# Chemical Alteration of Poly(tetrafluoroethylene) TFE Teflon Induced by Exposure to Electrons and Inert-Gas Ions

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In this study the chemical alterations of poly(tetrafluoroethylene) (TFE Teflon) by ∼1.0-keV electrons and 1.0-keV He and Ar ions have been examined using X-ray photoelectron spectroscopy (XPS). The initial F/C atom ratio of 1.99 decreases to a steady-state value of 1.48 after 48 h of electron exposure. Exposure to either $He^+$ or $Ar^+$ decreases the initial F/C atom ratio from ∼2 to a steady-state value of 1.12. The high-resolution XPS C 1s data indicate that new chemical states of carbon form as the F is removed and that the relative amounts of these states depend on the F content of the near-surface region. These states are most likely due to C bonded only to one F atom, C bonded only to other C atoms and C that have lost a pair of electrons through emission of $F^-$. Exposures of the electron-damaged and $He^+$- or $Ar^+$-damaged surfaces to research-grade $O_2$ result in chemisorption of very small amounts of O indicating that large quantities of reactive sites are not formed during the chemical erosion. Further exposure to the electron or ion fluxes quickly removes this chemisorbed oxygen. Exposure of the $He^+$-damaged surface to air at room temperature results in the chemisorption of a larger amount of O than the $O_2$ exposure but no N is adsorbed. The chemical alterations due to electrons and ions are compared with those caused by hyperthermal (∼5 eV) atomic oxygen (AO) and vacuum ultraviolet (VUV) radiation. The largest amount of damage is caused by AO followed by VUV, inert-gas ions, and then electrons.

## Introduction

Polymers are attractive and desirable materials for use in space applications because they are lightweight and typically much easier to process using techniques such as extrusion, casting, and injection molding at relatively low temperatures compared to metals and ceramics. They also tend to be more flexible and offer a wide variety of choices from optically transparent to opaque, rubbery to stiff, and conducting to insulating. Fluoroethylene propylene (FEP) Teflon[1] is one material that is widely used as a thermal blanket for spacecraft flying in low-earth orbit (LEO).[2] The reflectance of the FEP Teflon is increased by lining the FEP Teflon with aluminum or silver. Since FEP Teflon has a high thermal emittance, this system can both reflect a large fraction of the incident solar energy as well as effectively radiate heat away from itself.

However, over the last two decades, it has been well-established that polymers undergo severe degradation from exposure to the harsh orbital space environment resulting in reduced spacecraft lifetimes. These materials degrade because spacecraft surfaces are exposed to high fluxes of hyperthermal atomic oxygen (AO), bombardment by low- and high-energy charged particles, thermal cycling, and the full spectrum of solar radiation including ultraviolet (UV) radiation. AO is the main constituent of the atmosphere in LEO. It is formed by dissociation of $O_2$ by UV radiation from the sun, resulting in an AO concentration of approximately $10^8$ atoms/$cm^3$. The actual AO flux of $5 \times 10^{14}$ atoms/($cm^2 \cdot s$) impinging on a spacecraft is high due to orbiting speeds of approximately 8 km/s. At these relative speeds thermal AO collides orbital objects with a kinetic energy of ∼4.5 eV. These highly energetic collisions not only

result in surface chemical reactions but can also lead to a pure physical sputtering of the surface atoms. Many studies have been conducted in an effort to determine the mechanism of degradation caused by surface reactions with AO.[3−10] However, these studies have all been carried out after exposing these reactive surfaces to air prior to analysis, thus introducing the possibility of artifacts that do not represent the true space environment. A recent study has shown that exposure of AO-exposed Kapton[1] to air chemically alters the reactive surfaces formed during AO exposure.[11] Therefore, analysis of polymers exposed to LEO-simulated conditions must be carried out in vacuo to avoid artifacts induced by air exposure.

The space environment is very complex and quite inhomogeneous. Radiation and various types of particles are generated both within and beyond our solar system. Primary cosmic rays interact with gases and other matter in the upper atmosphere to produce secondary radiation in addition to radiation produced by the sun. Electrons and heavier nuclei as well as He nuclei are generated by fusion in the interior of the sun. All of these species (both charged and neutral) travel toward earth as the solar wind. This solar wind travels away from the sun in all directions, but the fluxes of these particles vary with sunspot activity and solar flares. Novas and supernovas generate heavy ions in our galaxy and beyond, which travel to earth. The Van Allen radiation belts contain trapped electrons in the outer belts and trapped protons in the inner belt. Space vehicles collide with these species. The compositions and intensity vary significantly with the trajectory of a space vehicle. Due to the complexity and inhomogeneity of the space environment, it is not possible to simulate the space environment in earth laboratories. Nevertheless, model studies such as this one are capable of providing useful information about the interaction

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of various types of species with materials used in space applications. This information is useful in selecting and developing new materials with improved survivability in space.

Several studies have been conducted on the deterioration of fluorinated polymers retrieved from spacecraft subjected to the LEO environment. The outer layer of the FEP Teflon multilayer insulation on the Hubble space telescope (HST) was significantly cracked at the time of the second HST servicing mission—6.8 years after it was launched into LEO.[12,13] Comparatively minor embrittlement and cracking were also observed in the materials retrieved from solar-facing surfaces on the HST at the time of the first servicing mission (3.6 years of exposure to LEO). Furthermore, an increased deterioration of fluorinated polymers may result from a synergistic effect of vacuum ultraviolet (VUV) radiation and charged particles such as electrons and ions in the presence of AO.[14] de Groh and Martin[15] studied pristine FEP Teflon multilayer insulation during X-ray irradiation over a temperature range from 50 to 200 °C. They found that degradation occurs more rapidly at elevated temperatures while no degradation occurs at elevated temperatures without irradiation.

Several forms of Teflon are available commercially and they have different chemical and physical characteristics. Poly-(tetrafluoroethylene) TFE Teflon was chosen for this study because it has the highest operating temperature ($\sim$260 °C) of all fluoropolymers, an extremely low coefficient of friction, good abrasion resistance, and good chemical resistance. This polymer is also referred to as PTFE Teflon on the Dupont website. The goal of this study is to examine the chemical alterations of a TFE Teflon surface caused by impinging electrons and He and Ar ions. Electrons and He$^+$ species were chosen because these are abundant in space. Ar$^+$ was chosen because it is a heavier ion and provides a comparison with He$^+$ since they are both inert-gas ions thereby eliminating chemical effects. The sources used are described below. There are two types of bonds in TFE Teflon: C—C bonds and C—F bonds, with bond strengths of approximately 83 and 111 kcal/mol, respectively. A single TFE Teflon surface was exposed to electrons for various time periods and then exposed to research-grade O$_2$ to test the chemical reactivity of the electron-exposed surface. Another TFE Teflon surface was exposed to He and Ar ions and then exposed to O$_2$ and air. A similar set of experiments have been carried out on TFE Teflon using AO[16] and VUV radiation.[17] Future studies are planned in which a TFE Teflon surface will be exposed simultaneously to AO, VUV radiation, electrons and ions to simulate more closely the LEO space environment.

This study is part of a larger study in which the goals are to characterize the effects of LEO on various types of polymers and to develop new polymers which will withstand the effects of LEO. Kapton is widely used as a thermal blanket for spacecraft, but it erodes severely in LEO due to exposure to AO. After ground-based exposure of Kapton to hyperthermal AO, XPS data indicate that the initial attack site is the carbonyl portion of the Kapton by reaction with AO to form CO$_2$, which desorbs.[11] This results in a reduction of the O content in the near-surface region. The Kapton surface becomes quite rough during AO exposure according to images taken using atomic force microscopy (AFM). Exposure of Kapton to 1.0-keV He$^+$ results in lowering the C and N surface contents.[18] AO exposure studies have been carried out on polyhedral oligomeric silsesquioxane (POSS)-containing copolymers, which are ceramic/polymer hybrid materials.[19−21] These are particularly interesting systems because when exposed to hyperthermal AO, the C and H are removed leaving a thin layer ($\sim$30 Å) of SiO$_2$, which

protects the underlying polymer from further erosion. This structure is also self-repairing in that SiO$_2$ forms again if the original layer is damaged.

A study was carried out by Pruden et al.[22] in which parylene-N and parylene-C were exposed simultaneously to oxygen and ultraviolet light. Using XPS and other surface-sensitive techniques, they found that aldehyde and carboxylic acid groups form in the near-surface region. Shyichuk et al.[23] have used quantum chemical methods to explain why the polystyrene photooxidation rates are slower than those of polypropylene. As shown by Nagata and Hizakae,[24] photocuring by UV irradiation at ambient temperature can be used to improve the mechanical properties of biodegradable copolymers based on 4,4′-(adipolydioxy)dicinnamic acid, **1**, 6-hexanediol, and poly(ethylene glycol)s. These studies[22−24] demonstrate that ultraviolet light can have a large effect on the chemical and physical properties of a wide variety of polymers under various circumstances. As stated above, Kapton is the most widely used spacecraft coating, FEP Teflon is used in certain space applications such as the Hubbel telescope, and POSS-containing copolymers provide great promise for future applications due to their low rate of degradation. More recently developed F-containing polymers,[25−28] F- and Si-containing polymers,[29,30] F- and Cl- and Si-containing polymers,[31] and F- and P- and Si-containing polymers[32] may also be potential candidates for space applications. Another interesting possibility would be to modify polymer surfaces by ion implantation for space applications. Hoffmann et al.[33] have modified Nafion surfaces by ion implantation with N$^+$ or F$^+$. Si$^+$ implantation could be used to form an implanted layer that may behave like POSS-containing copolymers when exposed to AO.

## Experimental Section

**Electron Source Characteristics.** The $\sim$1.0-keV electrons were generated in this study by operating an AO source[34] without oxygen present in the source and setting the electrostatic lens voltage to 0.0 V. Primary electrons (1.0 keV) from the filament struck a Ag membrane generating 1.0-keV electrons and a low, broad background of secondary electrons.[35] The electron flux used was approximately 5 $\mu$amp/mm$^2$ (3.1 electrons/(cm$^2$·s)).

**Inert-Gas Ion Source Characteristics.** The ion source used in this study was a PHI Model 04-161 Sputter Ion Gun with a PHI Model 20-045 Sputter Ion Gun Control. The ion source was operated at a primary beam energy of 1.0 keV with an emission current of 4 mA. The source was operated within an ultrahigh vacuum chamber backfilled to a pressure of $1 \times 10^{-5}$ Torr of He and Ar. The sample was exposed at an incident angle of $\sim$60° and a distance of 8 cm from the source, and the flux was $\sim$5 $\times 10^{13}$ ions/(cm$^2$·s) with the instrument settings used.

**Surface Characterization.** An as-received E.I. du Pont Nemours & Co., Inc. TFE Teflon film was wiped with ethanol and inserted into an ultrahigh vacuum (UHV) chamber (base pressure <1.0 $\times 10^{-10}$ Torr). XPS measurements were performed using a double-pass cylindrical mirror analyzer (DPC-MA) (PHI Model 25-270AR). XPS survey spectra were taken in the retarding mode with a pass energy of 50 eV, and high-resolution XPS spectra were taken with a pass energy of 25 eV using Mg K$\alpha$ X-rays (PHI Model 04-151 X-ray source). Data collection was accomplished using a computer interfaced, digital pulse counting circuit[36] followed by smoothing with digital-filtering techniques.[37] The sample was tilted 30° off the axis of the DPCMA, and the DPCMA accepted electrons emitted into a cone 42.6 $\pm$ 6° off the DPCMA axis.
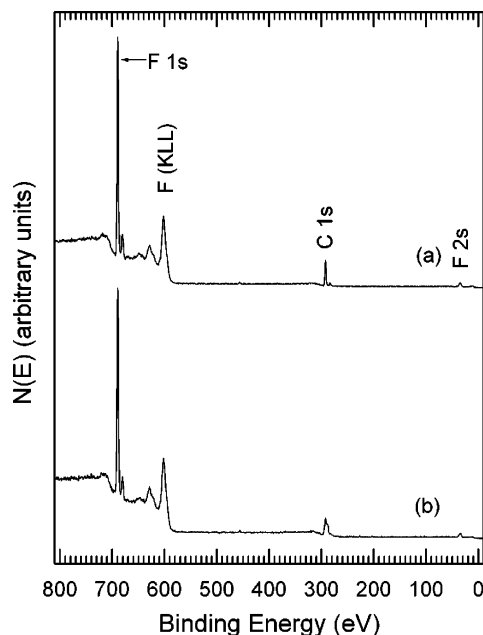
**Figure 1.** XPS survey spectra obtained from TFE Teflon (a) as entered and (b) after 2-h exposure to 1.0-keV electrons.

After wiping with ethanol the sample surface contained small amounts of hydrocarbon contamination according to the high-resolution XPS spectra. Ideally, the initial starting surface would be stoichiometric TFE Teflon with no hydrocarbon contamination. Unfortunately, this state cannot be attained. The hydrocarbons can be removed by ion sputtering. However, if they are completely removed, the TFE Teflon stoichiometry is damaged by removal of F because the sputtering process affects subsurface layers.[38] In practice the best starting surface that can be achieved is to remove as much of the hydrocarbon contamination as possible without altering the TFE Teflon. In this study the surfaces were presputtered with either 0.5 or 1.0 keV He$^+$ to remove most of the hydrocarbon contamination. The small amounts of hydrocarbon contamination remaining on the surfaces varied somewhat but reproducibility experiments have shown that this does not alter the F/C atom ratios or chemical-state information obtained as a function of time. Furthermore, the hydrocarbon C 1s feature is well-separated from the TFE Teflon C 1s species so it does not affect the calculated F/C atom ratios or peak shapes of the carbon species of interest.

The sample was then transferred in vacuo via a magnetically coupled rotary/linear manipulator into an adjoining UHV chamber that houses the electron source. There the surface was exposed to a flux of electrons and reexamined after various exposure times. The sample was not exposed to air after the exposures and before collecting XPS data. However, after the exposures the surface was exposed in vacuo to O$_2$ in another adjoining vacuum chamber to determine how this would affect the electron- or ion-exposed surface. The sample was maintained at room temperature during the exposures with a temperature increase to about 50 °C due to exposure to the X-ray source during XPS data collection. The substrate temperature was determined using a chromel−alumel thermocouple. The ion exposures were carried out in the same chamber that houses the XPS system.

## Results and Discussion

**Electron Exposures.** The XPS survey spectrum obtained from the as-received TFE Teflon surface prior to electron exposure is shown in Figure 1a. This spectrum is identical
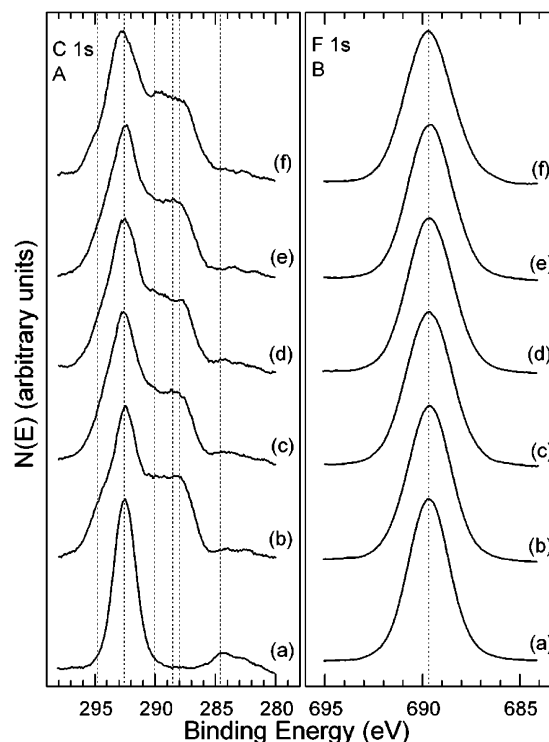


**Figure 2.** High-resolution XPS (A) C 1s and (B) F 1s obtained from TFE Teflon (a) as entered, (b) after exposure to 1.0-keV electrons for 2 h, (c) after exposure to 1.0-keV electrons for a total of 25 h, (d) after exposure to research-grade O$_2$ at room temperature and 150 Torr for 20 min, (e) after exposure to research-grade O$_2$ at room temperature and 150 Torr for 90 min, and (f) after exposure to 1.0-keV electrons for a total of 48 h.

(except for relative peak heights since different analyzers were used) to that given for PTFE in the polymer XPS handbook by Beamson and Briggs[39] with the characteristic C 1s, F 1s, F 2s, and F (KLL) peaks. There is no O 1s peak, which would appear near a binding energy (BE) of 530 eV. There are two states of carbon present indicated by a large peak due to TFE Teflon at a BE of 292.5 eV and a small peak due to adventitious carbon at 284.6 eV. These C 1s features are more apparent in the high-resolution XPS spectrum shown in Figure 2Aa. The corresponding F 1s spectrum shown in Figure 2Ba exhibits a single broad peak centered at 689.7 eV, which is characteristic of TFE Teflon.[39] Estimates of the near-surface compositions have been made from the peak areas in the high-resolution spectra using published atomic sensitivity factors[40] with the assumption of a homogeneous surface region. XPS probes the near-surface region of the sample and yields a weighted average composition with the atomic layers near the surface being weighted more heavily since the photoemitted electrons from these layers have a lower probability of scattering inelastically. The sampling depth is ∼4−6 nm, and ∼10% of the signal originates from the outermost atomic layer.[41] This near-surface region is nonhomogeneous because the electrons and ions react most strongly with the outermost few atomic layers. Therefore, the region that reacts to the greatest extent with the electrons and ions also makes the largest contribution to the XPS signal. This fact implies that XPS is an excellent technique for studying erosion of spacecraft materials. Even though the distribution functions involving the depth of chemical reactions in the near-surface region and the XPS determination of the weighted average composition of the near-surface region are complex, the compositional values provide a trend that is indicative of the chemical alterations occurring during electron or ion exposure. The compositions determined using the homogeneous

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**TABLE 1: Near-Surface Compositions (atom %) of TFE Teflon after Various Treatments (1-keV $e^{-1}$)**

|  | F | C | F/C |
|---|---|---|---|
| as entered | 66.5 | 33.5 | 1.99 |
| $e^-$ 2 h | 58.5 | 41.5 | 1.41 |
| $e^-$ 25 h | 60.8 | 39.2 | 1.55 |
| $O_2$ 20 min | 60.5 | 39.5 | 1.53 |
| $O_2$ 90 min | 60.6 | 39.4 | 1.54 |
| $e^-$ 48 h | 59.7 | 40.3 | 1.48 |

assumption are shown in Table 1 before and after various exposures to electrons and research-grade $O_2$. The F/C atom ratio obtained from the as-entered sample is 1.99, which is very close to the stoichiometric value of 2.0.

After 2 h of exposure to the 1.0-keV electron flux, distinct changes in the C 1s features are apparent in Figure 1b. On the basis of the high-resolution C 1s feature shown in Figure 2Ab, the feature due to adventitious carbon has been completely removed. The overall height of the high-BE peak due to TFE Teflon is decreased and a broad structure is apparent on the low-BE side. Although distinct peaks cannot be discerned, at least two peaks are present. A shoulder is also present at 294.8 eV. No detectable changes are observed in the F 1s, F 2s, or F (KLL) peaks in Figure 1b nor are any observed in the high-resolution F 1s spectrum (Figure 2Bb). The C concentration is increased from 33.5 to 41.5 atom % and the F concentration drops from 66.5 to 58.5 atom % resulting in a decrease in the F/C atom ratio to 1.41.

The surface was then exposed to the 1.0-keV electron flux for another 23 h for a total of 25 h. The data in Table 1 indicate that the F content is slightly increased while the C content is slightly decreased resulting in an increase in the F/C atom ratio from 1.41 to 1.55. This increase is consistent with the changes in the C 1s shown in Figure 2Ac. The peak at 292.5 eV due to carbon in TFE Teflon is increased in size relative to the shoulder. The features on the shoulder at 290.0 and 288.0 eV are more pronounced and there may be another small contribution just above 288.0 eV. Furthermore, the shoulder at 294.8 eV was eliminated by this exposure. No changes are apparent in the F 1s peak (Figure 2Bc).

Assigning these peaks to specific species is quite difficult for several reasons. Defining localized species, which yield features at specific BEs, may not be possible. For example,

$$ F \ - \overset{|}{\underset{|}{C}} - \ F $$
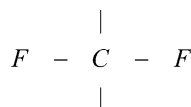
species are present in TFE and FEP Teflon and Tefzel[1] but the C 1s BEs are 292.48 and 290.9 eV, respectively. Also,

$$ H \ - \overset{|}{\underset{|}{C}} - \ H $$
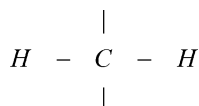
species are present in Tefzel and Tedlar[1] with BEs of 286.44 and 285.74 eV, respectively. XPS BEs result from the chemical environment around the given element. This fact implies that the chemical environment is larger than the species defined in TFE Teflon, Tefzel, and Tedlar. Since there are distinct peaks in these spectra, there are distinct chemical environments, but defining the nature of these chemical environments is difficult. Since the electron-exposed TFE Teflon surface is a damaged surface in that the composition is changed to a great extent, the structure is most likely altered in the following manner. The

two states with BEs of 290.0 and 288.0 eV may be carbons that have lost one and two fluorines, respectively. The presence of regions of lower concentrations of F implies that electron density on the C atoms is not decreased to such a large extent by withdrawal toward the F resulting in increased C 1s BEs.

The surface was then exposed to 150 Torr of $O_2$ for 20 min. Negligible changes are observed in the XPS survey spectrum (not shown). The C concentration increases to 39.5 atom %, the F concentration decreases to 60.5 atom %, and the F/C atom ratio drops to 1.53, all of which are similar to those after the 25-h, 1.0-keV electron exposure. No oxygen is adsorbed onto the surface. The surface was then exposed to $O_2$ for another 90 min. Negligible changes to the XPS survey spectra (not shown) are observed with the exception of the appearance of a very small peak at 530 eV, which is due to a small amount of oxygen adsorbed at the surface. The area under the O 1s feature is not large enough to quantify but is indicative of an O concentration less than 1 atom % in the near-surface region.

The high-resolution XPS spectra obtained after the two $O_2$ exposures exhibit subtle changes in the C 1s features (Figure 2Ad and 2Ae) while no changes to the F 1s spectra (Figure 2Bd and 2Be) are apparent. After the 20-min $O_2$ exposure, the high-BE C 1s peak (Figure 2Ad) broadens further on the low-BE side. The shoulder at 290.0 eV has a more definitive peak shape. The low-BE feature at 288.0 eV becomes more narrow and prominent, whereas the portion at 288.5 eV is decreased. After the additional 90-min $O_2$ exposure, the spectrum resembles that prior to any $O_2$ exposure. The peak at 288.5 eV becomes larger than the shoulder at 288.0 eV, and the peak at 290.0 eV becomes less prominent.

The surface was again exposed to the 1.0-keV electron flux for an additional 23 h (48 h total). The XPS survey spectrum (not shown) indicates no changes to the F 1s, F 2s, or F (KLL) peaks and that the small feature due to O is completely removed. The low-BE C 1s feature appears as a more defined peak, similar to that obtained after the 25-h, 1.0-keV electron exposure. The C composition of the surface increases to 40.3 atom %, the F 1s concentration decreases to 59.7 atom %, and the F/C atom ratio decreases to 1.48. As before, there is no noticeable change in the high-resolution F 1s spectrum shown in Figure 2Bf. Several changes to the C 1s spectrum are observed in Figure 2Af. The features at 290.0 and 288.0 eV begin to reemerge as peaks with the continued electron exposure. The high BE peak at 292.5 eV becomes broader with a shoulder now appearing on its high-BE side at 294.8 eV. This shoulder having a higher BE than carbon in the TFE Teflon environment indicates that electron-deficient species are formed under electron bombardment. This may occur by emission of $F^-$ species leaving carbon species which have lost an electron pair. The nuclei of these species then attract the C 1s electrons more strongly resulting in a larger C 1s BE. This feature is also apparent after the 2-h, 1.0-keV electron exposure (Figure 2Ab).

**He$^+$ Exposures.** The XPS survey spectrum obtained from the as-received TFE Teflon surface prior to ion exposure is identical with that shown in Figure 1a and only changes slightly after a 1-h exposure to 0.5-keV He$^+$ (not shown). As found above two states of carbon are present due to TFE Teflon at a BE of 292.5 eV and a small peak due to adventitious carbon at 284.6 eV (Figure 3Aa). The F/C atom ratio is 2.07 (Table 2), which is close to the expected value of 2.00. Comparison of the as-received survey spectrum and the He$^+$-exposed survey spectrum (not shown), as well as the high-resolution C 1s and F 1s spectra (Figures 3Aa, 3Ab, 3Ca, 3Cb), indicates that there are small changes to the surface induced by exposure to 0.5-
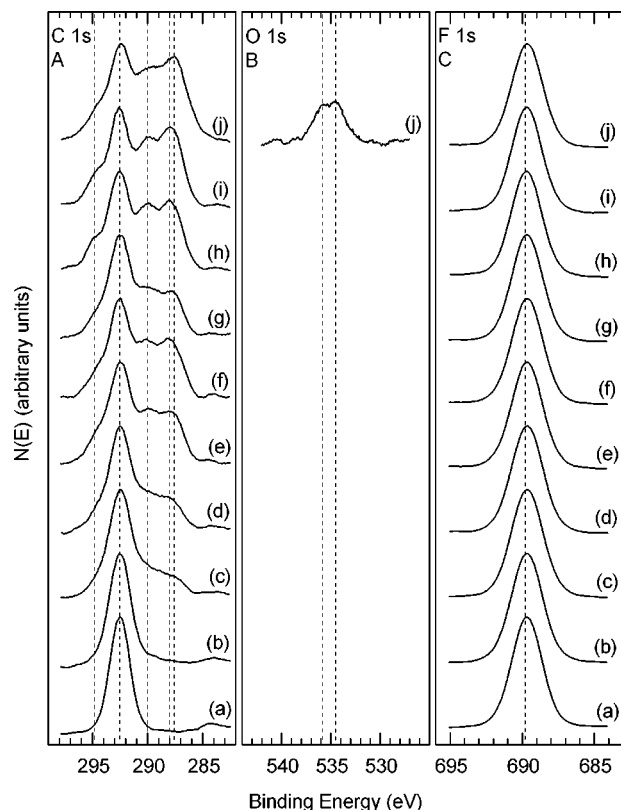
**Figure 3.** High-resolution XPS (A) C 1s, (B) O 1s, and (C) F 1s obtained from TFE Teflon (a) as entered, (b) after exposure to 0.5-keV He$^+$ for 1 h, (c) after exposure to 1.0-keV He$^+$ for 2 h, (d) after exposure to 1.0-keV He$^+$ for a total of 4 h, (e) after exposure to 1.0-keV He$^+$ for a total of 8 h, (f) after exposure to 1.0-keV He$^+$ for a total of 10 h, (g) after exposure to research-grade O$_2$ at room temperature and 150 Torr for 20 min, (h) after exposure to 1.0-keV He$^+$ for a total of 15 h, (i) after exposure to 1.0-keV He$^+$ for a total of 19 h, and (j) after exposure to air for 90 min at room temperature.

**TABLE 2: Near-Surface Compositions (atom %) of TFE Teflon after Various Treatments (1-keV He$^+$)**

|  | F | O | C | F/C | O/C |
|---|---|---|---|---|---|
| as entered | 67.4 | 0.0 | 32.6 | 2.07 | 0.0 |
| 0.5 keV He$^+$ 1 h | 68.5 | 0.0 | 31.5 | 2.18 | 0.0 |
| 1.0 keV He$^+$ 2 h | 64.1 | 0.0 | 35.9 | 1.79 | 0.0 |
| 1.0 keV He$^+$ 4 h | 60.2 | 0.0 | 39.8 | 1.51 | 0.0 |
| 1.0 keV He$^+$ 8 h | 75.8 | 0.0 | 42.2 | 1.37 | 0.0 |
| 1.0 keV He$^+$ 10 h | 57.4 | 0.0 | 42.6 | 1.35 | 0.0 |
| O$_2$ 20 min | 59.2 | 0.0 | 40.8 | 1.45 | 0.0 |
| 1.0 keV He$^+$ 15 h | 55.9 | 0.0 | 44.1 | 1.27 | 0.0 |
| 1.0 keV He$^+$ 19 h | 52.9 | 0.0 | 47.1 | 1.12 | 0.0 |
| 90 min air | 48.9 | 1.9 | 49.2 | 0.99 | 0.04 |

keV He$^+$. The F/C atom ratio increases slightly to 2.18, and the feature due to adventitious carbon is reduced in size.

Changes in the C 1s peak are observed in Figure 3Ac after a 2-h exposure to 1.0-keV He$^+$. The adventitious carbon peak is reduced further in size and at least one new state of carbon is apparent as a shoulder at 287.5 eV on the low-BE side of the C 1s peak. The F/C atom ratio is decreased to 1.79—a loss of nearly 18% of the F in the near-surface region. Negligible changes in the fluorine peaks are observed in Figure 3Cc. After an additional 2 h of 1.0-keV He$^+$ exposure, there is an increase in the size of the shoulder on the C 1s peak (Figure 3Ad). The C 1s feature is broader, the height of the shoulder is increased, and multiple carbon states are apparent. The low-BE feature from the previous exposure now appears to be a peak centered at 288.0 eV while another peak forms at 290.0 eV. The F/C atom ratio drops to 1.51, another 15% decrease in F concentra-

tion in the near-surface region. No changes are apparent in the F 1s, F 2s, and F (KLL) peaks.

Another 4 h of 1.0-keV He$^+$ exposure (8 h total) yields further change in the C 1s features as does a subsequent 2 h exposure. The high-resolution C 1s spectrum in Figure 3Ae indicates the presence of five distinct carbon features. The peaks at 288.0 and 290.0 eV each become more defined and make larger contributions to the carbon content at the surface. The F/C atom ratio is further reduced to 1.37—a loss of approximately 9% of the remaining near-surface F or 33% of the original F concentration. Also, a shoulder forms on the high-BE side of the TFE Teflon C 1s peak at 292.5 eV.

These changes are enhanced further by another 2-h, 1.0-keV He$^+$ exposure. The high-resolution F 1s spectrum (Figure 3Cf) indicates that the F 1s peak shape remains constant. The F/C atom ratio after this treatment only decreases nominally to 1.35. Assigning peaks to specific species is again difficult for the reasons stated above. Since the He$^+$-exposed surface is a damaged surface in that the composition is altered to a great extent, the structure is most likely altered in the following manner. The two states with BEs of 290.0 and 288.0 eV may be carbon species that have lost one and two fluorines, respectively. The presence of lower concentrations of F implies that electron density on the C atoms is not decreased to such a large extent by withdrawal toward the F resulting in decreased C 1s BEs. The shoulder at 294.8 eV, having a higher BE than carbon in the TFE Teflon environment, indicates that electron-deficient species are formed under He$^+$ bombardment most likely by emission of F$^-$ species leaving carbon species that have lost an electron pair. The nuclei of these species then attract the C 1s electrons more strongly resulting in a larger C 1s BE.

The sample was then exposed to research-grade O$_2$ at 150 Torr for 20 min and the XPS spectrum (not shown) indicates that only a very small amount (<1 atom %) of O$_2$ chemisorbs on the surface. This suggests that most of the broken bonds formed by the He$^+$ exposure cross-link on the TFE Teflon surface. The F/C atom ratio does, however, increase to 1.45. This may be due to removal of reactive C species by reaction with O$_2$ to form CO and CO$_2$. The C 1s and F 1s high-resolution spectra are shown in Figures 3Ag and 3Cg, respectively. As before the F 1s feature apparently is not altered by the O$_2$ exposure, but the C 1s shoulders are significantly altered in that they are decreased in intensity. This is consistent with loss of these species by reaction with O$_2$.

Five more hours of 1.0-keV He$^+$ exposure (15 h total) following the O$_2$ treatment results in complete removal of the O 1s feature in the survey spectrum (not shown). The C 1s feature shown in Figure 3Ah indicates that the shoulders become significantly larger and more well-defined. The peaks at 288.0 and 290.0 eV become larger with respect to the TFE Teflon peak at 292.5 eV. Also, the TFE Teflon peak is narrower and the shoulder on its high-BE side is larger and more prominent. The F/C atom ratio decreases further to 1.27. After another 4 h of 1.0-keV He$^+$ exposure (19 h total), it decreases further to 1.12. Approximately 46% of the fluorine originally present in the near-surface region is removed by this He$^+$ exposure. In the XPS spectrum in Figure 4a, changes to the C 1s feature are evident in that the two separate peaks merge into one large, broad feature. Furthermore, the 288.0-eV feature is broadened toward the low-BE side and is now considerably larger than the 290.0-eV feature.

After 19 h of 1.0-keV He$^+$ exposure, the sample was removed from the UHV system, exposed to air at room temperature for 90 min, and returned to the UHV system for analysis. The XPS
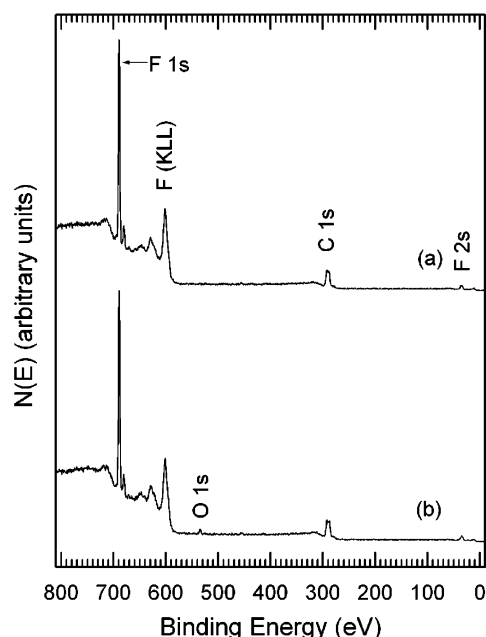
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**Figure 4.** XPS survey spectra obtained from TFE Teflon (a) after a 19-h exposure to 1.0-keV $He^+$ and (b) after a 90-min exposure to air at room temperature.



**Figure 5.** High-resolution XPS C 1s spectra obtained from TFE Teflon (a) as entered, (b) after exposure to 1.0-keV $Ar^+$ for 1 h, (c) after exposure to 1.0-keV $Ar^+$ for 8 h, and (d) after exposure to research-grade $O_2$ at room temperature and 150 Torr for 20 min.



**Figure 6.** High-resolution XPS C 1s spectra obtained from TFE Teflon after exposure to 1.0-keV $He^+$ for 8 h compared to C 1s spectra obtained after exposure to 1.0-keV $Ar^+$ for 8 h.

spectrum obtained after this exposure is shown in Figure 4b. Two noticeable changes from Figure 4a are the presence of an O 1s feature near 535 eV and further changes to the C 1s feature, which now has two peaks of nearly equal heights. The F 1s, F 2s, and F (KLL) features remain unchanged and no features due to N are evident. The C 1s features in Figure 3Aj are less defined after the air exposure and the feature as a whole is broader. The low-BE features are increased in height relative to the TFE Teflon feature at 292.5 eV. The F 1s peak in Figure 3Cj remains unchanged. The O 1s spectrum in Figure 3Bj appears as a broad feature with two peaks at 534.6 and 535.8 eV. The F/C atom ratio is decreased to 0.99.

**$Ar^+$ Exposures.** A fresh TFE Teflon sample was then sputtered with 1.0-keV $Ar^+$ for various times. The C 1s XPS spectra obtained after various $Ar^+$ exposures are shown in Figure 5. After a 1-h, 1.0-keV $Ar^+$ exposure, the spectrum shown in Figure 5b was obtained. Compared with the spectrum from the as-entered TFE Teflon, the adventitious carbon is mostly removed and carbon states with BEs of 287.5 and 290.0 eV are apparent. These changes are similar to those observed after a 2-h, 1.0-keV $He^+$ exposure (Figure 3c). The spectrum shown in Figure 5c was obtained after an 8-h exposure to 1.0-keV $Ar^+$. The C 1s feature at 286.9 eV is quite prominent while other features are not except for the peak at 292.5 eV due to TFE Teflon. The C 1s spectrum shown in Figure 5d was obtained after a 20-min exposure to $O_2$. The shoulders at ~295 and 290.5 eV are more prominent, and the low-BE energy feature is shifted to a higher BE by about 0.5 eV and broadened. The near-surface region O concentration is approximately 1.4 atom % after this treatment.

A comparison of the C 1s spectra obtained after exposure for 8 h to 1.0-keV $He^+$ and exposure for 8 h to 1.0-keV $Ar^+$ is shown in Figure 6. The spectra are quite different with regard to the carbon chemical states formed. Exposure to $He^+$ produces the two prominent damage states with BEs of 290.0 and 288.0 eV as discussed above. These two states may contribute to the C 1s spectrum obtained after $Ar^+$ exposure, but they are not apparent. Instead, a large, broad peak is present at a BE of 286.9 eV, which extends down to a BE of about 284 eV. The low-
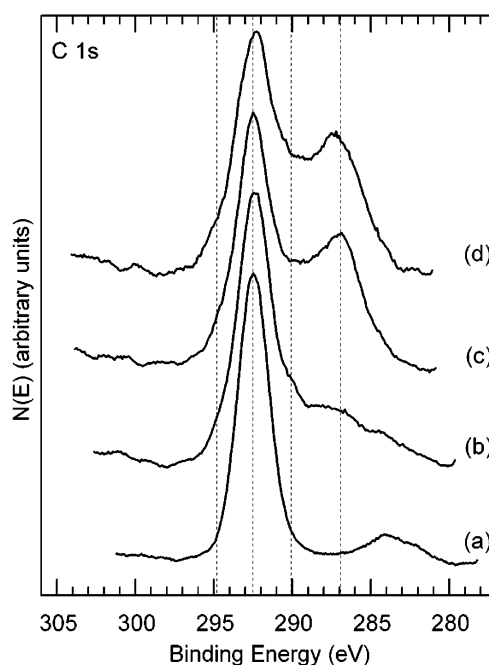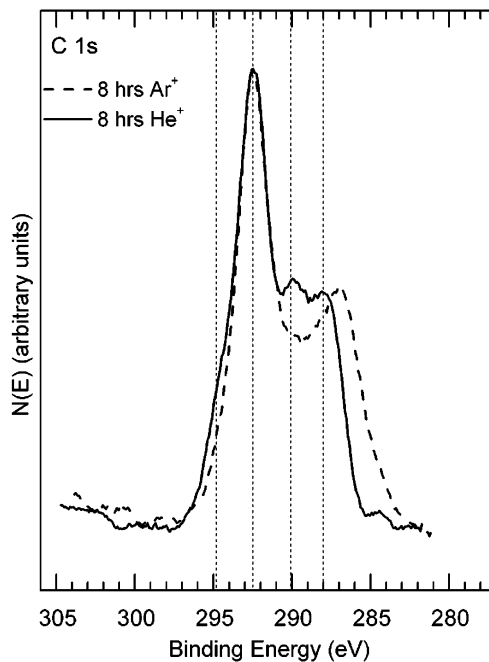
BE portion of the feature is due to a graphitic form of carbon, which has a BE of about 285 eV. The presence of F may result in an increased BE for this graphitic species due to withdrawal of electrons by the F. The $He^+$ exposure also produces a higher BE species at about 295 eV due to emission of $F^-$ leaving electron-deficient C species. This state is not present after exposure to $Ar^+$.

Both 1.0-keV $He^+$ and 1.0-keV $Ar^+$ have the same kinetic energy, but the velocity of the 1.0-keV $He^+$ is 3.16 times that of the 1.0-keV $Ar^+$ due to the mass difference while the ratio of the $Ar^+$ momentum to the $He^+$ momentum is 3.16. The F/C
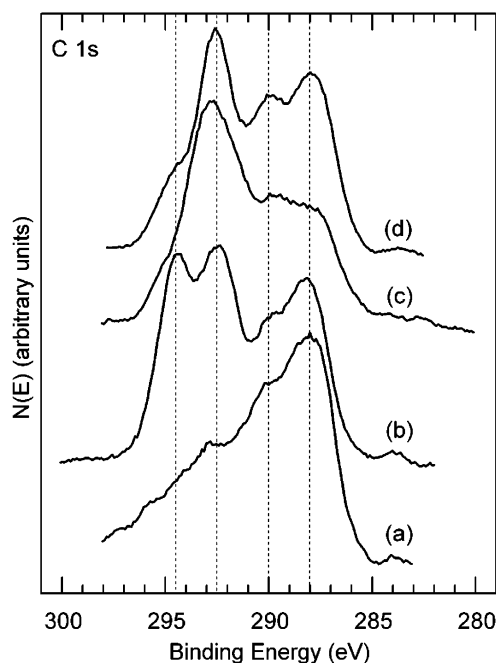
**Figure 7.** High-resolution XPS C 1s spectra obtained from TFE Teflon after exposure to (a) hyperthermal (~5 eV) AO for 74 h, (b) VUV for 74 h, (c) 1.0-keV e⁻ for 48 h, and (d) 1.0-keV He⁺ for 19 h. These spectra are all steady state because longer exposures do not result in different spectra.

atom ratio decreases with Ar⁺ exposure similarly to the He⁺ exposure but about twice as fast. In 8 h a steady-state F/C atom ratio of 1.13 is attained using 1.0-keV Ar⁺ while 19 h is required to attain a steady-state F/C atom ratio of 1.12 with 1.0-keV He⁺. This increased damage rate with Ar⁺ is most likely due to the fact that Ar⁺ has a larger cross section than He⁺.[41]

**Comparison of He⁺, e⁻, AO, and VUV data.** In two previous studies the chemical alteration of TFE Teflon by hyperthermal AO[16] and VUV radiation[17] has been studied. A comparison of C 1s features obtained from TFE Teflon after exposure to He⁺, e⁻, VUV, and hyperthermal (~5 eV) AO are shown in Figure 7. These are all steady-state exposures in that longer exposures do not result in different spectra. These four spectra are all quite different, but they all contain the same four features at 288.0, 290.0, 292.5, and 294.5 eV. None of these spectra exhibit a feature due to graphitic carbon as found in the case of Ar⁺ exposure. The greatest alteration occurs for the hyperthermal-AO exposure. The feature due to TFE Teflon is quite small as is the high-BE feature at 294.5 eV. The predominant peak at 288.0 eV is due to C species that have lost two F atoms, and the next largest feature at 290.0 eV is due to C species that have lost one F atom.

VUV radiation results in less alteration of TFE Teflon than hyperthermal AO. The lower BE features at 288.0 and 290.0 eV have a similar structure to those in the C 1s spectrum obtained after AO exposure, but they are smaller than the peak due to TFE Teflon, which is the predominant peak. Unlike the other spectra the high-BE peak at 294.5 eV is quite large and almost as large as the TFE Teflon peak.

Exposure to 1.0-keV He⁺ results in less alteration than VUV exposure. In this case the peak due to TFE Teflon is the predominant peak. The lower BE peaks are large and again have a similar structure to those obtained after AO exposure and VUV exposure. The high-BE shoulder at 294.5 eV is present on the TFE Teflon peak, which remains well defined.

The least amount of alteration occurs with the 1.0-keV e⁻ exposure. The lower BE C 1s states are present but they are

not well defined. The peak due to TFE Teflon is predominant, but it has a large shoulder at about 291.5 eV. The nature of the chemical species responsible for this shoulder is not understood. The high-BE feature at 294.5 eV is present as a shoulder on the TFE Teflon peak, but it is fairly small indicating that electron stimulated desorption (ESD) of F⁻ occurs less frequently than ESD of F neutrals.

## Summary

In this study the chemical alterations at a TFE Teflon surface caused by exposure to 1.0-keV primary electrons and 1.0-keV He⁺ and Ar⁺ have been studied using XPS. A 2-h exposure to 1.0-keV electrons results in a decrease in the F/C atom ratio from 1.99 to 1.41 and the formation of three new carbon chemical states assigned as C bonded to only one F, C bonded to other carbons, and carbons which have lost a pair of electrons by emission of F⁻. Adventitious C is not present in significant quantities on any of the surfaces examined in this study and what little is there initially is removed by a 2-h exposure to electrons and He⁺ and Ar⁺. Another 23 h of electron exposure results in a further decrease of the F/C atom ratio to 1.55 and an increase in the concentration of the three new carbon states, although the TFE Teflon state still predominates. Exposure of this electron-exposed surface to O₂ results in chemisorption of a very small amount of O due to bonding at reactive sites. The fact that so little O₂ chemisorbs indicates that the surface carbon may bond to other carbons, which is consistent with the formation of the new C chemical states. Further exposure of this surface to electrons for another 23 h results in removal of the chemisorbed oxygen and a further reduction in the F/C atom ratio to 1.48.

A 2-h exposure of a fresh TFE Teflon surface to 1.0-keV He⁺ ions reduces the initial F/C atom ratio from 2.07 to 1.79. Another 8 h of 1.0-keV He⁺ exposure further reduces the F/C atom ratio to 1.35 and the formation of three new carbon chemical states also assigned as C bonded to only one F, C bonded to other carbons, and carbons which have lost a pair of electrons by emission of F⁻. Exposure of this He⁺-altered surface to O₂ results in chemisorption of a very small amount of O at reactive sites. The fact that so little O₂ chemisorbs indicates that the surface carbons, which have lost F atoms, bond to other carbons, which is consistent with the formation of the new C chemical states. Nine more hours of 1.0-keV He⁺ exposure results in further reduction of the F/C atom ratio to 1.12 with the lower BE carbon states beginning to predominate. Finally this surface was exposed to air at room temperature and some O was chemisorbed resulting in a near-surface concentration of 1.9 atom %. A fresh TFE Teflon surface was also exposed to 1.0-keV Ar⁺ for various periods. Chemical alterations of TFE Teflon occur about twice as fast with 1.0-keV Ar⁺ versus 1.0-keV He⁺. This is believed to be due to the fact that Ar⁺ has a larger interaction (sputtering) cross section than He⁺. Comparison of the C 1s spectra obtained after exposure to 1.0-keV Ar⁺ and 1.0-keV He⁺ for 8 h indicates that different carbon chemical states are formed by Ar⁺. Specifically a significant amount of carbonaceous or graphitic carbon is formed by Ar⁺ exposure. This species is not formed by any of the other exposures.

The C 1s spectra obtained in this study using electrons and 1.0-keV He⁺ have been compared with C 1s spectra obtained using VUV and hyperthermal AO. The spectra compared are steady state in that extended exposures do not produce different spectra. Similar carbon species are present after all of the exposures, but the relative amounts vary greatly. The largest

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alteration is due to hyperthermal AO followed by VUV, He$^+$, and e$^-$. None of these treatments result in the formation of a graphitic species.

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