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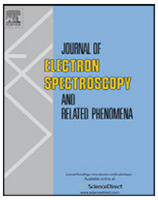

EUV-induced physico-chemical changes in near-surface layers of polymers

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ABSTRACT

In this work a laser-plasma EUV source based on a gas puff target was used for micro- and nanostructuring of polyethylene terephthalate (PET), polyethylene naphthalate (PEN) and poly-oxydiphenylene-pyromellitimide (Kapton HN) foils. The plasma radiation was focused using a gold-plated grazing incidence ellipsoidal collector. The collector allowed for effective focusing of Kr plasma radiation from the wavelength range $\lambda = 9–70$ nm. The polymer foils were irradiated in the focal plane or at some distance downstream the focal plane of the EUV collector. The surface morphology of the irradiated polymer samples was investigated using a scanning electron microscope (SEM) and the chemical changes by X-ray photoelectron spectroscopy (XPS). Different kinds of micro- and nanostructures created in near-surface layers of the polymers were obtained. The form of the structures depends on the type of polymer and the EUV exposure. In case of PEN even a single shot was sufficient to obtain visible changes in surface morphology. In case of Kapton clearly visible surface modification requires tens of EUV pulses. To investigate the changes in the chemical structure XPS spectra, corresponding to the valence band of the polymer samples, were measured. Significant differences were revealed in the XPS spectra of irradiated and not-irradiated polymers showing decrease of functional groups containing oxygen was indicated.

1. Introduction

Polymers are widely used in different kinds of industries. Depending on chemical composition and structure polymers have different physico-chemical properties. They can be used in a pure form or with additives modifying their bulk properties. Some of the polymer applications, however, require modification of their surface properties such as hydrophobicity, wettability, adsorption, adhesive or optical properties. These modifications include surface morphology and changes in the chemical structure of polymer molecules in a near-surface layer. Different methods are often used for surface structuring, including chemical [1], plasma [2], or radiation treatment. For the photo-induced modification of polymers, excimer lamps or excimer lasers are mainly used [3–5]. Photons emitted from these sources can excite electrons from the valence band of any organic material. The excited state can relax through a radiative or non-radiative process. In case of polymers one of the possible radiationless channels is a bond breaking of the polymer chain, other lead to increase of the polymer temperature. As a result polymer chains become shorter and their chemical structure and composition can change. Some volatile fractions can be released from the irradiated layer. The surface morphology can change due to preferential dry etching of amorphous polymer or melting of the near surface layer combined with a transient pressure of the ablation plume.

As a result of polymer irradiation chemical structure of the modified layer changes. The change is either in relative atomic concentrations or distribution of different functional groups, and can be investigated using different methods including energy dispersive spectroscopy (EDS), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The last method is very sensitive to the chemical composition and molecular structure in a very thin surface layer because of a very short photoelectron escape depth in the range of 1–5 nm in any material. For this reason the XPS was employed in many experiments on plasma or UV radiation treatment of polymer surfaces, for investigations of chemical changes in the near-surface layer [6–8]. Significant changes in atomic ratios and distribution of functional groups were revealed.

It was shown in our previous papers [9–12], that similar surface changes can be obtained using EUV sources. A single EUV photon carries enough energy to break many molecular bonds in a polymer chain. Some fragments of the chains or functional groups can then be released from the polymer surface changing its surface morphology and the chemical structure. The EUV radiation is strongly absorbed in any material, hence, the changes are limited to a very thin near surface layer of approximately 100–200 nm. Thus the polymer material in the bulk is not affected by the EUV radiation. In this paper we present our recent results of surface modifications of

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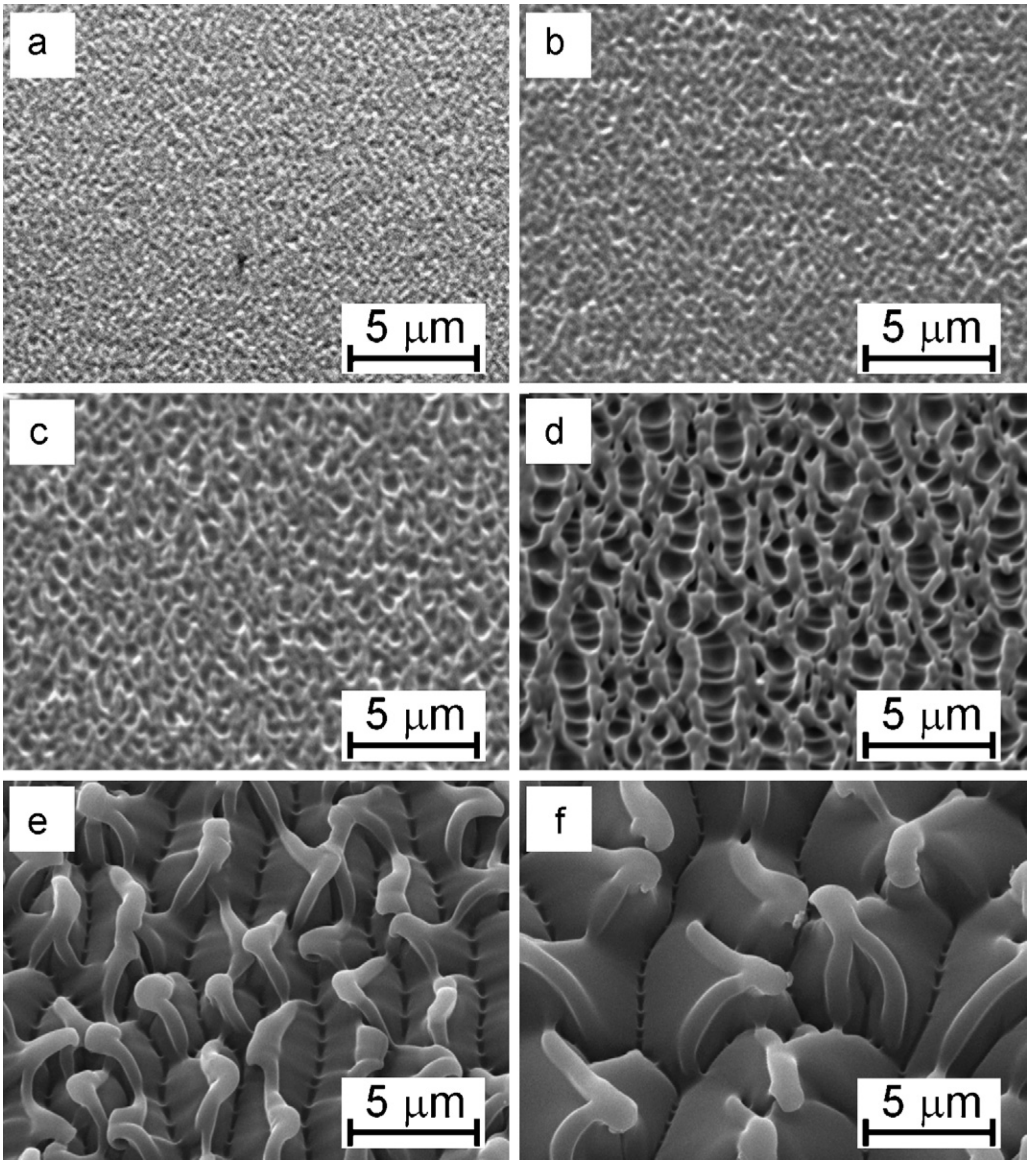

Fig. 1. Microstructures formed on PEN surface after irradiation with EUV pulses: (a) –1, (b) –3, (c) –5, (d) –10, (e) –50 and (f) 200 pulses.

PET (polyethylene terephthalate), PEN (polyethylene naphthalate) and Kapton HN (poly-oxydiphenylene-pyromellitimide) polymer foils, irradiated with a 10-Hz laser-plasma EUV source that is based on a gas-puff target. The EUV radiation was focused using an ellipsoidal grazing incidence mirror. The radiation fluence in the focal plane was sufficient for strong modification of polymer surface topography. Significant chemical changes in a near surface layer were also revealed.

2. Experiment

In the experiments, presented here, a 10-Hz laser-plasma EUV source based on the double-stream gas-puff target, irradiated with the 3-ns/0.8 J Nd:YAG laser pulse, was used. The target was created by pulsed injection of a krypton gas jet into a hollow stream of helium (Kr/He target) by employing electromagnetic valve system equipped with a double nozzle set-up. The focusing conditions and plasma parameters were adjusted to obtain maximum intensity in the EUV region. The radiation was focused using a gold-plated grazing incidence ellipsoidal collector, manufactured in Reflex s.r.o., (at present: Rigaku Innovative Technologies Europe s.r.o.), Czech Republic. The collector allowed for effective focusing of radiation emitted from Kr or Xe plasmas in the wavelength range $\lambda = 9–70$ nm. The most intense emission was in the relatively narrow spectral region centred at $\lambda = 10 \pm 1$ nm. The spectral intensity at longer wavelength range was much smaller, however, the spectrally integrated intensities in both ranges were comparable. The EUV fluence in the focal plane of the collector exceeded 60 mJ/cm^2 at the centre of the focal spot. FWHM diameter of the intensity distribution in the focal spot was 1.4 mm. Detailed description of the source and parameters of the focused EUV radiation can be found elsewhere [9].

A 50-μm thick PET, PEN and Kapton HN foils from Goodfellow utilized in the experiments, were used without any treatment. The samples were mounted on the XYZ translation stage and placed near the EUV collector focal plane. The translation stage allowed to adjust the sample position in respect to the focal plane. The samples were irradiated with a single or multiple EUV pulses. Irradiation with multiple pulses was performed at a 10-Hz repetition rate up to 600 pulses. The surface modifications were performed using the source radiation reflected from the collector without any additional thin-films filters. The surface morphology of the irradiated polymer