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Modification of a 5-eV Atomic-Oxygen Laser Detonation Source

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The present work describes the modification of a commercial pulsed laser detonation source, used for simulating the low Earth orbit 5-eV atomic-oxygen environment. In this facility the pulsed atomic-oxygen beam originates from a plasma and is accompanied by high levels of vacuum-UV radiation. Thus, the exposure of materials to the atomic-oxygen beam is therefore an exposure to a combined atomic-oxygen and vacuum-UV environment creating synergistic erosion effects. A simple, low-cost system, based on the selective reflection of oxygen atoms, was developed in order to remove the vacuum-UV component from the atomic-oxygen beam. This system reflected about 50% of the original atomic-oxygen content. The vacuum-UV content in the reflected atomic-oxygen beam was reduced to 0.03% of its content in the original atomic-oxygen beam. Chemical changes occurring in Kapton HN and Tefzel (ethylene-tetrafluoroethylene copolymer) under vacuum-UV irradiation were used to prove that the reflected residual vacuum-UV radiation has no effect on the tested polymers.

Introduction

THE main constituent of the residual atmosphere at low Earth orbit (LEO) at altitudes ranging from 200 to 700 km, that is considered hazardous to materials, is atomic oxygen (AO). Other space environmental hazards affecting polymers' properties at this environment are UV radiation, ionizing radiation (electrons, protons), high vacuum, micrometeorites and debris as well as thermal cycles. The interaction of the LEO constituents with the outer surfaces of a satellite can result in materials degradation, modifying their chemical, electrical, thermal, optical and/or mechanical properties.[1–4] The need for ground simulation systems to study the space environment stems from the high cost and very limited availability of in-flight experiments as well as the demands for accelerated tests simulating long-duration missions. A variety of ground simulation facilities is used for studying materials degradation under AO attack including plasma sources, ion neutralization, electron stimulation desorption, photodissociation, and supersonic and laser detonation sources.[5,6] The laser detonation source,[7,8] produces 5 eV oxygen atoms (same species and similar energy as AO in LEO), and sources based on this design are now used in several laboratories. One of the drawbacks of the source is the formation of plasma, which generates very high levels of vacuum-UV (VUV) radiance. Therefore, the laser detonation source should be considered more as a AO + VUV synergistic source, rather than a pure AO source, complicating and sometimes even preventing the characterization of AO effects on materials.

In the present work we demonstrate a simple and low-cost solution of excluding the VUV radiation from the AO beam. The method is based on using a quartz plate mounted in a way in which oxygen atoms are reflected toward the sample holder while UV/VUV radiation is absorbed by the quartz plate.

Experimental

A schematic diagram of the laser detonation source is shown in Fig. 1. The principle of its operation is based on introducing an O_2 gas pulse into a conical nozzle and firing a laser light pulse as the gas begins to expand into the nozzle. The laser pulse initiates plasma that expands into the conical nozzle, forming a detonation, and generates a beam, which consists mainly of fast neutral oxygen atoms. These atoms have an adjustable average velocity between 5 and 13 km/s. (The average velocity of O atoms in space is 8 km/s corresponding to 5eV.) This source is capable of producing beams containing O atoms fluxes of more than 10^{15} atoms/cm$^2 \cdot$ s at a distance of 50 cm from the edge of the conical nozzle. The VUV radiation associated with each atomic oxygen pulse for the spectral range of 115–180 nm, at a distance of 40 cm, was measured as 2.4×10^{-2} W/cm^2 (Ref. 9). Because the solar radiance at this spectral range is 2.4×10^{-6} W/cm^2 (Ref. 10), the samples are exposed to 1.0×10^4 equivalent suns (E.S.).

To separate between the AO beam and the VUV radiation associated with it, a reflection system was developed as described in Fig. 2. The main sample holder (SH1) is mounted perpendicular to the AO beam at a distance of 40 cm with an effective AO coverage area of 20×20 cm^2. Samples on SH1 are exposed to both AO and VUV in the main beam. The system was modified by adding a new sample holder plate (SH2) on the edge of SH1 in an angle of 79 deg in such a way that SH2 surface was parallel to AO beam. At this angle no VUV or nonreflected oxygen atoms could reach the samples attached to SH2. In addition, a quartz plate was placed in an angle of 45 deg to SH2 surface. The reflection plate is designed for 1) reflection oxygen atoms toward the sample holder mounted in parallel to the AO beam axis (SH2) and 2) elimination of UV radiation that could reach the sample holder by absorption.

Evaluation of the Quartz Plate VUV and AO Reflection Efficiencies

The reflected AO flux was evaluated by Kapton mass loss. The residual VUV flux was measured by a Cs-I phototube detector sensitive to UV in the range of 115–200 nm. The detector was mounted on SH2 in a way allowing only the quartz window reflected VUV to enter the detector active area. The main beam VUV radiation intensity was measured in a similar way, using a Cs-I phototube detector, which was located in front of the main beam source. To prevent saturation of this detector, because of the high intensity, a filter with a 2.5% transmittance was attached to it. Only a minute flux of reflected UV was measured by this technique. The effect of the residual UV flux on polymers degradation was assessed by studying the chemical changes which occur in Kapton and Tefzel TFE/ET irradiated by AO alone compared to AO + VUV.

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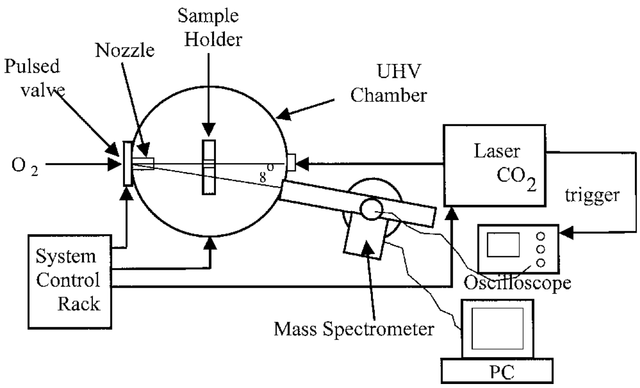

Fig. 1 Schematic diagram of the laser detonation AO source.

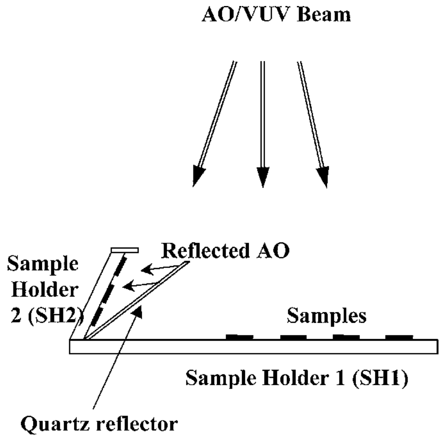

Fig. 2 Schematic diagram of the AO quartz reflection plate.

Exposure and Analyzing Procedures

The samples were exposed to various environments including AO + VUV, AO, and VUV. Exposure to AO + VUV was achieved by the direct beam (on SH1). Exposure to AO involved the indirect beam (samples on SH2). Exposure to VUV was achieved by covering the samples by MgF_2 window, which is fully transparent to VUV in the range of 115 nm and above. The AO fluence in the direct beam at ambient temperature was 5×10^{19} atoms/cm^2, determined by Kapton calibration (see next paragraph).

Mass loss measurements were used to evaluate the erosion yield of the exposed materials. Chemical changes, occurring at the surface as a result of the various radiation scheme, were measured by x-ray photoelectron spectroscopy (XPS). The XPS spectra were derived using a nonmonochromatized Mg Kα radiation (1253.6 eV) and a hemispherical CLAM 2 (VG microtech) analyzer operating at a pass energy of 100 eV for survey scans and 20 eV for high-resolution scans. The binding energy scale was calibrated using the Ag 3d5/2 line at 368.25 eV (Ref. 11). In the C-F-O system XPS data provide details about local bonding between C, F, and O as a result of wide separation of C1s peaks as a function of the degree of fluorination/oxidation. The binding energy of the C1s core level line changes from 285.7 eV for —C—H (—C—C—) to 292.5 eV for —C—F bonding states.[12] Sample charging, however, shifted the XPS lines between 2 and 5 eV. In the present study this shift was corrected by assuming that the binding energy of the lowest C 1s component is 284.7 eV for Kapton and 286.4 eV for ethylene-tetrafluoroethylene (TFE/ET).[13]

Materials

Kapton HN and Tefzel (ethylene-tetrafluoroethylene copolymer) TFE/ET were used in this research for evaluating the effect of the minute reflected VUV flux on polymers as well as for AO flux calibration. Kapton NH was used for calibration of the AO flux because its erosion rate is well established[14] and equals to 3.0×10^{-24} cm^3/O. Kapton was also used for evaluation of the reflected VUV effect because it exhibits a π-π^* shake-up peak in the C1s XPS core-level line (see details in the following).

Tefzel TFE/ET was used because it is a fluoropolymer that is etched under VUV radiation, revealing chemical changes. Tefzel has the following chemical structure:

$$[—CH_2—CH_2—CF_2—CF_2—]_n$$

The Tefzel samples were exposed to VUV generated by the main AO beam (samples covered by MgF_2 window mounted on SH1) and VUV reflected by the quartz plate (samples covered by MgF_2 window mounted on SH2). XPS was used to study the effect of the VUV radiation on the C—F bonds that are most sensitive to VUV bombardment. All samples were 2×2 cm^2 in size and were dry cleaned in a vacuum of 10^{-2} mbar at a temperature of 80°C for 4 h prior to the initial mass measurement and introduction into the simulation facility.

Results

VUV Flux

The average pulse intensity of the VUV radiation reflected by the quartz window was measured as 6.4×10^{-5} W/cm^2 as compared to VUV intensity of 2.4×10^{-2} W/cm^2 measured in the main AO beam pulse. In addition the full width at half-maximum (FWHM) of the main beam VUV pulse was eight times wider than the reflected VUV pulse, indicating an energy reduction factor of 3000. The solar irradiance at the range of 115–180 nm is 2.4×10^{-6} W/cm^2 (Ref. 10). Because the FWHM of the main beam VUV pulse is about 100 μs and 1×10^6 shots are required in order to achieve the maximal AO fluence in the main beam (5×10^{19} O atoms/cm^2), it can be shown that the maximal VUV fluence in the reflected beam was less than 0.1 equivalent sun hours.

Kapton XPS Spectra and Mass Loss

The pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide (Kapton) structure is shown in Fig. 3. As a result of the six different carbon bonding states of the carbon, the XP spectrum is composed of six peaks having different binding energies (BE). In addition, there is a π-π^* shake-up peak, originating from the aromatic group, at a higher BE. The assigned BE of the different peaks are summarized in Table 1.

Figure 4 shows high-resolution C1s core-level line of Kapton pristine sample and its curve fitting with C1s lines originating from carbon with the different chemical states. The peaks origin is described in Fig. 3, and the assigned BE are summarized in Table 1. A similar curve fitting was done for Kapton C1s spectra after exposure to net AO flux, VUV irradiation, and combined AO and VUV flux. The relative intensity of the shake-up peak, measured for each exposure condition, is shown as a function of the exposure conditions in the inset of Fig. 4 and here: 9.2% shake up for unexposed, 9.2%

Table 1 Poly(ether imide) (Kapton HN) C1s BEs

Parameter	BE, eV
1	284.7
2	285.6
3	285.7
4	285.8
5	286.3
6	288.6
7	290.8

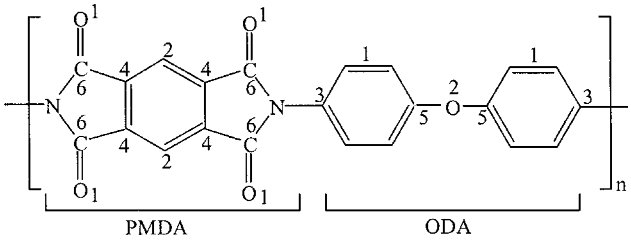

Fig. 3 Pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide (Kapton) structure.

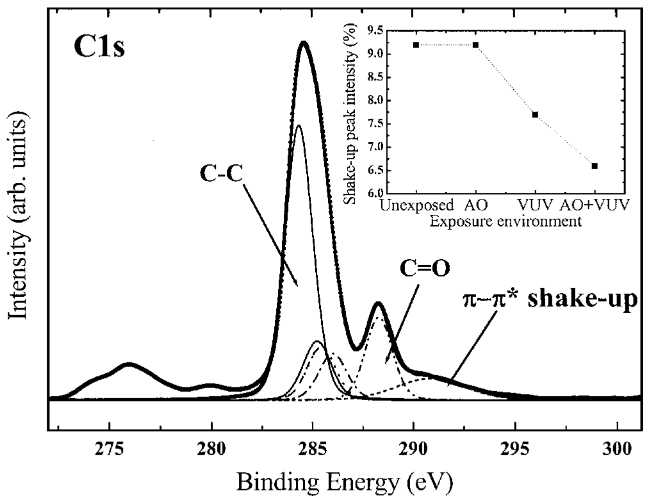

Fig. 4 Curve fitting of high-resolution XPS C1s core-level line of Kapton pristine sample. The inset shows the shake-up peak relative intensity as a function of the various exposures.

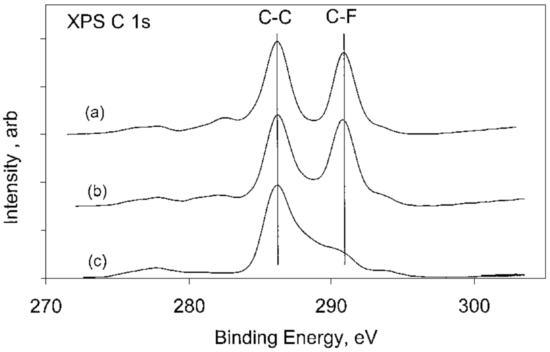

Fig. 5 High-resolution XPS C1s core-level lines obtained from Tefzel TFE/ET a) before and b) after exposure to reflected VUV and c) VUV originating from the main AO + VUV beam.

for AO exposure, 7.7% for VUV exposure, and 6.6% for AO/VUV exposure. The shake-up peak contribution of 9.2% for the pristine sample was not affected by the AO exposure. Exposure to VUV caused reduction of the shake-up peak concentration to 7.7% with further reduction to 6.6% after exposure to the combined environment of AO/VUV.

Kapton mass loss rates of about 18 and 9 μg/h were measured for samples exposed to the combined environment of AO + VUV and to the reflected AO beam, respectively. Exposure to VUV alone, originating from the main AO + VUV beam, as well as from the reflected quartz plate, revealed no mass loss at all.

Tefzel XPS Spectra

Figure 5 shows high-resolution XPS Tefzel TFE/ET (ethylene-tetrafluoroethylene copolymer) C1s spectra of pristine sample (a) after exposure to VUV flux generated by the main AO beam (b) and after exposure to the reflected VUV flux (c). The C1s spectrum is composed of two major peaks at 286.4 and 290.9 eV originating from two different carbon bonding states: —C—C— bonds (286.4 eV) and —CF_2 (290.9 eV). Figure 5 demonstrates the changes in the C1s line shape following an exposure to VUV generated by the main AO source and by the reflecting quartz plate. The main effect is the reduction of the C1s peak at 290.9 eV after exposure to the VUV generated by the main source. The sample exposed to the reflected VUV is showing a similar C1s curve to that of the unexposed reference sample. The reduction in the —CF_2 bonds (Fig. 5c) is associated with the reduction of the fluorine content of the sample (Table 2), estimated from the F1s line intensity. VUV irradiation originating from the main AO + VUV beam caused fluorine content reduction of about 30% (from 55.1% of pristine sample to 25.7%). The reflected VUV beam, however, did not cause any significant reduction in the fluorine content, (the fluorine content was reduced by only 1.5%). Table 2 displays these changes in the F/C ratio.

Table 2 C and F surface elemental composition of Tefzel before and after exposure to VUV from different sources

	C			
VUV source	C—C	C—F	F	F/C
Unexposed	24.3	20.6	55.1	1.23
Reflected	24.0	22.3	53.7	1.16
Main AO beam	56.6	17.7	25.7	0.35

Discussion

The laser detonation AO source developed by Physical Sciences (PSI) is one of the common advanced sources for generating hyperthermal (5 eV) atomic oxygen for simulating LEO environment. The source is based on firing a CO_2 laser beam at a nozzle in which O_2 gas is introduced through a pulsed valve. The light pulse produces high-temperature high-density plasma that expands, creating a detonation wave that forms the directional hyperthermal O/O_2 oxygen beam. One of the drawbacks of the laser detonation source is the formation of VUV radiation with each pulse of AO flux.[15] As demonstrated earlier, the samples could be considered as receiving a 1.0×10^4 E.S. Therefore, the laser detonation source environment should be considered more as a synergistic environment rather than an AO environment only.

One of the ways of removing the VUV radiation from the AO beam is using a chopper. However, the use of a chopper requires synchronization of the whole system and could be complicated and costly. A much simpler and cheaper solution is demonstrated in the present work. The present method is based on using a UV quartz plate mounted as described in the experimental part. The purpose of the plate is twofold: 1) it should reflect the oxygen atoms to a sample holder mounted in parallel to the AO beam axis, and 2) it should prevent the irradiation of the sample by VUV formed by the AO source.

Kapton mass loss was used for estimating the efficiency of the reflecting plate in regard to the AO flux. The Kapton erosion rate of samples exposed to the AO beam alone was about 50% of that obtained for samples positioned in front of the AO + VUV beam. The lower erosion rate could be a result of the lack of VUV radiation in the AO beam, lower reflected oxygen atoms energy, or low atoms reflection efficiency. Recent results,[16] using in situ quartz crystal microbalance measurements and thermal oxygen atoms, show also that the removal of the VUV from the AO beam affects the Kapton erosion rate by about 50%. Assuming inelastic collision between the AO and the reflector plate, this indicates that the reflection efficiency should be much higher then the measured 50%.

The main objective of using the reflecting plate was however to prevent any reflection of VUV radiation toward the irradiated samples. The phototube detector measurements indicated that the quartz reflecting window did not absorb the whole VUV radiation, and a small portion of it (6.37×10^{-5} W/cm^2, equivalent to 4.9×10^8 photons/cm$^2 \cdot$ s) was reflected toward the new sample holder (SH2). This flux represents only 1.6×10^{-4} % of the sun flux in the spectral range below 180 nm. Because the quartz reflection plate did not prevent the reflection of the VUV flux entirely, the question was whether the residual VUV flux could cause any detectable etching or synergistic effects in the exposed polymers.

Tefzel was selected for studying the residual VUV effect because its chemical content, and especially the fluorine to carbon (F/C) ratio, is very sensitive to VUV. The XPS C1s core-level line of Tefzel consists of two major peaks at 286.4 and 290.9 eV originating from two different carbon bonding states: C—C bonds (286.4 eV) and —C—F_2 (290.9 eV). Exposure of Tefzel to VUV results in scissioning of the —C—C— bond and release of volatile fragments C_nF_m (Ref. 17). The degradation is associated with a decrease in the fluorine content (Table 2) and in the C1s peak intensity at 290.9 eV (Fig. 5c) that originates from C—F bonds (see the preceding information). Exposure to reflected AO flux, however, shows almost no effect on the C1s peak at 290.9 eV (Fig. 5b), indicating that the minute amount of the VUV reflected by the quartz plate has no effect on the chemical structure of the Tefzel surface.

XPS spectrum of polymers with aromatic groups is characterized by the presence of a π-π^* shake-up peak, which is a result of electronic excitation of the π-electron system on an aromatic ring by a photoelectron.[18] The shake-up peak can be observed in the C1s and O1s spectra of unexposed Kapton samples. AO exposure causes surface reactions, modifying only the first few atomic layers ($\sim$1 nm).[5] Because the XPS probing depth is about 5–8 nm, the obtained spectrum is a combination of damaged and undamaged layers. Kapton samples that were exposed to AO in LEO environment revealed a π-π^* shake-up peak in the similar to the pristine samples XPS spectra.[19] However, exposure of Kapton in an oxygen radio frequency (rf) plasma asher reduced the π-π^* shake-up peak, indicating a much deeper damage compared to space exposed Kapton. Because the RF plasma species have thermal energies, the only plasma component energetic enough to penetrate and react with the bulk material well below the XPS probing depth is the VUV component.[19]

We used the π-π^* shake-up peak to detect whether the reflected VUV, reflected by the quartz plate, might affect the sample chemistry. Pristine Kapton sample shows (Fig. 4) a π-π^* shake-up contribution of 9.2%. Exposure to the reflected AO beam with residual VUV produced exactly the same result. Exposure to VUV originating from the main beam (obtained by using a MgF_2 window) exhibits a decrease in the π-π^* shake-up peak intensity from 9.2 to 7.7%, indicating a destruction of some of the aromatic groups by the VUV radiation. The result of exposing Kapton to a combined VUV + AO irradiation shows a lower π-π^* shakeup peak intensity with a value of 6.6%. The important conclusion of these experiments is that the residual VUV, associated with the reflected AO beam, did not cause any observable damage to Kapton samples.

Both XPS results, obtained from the Kapton and Tefzel samples exposed to reflected AO and VUV, clearly indicate that there is no measurable degradation effect as a result of the minute amount of reflected VUV. Therefore, the reflecting quartz plate can be considered as a device for producing "clean" AO environment, as opposed to the original AO + VUV beam.

Conclusions

A simple and a low-cost way for eliminating the VUV component in the AO beam of a laser detonation AO source was presented. The design is based on a quartz reflection plate that reflects the O atoms and absorbs most of the VUV flux. The reflection plate reflects the main beam O atoms with a reaction efficiency of about 50%. It was experimentally demonstrated that the very small amount of the VUV flux reflected by the quartz plate (0.03% of the VUV flux in the main AO + VUV beam) causes no chemical changes in the studied polymers (Kapton HN and Tefzel TFE/ET).

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