MICROMACHINING AND SURFACE MODIFICATION OF SOLIDS USING A LASER - PLASMA EUV SOURCE

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1. Introduction

Many works were devoted to micromachining or surface modification of polymers or inorganic solids using ultraviolet (UV) or soft X-ray (SXR) radiation generated in excimer lasers or synchrotrons respectively. In our previous papers we showed that surface processing of polymers can be also obtained using laser-plasma EUV (extreme ultraviolet) source. Extreme ultraviolet spans over a wavelength range of approximately 5÷50 nm corresponding approximately to photon energy range of 25÷250 eV. EUV photons can thus ionise any atom or molecule releasing one of the valence or even core electrons. Each of the resulting photoelectrons can have enough energy to break several molecular bonds. Interaction of the photoelectrons with molecules is not governed by the quantum mechanical selection rules like in the case of absorption of UV photons. Also relative probabilities of triplet states formation are greatly enhanced in respect to excitation with electromagnetic radiation. It means that radiationless deexcitation processes including bond breaking are predominant. Thus bond breaking in polymers irradiated with EUV is very effective and results in a very short penetration depth of the radiation in any kind of solids. In this paper results of investigation of ablation and surface modification of selected polymers irradiated with EUV pulses are presented. In experiments a 10-Hz laser-plasma EUV source based on a gas-puff target was used. The EUV radiation was focused on surface of an irradiated material using an ellipsoidal grazing incidence mirror. The radiation fluence in the focal plane was sufficient both for ablation and strong modification of surface topography of the polymers.

2. Experimental arrangement

In the experiments, a 10 Hz laser plasma EUV source based on a double stream gas puff target was used. The source was equipped with a gold plated grazing incidence EUV

collector. Spectrum of the focused radiation consists of a narrow feature with maximum close to 10 nm and a long-wavelength tail up to 70 nm. Maximum fluence in the wavelength range 8÷70 nm exceeded 60 mJ/cm^2. More detailed information concerning the source and the EUV focusing optics can be found elsewhere [1]. Polymer samples employed in the experiments were irradiated without any filters. The surface morphology of the irradiated samples was investigated using a scanning electron microscope (SEM) and atomic force microscope (AFM). The polymer decomposition products were identified using quadrupole mass spectrometry (QMS). The chemical changes were investigated by X-ray photoelectron spectroscopy (XPS).

3. Results

EUV irradiation of some polymers results in smooth ablation and these materials are suitable for creation of fine microstructures of controlled shape. Examples of such structures created in PVDF (polyvinylidene fluoride) and PMMA (polymethylmethacrylate) are presented in Fig. 1a,b. The structures were obtained by irradiation of the polymer foils with 100 EUV pulses through a copper mesh with 12,5 μm period and 5 μm bar width. Rough measurements of the ablation rate were performed using a 50 μm PMMA foil which was exposed to different number of EUV pulses. It was found that etching through the foil required irradiation with 500 pulses, hence, the average value of the ablation rate could be estimated to 100 nm per pulse. The microstructure shown in Fig. 1c was created in a FEP foil after 2 min exposure. It can be noticed that entire polymer material not screened by the contact mask was removed. The foil thickness was 50 μm while the smallest surface dimension 5 μm thus the aspect ratio of the structure could be estimated to about 10. Micromachining of other polymers is also possible but in this case the surface after ablation is very rough. The RMS of the surface can be comparable with the smallest dimension of the transferred pattern. An example of microstructure created in PET irradiated through a metallic grid with 100 μm period is shown in Fig. 1d. In Fig. 2 examples of micro- and nanostructures formed on polymer surfaces are shown. Forms of the structures depend on EUV fluence, number of pulses and material properties. Usually microstructures are created by irradiation with relatively high fluence while nanostructures are formed in areas irradiated with EUV fluence close to the ablation threshold. Normally formation of nanostructures requires irradiation with hundreds of pulses, however, in case of some polymers irradiation with a single pulse can result in creation of surface nanostructures. The surface modification

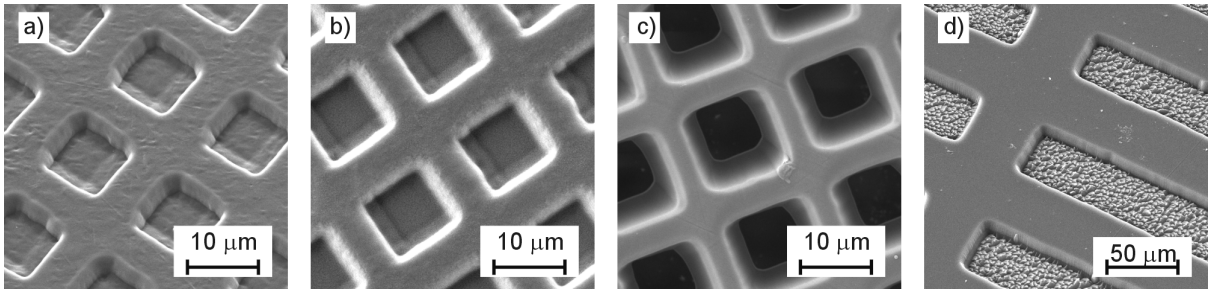

Fig.1: *Micromachining of polymer foils irradiated through a metallic grid: a) PVDF -100, b) PMMA -100, c) FEP -1200, d) PET 100 EUV pulses.*

can be also obtained in inorganic solids. Some interesting examples of the resulting structures are shown in Fig. 3. The images shown in Figs. 3a,b are surfaces of NaCl and CaF_2 monocrystals after 1min irradiation with 10 Hz repetition rate. In both cases a thin surface layer of the monocrystal was divided into microcrystals. The smallest crystal size shown here was about 5 μm for NaCl and 1 μm for CaF_2. In Fig. 3c microstructure formed in GaAs monocrystal irradiated with 100 of EUV pulses is presented. Form of the structure suggests that its origin is associated with melting of the near surface layer. The other possibility is

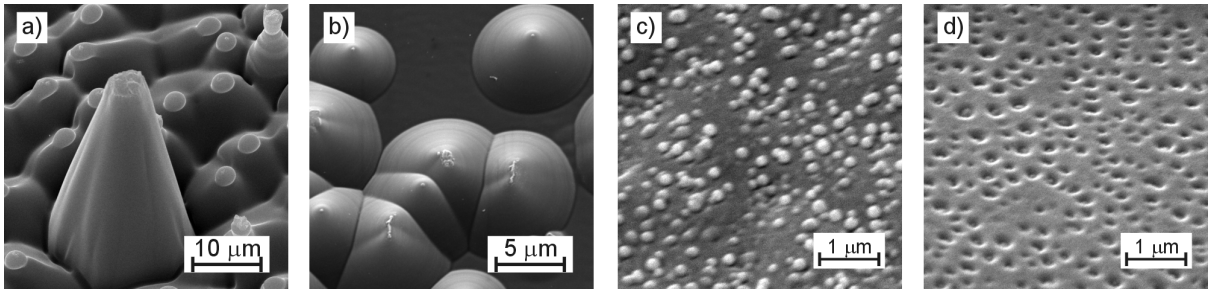

Fig.2: *Surface modification of polymer foils irradiated with 600 EUV pulses: a) PET , b) PI, c) PMMA, d) FEP. EUV fluence close to maximum - a,b) or close to ablation threshold - c,d)*

chemical decomposition of the material and melting of gallium (melting point 30 ºC). In the last image (Fig. 3d) surface of Ge monocrystal after 2 min irradiation with 10 Hz is shown. The resulting microstructure has a very small amplitude of the order of 20 nm. Its origin is probably also associated with melting of the near surface layer with the thickness corresponding to attenuation length of EUV radiation in Ge. In case of polymers additionally decomposition products were investigated using QMS and chemical changes were measured using XPS. Examples of the results for PET are shown in Fig. 4. The QMS spectrum contains a dominating peak associated with emission of molecules having a mass number 28 that can be attributed to both CO and C_2H_4 molecules and multiple peaks with significantly lower intensity corresponding to other decomposition products. The XPS spectra obtained for the

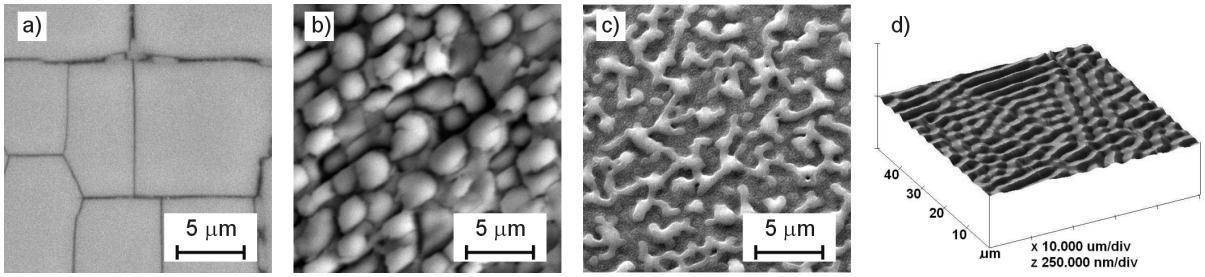

Fig.3: *Surface modification of inorganic monocrystals irradiated with maximum EUV fluence: a) NaCl 1 min , b)* CaF_2 *1 min, c) GaAs 10 s, d) Ge 2 min*

irradiated samples were compared to the spectra acquired for the pristine samples. As could be expected, the relative intensities of C and O signals in Fig 4b and 4c are different confirming the chemical changes.

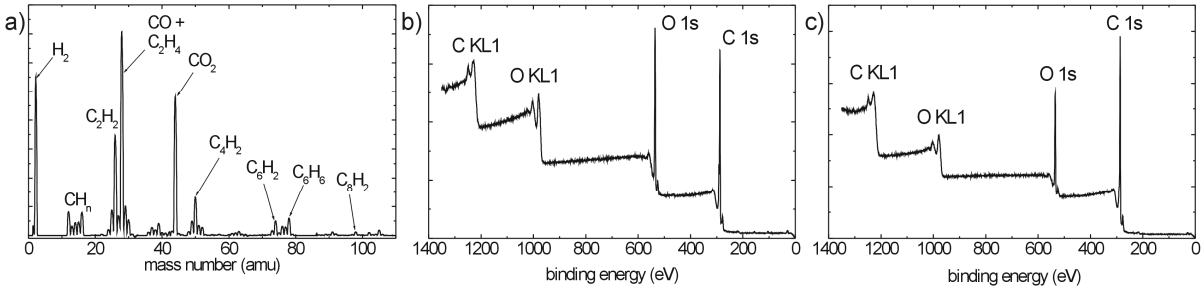

Fig.4: *Spectra acquired for PET; a) QMS - decomposition products, b) XPS - pristine sample, c) XPS - irradiated sample*

4. Conclusions

In this paper we presented the results of experiments concerning ablation and surface modification of organic polymers and inorganic monocrystals. Different kinds of surface structures were created in the investigated materials depending on the EUV fluence. It was shown that modification of the surface morphology of an irradiated polymer is accompanied by significant changes in its chemical structure.

Acknowledgement

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References:

[1] A. Bartnik, H. Fiedorowicz, R. Jarocki, J. Kostecki, A. Szczurek, M. Szczurek, *Appl Phys B* **96**, 727 (2009)