Plasma Polymerization of Tetrafluoroethylene. III. Capacitive Audio Frequency (10 kHz) and AC Discharge

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Synopsis

The plasma polymerization of tetrafluoroethylene (TFE) is studied in a capacitively coupled system with internal electrodes using a 10 kHz (af) and a 60 Hz (ac) source. The emphasis is on identifying conditions that are compatible with continuous coating of plasma polymer on a substrate moving through the center of the interelectrode gap. Operation at a pressure below 100 mTorr is most favorable for deposition of a substantial portion of the plasma polymer on this substrate. Plasma polymer deposited in this way is characterized by ESCA and by deposition rate data and compared to that deposited using rf power in both capacitively and inductively coupled systems. The polymers found in all systems are broadly similar and completely different from conventional poly(TFE). The distribution of power density in the various systems has been identified and compared. This is accomplished by using the known susceptibility of fluorine-containing polymers (including plasma polymer) to a high-power plasma as a probe of plasma power density within the interelectrode gap in the capacitively coupled system. The most active zone of the af or ac plasma is close to the electrode at a plasma pressure of approximately 40 mTorr. The use of a magnetic field leads to an intense localized glow such that etching by active fluorine atoms occurs at a specific locus on the electrode. By contrast, the low-pressure rf capacitively coupled glow discharge is the mildest of those investigated, and its most active zone is further from the electrode and much more diffusely localized by a magnetic field.

INTRODUCTION

In the preceding study[1] of the plasma polymerization of tetrafluoroethylene (TFE) in a capacitively coupled system using internal electrodes, the known susceptibility of TFE to high power densities (resulting in abstraction of fluorine atoms and a fluorine-poor polymer) was used as a probe of the power density distribution in the interelectrode gap for a radio frequency (rf) glow discharge. In the present work the same approach is used to reveal the power density distributions in the identical capacitively coupled system when frequencies of 10 kHz (af) and 60 Hz (ac) are employed. The goal of these studies is to obtain a fundamental understanding of the capacitively coupled system that will allow the deposition of plasma with useful properties on a substrate pulled continuously between electrodes. A minimum deposition rate of plasma polymer on the electrodes and other surfaces of the reaction chamber is desirable in such an application. For this reason conditions which tend to favor deposition at a site midway between electrodes, i.e., relatively low pressure (<100 mTorr) are in-

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vestigated most extensively. The deposition rate and chemical nature (by means of ESCA) of TFE plasma polymer have been determined as a function of glow discharge current. The effect of the magnetic field has also been studied.

In contrasting the results presented here with those obtained using an rf glow discharge,[1] it is well to bear in mind the fundamental difference between the two types of glow discharges.[2,3] The ac and af glow discharges may be considered to be dc glow discharges of alternating polarity. Positive ions hitting the cathode give rise to secondary electrons. These are accelerated through the Aston dark space, cathode glow and Crookes dark space gaining enough energy to ionize neutral species in the negative glow. These ions can then reinitiate the process ensuring a self-sustaining glow discharge. Free radicals and other active species are formed in or near the negative glow and react yielding a plasma polymer. Internal conducting electrodes are necessary to sustain such a discharge as buildup of a positive charge on the cathode would repel cations thus shutting off the required source of secondary electrons. In an rf glow discharge, electrons oscillate in the field set up between (and/or around the electrodes) gaining enough energy to form free radicals, ions, and other active species by random collisions. Conducting electrodes are therefore not required.

EXPERIMENTAL

The apparatus used in this study has been described in the preceding paper.[1] The method of achieving magnetic enhancement of the glow discharge is the same as already described.[1] In addition, samples for deposition rate determination and for ESCA analysis were obtained as previously described.[1]

The audio-frequency runs were made using a Hewlett–Packard Model 2 CD wide-range oscillator set at 10 kHz driving a Crown M-600 laboratory amplifier. The output from the amplifier, which varied from 0 to 72 V, was fed to a special transformer, where the voltage was increased to as much as 1500 V. This high voltage was then conducted to the electrodes inside the reaction chamber. The current and voltage levels at the electrodes were determined with a Hewlett–Packard 3435A digital multimeter.

AC power was fed to the electrodes as follows: The output (0–115 V) of a variable transformer, connected to the power mains, was used to feed the primary of a Stancor Model PC8304 transformer. The Stancor transformer output, a maximum of 1500 V, was conducted to the electrodes inside the reaction chamber. The voltage was read with a GE 0–500 V ac panel meter connected between the center tap and one side of the high-voltage transformer. The current was measured with a GE 0–500 mA ac panel meter.

RESULTS

Visual Observation of Audio-Frequency Glow Discharge

The most pronounced differences between rf, af, and ac glow discharges are between rf on the one hand and af and ac on the other. Only the visual observations for af will therefore be described.

No Magnets

The most even glow patterns are obtained at low flow rates and low pressures. Increasing either the flow rate or pressure results in an increase in intensity of the glow pattern. However, most of the increase is observed at the electrode thus making for a more uneven glow pattern with increasing pressure and flow rate. These effects can be seen in Figures 1, 2, 3, and 4. In Figure 4 there is a band of even intensity in the center of the interelectrode gap at p_g = 260 μm clearly separated from the intense glow on the electrode. The overall intensity of glow decreases however as the flow rate is increased to 99 cm^3/min with p_g = 460 μm. Arcing is a problem at all flow rates and pressures, particularly at high powers. As seen by the exposure times for Figures 1 through 4, the intensity of glow is considerably weaker for the audio-frequency glow discharges without magnets than it is for either the audio-frequency discharges with magnetic enhancement (cf. seq.) or for radio-frequency discharges.

With Magnetic Enhancement

All af glow discharges with magnetic enhancement are characterized by an annular zone of intense glow close to the electrodes. However, whereas the most *even* glow without magnetic enhancement was obtained at low flow rates, with magnetic enhancement the most *uneven* glow is obtained at the same low flow rate.

Figure 5 shows the glow discharge at F = 1 cm^3/min with p_M = 25 mTorr, p_g = 21 mTorr. Almost all the glow is close to the electrodes. Increasing the pressure or flow rate and pressure tends to increase the glow in the center of the gap without increasing the glow at the electrode, as seen in Figures 6 and 7.

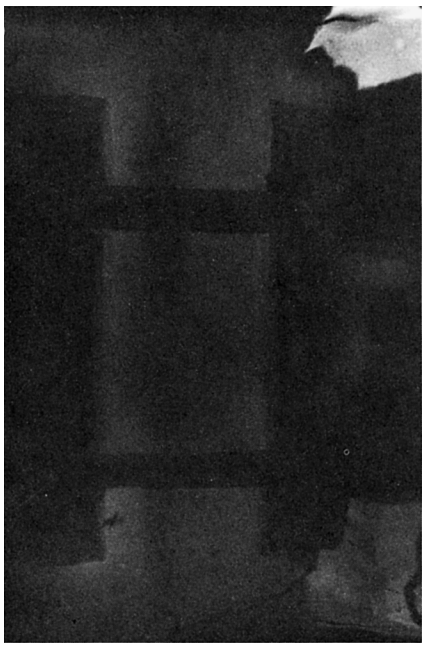


Fig. 1. Glow discharge obtained with a TFE flow rate of 1 cm^3 (S.T.P.)/min, p_M = 25 mTorr, and no magnets. Exposure time = ½ sec.

Fig. 2. Glow discharge obtained with a TFE flow rate of 1 cm^3(S.T.P.)/min, p_M = 300 mTorr, and no magnets. Exposure time = ½ sec.

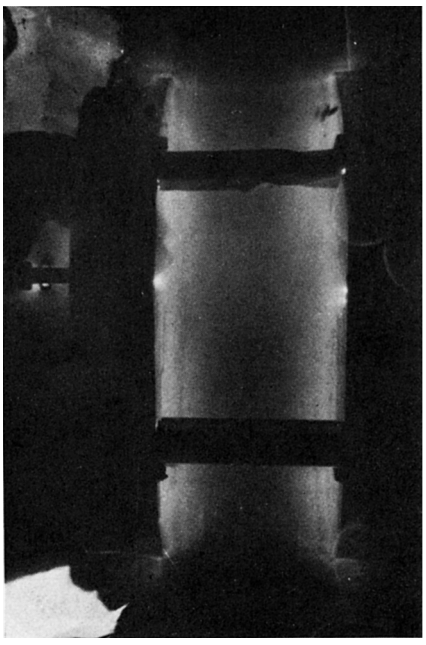


Fig. 3. Glow discharge obtained with a TFE flow rate of 4.9 cm^3(S.T.P.)/min, p_M = 300 mTorr, and no magnets. Exposure time = ½ sec.

Figure 7(b) is equivalent to Figure 7(a) but taken at the same exposure time as for the photographs of glow discharges obtained without magnetic enhancement. Thus, the effect of magnetic enhancement at F = 9.9 cm^3/min, P_0 = 500 can be

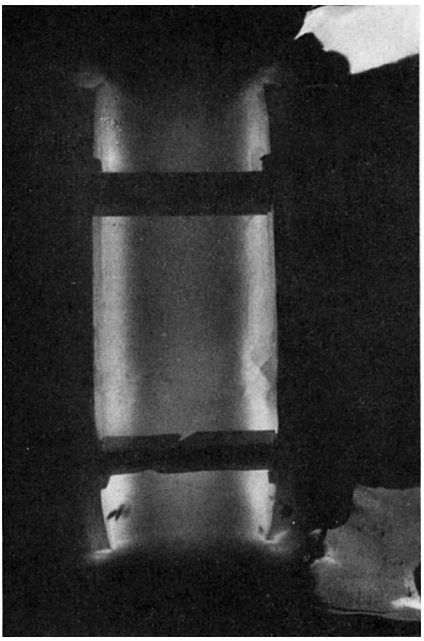


Fig. 4. Glow discharge obtained with a TFE flow rate of 9.9 cm^3(S.T.P.)/min, p_M = 500 mTorr, and no magnets. Exposure time = ½ sec.

seen by comparing Figure 7(b) with Figure 4. It is seen that the main difference is that there is an annular glow with magnetic enhancement which extends out from the electrode to a lesser extent than without magnetic enhancement. The glow in the center of the interelectrode gap is also somewhat more intense with magnetic enhancement. Nevertheless the differences are minor when compared to those that exist at low flow rates and pressures. As with rf, the greatest effect of magnetic enhancement is observed at low flow rates and pressures. The similarity between glow discharges at high pressures and flow rates regardless of the presence of magnets is completed by the observation that on increasing F to 99 cm^3/min, p_M to 500 mTorr, and p_g to 440 mTorr, the intensity of glow with magnetic enhancement decreases as seen comparing Figure 7(a) with Figure 8. The same effect was observed in the absence of magnetic enhancement.

Deposition Rates

A preliminary survey of the effect of flow rate and pressure was run as for rf, i.e., at F = 2 cm^3(S.T.P.)/min, P_0 = 40 μm, and a relatively low current level and at F = 99 cm^3(S.T.P)/min, P_0 = 500 μm, and the same relatively low current level. The same current level was used at both pressures in contrast to the rf case where a higher power was required for the high-pressure case to fill the interelectrode volume with glow. The effect of increasing flow rate and pressure is similar to that observed for radio frequency, i.e., a very large increase (relative to the low flow rate case) in deposition rate on the electrodes, a decrease at a point midway between electrodes. For this reason only glow discharges at the lower flow rate were investigated further.

Deposition rate profiles were obtained for a flow rate of 2 cm^3(S.T.P.)/min

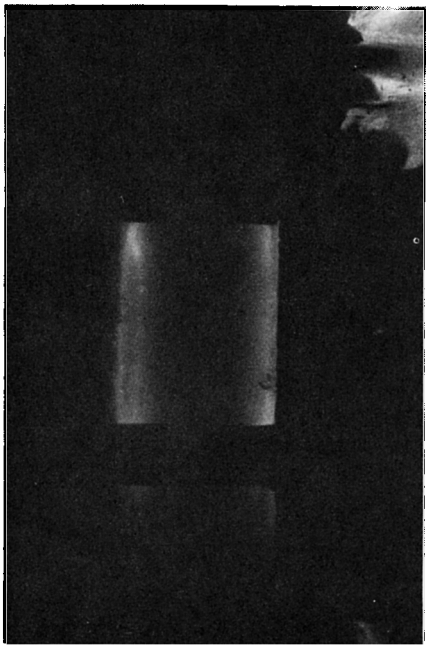


Fig. 5. Glow discharge obtained with a TFE flow rate of 1 cm^3(S.T.P.)/min, p_M = 25 mTorr, with magnetic enhancement. Exposure time is 1/8 sec for this and subsequent photographs unless otherwise noted.

and a pressure, before initiation of the glow discharge, of 60 mTorr. Further details of the polymerization are given in Table I. The deposition rate profiles obtained on the electrode and on an aluminum foil substrate placed midway between electrodes are given for glow discharges using audio frequency in Figure 9 when no magnets are used and in Figure 10 for the magnetically enhanced case. Corresponding profiles for 60-Hz plasma are shown in Figures 11 and 12, respectively.

The following general observations can be made: (i) The deposition rate profile is considerably more even without magnets than when magnets are used. (ii) Increases in current have much greater effects at the electrode than at the substrate.

Negative deposition rates are observed at the higher current levels at the electrode only, in the absence of magnets (see Fig. 9). The deposition rate is also decreased somewhat at the substrate when the af current is increased from 19 mA to 71 mA. Similar results are obtained with magnetic enhancement as well. Because of the concentration of the glow discharge on a ring 4 cm in diameter close to the electrode, the greatest effect is seen at the sampling point closest to this ring of intense glow, i.e., on the electrode at a radius of 4 cm. Negative deposition rates, indicating sputtering and ablation of plasma polymer and aluminum, are obtained at this site on the electrode at the higher af and ac currents. The deposition rate profile on the substrate is much more even and much less sensitive to power. This indicates less ablation with increased power at the substrate. However, some of the material sputtered from the electrode may be deposited on the substrate, also contributing to the apparent deposition rate.

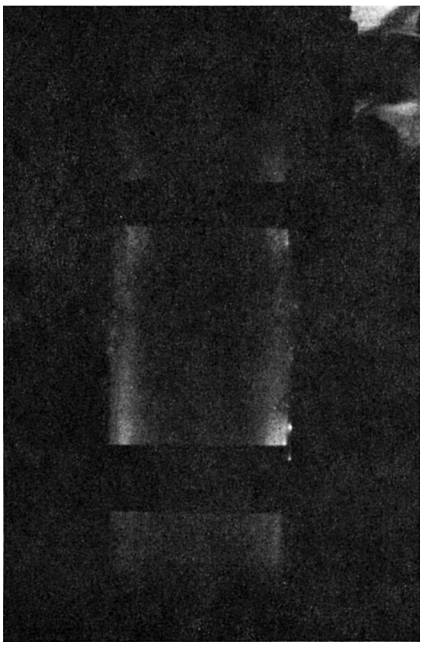


Fig. 6. Glow discharge obtained with a TFE flow rate of 1 cm^3/min, p_M = 300 mTorr, and magnetic enhancement.

ESCA Data

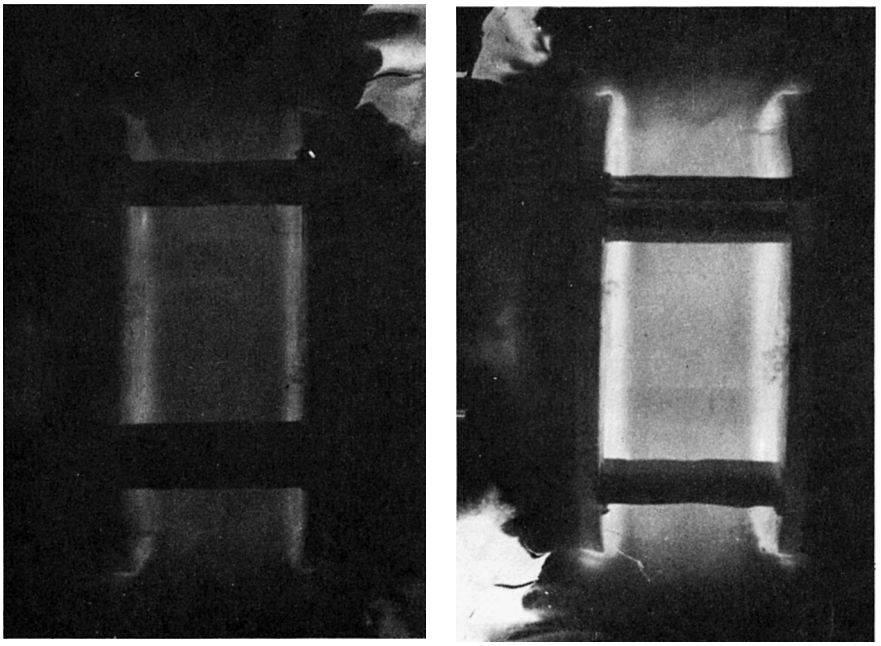
A summary of the ESCA data obtained for af samples is given in Table II and for ac samples, in Table III. As seen previously for the inductively and capacitively coupled rf cases, high power tends to decrease CF_n groups (n = 1, 2, 3) as seen by a decrease in the ratio of the peak height at 291.5 eV as compared to that at 284.6 eV. In addition, the Al/C and O/C ratio is observed to increase with increase in power. This is caused by the tendency of active fluorine atoms to etch the sample, resulting in C–F bond breakage, sputtering of the aluminum substrate, and the formation of radicals that subsequently react with oxygen in the air. The O peak is always found at a binding energy of 532–534 eV (after correction for charging), indicating that the oxygen is bound to carbon atoms in the plasma polymer, not to aluminum. When magnets are used, the increased power density at a radius of 4 cm close to the electrode is reflected in the most marked evidence of ablation by fluorine (low C_{1s} peak height ratio, high Al/C and O/C ratios) at the electrode at a radius of 4 cm.

The F/C ratio does not appear to be very sensitive to high power density, probably because at high power densities fluorine atoms are bonded to aluminum whereas at low power levels they are bonded to carbon in plasma polymer.

It may be noted that generally the power density is less at the substrate than at the electrode on the basis of the ESCA data. This is in agreement with the decreased sensitivity of deposition rate to changes in applied power at the substrate as compared to the electrode. The one notable exception to this trend is the ESCA data for a sample taken from the center of the electrode for an ac plasma using a current of 100 mA and magnetic enhancement. The deposition rate for this case is also abnormally high.

TABLE I
Conversion Rates for TFE Plasma Polymerization (Flow Rate = 2 cm^3(S.T.P.)/min, p_M = 60 mTorr)

Frequency	Magnets	Power, W	Current, mA	W/FM, (J/kg) × 10^{-8}	p_g, mTorr	TFE Conversion to plasma polymer	
						Electrode, %	Substrate, %
af	no	11	19	0.74	40 and up	5.2	2.0
af	no	72	71	4.82	37 and up	—	0.6
af	MAG	6.6	15	0.44	44	8.4	9.4
af	MAG	25	50	1.68	38	—	4.7
af	MAG	50	100	3.35	35	—	8.6
ac	no	36	50	2.41	40	4.2	0.5
ac	MAG	21	50	1.41	39	6.3	7.0
ac	MAG	74	150	4.96	35	—	4.6



(A) (B)

Fig. 7. Glow discharge obtained with a TFE flow rate of 9.9 cm^3/min, p_M = 500 mTorr, and magnetic enhancement: (a) exposure time = 1/8 sec; (b) exposure time = 1/2 sec.

DISCUSSION

The properties of ac and af glow discharges can be understood from the known features of dc glow discharges. The ac and af glow discharges may then be considered dc glow discharges of alternating polarity.[3] A dc glow discharge is observed to have several lighter and darker zones. The most important zone for our purposes is the zone between the electrode and the negative glow. In this zone, consisting of the Aston dark space, cathode glow, and Crooke's dark space, a major portion of the potential drop between the electrodes is found. The thickness of this zone is approximately the mean distance travelled by an electron from the cathode before it makes an ionizing collision.[3] The thickness is therefore inversely proportional to pressure and decreases with increasing potential drop between the electrodes. The negative glow which occurs after the Crooke's dark space is a zone of high concentration of positive ions formed by collision with energetic electrons emerging from the Crooke's dark space. These positive ions then are accelerated toward the electrode through the large potential drop existing between the negative glow and the cathode where they generate the secondary electrons which ensure a self-sustained glow discharge.

The important points in this description of af and ac glow discharge are the following:

1. The electrons in these discharges originate in large part at the electrodes by secondary emission following ion impact.
2. The ions originate by collision of energetic electrons with gas atoms in the

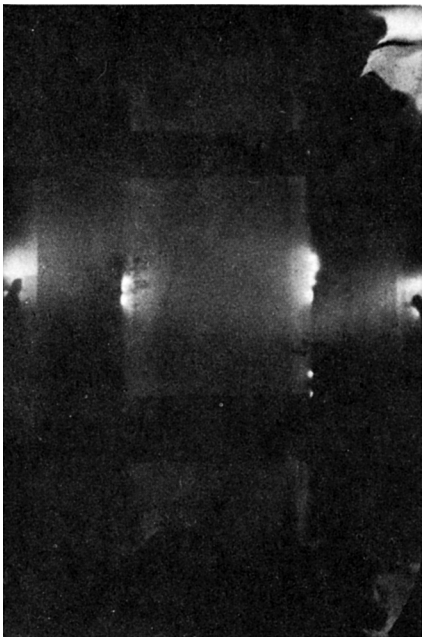


Fig. 8. Glow discharge obtained with a flow rate of 99 cm^3/min, p_M = 500 mTorr, and magnetic enhancement.

negative glow region. These energetic electrons would also produce a high concentration of free radicals and other reactive species in or near the negative glow.

3. A large fraction of the potential drop between electrodes is between the electrode and negative glow.

4. The distance between the electrode and negative glow is inversely proportional to the pressure. This is because the number of ionizing collisions per unit distance increases with pressure. This distance also decreases as the potential drop between electrodes is increased.

A consequence of the above points is that one would expect the reactive species necessary for plasma polymerization would be formed in the negative glow. This reactive zone would be expected to move closer to the electrode as pressure is increased, closer to the center of the interelectrode gap as pressure is decreased. This prediction agrees well with the observed concentration of glow close to the electrode at high pressure and a glow extending further from the electrode at low pressures. It is also in agreement with the observed increased proportion of the total deposition at a substrate placed midway between electrodes as the pressure is lowered.

The magnet field setup which we use is donut-shaped, with the midsection of the donut lying on the electrode surface and the hole at the electrode center. Electrons trying to pierce the surface of the donut must follow spiraling convoluted paths. They are therefore (1) impeded from escaping from the confines of the donut-shaped field, and (2) ionize molecules and atoms closer to the electrode than they would at the same pressure without magnets. The effect at high pressures, where the glow is close to the electrode in any case, is merely

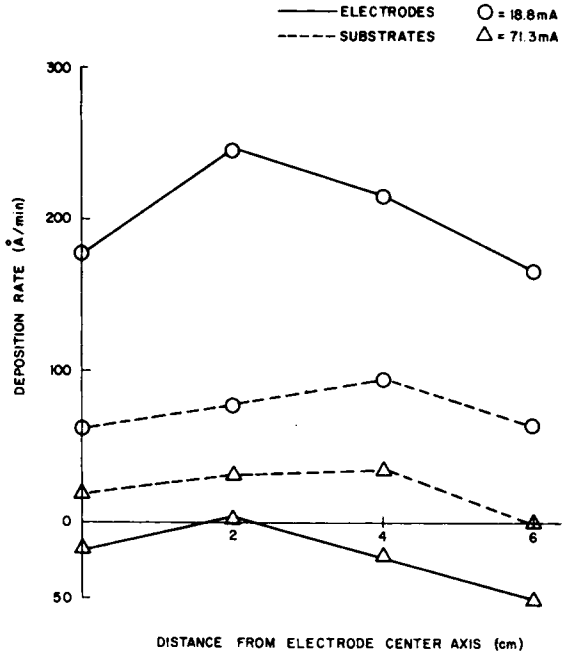


Fig. 9. Deposition rate profile on electrodes and on substrate for af plasmas of a flow rate of 2 cm^3(S.T.P.)/min, p_M = 60 mTorr, and no magnets.

to concentrate the glow in a ring in a plane close to the electrode surface, coaxial with the electrode centers. The effect at low pressures is more dramatic. The glow is concentrated into the same ring as for the high pressure case but is in addition moved closer to the electrode surface.

These considerations may be presented in terms of distribution of power in the plasma. As one lowers the pressure, power is distributed more evenly throughout the interelectrode gap than at high pressures. For this reason we found that low pressures (below 100 mTorr) were more conducive to a high deposition rate of plasma polymer on a substrate placed in the middle of the electrode gap. The tetrafluoroethylene glow discharge system is especially suitable for a study of power distribution in a plasma because, at high energies, ablation and etching caused by fluorine ions occurs. Thus, as the power is increased we may identify the sites of high power concentration by decreased deposition rate and by the decreased frequency of C–F bonds in the polymer as revealed by ESCA.

The data presented in Tables I–III and Figures 9–12 reveal that the power density is usually higher nearer the electrode than at the center of the interelectrode gap at a pressure of 40 mTorr in the glow discharge. The use of a magnetic field concentrates the power in a ring of radius 4 cm (in our case) near the electrode. Negative deposition rates are found near this ring on the electrode with the higher current levels due to etching of the aluminum by fluorine ions. However, plasma polymer is present on the electrode at a radius of 4 cm as revealed by the ESCA data. At high powers it is low in C–F_n bonds, as would be expected and contains a high O/C elemental ratio. The polymer near the center

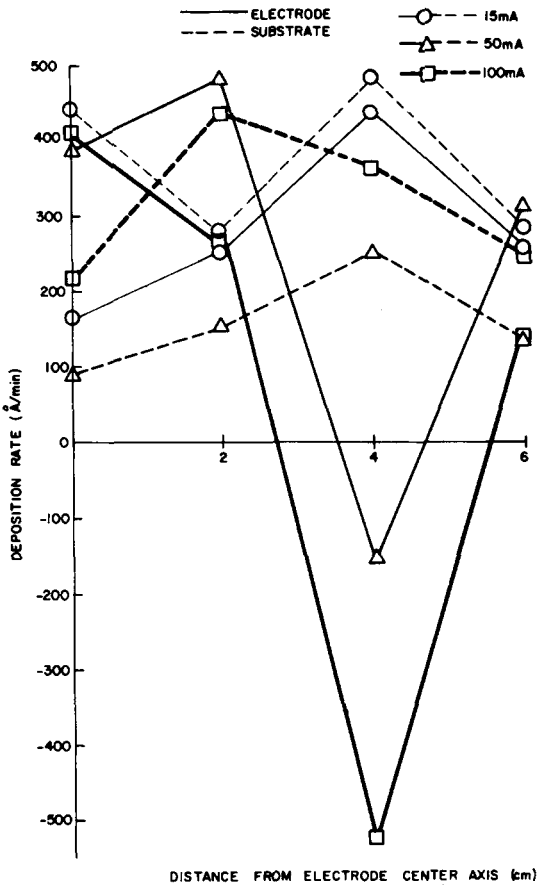


Fig. 10. Deposition rate profile on electrodes and on substrate for af plasma at a flow rate of 2 cm^3(S.T.P.)/min, p_M = 60 mTorr, with magnetic enhancement.

of the electrode invariably contains more C–F_n bonds and less oxygen. Scanning electron micrographs of the aluminum blanks on which polymer was deposited for ESCA studies reveal that fluorine is uniformly distributed on the surface even in regions of negative polymer deposition. The most tenable explanation of the presence of polymer at zones of extreme etching is that plasma polymer deposition competes with etching. The etching process removes both plasma polymer and aluminum.

In all cases the substrate placed midway between the electrodes is found to be in a less energy-dense region than the electrode. This is manifested in a much smaller sensitivity to increase in power both in deposition rate and in depletion of C–F_n bonds than is found at the electrode.

The one exception to these generalizations is found at a current of 150 mA using ac and magnetic enhancement. Here, the site of least energy density appears to be the center of the electrode where a very high deposition of polymer containing the highest proportion of C–F_n bonds is formed.

The following differences are noted between the rf glow discharge described in the preceding paper[1] and the af and ac discharges:

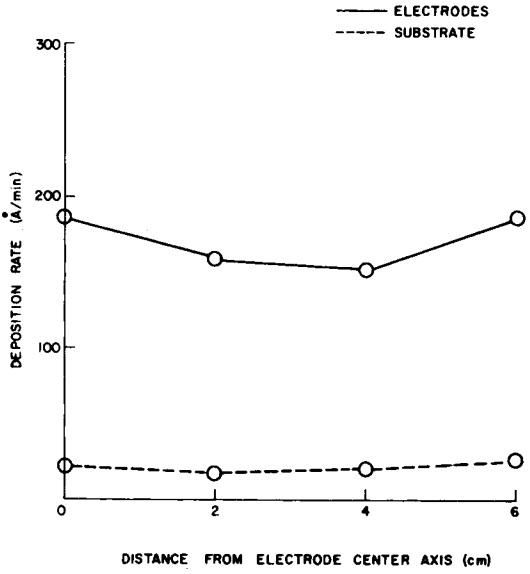


Fig. 11. Deposition rate profile on electrodes and on substrate for an ac plasma at a flow rate of 2 cm^3(S.T.P.)/min, p_M = 60 mTorr, and no magnets. Current is 50 mA.

No Magnets

At low pressures a glow concentration is observed close to the electrode for af, ac but not for rf glows. The af, ac glows are always confined to the interelectrode gap, whereas at high power and low pressures an rf glow may escape from the interelectrode gap and fill the reaction chamber. A negative deposition rate was observed *at the electrode* at high power for the af plasma, whereas the trend to decreasing deposition with increasing power was most marked *at the substrate* for the rf plasma. No negative deposition rates were observed for rf.

The ESCA spectra reveal that when there are differences in the nature of the polymer formed at electrode and substrate for af and ac, the more fluorine poor polymer is formed at the electrode. The opposite was the case for rf. For af, and ac, the F/C ratios are not as constant, independent of reaction conditions, as was observed for the rf capacitively coupled plasma but more so than for an rf inductively coupled plasma.[4] The most revealing information concerning fluorine in the plasma polymer is given by the C_{1s} spectrum. The peak height ratios of the 291.5 to 284.6 eV portions of the C_{1s} spectra are considerably lower for the low-energy af and ac samples than for the low-energy rf samples. This means that a polymer somewhat richer in CF_2 groups is found in an rf plasma under conditions (including power) otherwise identical to those for af plasma. In this respect the plasma polymer formed in an af plasma is more nearly similar to the rf inductively coupled plasma polymer[4] than to the rf capacitively coupled plasma polymer.

Another noticeable difference between the rf capacitively coupled plasma (with or without magnets) and the ac and af plasma is found in the position of oxygen ESCA peak. For the rf plasma, the oxygen peak is at 532–535 eV when no aluminum is detected on the surface. However, the oxygen peak position shifts to

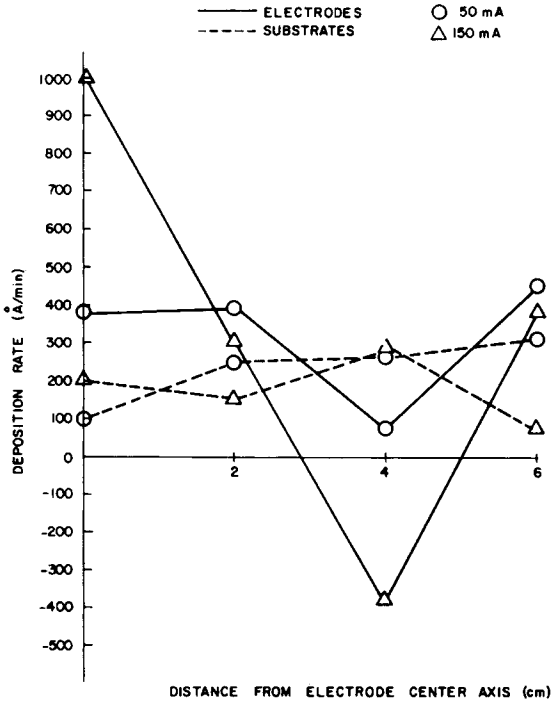


Fig. 12. Deposition rate profiles on electrode and on substrate for an ac glow discharge at a flow rate of 2 cm^3(S.T.P.)/min, p_M = 60 mTorr, and magnetic enhancement.

less than 531.5 eV whenever aluminum is present on the surface, presumably indicating aluminum–oxygen bonds. For the ac and af glow discharges, the oxygen peak position is always characteristic of oxygen covalently bound (to plasma polymer). In addition, at the high power levels where aluminum is detected on the surface, the O/C ratio is always higher for the rf case than for the af, ac case. Thus, aluminum–oxygen bonds are detected at the surface for a high-power rf plasma but not for high-power af, ac.

With Magnetic Enhancement

The outstanding visual difference seen in comparing the ac and af magnetically enhanced glow discharge with the corresponding rf discharge with the corresponding rf discharge is that a discrete ring (see Fig. 5) is formed at the electrode for the low-frequency discharge in contrast to the rather diffuse ring observed for the rf plasma. A direct consequence of this is that a negative deposition rate is observed at high power at a position on the electrode corresponding to the radius of the ring for both af and ac, whereas no negative deposition rates were observed for the rf glow discharge.[1] The negative deposition rate is caused by etching by activated fluorine atoms and/or sputtering.

The ESCA spectra again show that the most fluorine-poor polymer is formed at the electrode and particularly at a radius of 4 cm. This confirms the impression gained from visual observation that the power density is greatest at the

TABLE II
Summary of ESCA Data for Plasma Polymer of Tetrafluoroethylene Deposited in a Capacitively Coupled af Glow Discharge
(F = 2 cm^3 (S.T.P.)/min, p_M = 60 mTorr)

Code[a]	Peak area corrected for photoelectric cross-section, (counts eV) × 10^{-4}				Elemental ratio			Peak height ratio
	O_{1s}	F_{1s}	C_{1s}	Al_{2s}	O/C	F/C	Al/C	C_{1s} 291.5 eV/C_{1s} 284.6 eV
0E 19N af	0.12	2.72	2.29	0	0.052	1.19	0	1.14
4E 19N af	0.12	2.63	2.27	0	0.053	1.16	0	1.16
0S 19N af	0.059	3.29	2.17	0	0.027	1.52	0	1.61
4S 19N af	0.076	3.19	2.27	0	0.033	1.41	0	1.61
0E 71N af	0.45	2.61	1.80	0.75	0.25	1.45	0.41	0.12
2E 71N af	0.45	2.65	1.79	0.78	0.25	1.48	0.43	0.11
4E 71N af	0.37	2.35	1.79	0.77	0.21	1.31	0.43	0.10
0S 71N af	0.38	2.91	1.56	0.66	0.24	1.87	0.42	0.15
4S 71N af	0.38	2.56	1.64	0.57	0.23	1.56	0.35	0.19
0E 15MAG af	0.14	2.77	2.34	0	0.060	1.18	0	1.11
4E 15MAG af	0.22	2.35	2.43	0	0.091	0.97	0	0.89
0S 15MAG af	0.095	3.19	2.30	0	0.041	1.39	0	1.52
4S 15MAG af	0.092	3.03	2.35	0	0.039	1.29	0	1.41
0E 50MAG af	0.14	2.82	2.25	0.053	0.063	1.25	0.024	1.11
4E 50MAG af	0.41	2.03	1.36	0.75	0.30	1.49	0.55	0.10
0S 50MAG af	0.070	3.92	2.56	0	0.027	1.53	0	1.64
4S 50MAG af	0.12	3.66	2.52	0.064	0.046	1.45	0.025	1.19
0E 100MAG af	0.35	1.88	1.60	0.49	0.22	1.18	0.30	0.13
4E 100MAG af	0.29	2.06	1.40	0.66	0.21	1.47	0.47	0.065
0S 100MAG af	0.22	2.58	1.85	0.21	0.12	1.39	0.11	0.55
4S 100MAG af	0.17	2.68	1.95	0.16	0.086	1.37	0.084	0.76

[a] 0E 71N af indicates a sample taken 0 cm from the center of the electrode prepared with a current of 71 mA using no magnets and af power. 4S 50MAG af indicates a sample taken 4 cm from the electrode center axis on the substrate prepared with a current of 50 mA using magnetic enhancement and af power.

TABLE III

Summary of ESCA Data for Plasma Polymer of Tetrafluoroethylene Deposited in a Capacitively Coupled af Glow Discharge (F = 2 cm^3 (S.T.P.)/min, p_M = 60 mTorr)

	Peak area corrected for photoelectric cross section, (counts eV) × 10^{-4}				Elemental ratio			Peak height ratio
Code[a]	O_{1s}	F_{1s}	C_{1s}	Al_{2s}	O/C	F/C	Al/C	C_{1s} 291.5 eV/C_{2s} 284.6 eV
0E 50N ac	0.26	2.68	2.52	0.23	0.102	1.06	0.092	0.54
4E 50N ac	0.33	2.75	2.20	0.35	0.152	1.25	0.158	0.44
0S 50N ac	0.105	3.47	2.66	0	0.039	1.30	0	1.20
4S 50N ac	0.116	3.40	2.56	0	0.045	1.33	0	1.06
0E 50MAG ac	0.080	3.31	2.34	0	0.034	1.41	0	1.33
4E 50MAG ac	0.43	2.22	1.39	0.82	0.31	1.60	0.59	0.085
0S 50MAG ac	0.079	3.38	2.34	0.027	0.034	1.44	0.012	1.43
4S 50MAG ac	0.055	3.33	2.33	0	0.024	1.43	0	1.52
0E 150MAG ac	0.185	3.26	2.35	0.12	0.079	1.39	0.051	0.85
4E 150MAG ac	0.44	2.11	1.35	0.93	0.33	1.56	0.64	0.059
0S 150MAG ac	0.41	2.44	1.82	0.47	0.23	1.34	0.26	0.25
4S 150MAG ac	0.38	2.56	1.82	0.40	0.21	1.41	0.22	0.31

[a] 4E 50N ac indicates a sample taken 4 cm from the center on the electrode prepared with a current of 50 mA using no magnets and ac power. 0S 150 MAG ac indicates a sample taken 0 cm from the electrode center axis on the substrate prepared with a current of 150 mA using magnetic enhancement and ac power.

electrode on the ring of intense glow. There appear to be more distinct differences between the chemical nature of the polymer formed at a radius of 4 cm on the electrode and the polymer formed at the electrode center for ac than for af. The greatest difference in the chemical nature of all samples (on the electrode and substrate) is between samples on the electrode for ac. Conversely, the greatest difference for af is between electrode samples as a class as opposed to substrate samples. This may be caused by a more effective localization of glow for ac than for af. Particularly striking are the peak height ratios obtained for the center and a radius of 4 cm on the electrode for an ac plasma at 150 mA. The polymer richest in fluorine is formed at the electrode center.

CONCLUSIONS

The polymers made in parts I, II, and III all show the salient characteristics of plasma polymers, regardless of whether they are made in a straight-tube inductively coupled reactor (part I),[4] a capacitively coupled reactor using rf power (part II),[1] or a capacitively coupled reactor using ac or af power. None has the linear $(CF_2)_n$ structure of a conventional poly(tetrafluoroethylene). Rather, a highly branched structure which may contain CF_2 and CF_3 groups results.

The relative proportion of CF_3 and CF_2 groups on one hand and aliphatic or graphitic carbons on the other, in the plasma polymer, depends on the power density of the glow discharge from which the plasma polymer deposits. At high power inputs all TFE plasma polymer is generally fluorine poor, regardless of the reactor in which polymerization occurs. Such a fluorine-poor polymer generally contains oxygen because of reaction of plasma polymer free radicals with oxygen in the atmosphere. Additionally, when deposited on aluminum, the element (i.e., aluminum) is detected on the surface because of ablation by activated fluorine species. At low power inputs the chemical nature of the plasma polymer depends on location in the reactor. When deposited species have not been exposed to localized high power densities, a plasma polymer rich in CF_2 and CF_3 groups is laid down, the relative amount of oxygen at the surface is very low, while aluminum is undetectable by ESCA. For an inductively coupled system, plasma polymer deposited downstream from the coil, i.e., from the region of highest power density, is fluorine poor. For the capacitively coupled systems we have inferred the power density at various locations from the chemical nature and deposition rate of TFE plasma polymer. A low pressure glow discharge has been found to result in increased deposition of plasma polymer at a substrate placed midway between electrodes. For such a low pressure discharge, power density tends to be greater in the center of the interelectrode gap than at the electrodes, for rf. The opposite is true for af and ac. The use of a magnetic field moves the high power density region of the glow discharge closer to the electrodes. For af and ac, magnetic enhancement results in a concentration of power in a ring 4 cm in diameter coaxial with the electrode center axis and close to the electrodes. Power concentration is significantly greater on this ring than it is at the electrode center as revealed by deposition rates and ESCA spectra. Such radical differences on the electrode were not observed for a magnetically enhanced rf glow discharge under otherwise similar conditions.

The mildest conditions, as judged from ESCA data for the four types of glow discharges, were obtained with the rf capacitively coupled system at low power

input. The most active plasma was present in the high-power ac and af magnetically enhanced glow discharges, which led to negative deposition rates, at the electrodes, caused by plasma etching.

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