Nuclear Instruments and Methods in Physics Research B 410 (2017) 60–67

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Combined impact of 500 keV protons and oxygen plasma on polyimide films

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ARTICLE INFO

Article history:
Received 25 May 2017
Received in revised form 5 August 2017
Accepted 10 August 2017

Keywords:
Polyimide
Space environment
Proton irradiation
Atomic oxygen
Spectroscopy

ABSTRACT

This paper presents results of experimental investigation of combined impact of 500 keV protons with fluences of 10^{15}–10^{16} cm^{-2} and oxygen plasma with fluences of (0.8–3.5) 10^{20} cm^{-2} on polyimide films. Measured UV–vis transmission, Raman and XPS spectra of polyimide specimens before and after combined impact and data on the sample mass losses as a result of erosion due to oxygen plasma exposure are given. On the base of the obtained spectroscopic results, the changes in the polyimide structure caused by the proton and oxygen irradiation are analyzed and discussed.

1. Introduction

A spacecraft in a near-Earth orbit is subjected to the influence of various space environment components including space radiation, high vacuum, solar electromagnetic radiation, atomic oxygen, micrometeoroids and space debris, etc. Polyimide (PI) films are widely used on the external spacecraft surface as thermal control coatings (TCC) and other film constructions for various applications. When exposed to the space environment, materials on the external spacecraft surface may degrade, and, therefore, the improvement of their durability to the space component influence is a task of critical importance [1].

Many studies were carried out to investigate radiation-induced damage processes in polyimide and their effects on mechanical, optical, and electrophysical properties of PI materials [2–7]. For example, it was shown that irradiation with low-energy (less than 200 keV) protons leads to a significant reduce of PI reflective properties and the following increase of the solar absorptance which is of critical importance for TCC ability to maintain a given thermal regime [8,9]. The most serious degradation of PI properties was observed due to the irradiation by heavy ions at high energy (*e.g.*, [3–5]), but for spacecraft in near-Earth orbits it is very important to investigate the effects of protons of the Earth's radiation belts with the energies higher than 500 keV [10]. In this work PI specimens were irradiated by 500 keV protons, and to the authors' knowledge, little or no work has been carried out to study damaging effects on PI films induced by protons with intermediate energies.

Another dangerous space environment in low-Earth orbits is atomic oxygen. It is the main component of the upper Earth's atmosphere in the ~200–800 km altitude range, where manned space flights take place, and causes the erosion and damage of polymeric materials on the spacecraft external surface. High translational energy (~5 eV) of O atoms due to the spacecraft orbital velocity enhances their reactivity and opens additional pathways of their reaction with near-surface layers of materials. A hyperthermal O atom flux causes erosion of PI film coating due to the breakage of chemical bonds and the formation of volatile species (first of all, CO and CO_2) [11]. This impact results in substantial mass loss of the materials and the deterioration of their properties.

It is possible to expect that the combined impact of protons and oxygen plasma may enhance the destruction of surface film layers. In this paper, we report the results of the experimental study of the combined impact of 500 keV protons and oxygen plasma on PI films. Measured UV–vis transmission, Raman and XPS spectra of PI specimens before and after combined impact and data on the sample mass losses as a result of erosion due to oxygen plasma exposure are presented.

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http://dx.doi.org/10.1016/j.nimb.2017.08.012
0168-583X/

2. Materials and methods

The films used in our study are commercial PI films with thickness of ~35 μm and density of 1.43 g/cm^3. Proton irradiation of PI specimens with size of 35 × 35 mm was performed on a KG-500 cascade generator (Skobeltsyn Institute of Nuclear Physics of Lomonosov Moscow State University, SINP MSU) at average flux density of $1.2{\cdot}10^{12}$ cm$^{-2}{\cdot}$s^{-1} up to fluence of 10^{14}–10^{16} cm^{-2}. The residual pressure in the vacuum chamber was ~10^{-5} Torr, and the specimen temperature during irradiation did not exceed 50 °C to avoid thermal damage of the films.

Magnetoplasmodynamic accelerator, developed at SINP MSU, was applied to generate oxygen plasma flow, consisting of neutral O atoms and O^+ions [12]. The facility provided average particle energy in the plasma beam of ~20 eV at flux density of $(1-5){\cdot}10^{16}$ cm$^{-2}{\cdot}$s^{-1}; the samples under study were irradiated with fluences of $(0.8–3.0){\cdot}10^{20}$ cm^{-2}. The equivalent atomic oxygen fluence was determined by the change in thickness of a reference sample (Kapton HN, DuPont) with erosion yield of $3{\cdot}10^{-24}$ cm^3/atom O [11,13]. The thickness of the reference samples was measured with accuracy up to 1 μm. The mass erosion yield, R_m, characterizing the polymer durability to oxygen attack was calculated on the base of weight measurements with a microbalance HR-202i (an accuracy of 10^{-5} g) after reaching a steady state in terms of humidity absorption.

The optical transmittance of the specimens was measured with a two-channel Shimadzu UV–3600 spectrometer. The surface of the samples was investigated with Carl ZEISS AxioImager A1m optical microscope and VEGA3 TESCAN scanning electron microscope (SEM). Raman spectra were obtained using NTEGRA Spectra nanolaboratory with an LM473 solid-state laser (wavelength of 473 nm, power of 8.4 mW). Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer (XPS) with monochromatic AlK and a charge neutralizer was used to obtain XPS spectra of pristine and irradiated specimens.

3. Results and discussion

3.1. 500 keV proton irradiation

As a result of 500 keV proton irradiation with fluence of 10^{14}–10^{16} cm^{-2} (see Table 1) the surface of the specimens remained glossy, but the color changed from initial golden yellow to dark brown and almost black in the case of the highest fluence of protons. This darkening remained unchanged for a long time. The irradiation was carried out in a vacuum chamber, and after the irradiation all the samples were removed from the chamber and weighed. The weight measurements were performed in air, and no noticeable changes in samples mass were detected. The films exposed to higher proton fluence twisted, and their bended form was maintained for a long time.

The measured transmission spectra of the initial and proton-irradiated samples are presented in Fig. 1. They demonstrate clearly a decrease in the spectral transmittance of PI with increasing the proton fluence. The transmission spectrum of the initial film (specimen PI1) is typical for PI films: strong absorption is observed in the ultraviolet (UV) range, which is due to the presence of chromophores (carbonyl C=O groups and aromatic rings) [2], then there is a sharp increase in the transmittance followed by a smooth transition to a plateau at a level of 80–85% in the infrared range.

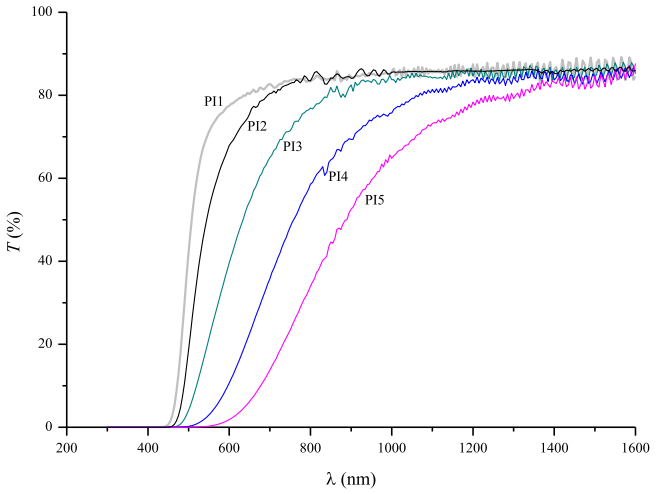

Fig. 1. Transmission spectra of the samples: PI1 – non-irradiated; PI2–PI5 irradiated with protons (fluence values are given in Table 1).

For the proton-irradiated samples (specimens PI2–PI5, see Table 1), the absorption increases with increasing proton fluences and the threshold wavelength at which the transmittance is zero shifts to longer wavelengths. The most significant changes in the transmission spectrum occur in the optical range: *e.g.*, for specimen PI5 irradiated by protons with a fluence of $7.5{\cdot}10^{15}$ cm^{-2}, the integrated transmittance in the optical range decreased by factor of six or more.

The effect of the optical darkening of the polymer film due to ion irradiation is well known and has been described in many studies, *e.g.* [2,14]. The shifting in the edge of optical absorption from UV to the visible region was related to the gradual reduction of the optical energy gap. This is usually explained by the appearance of carbonized structures, such as unsaturated C=C double bonds, aromatic ring structures, graphite-like planes, *etc.*, in the near-surface layers, leading to the increase in absorption at the shorter wavelengths in the visual region [2]. The formation of carbon-enriched structures is associated with the appearance of free radicals, and in irradiated PI only pyrolytic (carbon) free radicals with *g*-value of 2.0025 were registered by EPR method [9]. The degree of carbonization which causes strong darkening was observed in PI films as a result of heavy ions irradiation (*e.g.*, [3]), however, it did not occur in the case of low-energy protons at the same fluences [8,9].

Irradiation effects in polymers are associated with both nuclear stopping and ionization losses. Calculated with SRIM/TRIM software [15] nuclear and ionization energy losses of protons in a PI target are given in Fig. 2a. At protons energies up to ~50 eV, nuclear stopping due to atoms displacement is greater than electronic stopping, but at higher energies ionization losses dominates. The average proton ranges in PI materials are ~7.3 μm with range straggling ~0.3 μm. The main energy losses of 500 keV protons in PI occur due to the target ionization, so atom displacements begin only at a relatively large penetration depth when the protons have already lost much of its original energy (Fig. 2b). Specific ionization losses achieve their maximum (~10 eV/Å) at the depth of ~6.6 μm (Fig. 1c), and near the surface they are about a half of this value being much higher than nuclear losses. As it will be shown below

Table 1
Proton fluences used at the irradiation of PI samples.

Specimen	PI1	PI2	PI3	PI4	PI5
Proton fluence, cm^{-2}	0	$1.0{\cdot}10^{15}$	$2.5{\cdot}10^{15}$	$5.0{\cdot}10^{15}$	$7.5{\cdot}10^{15}$