

SOFT X-RAY AND EUV TREATMENT OF SOLIDS

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1. Introduction

The soft X-ray (SXR) photons can ionize any atom or molecule releasing one of the core or valence electrons. Each of the resulting photoelectrons can have enough energy to break several molecular bonds. Thus bond breaking in polymers irradiated with SXR is very effective. Many experiments concerning micromachining and surface modification of polymers were performed using synchrotron SXR sources. A possibility of high aspect ratio micromachining by direct photo-etching was demonstrated for polytetrafluoroethylene (PTFE) [1,2]. In this case the polymer chains were fragmented to C and F containing volatile fractions that were ejected from the surface. Another behaviour was reported for polyvinylidene fluoride (PVDF). Irradiation of this polymer with synchrotron radiation resulted in dehydrogenation and defluorination. This way carbonization of the near-surface layer was obtained leading to strong increase of surface conductivity [3,4].

In our previous papers we show that efficient ablation or surface modification of polymers can be also obtained using laser-plasma EUV (extreme ultraviolet) source. Extreme ultraviolet spans a wavelength range of approximately 5÷50 nm corresponding approximately to photon energy range 25÷250 eV. EUV photons can thus ionize any atom or molecule releasing one of the valence or even core electrons. The mechanism of interaction with matter of EUV photons is thus similar to SXR. The essential difference concerns the penetration depth which for EUV is an order of magnitude smaller comparing to SXR. In this paper results of investigations concerning EUV irradiation of polymers and inorganic solids are presented. Different kinds of decomposition products were identified using quadrupole mass spectrometry (QMS). Significant chemical changes in a near surface layer were revealed using X-ray photoelectron spectrometry (XPS).

2. Experimental arrangement

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/0.8J Nd:YAG laser pulse was used. The target was created by pulsed injection of a gas mixture (90% krypton + 10% xenon) into a hollow stream of helium (KrXe/He target) by employing the electromagnetic valve system equipped with a double nozzle set-up. The radiation was focused using a gold-plated grazing incidence ellipsoidal collector manufactured in Rigaku Innovative Technologies Europe s.r.o., Czech Republic. The most intense emission was in the relatively narrow wavelength range centred at 11 ± 1 nm. The EUV fluence in the focal plane of the collector exceeded 60 mJ/cm^2 at the centre of the focal spot. FWHM of the fluence distribution in the focal spot was 1.4 mm. Detailed description of the source and parameters of the focused radiation can be found elsewhere [5].

The surface morphology of the irradiated samples was investigated using a scanning electron microscope (SEM). The chemical changes were investigated by X-ray photoelectron

spectroscopy. The ablation process was investigated using a quadrupole mass spectrometry (QMS).

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, PMMA, PA6 (polyamide, nylon 6) and FEP are presented in Fig. 1. The structures were obtained by irradiation of the polymer foils with multiple EUV pulses through a copper mesh with 12,5 μm period and 5 μm width bar. The microstructures created in PVDF, PMMA and PA6 having similar depth were obtained after 10 s exposure. The microstructure shown in Fig. 1d was created in a FEP foil after 2 min exposure. Rough estimation of the ablation rate for these polymers was performed using 50 μm foils which were exposed to different number of EUV pulses. It was found that etching through the foils required irradiation with 500 pulses, hence, the average value could be estimated to 100 nm per pulse.

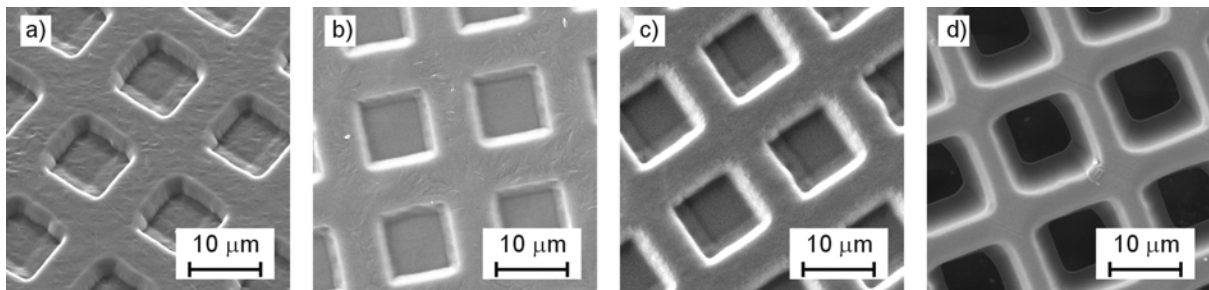


Fig.1: SEM images of polymer foils irradiated through a metallic grid with 12,5 μm period: a) PVDF 100 EUV pulses, b) PA6 100 EUV pulses, c) PMMA 100 EUV pulses, FEP 1200 EUV pulses

Possibility of efficient micromachining is especially important in case of the PVDF fluoropolymer. This polymer has piezoelectric, pyroelectric and ferroelectric properties but its micromachining using other methods is difficult. Many works have been performed on surface processing of PVDF using ion beams synchrotron X-ray and UV laser radiation. Irradiation of PVDF with these sources resulted in strong modification of the molecular structure in a near surface layer of the polymer. The chemical changes are associated with dehydrogenation, defluorination and crosslinking between the polymer chains. The changes, especially the defluorination, strongly influence the ablation process. In case of utilizing the synchrotron radiation for photomachining the maximum achievable etch depth was ~ 10 μm due to a saturation behavior [4]. QMS (quadrupole mass spectrometry) showed that only H_2 , F and HF gaseous species were emitted from the surface during irradiation. The removal of the fluorine atoms resulted in decrease of the irradiated region volume, hence, was responsible for the photomachining mechanism. Simultaneously the F fraction in PVDF decreased gradually as the etching progressed and finally the process stopped. Similar behavior was reported for PVDF irradiated with ion beams and excimer lasers.

QMS measurements performed in this work showed quite different behaviour. A typical spectrum of the ablation products is presented in Fig. 2. The spectrum is consisted of multiple peaks corresponding to decomposition products of the irradiated polymer. As could be expected from the irradiation experiments using synchrotrons there are two intense peaks corresponding to the H_2 and HF molecules [3,4]. Our results, however, are significantly different in respect to these measurements because of the presence of many other peaks corresponding to the molecules or radicals containing C atoms. Such peaks are not present in

the spectra obtained with synchrotron irradiation. Apart from that intensities of H₂ and HF peaks are similar in our case while H₂ emission in case of X-ray irradiation is over 3 times larger comparing to emission of HF. In case of EUV irradiation intensity of a peak corresponding to CF radical is the same as the H₂ peak, intensities of other peaks, corresponding to the presence of C containing molecules, are lower but still very well defined. Their spectrally integrated intensities are about 4 times higher in relation to the H₂ and HF peaks. The mass spectrum revealed the presence of numerous molecular species containing one to three C atoms in the mass range up to 120 amu. These are radicals or unsaturated molecules being fragments of the polymer chain. The C:H:F ratio obtained from the spectrum is 1:1:0.9, respectively which is in good agreement with the ratio in PVDF molecules (1:1:1). It means that an average atomic composition of the ablated material is similar to the atomic composition of the polymer and thus there should be no significant changes in chemical composition of the material remained on the polymer surface after the ablation.

Chemical changes in the near-surface layer of PVDF were additionally investigated using X-ray photoelectron spectroscopy (XPS). The XPS spectra were acquired for polymer samples exposed to different number of EUV pulses with low and high fluence. For comparison the XPS measurements were performed also for a pristine PVDF sample. Typical XPS spectra obtained for the samples irradiated with 450 EUV pulses are presented in Fig. 2 b,c. In all cases two characteristic peaks corresponding to photoelectrons

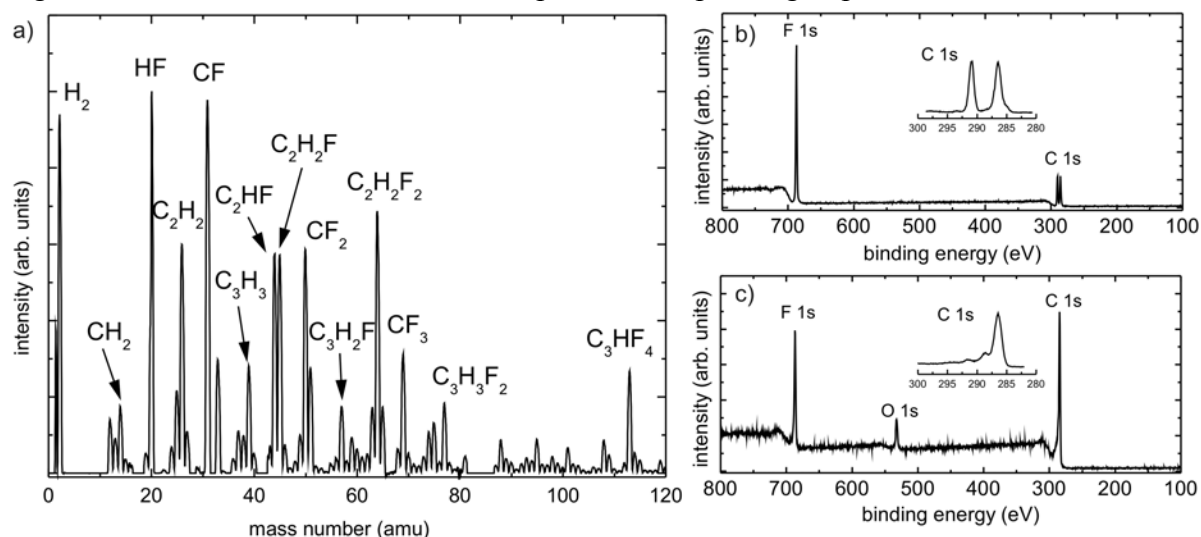


Fig.2: *Experimental results for PVDF: a) QMS spectrum, high fluence irradiation, b,c) XPS spectra – b) remaining surface material after ablation, high fluence), c) chemically modified material in the near-surface layer, low fluence)*

coming from fluorine (F1s) and carbon (C1s) atoms are present. Their relative intensities in case of the untreated polymer sample and the sample irradiated with high fluence are almost identical. The relative concentration of F/C atoms in this case (Fig. 2b) calculated from the peak intensities taking into account the corresponding weights is 49/51 %. This ratio is similar to a theoretical value. It means that the polymer material that remains on the surface after ablation is chemically unaffected. Completely different is the situation in case of PVDF irradiated with low fluence. In this case the C1s peak is much stronger comparing to F1s peak. The calculated fluorine concentration decreased to 12,5 % while carbon concentration increased to 79,7 %. Additionally form of the C1s peak acquired with high resolution differs significantly from C1s peaks obtained for the pristine sample. The high resolution C1s spectrum of untreated PVDF contains two dominating peaks corresponding to -CH₂ (binding

energy 286,44 eV) and $-CF_2$ (binding energy 290,9 eV). In case of the polymer irradiated with low fluence the peak corresponding to binding energy 290,9 eV is strongly decreased. It means that irradiation of PVDF with low fluence results in carbon enrichment in the near surface layer similarly as in case of X-ray irradiation [3,4]. An additional O1s peak corresponds to 7.8 % of oxygen incorporated at the polymer surface exposed to air after irradiation.

The images shown in Fig. 3a,b are surfaces of GaAs irradiated with 100 pulses in the focal plane and 1 mm downstream the focal plane respectively. In both cases micro and nanostructures occurred, however, there are significant differences between them due to different fluences. Forms of the structures suggest that their origin is associated with melting of the near surface layer. Attenuation length of EUV used for irradiation in this case is about 20 nm. Thus the volume density of the energy deposited in a single shot is sufficiently high for melting. The other possibility is chemical decomposition of the material and melting of gallium (melting point $30^{\circ}C$). In Fig. 3c,d images of a lead (Pb) plate irradiated in similar conditions as the GaAs sample are shown. Also in this case forms of surface morphologies suggest the consecutive melting and freezing of the material during irradiation.

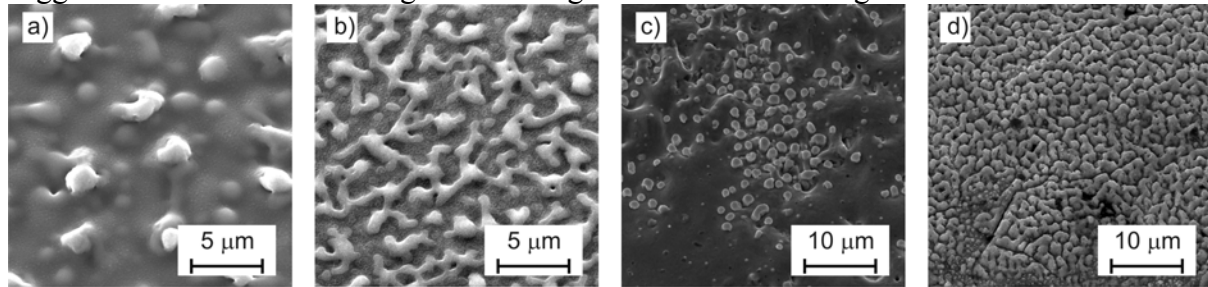


Fig.2: Surface modification of irradiated inorganic solids: a) GaAs - 100 EUV pulses in the focal plane, b) GaAs - 100 EUV pulses 1 mm downstream the focal plane, c) Pb - 25 EUV pulses in the focal plane, d) Pb - 25 EUV pulses 1 mm downstream the focal plane

4. Conclusions

In this paper we presented the results of experiments concerning ablation of organic polymers and surface modification inorganic solids. Ablation products and chemical changes in a near-surface layer of the irradiated PVDF were investigated. Different kinds of surface structures in case of irradiated GaAs and Pb were created. In the experiments EUV radiation from a laser plasma was used. Similar experiments with soft X-rays are prepared.

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