Thermal Stability of Fluorocarbon Films Deposited from Pentafluoroethane/Argon Plasmas

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Fluorocarbon films were deposited from pentafluoroethane/argon mixtures in a parallel-plate reactor at a pressure of 1 Torr and substrate temperatures between 120 and 210°C. Films deposited on substrates placed on the heated, grounded electrode as well as films formed on the powered electrode were analyzed using infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). Polymer deposition rates decreased with an increase in substrate temperature indicating that reactant adsorption is the rate-limiting step. Films deposited on the powered electrode had an O/C ratio of 0.14, which was significantly higher than that of films deposited on the grounded electrode at elevated temperatures. Likewise, IR spectra of films on the powered electrode also showed significant contributions from C=O related groups. TGA data indicated that the powered electrode films had ~3% weight loss at 250°C, while films deposited on the grounded electrode had ~1% weight loss at 250°C. The thermal stability of films deposited on the grounded electrode was significantly enhanced when deposited at higher substrate temperatures. XPS analyses indicated a decrease in the F/C ratio of the deposited films with an increase in substrate temperature. TGA analyses indicated that weight loss below 250°C was due primarily to the outgassing of low-molecular weight species from the fluorocarbon films. The higher weight loss region between 320 and 425°C was ascribed to polymer degradation due to scission of main chain C–C bonds and to evolution of HF and CO₂.

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Plasma deposited fluorocarbon films have received considerable attention recently as potential interlayer dielectrics for future generation integrated circuits (ICs). Apart from their low dielectric constant (<2.6), they also possess other favorable characteristics such as low moisture absorption, high chemical inertness, and plasma-assisted conformal step coverage. However, one of the critical requirements for successful integration of these materials into IC manufacturing processes is thermal stability in excess of 350–400°C. Recently, fluorocarbon films deposited from C₂F₅ precursors at substrate temperatures of 400°C have been reported to have adequate thermal stability at 400°C. The precursor and the substrate temperature were important parameters in determining the thermal stability of the film. However, the effect of substrate temperature on the deposition rate, chemical structure, and degradation mechanism of the fluorocarbon films was not evaluated. Another study reported that the presence of oxygen-containing moieties in fluorocarbon films enhances outgassing of CO and CO₂ at lower temperatures and thus reduces the thermal stability of these films. Although the effect of deposition conditions on the oxygen content and thus the corresponding weight loss of the polymer are critical to the thermal stability of the film, these issues have not been investigated.

In this study, the effect of applied power and substrate temperature on the chemical structure, chemical composition, and thermal stability of the plasma-deposited fluorocarbon films was investigated by means of X-ray photoelectron spectroscopy (XPS), IR spectroscopy, and thermogravimetric analysis (TGA). The monomer studied, pentafluoroethane (CF₃CHF₂), was selected because of its shorter atmospheric lifetime relative to that of pure fluorocarbon gases. The chemical composition of the deposited films was monitored as a function of postdeposition annealing temperature in order to identify the thermally labile moieties present in the polymer. Mass spectrometry was used to monitor the species evolved from the polymer as a function of annealing temperature in order to gain insight into film degradation mechanisms. The effect of oxygen content on thermal stability was studied by characterizing films deposited on both the powered electrode (high oxygen content in the deposited films) and the temperature-controlled, grounded electrode (low oxygen content in the deposited films). Note that plasma-deposited films are highly cross-linked networks with undefined molecular weights and are thus different from conventional polymers. Despite these differences, we follow the convention of referring to these films as polymers in subsequent sections of the paper.

Experimental

A parallel-plate radio frequency (rf) plasma reactor was used for the deposition of fluorocarbon films from pentafluoroethane/argon mixtures. Details of the reactor setup and operation are given elsewhere, so only a brief description is presented here. The distance between the 4 cm diам, parallel-plate, stainless steel disk electrodes was fixed at 2.9 cm for all experiments. RF power at 13.56 MHz from an ENI power systems HF-300 rf generator was coupled to the top electrode using a Heathkit SA-2060A antenna tuner. Substrates were placed on the grounded electrode whose temperature was regulated with a Syskon RKC temperature controller. Depositions were carried out at substrate temperatures of 120, 180, and 210°C, and a constant operating pressure of 1 Torr. The flow rates of pentafluoroethane and argon were set at 20 and 75 sccm, respectively, for all depositions. In some cases, films deposited at a specific substrate or deposition temperature were heated to 200°C in the reactor immediately after deposition and held there for 2 h in vacuum. In the following discussions, this heat-treatment of the deposited films in vacuum is referred to as postdeposition annealing. In this study, films deposited onto the temperature-controlled, grounded electrode and the powered electrode without temperature control, were characterized by various analytical techniques including TGA, IR, XPS, and mass spectrometry.

IR spectra of the deposited films were collected in reflection mode at a grazing angle of 70° using a Nicolet Magna-IR 560 Fourier transform infrared (FTIR) spectrometer. All spectra were recorded at a resolution of 4 cm⁻¹ and averaged over 512 scans. In order to improve the signal-to-noise ratio, fluorocarbon films were deposited onto silicon substrates that had been sputter coated with a 300 nm layer of aluminum. Films deposited on the powered electrode were analyzed directly on the stainless steel powered electrode.

XPS was used to obtain the chemical composition and bonding structure of polymer films. Spectra were collected using a PHI model 1600 XPS system equipped with a monochromator. The sample was exposed to monochromatized Al Kₐ X-rays, and the ejected photoelectrons were detected by a multichannel hemispherical detector that provided high-energy sensitivity and resolution. Chamber pressure was typically below 5 × 10⁻⁹ Torr during analysis. High-resolution spectra were collected for C 1s, O 1s, N 1s, and F 1s.

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regions at a pass energy of 11.75 eV. Spectra were corrected for binding energy shifts by assigning the highest binding energy CF₃ component of the C 1s peak to 293.2 eV. Relative compositions of the various species in the deposited films were determined by peak deconvolution of each spectral region assuming all peaks to be perfectly Gaussian with a constant full width half maximum (fwhm).

TGA was performed to monitor the weight loss of freestanding polymer films with temperature in a nitrogen environment. Freestanding polymer films were obtained by depositing the polymer on silicon (with native oxide) substrates and etching away the native oxide in HF. Films deposited on the powered electrode were removed by peeling films from the electrode for analysis. The sample temperature was initially ramped to 100°C at 3°C/min and held for 30 min in order to remove moisture present in the films. The temperature was then raised from 100 to 425°C at a rate of 2°C/min and held at 425°C for 1 h.

XPS and IR analyses were also performed on samples held at intermediate temperatures of 250, 300, 350, and 400°C for 1 h in a furnace under a nitrogen atmosphere. The samples were ramped to these temperatures in the furnace with the same ramp rates and intermediate hold steps used in the TGA analysis. These postdeposition treatments are designated by the term annealing temperature in subsequent sections of this paper.

Mass spectrometry was performed using a VG Instruments model 70-SE spectrometer. Freestanding polymer films were placed in a capillary tube that was heated at 10°C/min to the final temperature of 425°C. Evolved species from the polymer films with mass-to-charge ratios in the range 10-700 amu were detected by the mass spectrometer. The ionizer potential was fixed at 70 eV. The total pressure inside the spectrometer was below 10⁻⁶ Torr during analysis.

Results

Recent studies on the plasma deposition of fluorocarbons have recognized the effect of substrate temperature⁴ and polymer O/C ratio⁵ on the thermal stability of the deposited films. However, little work has been done that focuses on understanding the effect of substrate temperature on the chemical bonding structure and composition of deposited films. Such information is critical, in that it will determine the type of polymer degradation mechanism and consequently, the thermal stability of the film. In this paper, fluorocarbon films deposited on the powered electrode (no external heating or cooling) and the heated grounded electrode were analyzed by various techniques including IR, XPS, TGA, and mass spectrometry in order to compare and correlate thermal stability with chemical structure and bonding configurations. Although the powered electrode heats up during deposition due to ion bombardment, its temperature is lower than that of the externally heated grounded electrode due to low ion energies at the reactor operating pressure of 1 Torr. Indeed, when the lower electrode was not intentionally heated, its temperature rose to only 95°C. This observation suggests that films deposited on the powered electrode may be expected to have higher concentrations of trapped low-molecular-weight species as well as a higher O/C ratio (due to the higher concentration of dangling bonds and trapped radicals) than films deposited on the grounded electrode. Hence, a comparison of the films deposited on the ground and powered electrode should provide additional insight into the effects of oxygen incorporation on the thermal stability of plasma-deposited films.

As shown in Fig. 1, the deposition rate of fluorocarbon films on the grounded electrode decreased from 65.9 to 31 nm/min with an increase in substrate temperature from 120 to 210°C. The apparent activation energy for the film deposition was calculated to be ~13.2 kJ/mol. A negative activation energy suggests that reactant adsorption is the rate-determining step.⁸

**XPS studies.**—XPS analyses of the deposited films indicate a fluorine-to-carbon (F/C) ratio between 0.8 and 1.2 for all deposition conditions, suggesting extensive cross-linking of the polymer chains. Specifically, the F/C ratio decreases slightly from 1.12 to 0.95 with an increase in substrate temperature from 120 to 210°C and is nearly independent of applied rf power within the range of 20-30 W. The effect of substrate temperature on the concentrations of CF₃, CF₂, CF, C–CFₓ, and C–C or C–H in the deposited films is shown in Fig. 2 (the underline indicates the atom analyzed). The observed increase in the concentration of nonfluorinated C–C moieties with temperature suggests that the deposited polymer films are more graphitic at higher substrate temperatures and should therefore have higher thermal stability. Also, there is a slight decrease in the concentration of CF₃ end groups with substrate temperature. These CF₃ groups are highly volatile and hence thermally labile. The O/C ratio of films deposited on the grounded electrode is ~0.03 for all substrate temperatures. In contrast, films deposited on the powered electrode have an O/C ratio of 0.14, consistent with postdeposition oxidation of trapped radicals upon air exposure. XPS deconvolution of the O 1s spectra indicates three primary peaks corresponding to CFₓO, –O (carboxylic acid, ester, or anhydride) at 533.9 eV, and –(C=O)O (ketone) or –(C=O)O at 532.6 eV. However, there could also be contributions of peroxides to the O 1s spectrum.

The effect of furnace annealing on the concentration of CFₓ and C–C moieties in the film is shown in Fig. 3. It is evident from the figure that there is a drastic decrease in the CFₓ, CF₂, and CF concentrations and a corresponding increase in the C–CFₓ and C–C concentrations after the final anneal of 425°C for 1 h in a nitrogen atmosphere. Consequently, the F/C ratio of the films decreases from 0.9-1.2 to 0.59-0.72 after the final anneal, indicating extensive defluorination and loss of fluoride-rich CFₓ species. Further, there is no change in the relative CFₓ concentrations of the deposited films until a temperature of 300°C, suggesting that film degradation is negligible below this temperature.
the presence of randomly distributed saturated CF₆₈ groups typical of plasma-polymerized fluorocarbons. IR spectra of the deposited fluorocarbons such as –C–F also to oxygenated species such as –C–O. It is evident from the IR spectra that the peaks between 1600 and 1880 cm⁻¹ (oxygen containing groups) are much more prominent in polymer films deposited on the powered electrode than those deposited on the grounded electrode. This indicates the presence of high concentrations of C=O related moieties in films deposited on the powered electrode and is consistent with the high O/C ratio indicated by XPS analysis. The prominent peak between 1100 and 1400 cm⁻¹ could have significant contributions from C-O-C stretching vibrations, which occur around 1100 cm⁻¹. The difference in the peak shape and peak position between films deposited on the powered and grounded electrodes indicates different bonding environments and chemical compositions of these films. Furthermore, the powered electrode films have an extra peak at 870 cm⁻¹, which can be attributed to several carbon skeletal modes as well as peroxo (–O–O–) groups. Peroxy radicals are very likely to be formed due to atmospheric oxidation of dangling bonds and have been detected in e-beam-irradiated Teflon by electron spin resonance. Also, films deposited on the powered electrode have higher CH₃ concentrations than films on the grounded electrode.

Figure 5 shows the variations in the IR spectrum of a polymer film deposited on the grounded electrode that has been subjected to various furnace anneals in a nitrogen environment. Clearly, there is a decrease in the intensity of the saturated fluorocarbon peak (between 1100 and 1400 cm⁻¹) with an increase in the annealing temperature, indicating defluorination as well as loss of CₓFₓ fragments due to film degradation. Further, there is a significant decrease in the C=O related moieties in the 1700 and 1800 cm⁻¹ regime. The peak maximum shifts from ~1690 to ~1620 cm⁻¹ (corresponding to –C=O–C groups) at annealing temperatures above 350ºC, indicating a preferential loss of carbonyl and carboxyl groups with respect to unsaturated carbon groups. Loss of C=O related moieties from plasma-deposited fluoropolymers at elevated temperatures has been observed by other researchers.5

TGA studies.—The effect of different deposition temperatures on the observed weight loss of the resulting polymer films is shown in Fig. 6. It is evident from the figure that higher substrate temperatures increase the thermal stability of the polymer both in terms of the TGA temperature for 5% weight loss as well as the final residue obtained. As expected, films deposited on the powered electrode had the least thermal stability of all the examined films. The effect of postdeposition annealing is shown in Fig. 7. Postdeposition annealing of the films increases the temperature for 5% weight loss. Table I summarizes the important characteristics of the TGA data for all the deposition conditions in terms of parameters such as temperature for 5% weight loss, residue at 425ºC (no hold time), and residue after a furnace anneal of 425ºC for 1 h. Clearly, the effect of applied power on the thermal stability of the polymer is minimal within our range of operation. Films deposited at rf powers of 20 and 30 W yield nearly the same residue after a 425ºC furnace anneal for 1 h.

Figure 3. Effect of furnace annealing temperature on relative concentrations of CF₃, CF₂, CF, C–CF₂, and C–C or C–H. Deposition conditions: 30 W, 1 Torr.

**FTIR studies.**—IR spectra of the films deposited on the powered and grounded electrodes are shown in Fig. 4. These spectra consist of a broad absorption peak between 1100 and 1400 cm⁻¹, indicating the presence of randomly distributed saturated CF₆ groups; this peak is typical of plasma-polymerized fluorocarbons. IR spectra of the deposited films also show a broad peak between 1600 and 1800 cm⁻¹ and another peak between 1820 and 1880 cm⁻¹. The peak between 1600 and 1800 cm⁻¹ can be attributed to unsaturated hydrocarbons and fluorocarbons such as –C=C– and –C=CF₂ and also to oxygenated species such as –C=O (ketones, 1720 cm⁻¹), –C=O–OH (carboxylic acid, 1750-1785 cm⁻¹ in fluorocarbon systems), and -COOR (ester). The intensity of this peak decreases slightly in films deposited at higher substrate temperatures, indicating a lower content of C=O related groups in these films. The bonding structure corresponding to the peak between 1820 and 1880 cm⁻¹ is unclear. This peak could have contributions from acid fluorides [-C(O)=O]F which occur between 1870 and 1900 cm⁻¹ and from acid anhydride groups [-C(O)=O–C=O–O]F which occur between 1800 and 1840 cm⁻¹. The C=O related peaks arise from the atmospheric oxidation of dangling bonds typical of plasma deposited polymers. It is evident from the IR spectra that the peaks between 1600 and 1880 cm⁻¹ (oxygen containing groups) are much more prominent in polymer films deposited on the powered electrode than those deposited on the grounded electrode. This indicates the presence of high concentrations of C=O related moieties in films deposited on the powered electrode and is consistent with the high O/C ratio indicated by XPS analysis. The prominent peak between 1100 and 1400 cm⁻¹ could have significant contributions from C-O-C stretching vibrations, which occur around 1100 cm⁻¹. The difference in the peak shape and peak position between films deposited on the powered and grounded electrodes indicates different bonding environments and chemical compositions of these films. Furthermore, the powered electrode films have an extra peak at 870 cm⁻¹, which can be attributed to several carbon skeletal modes as well as peroxo (–O–O–) groups. Peroxy radicals are very likely to be formed due to atmospheric oxidation of dangling bonds and have been detected in e-beam-irradiated Teflon by electron spin resonance. Also, films deposited on the powered electrode have higher CH₃ concentrations than films on the grounded electrode.

Figure 4. IR spectra of films deposited on (a) powered electrode (no external heating) and (b) grounded electrode at 180ºC. Deposition conditions: 30 W, 1 Torr.

Figure 5. Infrared spectra of grounded electrode films annealed in a nitrogen purged furnace at 250, 300, 350, 400, and 425ºC.
Mass spectrometer studies.—Mass spectrometry was performed to identify the prominent chemical species evolved as freestanding polymer films are heated from 70 to 425°C at a rate of 10°C/min. Analysis of the evolved species shows primarily mass numbers 69, 51, 44, 20, 131, and 181 corresponding to CF₃, CHF₂, CO₂, HF, C₃F₅, and C₄F₇. The effect of temperature on the detected intensities of these species is shown in Fig. 8 for a film deposited on the grounded electrode. In Fig. 8, intensities of each species are normalized to the intensity of the CF₃ fragment, which is assigned a value of 100. The same mass numbers and trends are observed for films deposited on the powered electrode. Although CO may have been released from the films during the heating cycle, its concentration is difficult to track due to the presence of nitrogen in the spectrometer background. The CF₃ concentration is the highest among all detected species for all the deposited films and is characteristic of saturated fluorocarbons. The detection of CF₃ and CHF₂ is consistent with the chemical composition of the pentafluoroethane monomer used for film deposition. There are also significant concentrations of mass numbers 113 and 163 detected. These mass numbers may be attributed to oxygenated moieties such as C₂F₃O₂ and C₃F₅O₂ arising due to decarboxylation or to partially hydrogenated species such as C₃F₄H and C₄F₆H. As expected, concentrations of all evolved species increase with the annealing temperature. However, there is a drastic increase observed in the concentration of evolved species between 350 and 425°C, suggesting that significant degradation of the polymer occurs in this temperature range. Furthermore, there is a significant increase in the concentration of high molecular weight fragments (Mw > 200) at temperatures greater than 350°C. However, the intensities of high molecular weight fragments are much lower than those of lower molecular weight fragments.

The detection of CO₂ by mass spectrometry supports the loss of carbonyl and carboxyl groups, as indicated by FTIR analysis. However, trace CO₂ is present in the instrument background so that desorption of CO₂ may arise from the spectrometer walls, especially at high temperatures.

### Discussion

It is clear from the TGA data in Fig. 6 and 7 that all the deposited polymers have a low weight loss region below 250°C and a high weight loss region between 320 and 425°C. We believe that polymer weight loss in these temperature regimes occurs by different mechanisms. At low temperatures, weight loss is due to outgassing of low

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**Table I. Summary of the TGA results for films deposited on the grounded and powered electrodes at various deposition conditions.**

<table>
<thead>
<tr>
<th>Deposition conditions</th>
<th>Temperature for 5% weight loss (°C)</th>
<th>Residue after heating to 425°C (wt %)</th>
<th>Final residue after 1 h at 425°C (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground electrode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 W, 120°C, 1 Torr</td>
<td>293.3</td>
<td>43.3</td>
<td>32.4</td>
</tr>
<tr>
<td>30 W, 180°C, 1 Torr</td>
<td>321.9</td>
<td>65.4</td>
<td>57</td>
</tr>
<tr>
<td>30 W, 210°C, 1 Torr</td>
<td>341</td>
<td>66.4</td>
<td>59.4</td>
</tr>
<tr>
<td>20 W, 120°C, 1 Torr</td>
<td>297.7</td>
<td>44.4</td>
<td>35.1</td>
</tr>
<tr>
<td>30 W, 120°C, 1 Torr, 200°C anneal</td>
<td>310.5</td>
<td>49.7</td>
<td>39.6</td>
</tr>
<tr>
<td>Powered electrode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 W, 1 Torr</td>
<td>271.2</td>
<td>28</td>
<td>19</td>
</tr>
</tbody>
</table>
molecular weight species, and at high temperatures, it is due to degradation of the polymer. The temperature range between 250 and 320°C is a transition region between the two weight loss regimes. Hence, this discussion section focuses on the weight loss mechanisms at low and high annealing temperatures, followed by the effect of deposition temperature on the thermal stability of the deposited films.

Low temperature weight loss region (<250°C).—The weight loss in this region (<250°C) appears to be due to outgassing of low molecular weight species trapped in the film, or to loosely bonded (non-cross-linked) segments of the polymer. Mass spectrometric analysis of the evolved species indicates low concentrations of mass numbers 20, 43, 44, 51, 57, 71, 85, 97, and 69, which are assigned to HF, C₂F, CO₂, CHF₂, C₂F₂H, C₂F₃O, C₂F₅O, and CF₃, respectively. Although C₂F, C₂FN, C₂FN₂, and CF₃O are the primary constituents evolved at temperatures below 250°C, their concentrations are negligible at higher temperatures. The nitrogen content in the films could be attributed to the use of nitrogen as a purge gas in the reactor. XPS elemental analysis shows less than 1% nitrogen in all deposited films, yet it makes up a large fraction of the evolved material below 250°C. Indeed, low-temperature outgassing of nitrogen-containing species from plasma-deposited fluorocarbon films has been observed by other researchers. Further, only trace quantities of high molecular weight (>200 amu) fragments are detected below 250°C, consistent with our hypothesis.

XPS analyses of the grounded electrode films in a nitrogen-purged furnace at 250°C for 1 h show little change in the relative concentration of CF₃ species from the as-deposited polymer, suggesting negligible change in the chemical structure and composition of the polymer. Further, the IR spectra of the polymers subjected to a 250°C furnace anneal in nitrogen are also essentially unchanged from that of the as-deposited polymer except for a small amount of defluorination as indicated by the slight decrease in the intensity of the peak between 1100 and 1400 cm⁻¹ (Fig. 5). Finally, XPS analyses indicate ~1% weight loss for all the grounded electrode films below 250°C, confirming that negligible degradation occurs at these temperatures.

However, films deposited on the powered electrode show a relatively high weight loss of ~3% at 250°C. Apart from the outgassing of low molecular weight species, significant concentrations of COF and COF₂ are detected by mass spectrometry, which is consistent with acid fluoride and peroxo groups detected in powered electrode films by IR analysis. Further, there is an interesting trend of evolution of COF, COF₂, CO₂, and HF in this temperature range, as shown in Fig. 9. In Fig. 9, the normalized intensity corresponds to the ratio of the intensity of a fragment to the maximum intensity detected by the mass spectrometer for the same fragment. In all cases, the maximum intensity of all fragments is observed at the highest annealing temperature, 425°C. The increase in COF and COF₂ may be due to the scission of acid fluoride end groups (−COF) or more likely to the decomposition of peroxo radicals from the polymer chain, which typically occurs below 300°C.15,16 The COF₂ can further react with moisture present in the spectrometer background to form CO₂ and HF.16 This mechanism may also contribute to the relatively high weight loss of these films compared to that of the grounded electrode films. Furthermore, acid fluoride groups partly hydrolyze in the presence of water vapor to form acid (−COOH) groups,17 which decompose, liberating CO₂ at higher temperatures.

High temperature weight loss region (>320°C).—The high weight loss region observed in the TGA at temperatures above 320-350°C (exact results depend on the deposition conditions) is due to polymer degradation. Although the degradation mechanisms are difficult to specify precisely, they can be interpreted in terms of two competing pathways,18 that involve (i) the decomposition of chain carbon bonds and (ii) dehydrofluorination reactions involving the evolution of HF. If the polymer decomposes completely by the first path, no residue should remain, while decomposition by the second pathway yields a residue. The detection of significant concentrations of large fragments such as C₅F₅, C₆F₇, C₆F₉H, and C₅F₆H by mass spectrometry (Fig. 8) supports the decomposition of carbon-carbon chain bonds while the detection of HF is indicative of the second pathway. The liberation of HF may be due to the reaction between adjacent pendant hydrogen and fluorine atoms which results in the formation of unsaturated −C≡C− moieties in the polymer. Indeed, IR spectra of the deposited films (Fig. 5) after a 425°C furnace anneal show a prominent absorption peak at ~1630 cm⁻¹ corresponding to unsaturated carbon moieties. The dehydrofluorination mechanism would likely involve the cleavage of the relatively weak C−H bond and the subsequent scavenging of fluorine by the liberated H free radical. Hence, this mechanism is favored when the hydrogen concentrations in the deposited films are high. Indeed, previous studies19 have shown that more HF is liberated during the pyrolysis of [−C₅H₅F−]ₙ than of [−C₅H₇F₃]ₙ. However, the presence of oxygenated species could have a significant effect on the degradation mechanism and consequently the final residue. For instance, films deposited on the powered electrode have a high O/C ratio of 0.14 and yield only 19% residue after a 425°C anneal for 1 h. In contrast, films deposited on the temperature-controlled, grounded electrode have an O/C ratio of ~0.03 and yield much higher residues in the range of 40-65%. The increase in the concentration of CO₂ as detected by the mass spectrometer between 350 and 425°C confirms the loss of oxygenated moieties from the polymer. This is corroborated by the IR spectrum of the grounded electrode film (Fig. 5), which shows a dramatic reduction in the intensity of C=O related peaks (1700-1800 cm⁻¹) upon heating the deposited films above 350°C. The decrease in the FTIR intensity of C=O related peaks may be partially attributed to decarboxylation, which occurs at temperatures greater than 300°C.15 These reactions not only reduce the molecular weight but also give rise to free radicals that can further break down the polymer chains into smaller fragments. This could be one of the factors responsible for the extremely low residue obtained on heating the powered electrode films where the first pathway appears to dominate. Hence, the presence of oxygen-related species has a detrimental effect on the thermal stability of the polymer.

The other important factor affecting the thermal stability is the concentration of volatile end groups such as CF₃ and CHF₂. High concentrations of end groups signify lower molecular weight and extent of cross-linking and consequently, lower thermal stability.20 XPS analyses indicate 12-16% CF₃ in the as-deposited polymer films, indicating a significant fraction of end groups in the polymer. Also, a part of the CF₂ detected by the XPS in the film could be due to CHF₂ end groups. Indeed, CF₃ and CHF₂ are the major components of the evolved species, although only a fraction of them may result from the loss of end groups. Furthermore, XPS analyses indicate a significant decrease of CF₃ and CF₂ moieties in films furnace annealed between 350 and 425°C, corroborating the mass spectrometry data. The final

![Figure 9](https://example.com/figure9.png)
F/C ratio of the films varies between 0.6 and 0.72 after the 425°C temperature step, suggesting that films of the type C$_2$F$_x$ (x > 1.2) are more thermally stable. In fact, polymers of the type C$_2$F$_x$ have been shown to be thermally stable up to 590°C in vacuum.

**Effect of deposition temperature.**—As indicated in Table I, deposition at higher substrate temperatures significantly increases the incipient degradation temperature of the polymer films and results in lower weight loss. XPS analyses indicate a decrease in the F/C ratio of the polymer with an increase in deposition temperature, probably due to a higher degree of cross-linking and to a reduction in the thermally labile fluorine-rich CF$_3$ and CHF$_2$ groups. Both these factors significantly enhance the thermal stability of the polymer. Higher deposition temperatures significantly reduce low molecular weight species trapped in the films either by more efficiently reacting and incorporating them into the growing network or by desorbing them in the case of incomplete polymerization. The low deposition rates at high temperatures further aids this reaction-desorption mechanism. IR spectra indicate lower concentrations of oxygen-related moieties for films deposited at higher substrate temperatures, probably due to a decrease in the concentrations of trapped free radicals and dangling bonds. Further, the reacting species as well as the growing polymer chains have higher mobility at higher temperatures, thereby allowing the formation of a dense network. Hence, deposition at higher temperatures is definitely more beneficial than postdeposition annealing of the films in terms of the thermal stability of the resulting films. Postdeposition annealing removes only the thermally labile low molecular weight fragments but does not cause a significant increase in the extent of film cross-linking. As a result, there is a decrease in the polymer weight loss at low temperatures but a minimal change in the residue after a final 425°C anneal.

As shown in Table I, there is a minimal effect of the applied rf power on the thermal stability of the polymer within our narrow range of operation. This is consistent with the relatively constant concentrations of CF$_3$ species and F/C ratio detected by XPS for the films deposited at different rf powers and with the fact that the deposition mechanism did not change significantly with rf power. However, films deposited at higher power densities could exhibit significantly different chemical structures and oxidation rates and hence, may be expected to have different thermal stabilities.

There are several other parameters that influence the film thermal stability, such as operating pressure, argon partial pressure, and plasma frequency. The effects of these parameters are beyond the scope of this paper and may be investigated in future studies. However, the proposed degradation mechanisms are applicable to any plasma-deposited hydrofluorocarbon film. The relative importance of the individual degradation steps varies depending on the exact chemical structure of the deposited films.

**Conclusions**

Fluorocarbon films deposited from perfluorooctane/argon plasmas at substrate temperatures between 120 and 210°C and rf powers between 20 and 30 W were analyzed for their thermal stability in terms of changes in their chemical structure, composition, and weight loss. TGA analyses of the deposited films indicate a low weight loss regime below 250°C and a high weight loss regime between 320 and 425°C; these regimes result from different weight loss mechanisms. The weight loss below 250°C is attributed to the outgassing of low molecular weight species from the deposited films and represents ~1% weight loss for films deposited on the grounded electrode. Virtually no film degradation occurs in this regime, as indicated by IR and XPS results. The weight loss in this regime is significantly reduced either by postdeposition annealing or by increasing the deposition temperature, both of which assist in the removal of low molecular weight species from the film. In contrast, films deposited on the unheated powered electrode had a much higher weight loss of ~3% below 250°C, which is attributed to the higher concentration of trapped low molecular weight species as well as the loss of oxygenated groups in the form of COF, COF$_2$, and CO$_2$. The high weight loss region between 320 and 425°C results from extensive polymer degradation. The degradation mechanism involves several pathways, which include loss of C$_2$F$_x$ species through scission of main chain C–C bonds, dehydrofluorination (loss of HF) involving scavenging of fluorine by hydrogen free radicals, decarboxylation involving loss of acid and ester groups through evolution of CO$_2$, and loss of volatile end groups such as CF$_3$ and CHF$_2$. Higher deposition temperatures reduce the polymer weight loss in this regime. Fluorocarbon films deposited at 210°C yield a residue of 65% after a 1 h 425°C anneal, while those deposited at 120°C gave a residue of 40%. This enhancement in thermal stability is attributed to more extensive film cross-linking and lower concentrations of volatile end groups, as indicated by XPS analyses. Furthermore, IR spectra indicated a slight decrease in the C=O related species in the deposited films with an increase in substrate temperature. The presence of oxygen-related species in the film not only enhances outgassing at lower temperatures but also significantly enhances film degradation at higher temperatures. Indeed, TGA analyses of the oxygen-rich powered electrode films indicate a weight loss of 5% by 270°C and a residue of only 19% after a 1 h 425°C anneal.

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