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Assessment of Atomic-Oxygen Flux in Low-Earth-Orbit Ground Simulation Facilities

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A common method for assessing the atomic-oxygen flux in low-Earth-orbit (LEO) ground simulation facilities is measuring the mass loss of attached Kapton coupon and assuming a known erosion yield of 3×10^{-24} cm^3/O atom. However, in most ground simulation facilities additional components, for example, UV radiation, excited and ionized oxygen atoms and molecules or reactive volatile products of degraded samples might be involved in Kapton-atomic-oxygen interaction. The present work demonstrates the effect of simultaneous atomic oxygen and other reactive species irradiation on the Kapton etching rate. The Kapton mass loss was measured in situ using quartz crystal microbalance. The etching rate was assessed as a function of atomic oxygen and either VUV radiation, sample temperature, or reactive volatile products. Kapton reactivity was found to be dependent on the examined system parameters resulting in ambiguous determination of the atomic-oxygen flux. The validity of the use of Kapton as a reference material for ground simulation testing (of spacecraft candidate materials for LEO applications) should be critically reassessed in the context of the present findings.

Introduction

THE space environment of low Earth orbit (LEO), at altitudes ranging from 200 to 700 km, is considered hazardous to materials and especially polymers. The main constituent of the space environmental hazards affecting polymers' properties is atomic oxygen (AO) having an impact energy of 5eV because of the spacecraft high velocity. The interaction of AO with the outer surfaces of a spacecraft can result in materials degradation affecting their chemical, electrical, thermal, optical, or mechanical properties.[1–4] The high cost and very limited availability of the in-flight experiments as well as the demands for accelerated tests simulating long-duration missions result in development of ground simulation systems to study the space environment. A variety of ground simulation facilities is used for studying materials degradation under AO attack including rf and dc plasma sources and ion neutralization, electron stimulation desorption, photodissociation, supersonic, and laser detonation sources.[5,6] Although the main purpose of these sources is generating AO flux, the produced AO could be associated with one or more of other source components such as UV radiation, ions, electrons, excited species, as well as varying the sample temperature. All of these sources share also a common problem of how to assess the LEO 5-eV equivalent AO flux. A common and recommended[7] way of evaluating the AO flux is by measuring the mass loss of Kapton coupon exposed simultaneously with the tested samples. By assuming a reaction yield of 3×10^{-24} cm^3/O atom (as measured for Kapton exposed in space), an equivalent of the 5-eV AO flux could be calculated. However, the Kapton erosion rate could be affected by other simulation facility factors such as one of the associated components (e.g., UV, ions, etc.), sample temperature, or volatile products of tested materials, thus resulting in an erroneous AO flux calculation.

In the present work we study the effect of several AO-flux-associated components on Kapton erosion rate. RF plasma asher was used as an AO simulation system. In addition to AO, it contains also UV radiation, ions, electrons, molecular oxygen, and excited species. Although we used a specific simulation facility in this study, the conclusions drawn for Kapton etching rate dependence on the AO-accompanying components are generalized for the use of Kapton as a reference material for determining the AO flux in various simulation systems.

Experimental

Kapton samples were spin coated on quartz-crystal-microbalance (QCM) crystals using a Dupont procedure for deposition of polyimide (Pyralin® PI 2545). The deposited polyimide films were tested to be similar to Kapton HN films in their chemical structure and their sensitivity to AO irradiation. Fourier-transform-infrared spectroscopy (FTIR) measurements of the deposited polyimide films have shown that their chemical structure (not shown in the paper) is similar to that of Kapton HN. The AO irradiation sensitivity was tested by a simultaneous exposure of both materials (Kapton HN and deposited polyimide) to AO flux and by measuring a similar mass loss.

The Kapton erosion rate measurements were carried out using a QCM mounted in an rf plasma system equipped with an automatic matching unit and a power of 75–1200 W (see Fig. 1). The coated crystals were located on a sample holder enabling positioning of the QCM in a selected downstream position. The samples were exposed to different environment type [AO, AO + VUV, or vacuum ultraviolet (VUV) alone]. This was achieved by using a specially designed target holder assembly causing the plasma afterglow flow to reach the sample sideways while the top is covered by MgF_2 window, as shown in Fig. 1. In such a configuration, the sample is exposed to all rf plasma afterglow components, while the VUV radiation-only pathway is through the MgF_2 window. Shielding the MgF_2 window with Al foil eliminates the sample direct VUV irradiation. Blocking of the sample holder sideways prevents the sample exposure to all rf plasma components except for the VUV radiation penetrating through the MgF_2 window. At this configuration it is also possible to cover the MgF_2 window, thus studying the net effect of vacuum environment on the sample erosion. The cooling system of the QCM

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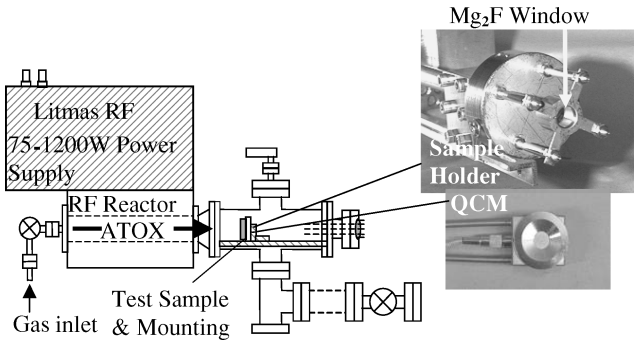

Fig. 1 Schematic diagram of the AO simulation system.

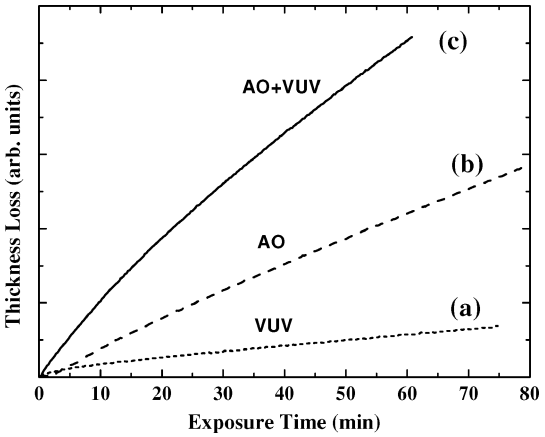

Fig. 2 QCM measurements of the Kapton thickness loss under a) VUV, b) AO, and c) AO + VUV irradiation.

was used for adjusting the crystals temperature to the desired ones in the range of 0–55°C. The samples were also exposed to different environments of volatile products obtained from AO exposure of attached fluoropolymers, silicones, as well as reference Kapton samples.

At operating pressure of 120 mtorr and sample location of 100 mm downstream from the rf plasma reactor end, the 5-eV equivalent AO flux was calculated (by measuring Kapton mass loss and assuming erosion yield of 3×10^{-24} cm^3/atom) to be about 5×10^{15} atoms/cm^{2}s. The VUV flux was assessed by a phototube sensor (Hamamatsu Model R1187) positioned at the location of the exposed sample. The phototube is a Cs-I detector with a spectral response in the range of 115–200 nm. Therefore only VUV flux in this range was measured. The measurements were performed using a 1% transmittance filter to reduce the intensity to the working range of the sensitive sensor. The VUV flux was 1.6×10^{16} photons/cm^{2}s at 300 W, 100 mm away from the reactor.

The surface morphology of the irradiated Kapton was analyzed under ambient conditions by atomic force microscopy (AFM), using a NanoScope II. The surface vertical roughness Rq $\{Rq = [\sum (Z_i - Z_{\text{ave}})^2 / N]^{1/2}$, where Z_{ave} is the average Z height value within a given area, Z_i is the current Z value, and N is the number of points within the given area$\}$ was measured and averaged by the system.

Results

The effect of various environmental parameters on the Kapton etching rate and morphology is described next. The parameters investigated were separate or combined AO and VUV irradiation, sample temperature and type of neighboring samples.

AO, VUV, and AO + VUV Effects

Erosion Rate

Figure 2 shows the thickness loss of eroded Kapton polyimide coating under irradiation of a) VUV radiation alone, b) AO flux, and c) combined AO + VUV. It is clearly seen that excluding VUV radiation from the AO flux decreased the etching rate by about a factor of two. Some etching of the Kapton was observed also under VUV radiation alone. The exposure was done using a sample holder covering the QCM and preventing all plasma active species from reaching the sample except for VUV radiation penetrating through a MgF_2 window. It is believed that the observed erosion is an artifact, and it results from interaction of the VUV radiation with residual oxygen molecules exist in the sample holder cavity at operating pressure of 120 mtorr. This interaction forms oxygen atoms that are reactive and cause the measured etching. A similar experiment was done with Ar plasma and the results (not shown) indicate that VUV alone did not cause any etching of the exposed Kapton.

Morphology Modification

The effect of the irradiation type on the Kapton morphology is demonstrated in Fig. 3 showing AFM images of 2×2 μm scan size. Pristine Kapton (Fig. 3a) has an initial roughness of 1 nm and no specific features on the surface. After AO exposure (Fig. 3b) the surface is eroded and is characterized by higher roughness of 5 nm and grains of about 300 nm in diameter. Addition of VUV to the

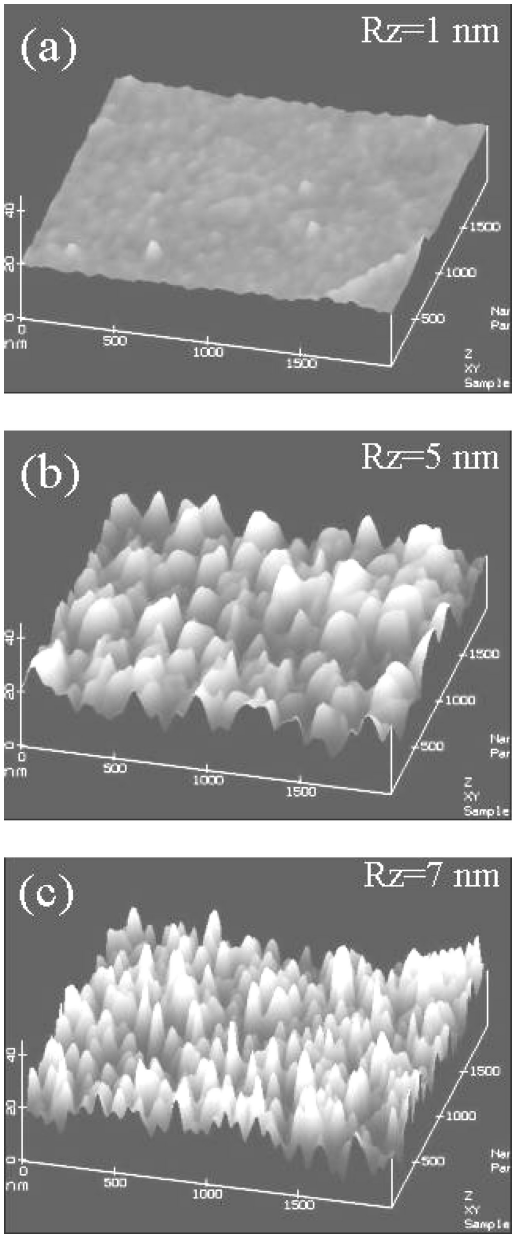

Fig. 3 AFM images of a) unexposed, b) AO irradiated, and c) AO + VUV irradiated Kapton films: Rz = surface roughness, images size 2×2 μm, and Z-scale 40 nm.

AO resulted in slightly higher surface roughness ($Rz = 7$ nm) with the main effect on the grain size. The AO + VUV exposed Kapton is characterized by a needle-like surface with small grains of about 100 nm in diameter (Fig. 3c).

Sample Temperature

The effect of the sample temperature on the Kapton erosion rate is shown in Fig. 4. The Kapton was exposed to oxygen plasma while keeping all plasma parameters constant except for the sample temperature. Increase of the sample temperature results in higher erosion rate. The erosion rate follows Arrhenius behavior as can be seen by the linear curve in the inset of Fig. 4. The activation energy calculated from this curve was found to be about 17 kJ/mole ($\sim$ 0.2eV).

Volatile Products

Different types of accompanying samples were located in the vicinity of the Kapton-coated QCM crystal in order to study the effect of volatile products resulted from neighboring samples erosion on the Kapton etching rate. The accompanying samples were 6 cm in diameter with a centered hole used for mounting the samples around the QCM. In this configuration the samples were kept at the same plane thus ensuring a similar AO flux. The results are shown in Fig. 5. Each type of accompanying samples, that is, poly(dimethyl)siloxane-based coating (PDMS), Teflon FEP film, and Kapton film (reference material), was exposed in a separate experiment keeping similar dimensions and location of the sample

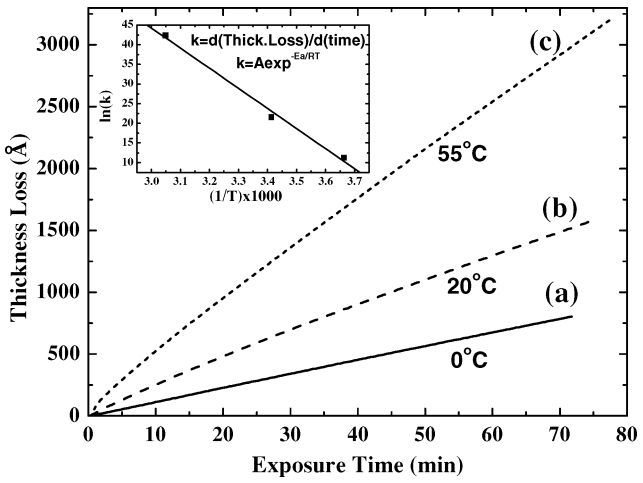

Fig. 4 QCM measurements of the Kapton thickness loss as a function of sample temperature: a) 0°C, b) 20°C, and c) 55°C. The inset shows an Arrhenius plot of erosion rate constant as a function of temperature.

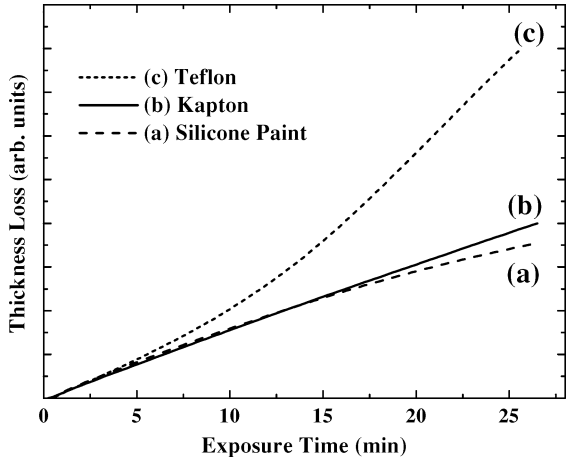

Fig. 5 QCM measurements of the Kapton thickness loss as a function of volatile products of coexposed samples: a) PDMS, b) Kapton, and c) fluoropolymer (Teflon FEP).

in order to ensure similar flow conditions. No attempt was done to measure the samples' erosion volatile products flux at the Kapton surface. The results show that the presence of PDMS does not affect significantly the Kapton etching rate, whereas the presence of fluoropolymer results in a drastic increase of the Kapton etching rate after a short incubation period.

Discussion

The space environment effects on spacecrafts' materials are of obvious interest resulting in many in-flight experiments. However, these experiments are expensive and are of limited availability, and most of them are very short in exposure terms. All that lead to development of a variety of ground simulation facilities for studying the effect of the main space environment hazard constituent (AO) on materials degradation. A major problem in using an AO simulation facility for materials degradation studies is the way of assessing the AO flux. A common way is exposing a Kapton coupon in close vicinity to the tested materials. By measuring its mass loss and assuming a reaction yield of 3×10^{-24} cm^3/O atom, an equivalent of the 5-eV AO flux could be calculated.[7]

The generated AO beam in most AO sources is associated with accompanying reactive elements such as UV radiation, ions, electrons, and other energetic species that could affect the etching rate of the Kapton reference coupon. The AO source reactor atmosphere could also contain reactive volatile products (obtained by degradation of tested materials) and could also affect the Kapton coupon temperature; both might influence the Kapton erosion yield.

The purpose of this study was to evaluate the validity of the method of assessing the AO flux by measuring the mass loss of Kapton coupon exposed to AO beam simultaneously with the tested material. The study was done by exposure of Kapton-coated QCM crystal to different AO simulation environments. As an AO source, we used an rf plasma system that although is widely used as a common source for material screening with respect to AO degradation in LEO it produces oxygen atoms at thermal energies ($\sim$ 0.04 eV)(Ref. 8). In addition to thermal AO, other species are also present in the rf plasma environment including molecular oxygen, atomic and molecular oxygen ions and electrons at energies of tens eV, excited neutral and ionic species, and also $\sim$130 nm VUV radiation with flux of 10^{13}–10^{16} photons/cm^{2}s (Refs. 9 and 10). By using a special sample holder design, we could expose the Kapton-coated QCM crystals to all rf plasma afterglow components (denoted as AO + VUV), VUV irradiation alone (VUV), and rf plasma afterglow excluding VUV radiation (AO).

Let us discuss first the effect of the VUV radiation on the Kapton erosion rate. As is shown in Fig. 2, the elimination of direct VUV radiation (flux of 1.8×10^{16} photons/cm^{2}s) from the AO beam results in a significant decrease in the Kapton etching rate. The phenomenon can be explained by the damage created by the VUV radiation to the polymer structure. AO exposure causes surface reactions, hence modifying only the first atomic layers ($\sim$1 nm) (Ref. 5). As was shown by Grossman et al.,[11] exposure to VUV causes destruction of some of the aromatic groups well below the AO bombarded eroded layer. The measured increase of the Kapton erosion rate caused by AO + VUV combined bombardment can therefore be explained by the following erosion mechanism: VUV radiation initiates a destruction of the aromatic groups in underneath layers, and as a consequence the AO is reacting with already damaged layer thus resulting in a higher etching rate. The effect is also shown by the morphology modification (Fig. 3). A VUV irradiation simultaneously with the AO caused the modified damaged layer to have an increase in the oxygen reactive sites. The result is smaller grain size (100 Å compared to 300 Å for AO exposure alone) and higher surface roughness.

Other parameters shown to affect the Kapton sensitivity towards AO attack were the sample temperature and the presence of reactive volatile products in the plasma atmosphere. The temperature effect on the Kapton erosion rate (Fig. 4) is showing Arrhenius behavior with activation energy of about $\sim$17 kJ/mole. It is assumed that the etching is a thermal process in which the reactive gaseous

species have come into thermal equilibrium with the surface before reacting. Thus, the high sensitivity of Kapton erosion rate to sample temperature could be a result of phenomena such as 1) increase in the oxygen atoms surface diffusion or 2) increase in the volatile products desorption rate. However, it is not clear which of the preceding processes is the limiting process, and further studies are needed to elucidate the detailed mechanism of the observed effects. A similar experiment using oxygen atoms with varied energies (0–5 eV) (Ref. 12) revealed a comparable activation energy for thermal oxygen atoms reacting with Kapton. At higher atoms energy of 5 eV, no activation energy was measured. Because the activation energy required for surface diffusion or volatile products desorption is supplied already by the impinging atoms, the eroded Kapton temperature (in the measured range of 25–150°C) has negligible effect on the etching process.

The rf plasma environment, modified by reactive volatile degradation products (Fig. 5), was found to affect the Kapton erosion rate for a given AO flux. A significant Kapton reaction yield increase was measured because of the addition of fluorine-containing materials. It can be suggested that the Teflon® forms reactive volatile products, such as HF and $C_xH_yF_z$ (Ref. 13), which can react with Kapton increasing its erosion yield.

Although the study is based on one specific simulation facility, the conclusions drawn are general in nature and apply to all other relevant facilities and especially to the use of Kapton as a reference material for assessing the AO flux. It was found that evaluation of the simulated AO flux based on a Kapton coupon sample could result in a massive error. The results shown indicate a flux measurement error of about one order of magnitude for relatively short exposure times. Higher AO fluences will result in much higher deviations from the correct fluence value. Kapton is used as a reference material for evaluating AO fluxes because of its extensive exposure in space and accurate erosion yield calculated from these experiments. It is, however, shown that its erosion yield could be significantly affected by other reactive elements in the AO source leading to inaccurate AO flux measurements. The study shows that there is a need for a better and more accurate method for evaluating the AO flux of ground simulation facilities.

Conclusions

The most common way for assessing the AO flux in ground simulation facilities is by measuring the mass loss of a Kapton coupon attached to the tested materials. However, most LEO environment simulation sources generate AO beam associated with other reactive elements such as UV radiation, ions, electrons, and other reactive fragments that could affect the etching rate of the Kapton reference coupon. The AO source reactor atmosphere could also contain reactive volatile products (obtained by degradation of tested materials) and could also affect the Kapton coupon temperature; both might influence the Kapton erosion yield.

The study includes in situ measurements erosion rate of Kapton exposed to AO simultaneously with other simulation facility components, such as VUV, coexposed samples reactive volatile products, and sample temperature. The results indicate that the erosion rate could be severely affected by the presence of AO-accompanying components. It is concluded that the Kapton erosion rate is system dependent. Thus, a simple and unambiguous method for measuring the AO flux is needed.

Acknowledgment

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