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GROUND-BASED SIMULATION OF LEO ENVIRONMENT: INVESTIGATIONS OF A SELECT LDEF MATERIAL—FEP TEFLON™

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SUMMARY

The Long Duration Exposure Facility (LDEF) has produced a wealth of data on materials degradation in the low-Earth orbit (LEO) space environment and has conclusively shown that surface chemistry (as opposed to surface physics-sputtering) is the key to understanding and predicting the degradation of materials in the LEO environment. It is also clear that materials degradation and spacecraft contamination are closely linked and that the fundamental mechanisms responsible for this linking are in general not well understood especially in the area of synergistic effects. The study of the fundamental mechanisms underlying materials degradation in LEO is hampered by the fact that the degradation process itself is not observed during the actual exposure to the environment. Rather the aftermath of the degradation process is studied, i.e., the material that remains after exposure is observed and mechanisms are proposed to explain the observed results. The EOIM-3 flight experiment is an attempt to bring sophisticated diagnostic equipment into the space environment and monitor the degradation process in real time through the use of mass spectrometry. More experiments of this nature which would include surface sensitive diagnostics (Auger and photoelectron spectroscopes) are needed to truly unravel the basic chemical mechanisms involved in the materials degradation process. Since these in-space capabilities will most likely not be available in the near future, ground-based LEO simulation facilities employing sophisticated diagnostics are needed to further advance the basic understanding of the materials degradation mechanisms. The LEO simulation facility developed at Los Alamos National Laboratory has been used to investigate the atomic oxygen/vacuum ultraviolet (AO/VUV) enhanced degradation of FEP Teflon® (®E.O. Du Pont de Nemours, Inc.). The results show that photo-ejection of polymer fragments occur at elevated temperature (200 °C), that VUV synergistic rare gas sputtering of polymer fragments occur even at 25 °C, and that combined AO/VUV interaction produces a wide variety of gas phase reaction products.

INTRODUCTION

The results of polymer material degradation studies in the LEO environment (refs. 1,2) and ground-based LEO simulation environments (refs. 3,4,5) have shown a strong synergistic interaction between AO and VUV radiation when interacting with fluorocarbon polymers: fluorinated ethylene propylene-FEP Teflon™ and polytetrafluoroethylene-PTFE). The degradation effects are of great practical importance since FEP Teflon™-coated silvered thermal blanketing material is routinely used on spacecraft and is being considered for use on large permanent space platforms (Space Station *Freedom* (S.S. *Freedom*), etc.). These future missions call for long-lived materials, requiring little servicing or replacement—thus the importance of determining materials service life from accelerated testing and fundamental degradation mechanism studies.

Early extensive investigations of γ-radiation damage to FEP and PTFE fluorocarbon polymers have been reported (refs. 5,6,7) with electron spin resonance (ESR) detecting surface absorbed free radicals such as ($-CF_2\bullet$) and ($-CF_2CF\bullet CF_2-$) (ref. 8) and mass spectrometer detection of CF_4 liberation (ref. 9) into the gas phase. The conclusions presented in reference 9 show that for photons having an energy below the F(1s) binding energy ($\approx$690 eV), the total energy deposited in PTFE (per photon) is roughly constant at 2 percent/Å up to a depth of several microns. The primary gas phase reaction product was CF_4 as detected by CF_3^+ and that extensive cross linking occurred which resulted in an increase in resistance to chemical etching by sodium hydroxide. The cross linking reaction is initiated by low-energy valence excitations resulting from direct absorption of VUV radiation or the production of low-energy secondary electrons. While these studies were undertaken to investigate the primary photolysis degradation, other investigations (ref. 10) undertook studies of the subsequent reactions of the surface absorbed free radicals with O_2. In this study mass spectrometric probing of high pressure (10^4 Pa) oxygen flowing over the irradiated PTFE sample showed a wide range of complex reaction products some of which contained oxygen and others not containing oxygen: CO_2, CF_2O and CF_4, C_2F_6, C_3F_6, C_3F_8, C_4F_8, C_4F_{10}, C_5F_{14}, etc. This study also found that irradiation of PTFE in the absence of O_2 resulted in a similar nonoxygen containing reaction products but with intensities $\approx$50 time less than with O_2 present. It was also concluded that free fluorine was produced which resulted in the formation of unsaturated COF_2 when O_2 was present and CF_4 when oxygen was not present. The general conclusions drawn from information found in the literature are that all formulations of fluorinated polymer (FEP, PTFE, etc.) give similar results in terms of the types of gas phase products and surface absorbed products produced, that the extent of damage extends deep (several microns) into the polymer bulk, that there are large changes in mechanical properties after exposure to radiation and oxidants, and the surface becomes cracked and rough.

Exposure of these polymers to the LEO space environment results in similar effects except that polymers exposed to the direction of travel (ram) have the cross-linked material removed through AO oxidation, while material facing the direction opposite to ram (wake) retains the cracked cross-linked layer. The effect of the LEO environment on spacecraft materials has been well documented (ref. 11) and results from the high collision energy (5 eV) and flux of atomic oxygen on the ram facing surfaces. In the case of polymers containing only C, O, H, and N, the effect of collision energy is very severe, with oxidation reactivities increasing three to four orders of magnitude in going from thermal energy (0.05 eV) AO to 5 eV AO. Fluorocarbon polymer oxidation rate dependence on collision energy has not been as extensively studied as with polyimides, but indeed does show a high anisotropic reaction rate when AO is combined with VUV radiation indicative of a strong collision energy dependence. There is indeed evidence that fluorocarbons can exhibit reactivities as high as polyimides ($\approx$10 percent of the AO flux results in volatile reaction products) when VUV radiation intensities are high. The purpose of this paper is to present a preliminary investigation of the mechanism of the synergistic degradation effects between VUV radiation and hypervelocity atomic oxygen on FEP Teflon™.

EXPERIMENTAL

The LEO simulation facility has been described in detail elsewhere (ref. 12), thus only a short description will be given here. A cw laser sustained discharge is employed to form a high intensity beam of AO. Since the source uses a rare gas/oxygen mixture, samples are exposed to a cw beam of rare gas and oxygen atoms (percent dissociation of O_2 into AO $\approx$ 90 to 100 percent) along with roughly 2 suns of VUV radiation in the wavelength range of 3,000 to 1,000 Å. Figure 1 shows the VUV spectrum produced using a 50-percent mixture of O_2 and argon. The AO flux in position closest to the nozzle is $\approx$5-10$\times10^{16}$ AO/cm^2-s, whereas the experiments reported in this paper were performed in a position where fluxes are 5-10$\times10^{14}$ AO/cm^2-s. In situ Auger and XPS surface sensitive diagnostics have also been recently added though not used in this investigation. The following equipment has been incorporated into the turbomolecular/liquid nitrogen cryoshroud pumped experimental station shown in Figure 2—a VUV krypton low pressure resonance lamp having a MgF_2 window which produces $\approx10^{14}$ VUV photons/cm^2-s at 1,236 Å and a quadrupole residual gas mass spectrometer operated in the pulse counting mode which can be swung into the primary AO beam to measure composition and modulation spectra. When the residual gas analyzer is out of the beam, a sample can be positioned in the AO beam with the analyzer ion source $\approx$1.5 cm from the surface at 45° to the surface normal. These configurations allow measurements to be taken of the primary beam velocity distribution and prompt photon signal and then modulated gas phase reaction product spectra with the detector positioned out of the beam. The time delays seen in the product spectra compared to the direct beam are due primarily to surface desorption kinetics and not time-or-flight effects (short flight path from surface to detector). The primary AO beam is modulated near the source by a four sector 50-percent duty cycle (378 Hz) chopper wheel driven by a hysteresis motor and variable frequency power source. A photocell/light detector is used to provide a timing signal to drive a pulse counting multichannel scalar which is used to record the modulation spectra. The cw krypton resonance lamp is positioned on the opposite side of the beam with respect to the mass spectrometer. A sample manipulator is employed to position the material under study in the AO beam and to heat the sample above room temperature. A pressure of 8×10^{-10} torr is obtained with the AO beam off and a background pressure of 2×10^{-6} torr when the beam is on. Tests were conducted to ensure that the average background pressure was not modulated at 378 Hz by removing the sample from the beam while keeping the mass spectrometer out of the direct beam. Integration times of 10-min duration on masses 40, 32, 16, 28, and 44 showed no discernible modulation. Reaction product integration times were all less than 10 min.

RESULTS

We report results for three different experimental conditions: VUV lamp on and hypervelocity beam off, VUV lamp off and hypervelocity pure argon beam on, and finally VUV lamp off and hypervelocity AO/Ar beam on. The beam source is not yet configured to eliminate the photon component using a slotted disk velocity selector. A photomultiplier was employed to detect the photon modulation reference signal.

VUV 1,236 Å Photodesorption Results

Mass spectra results were obtained with the FEP Teflon™ sample at three temperatures: 60 °C, 148 °C, and 248 °C by taking spectra with the lamp on and then subtracting spectra taken with the lamp off. The summary spectra are shown in Figure 3 as a function of sample temperature. Note that at the low temperature, no gas phase products are seen while at higher temperatures CF_3^+ along with lower molecular weight ion radicals are observed. The CF^+ ion is produced primarily (ref. 13) from dissociative ionization of C_2F_4 in the mass spectrometer ion source where as the CF_4^+ ion can be produced from dissociative ionization of CF_4, C_2F_6, C_3F_8, and C_4F_{10}. The large change in the ratios of CF_3^+/CF^+, and the fact that no ions of mass greater than 100 amu were observed is indicative that at the highest temperature only CF_4 and C_2F_4 are being desorbed. An Arrhenius plot of the data gives a thermal activation energy of ≈0.2 eV for thermal assisted ejection of photo-produced radicals. There was no evidence for C or F atom release from the surface probably because these species are tightly bound and recombine to form high molecular weight fragments, i.e., CF_4 is not part of the polymer chain and must be formed by recombination of CF_3 and F.

Figure 4 shows the time history of the rate of emission of CF_4 product into the gas phase. The data were taken by turning the krypton lamp on and off while recording the mass 69 intensity. Signal averaging techniques were not employed for this particular data set. Note the very long times (10's of seconds) associated with the photo-induced desorption. From data presented in the literature it is known that photodissociation in Teflon™ occurs over a depth of 1 to 2 μm with ≈2 percent/Å of the photon energy being deposited. The data shown in Figure 4 therefore are interpreted as exhibiting diffusion limited release of photoproducts, i.e. upon lamp turn-on ≈2-percent photon energy eV/Å is deposited in the near surface region. Upon lamp turn off, diffusion and recombination of radical occurs resulting in long-term release of gas phase products. From these data, it is concluded that modulation of VUV photon intensity on the millisecond time scale would not produce observable modulated photo-produced gas phase products. As will be shown this indeed is the case.

Neat Hyperthermal Argon Beam Results

Gas phase products produced by the interaction of hyperthermal argon and its associated VUV spectral component with FEP Teflon™ are shown in Figure 5 at three temperatures. Note that at the low temperature CF_4 is observed in the mass spectrum in contrast to the data in Figure 3 where VUV alone does not release CF_4 at low temperature. The presence of hypervelocity (≈2 to 3 eV) argon appears to produce sputtering of the weakly bound CF_4 which therefore must reside on the Teflon™ surface. No CF is observed indicating that C_2F_4 must reside in the subsurface region where sputtering release will not occur. At the higher surface temperature of 255 °C, both CF_4 and C_2F_4 are produced. Modulated beam spectra in Figure 6 shows the results from the interaction of hyperthermal argon (3 eV) and VUV radiation with FEP Teflon™ held at a temperature of 60 °C. The curves labeled photons and direct Ar are the direct beam photon component and neutral argon, respectively, while the resulting gas phase product CF_4 is represented by the CF_3^+. Note that the CF_4 product correlates with the neutral argon beam component and not the photon component, i.e., the CF_3^+ intensity does not begin to rise before the arrival of the modulated argon. The direct photon modulation produced species is damped out by diffusional effects but does prepare the surface and subsurface regions with low concentrations of free radicals. The high kinetic energy (≈3 eV) argon arrives later in time and produces sputtering of low binding energy surface absorbed species. Free radicals are most likely chemisorbed with binding energies greater than 3 eV while CF_4 with fully occupied orbitals is physisorbed with a binding energy <3 eV. Note that the CF_3^+ signal is complex. The initial rate of CF_4 ejection just after the argon arrives is much higher than later in the argon pulse, i.e., the surface absorbed CF_4 concentration is high resulting in a high removal rate compared to later times when the surface concentration is replenished by diffusion of CF_3 and F on the surface or from the Teflon™ interior to form CF_4. The diffusion is slower than the initial CF_4 removal rate thus producing a diffusion limited removal. After the beam is turned off, a slowly decreasing intensity of CF_4 is observed which is nearly linear with log(t) indicating a diffusion controlled release.

AO/Argon/VUV Combined Interaction Results

The gas phase reaction product relative intensities for the interaction of hyperthermal AO and argon along with the associated VUV component from the beam source are shown in Figure 7. The mass spectral intensities are 20 to 50 times that produced by hyperthermal argon alone. It is evident from the spectrum that there are two classes of reaction products, ones containing oxygen and those that do not. The oxygen containing molecules are CO, CO_2, and COF_2 (COF comes from cracking of COF_2 in the ion source and O_2F_2 represents a minor channel). The methane equivalent, CF_4, appears to be a major fraction of the nonoxygen containing molecules although a substantial amount of high molecular weight polymer fragments must also be present and may crack to form CF_3^+ in the ion source. Fragments with molecular weight above 131 amu were not observed and are most likely not present as the signal to noise was especially favorable to observe high molecular weight species if they were present. It appears that C_3F_8 or C_2F_6 are the highest molecular weight gas phase fragments desorbed into the gas phase. Modulated mass spectra (not shown) give the same qualitative diffusion effects shown for hyperthermal argon interaction.

DISCUSSION AND CONCLUSION

Fluorocarbon polymers appear to exhibit a complex response to the LEO environment. The results presented here indicate that surface recession of FEP Teflon™ can occur in the presence of VUV radiation alone even without the presence of AO. VUV radiation forms free radicals over a wide depth range (several microns) which at low temperatures (<50 °C) remain on the material surface and bulk forming crosslinked material. The crosslinked material is chemically different from the virgin material but is susceptible to removal by hypervelocity AO. At high surface temperature (>100 °C) VUV produced reaction products are thermally desorbed as fully bonded stable saturated and unsaturated fluorocarbon gases, i.e., CF_4, C_2F_4, C_2F_6, etc. The results presented here also indicate that hypervelocity nonreactive species such as argon can produce sputtering of surface absorbed fluorocarbon gases which would normally only desorb at higher temperatures. The interaction of VUV and hypervelocity AO produces a wealth of gas phase reaction products which can be classed as oxygen and nonoxygen containing species. The most abundant oxygen containing products are low molecular weight species such as CO and CO_2. The gas phase products not containing oxygen are high molecular weight fluorocarbon gases up to C_3F_8 and C_2F_6. All gas phase products irrespective of their oxygen content appear to desorb in at least two steps. The first step being prompt, is most likely due to desorption of surface absorbed gas while the second, extending over a much longer period of time, is produced by diffusion limited desorption. This second long time step appears to be diffusion controlled either from surface mediated diffusion or diffusion from deep (several microns) within the material.

The preliminary mechanism of fluorocarbon polymer oxidation by combined VUV and hypervelocity AO indicates that diffusion mediated steps are active and that care must be given to the development of accelerated testing methodologies. It remains to be seen whether fluorocarbon polymer reactivity is linear with VUV and/or AO flux. Under low flux conditions and suitable temperatures where diffusion rates are fast compared to oxidation, the oxidation rate may appear first order in AO flux. There may be other regimes at high flux and low temperatures where the oxidation rate may be diffusion limited and relatively insensitive to changes in AO flux when the flux is high. We are presently investigating this parameter space in order to develop guidelines for the development of accelerated testing strategies.

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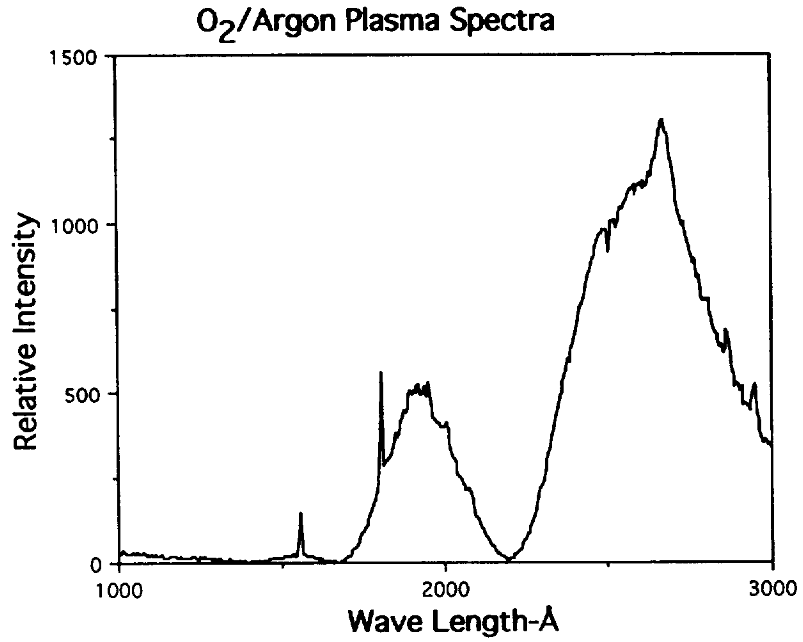

Figure 1. O_2/argon plasma spectrum. Intensity is ≈1-2 UV suns.

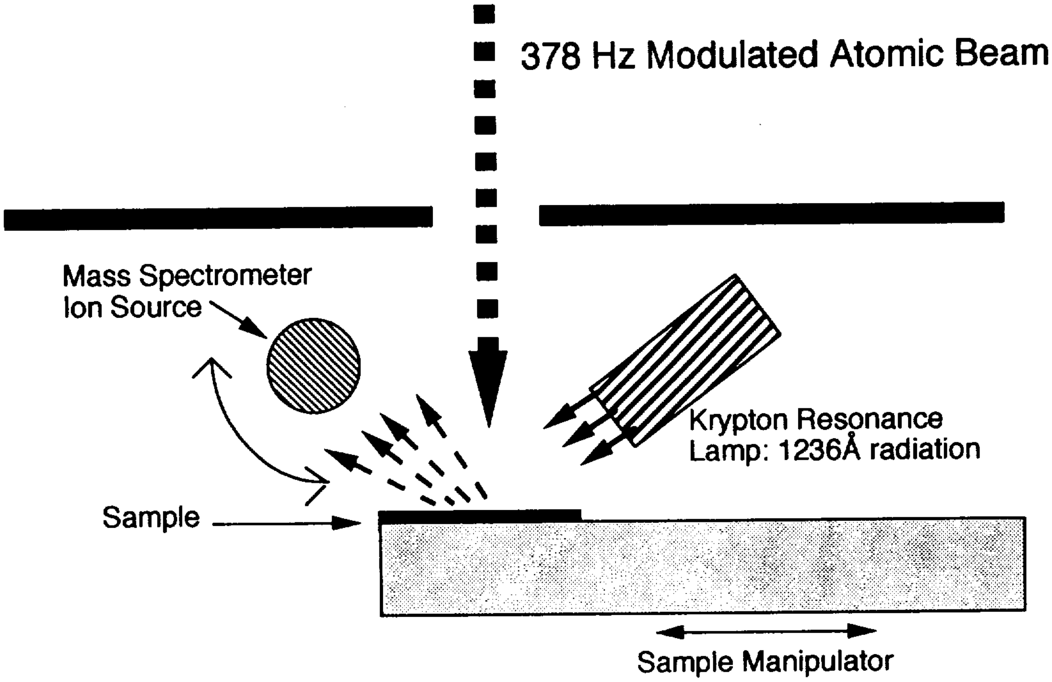

Figure 2. Experimental configuration. Modulated atomic beam scatters from sample and is detected by a residual gas analyzer in line-of-sight pulse counting mode. Source to sample distance is 1.25 meters. Krypton resonance lamp (1236Å) is ≈2 cm from the sample and is operated in cw mode. Photon flux from lamp is ≈ 10^{14} photons/s-cm^2.

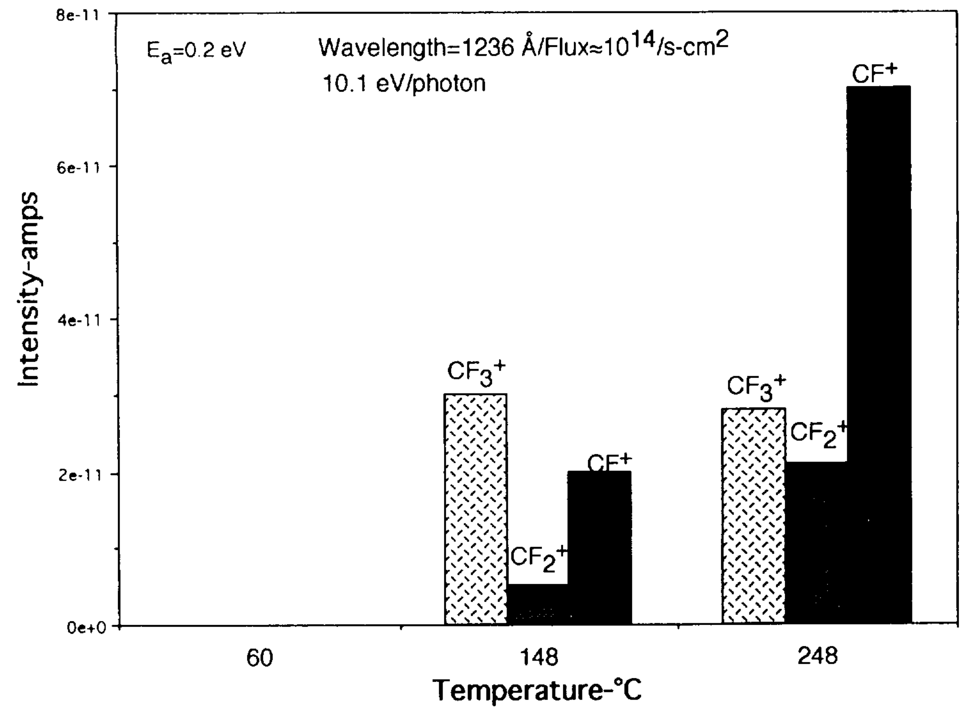

Figure 3. Temperature dependence of VUV photo produced reaction products from FEP Teflon™. Thermal activation energy is ≈0.2 eV and CF_4 and C_2F_4 are the major products. Note no measurable mass signals at low temperature.

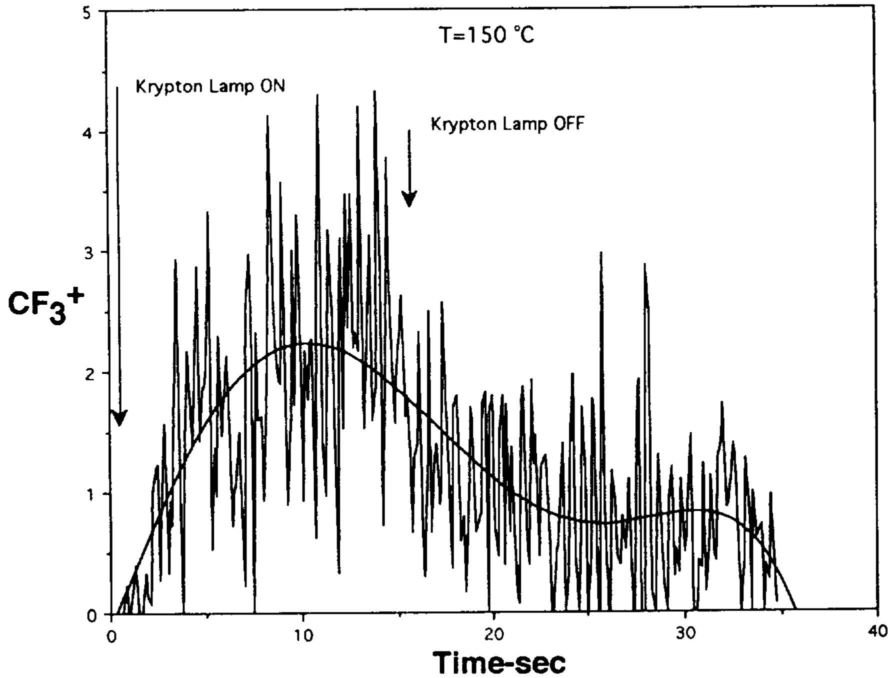

Figure 4. Time history of CF_4 VUV (1,236 Å) photo-produced product from FEP Teflon™. The time scale indicates the products are desorbing through a diffusion limited mechanism.

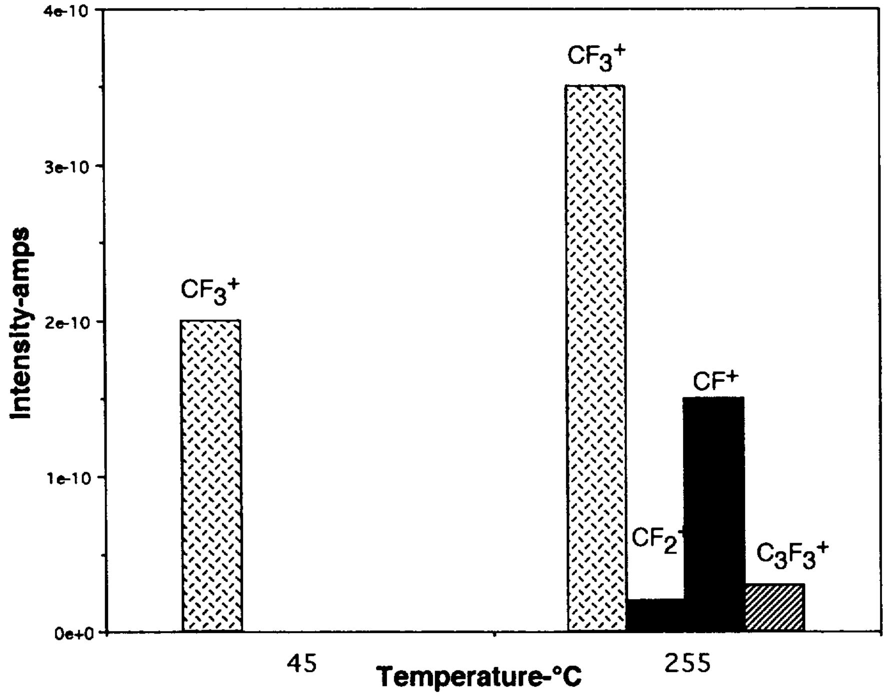

Figure 5. Temperature dependence of VUV/hyperthermal argon produced reaction products from FEP Teflon™. The CF_4 product observed at low temperature is due to hyperthermal argon sputtering. At higher temperature a mixture of CF_4 and C_2F_4 is observed.

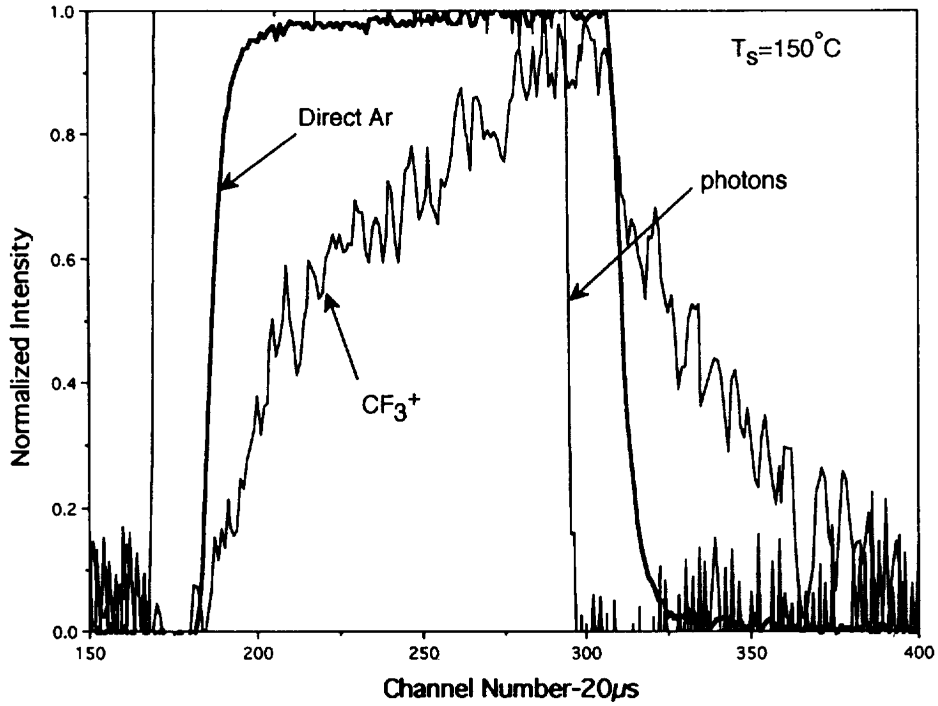

Figure 6. Modulation spectra of VUV/hyperthermal argon produced CF_4 gas phase product from FEP Teflon™. The CF_4 product correlates with the hypervelocity argon and not VUV radiation and is released in a two step process.

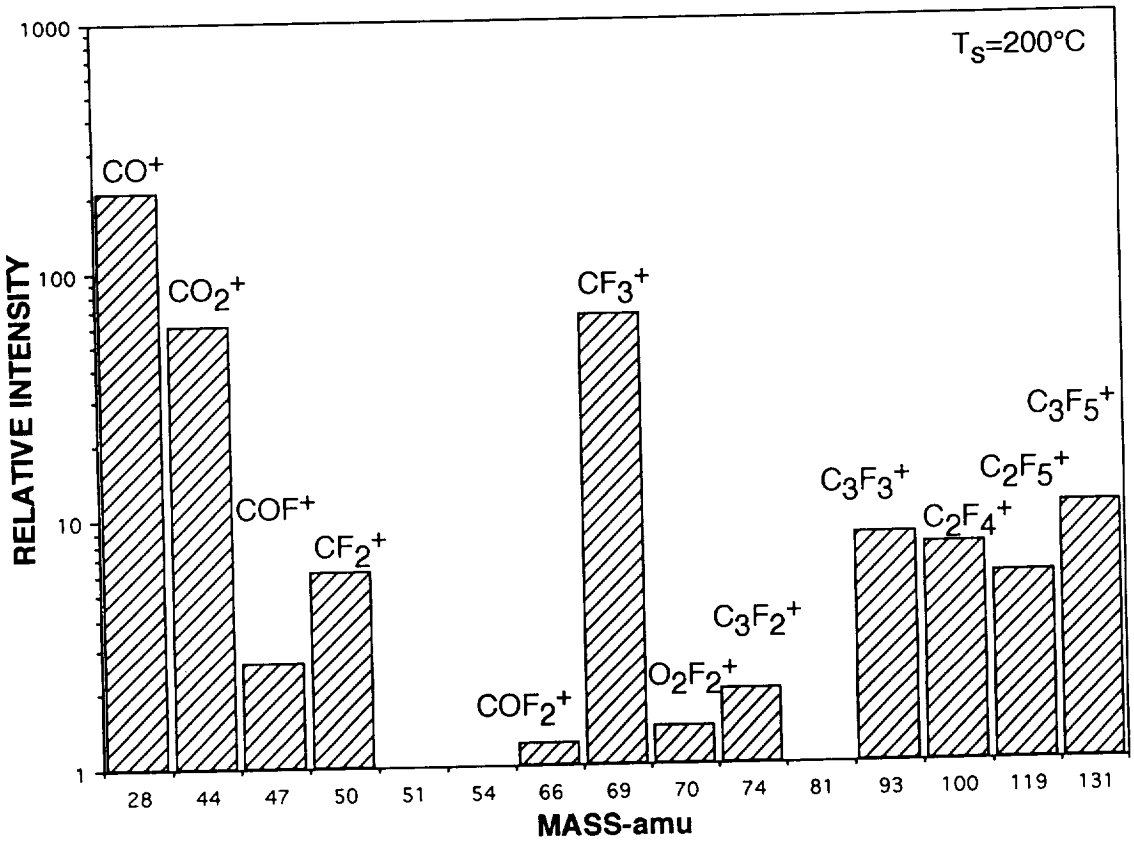

Figure 7. AO/VUV produced gas phase products from FEP Teflon™. Products are classed as oxygen containing and nonoxygen containing. Note high molecular weight products are produced when AO is present.