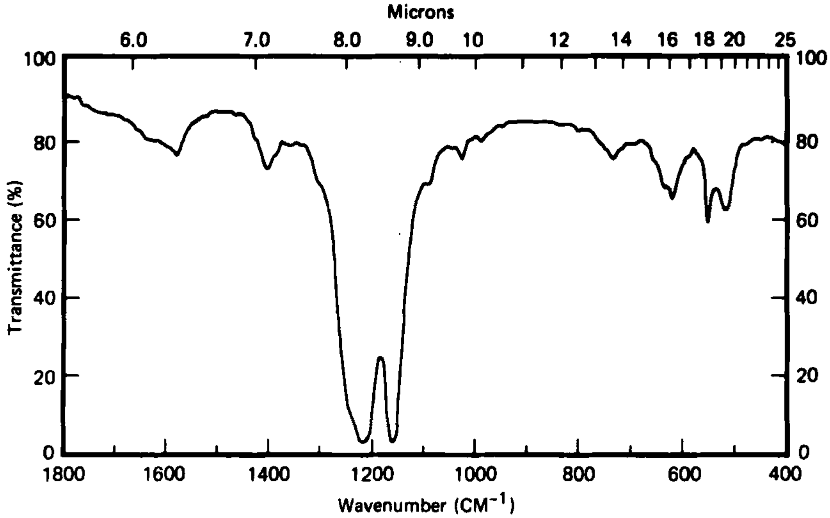


FIG. 4. Infrared absorption spectrum for a glow discharge fluorocarbon-type polymer film.

indicated by CLA (center line average) and RMS (root mean square) of the peak to valley distances measured on the microtopographer. The films deposited in the chamber (D) were insoluble in Freon TF.

The polymer films deposited on the smooth substrates were examined under low magnification and found to be continuous and free of cracks. Atmospheric testing to "decorate" microscopic pores in the films showed evidence of pitting. The corrosion spots on the metal substrate due to the pits grew in size with time; however, the density remained constant. For a 30 nm, film pit densities of approximately 200/mm^2 were measured, while the 80 nm thick film dropped to 40. These pit densities are much less than metal coatings of similar thickness. This points to the potential of polymer films in the very thin film range to protect sensitive metallurgies.

The wettability of organic surfaces is determined by the nature and packing of the surface atoms and exposed groups. Zisman has shown a close correlation between critical surface tension for spreading (γ_c) and the constitution of the solid surface. A rectilinear relation has been established between the cosine of the contact angle and the surface tension at the interface of the liquid and vapor phases (γ_{LV}) for each homologous series of organic liquids. γ_c for each series is defined by the intercept of the straight line plot of cos θ vs γ_{LV} with the cos $\theta = 1$ axis. The surface of lowest energy (lowest γ_c) is that comprised of closed pack $-CF_3$

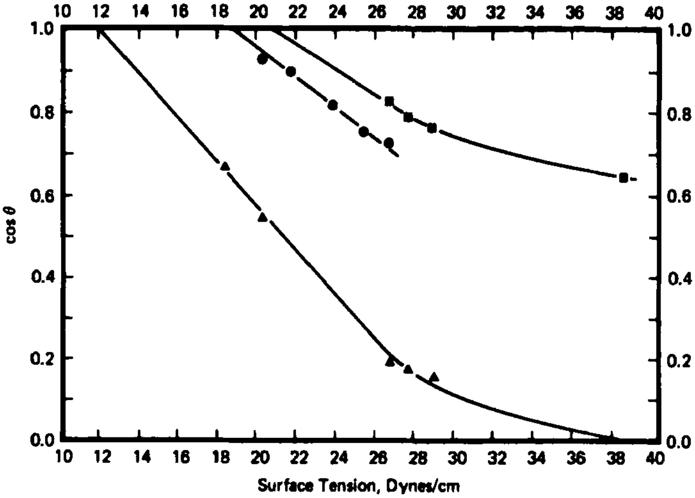


FIG. 5. Wettability of fluorocarbon-type polymers. Teflon measured by Chan (●), and glow discharge polymers from the deposition chamber (▲) and the plasma zone (■) described in Fig. 1.

groups [3] where γ_c is 6 dyn/cm for a condensed absorbed monolayer of perfluorolauric acid. γ_c has a value of 19 dyn/cm for n-alkanes on the surface of Teflon [14]. The contact angle measurements are shown in Fig. 5 for the glow discharge fluorocarbon-type polymers from two regions of the deposition system and for Teflon [14]. The samples from the deposition chamber (region D, Fig. 1) have higher contact angles than Teflon [14]. γ_c for the deposition chamber films is 12 dyn/cm. The presence of some CF_3 groups and the large CF_2 group concentration observed in XPS (Fig. 3) would account for this low γ_c value. Polymers closer to the plasma zone are more wettable; this can be explained by the presence of functional groups other than CF_2 and CF_3 as shown in the XPS data of Fig. 3.

SUMMARY

The composition of polymer films prepared by electrodeless glow discharge polymerization of TFE was shown to be dependent on the distance of the deposited film from the rf plasma zone.

The most distant fluorocarbon films had a lower surface energy than Teflon and provided a reasonably good protective coating (80 nm) for metals in a corrosive atmosphere.

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