acta physica slovaca vol. 54 No. 3, 277 – 284 **June 2004**

INFLUENCE OF IRRADIATION CONDITIONS ON POLYTETRAFLUOROETHYLENE ABLATION INDUCED BY SOFT X-RAYS EMITTED FROM LASER-PRODUCED PLASMA

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Received 7 April 2003, accepted 28 February 2004

The ablation efficiency in polytetrafluoroethylene of single soft x-ray pulses emitted by laser-produced plasmas was investigated. Placement of samples at different distances from the x-ray source made it possible to investigate dose and dose rate effects on the ablation processes for constant spectral properties of the x-ray source. The high-temperature plasma was created by focusing a 1315 nm laser beam from the PALS iodine laser system (Institute of Physics, ASCR, Prague) on the surface of a metallic target placed in a vacuum interaction chamber. A gas fill in the chamber was used to reduce charged particle emission from the plasma before it arrived at the sample surface. Nonthermal processes in ablation induced by x-ray radiation are discussed. An ablation mechanism based on radiation-chemical scissions of polymer chains followed by blow-off of low-molecular fragments into the vacuum is proposed.

PACS: 52.38.Ph, 52.50.Jm, 61.80.Cb, 36.203Ng

1 Introduction

Earlier experiments using XUV radiation (for a review see [1]) have demonstrated that the interaction of short-wavelength radiation with a solid material in vacuum induces the transfer of macroscopic amounts of the material into the vacuum. Ablated material can be collected on a chosen substrate so that high-quality thin films are produced. Short wavelength radiation sources used for material removal can have either low (synchrotron radiation) or high (FEL and hot dense plasma) peak power. With low-peak-power sources, materials components are removed by photon-induced desorption (often called direct dry etching or synchrotron radiation induced evaporation). Each x-ray photon carries enough energy to break any chemical bond and its energy is also usually higher than any crystal's cohesive energy. These photons are able to excite electrons from inner atomic shells, followed by an Auger cascade of other electrons. This leads to

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the formation of electron-depleted regions in the material structure, which rapidly decompose by Coulomb explosion. Therefore, the photons absorbed in the near-surface region may create small fragments of the sample material, which are emitted into the vacuum. It is necessary to underline that, in the case of low-peak-intensity irradiation, material is removed only from the surface and a very thin near-surface layer. Quite a different situation is expected when a high-peak-power source delivers a single high-energy pulse onto the sample. The sample is exposed to a high local dose of radiation (given by the energy content of the pulse and the absorption length of the radiation in the irradiated material) in a short period of time (given by the pulse duration) – thus a very high dose rate. This means that a large number of events which cause radiation-induced structural decomposition (i.e. polymer chain scissions, etc.) occur almost simultaneously in a relatively thick layer of irradiated material. Since a significant part of the radiation energy absorbed in the material is thermalized, sudden overheating of the layer, which is also chemically altered by the radiation, must be taken into account. The overheated fragmented region of the sample represents a new phase, which tends to blow off into the vacuum.

In this contribution we present the results of a study of the ablation of polytetrafluoroethylene (PTFE) irradiated by intense soft x-ray radiation emitted from laser-produced plasmas. By varying the distance, d, of the polymer samples from the plasma source, we covered a wide range of fluences, while photon energy and pulse duration of the short wavelength radiation pulses were kept constant.

2 Experimental

The polytetrafluoroethylene (PTFE) samples used in our studies were 1 mm thick sheet purchased from Goodfellow (UK), fabricated into 3 mm diameter discs, and polished. Since PTFE is a very soft material, the mechanical polishing was not fully successful. Ripples due to polishing powder movement over the surface were indicated by a profiler and SEM. Their typical depth is ~ 10 nm. The samples were placed behind masks, a nickel or an iron mesh and irradiated by soft x-ray radiation. The wires of the mesh were in close contact with the sample surface. The samples were located 45 mm, 87 mm, and 157 mm from the laser-produced plasma. The x-ray radiation was emitted from hot dense plasma produced by a focused laser beam. The pressure of the buffer gas (air) in the chamber in our experiments was typically ~ 10 Pa. High temperature plasma was created by focusing a 1315 nm laser beam with available pulse duration 400 ps and laser energy E_{L} up to 1 kJ from the PALS, (high-power iodine photodissociation laser system [2], Institute of Physics and Institute of Plasma Physics, AS CR, Prague) on the surface of planar metal-slab molybdenum targets.

Highly charged particles emitted from the plasmas were slowed down before arriving at the sample surface by a buffer gas, which stops the slow highly charged ions while transmitting a significant portion of the photons. Absence of ion current was checked using ion collectors.

Depth profiles of the structures formed due to ablation and expansion of the irradiated material were measured using an Alpha-Step 500 Surface Profiler (Tencor; USA). Raman measurements were made with Ar^+ laser (514.5 nm) micro-beam in the usual back scattering geometry (Model 1000 Renishaw Ramanscope; UK). The system was equipped with a CCD camera and a Leica DMPL microscope. This tool enables the probing of chosen places on the sample surface. Typically, laser spots with a diameter of 4 μm were used.

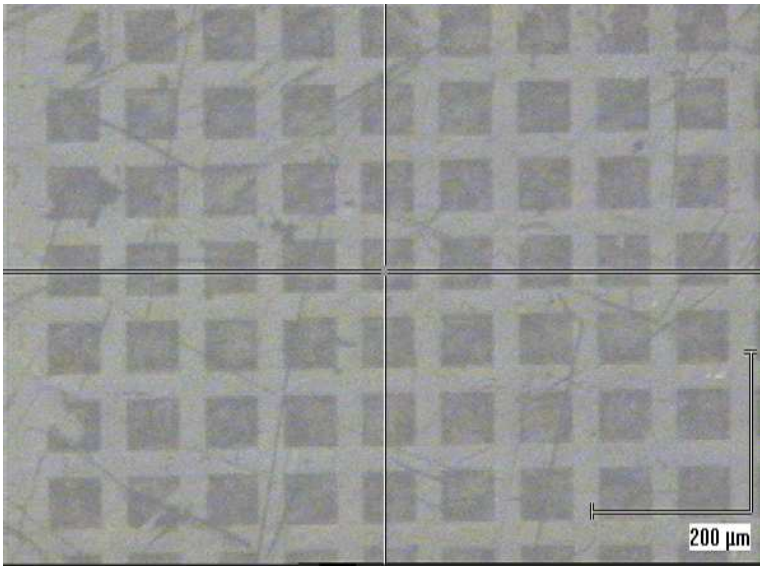

Fig. 1. Optical micrograph of a PTFE sample irradiated through a mesh contact mask by soft x-rays from a laser-produced molybdenum plasma. Distance between the x-ray source and the sample $d = 157$ mm and $E_{\mathrm{L}} = 747$ J.

3 Results and discussion

PTFE was successfully ablated with the XUV source based on laser-produced plasmas at all of the three chosen distances. The result of the first experiment carried out with the PALS is presented in Fig. 1, which shows an optical micrograph of the structure formed in a PTFE sample irradiated through a mesh contact mask by soft x-rays emitted from plasma produced by a 747 J laser pulse interacting with a molybdenum target. The plasma was formed with the laser beam focus located 2 mm behind the target surface. Under these conditions the plasma emission spectrum is dominated by a very soft radiation component. Just this component is modified by transmission of the ambient gas left in the chamber. Although the PTFE sample was located at the longest of the 3 distances from the source, quite a clear and sharp structure was formed due to ablation (Fig. 1).

Varying the position of the laser beam focal point with respect to the target surface can control the ratio of softer to harder x-ray emission from the laser-produced plasma. If the focus is located right at the surface, the laser radiation intensity is high and the fraction of hard emission is at a maximum. Moving the target toward the focusing lens by 2 mm produces maximum soft x-ray emission due to increased plasma volume, while harder radiation is suppressed due to decreased laser beam intensity.

In Fig. 2 the results of the profiler measurement are shown for a sample irradiated under the optimum conditions for generation of soft x-rays, i.e. with the focus of the laser beam 2 mm in front of the molybdenum slab target surface. If the samples are located nearest the plasma source the deeper structure is produced, which can be see in Fig. 3.

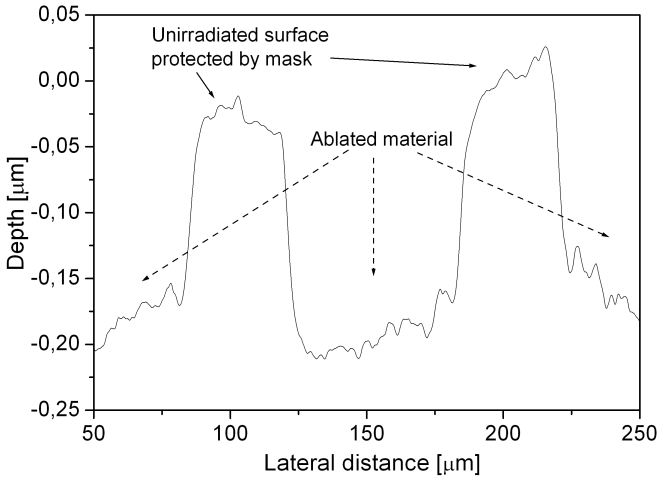

Fig. 2. Depth profiles of ablated PTFE samples, measured with an Alpha-Step 500 surface profiler (Tencor, USA). Target material Mo, $E_{\mathrm{L}} = 716$ J, $d = 87$ mm, $p = 50$ Pa.

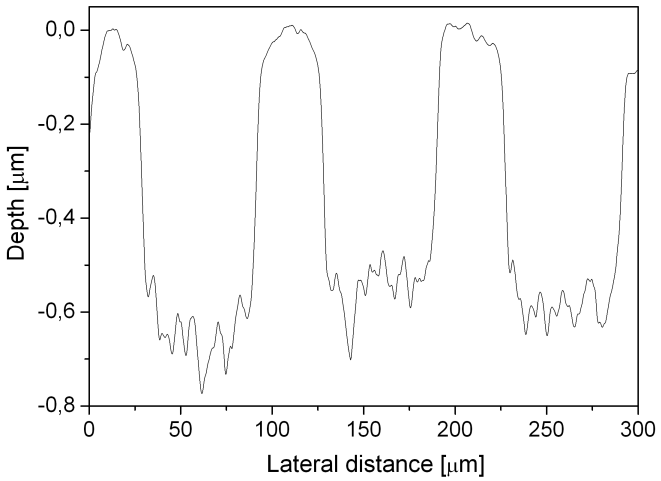

Fig. 3. PTFE sample irradiated through a nickel mesh by short-wavelength radiation from a molybdenum-target surface, laser pulse energy 747 J, $d = 45$ mm, $p = 46$ Pa.

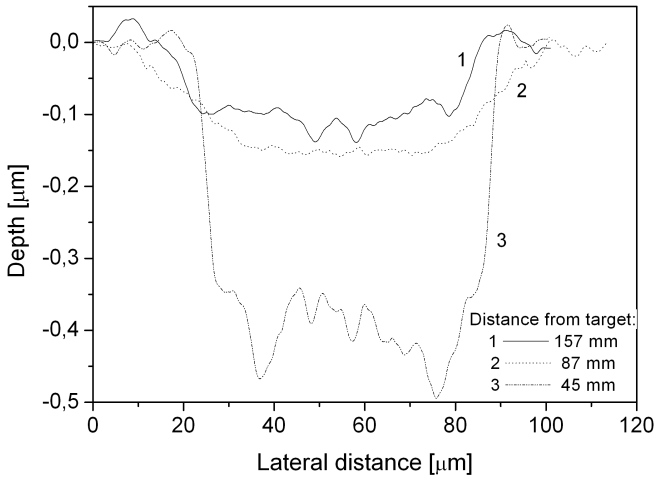

Fig. 4. Ablation of PTFE by laser-produced plasma for different distances from the laser target. $E_{\mathrm{L}} = 711$ J.

Reduction of the soft x-ray fluence by increasing distance of the sample (45 mm to 157 mm) from the Mo target results in a decrease of ablation efficiency due to the decrease in the amount of soft x-ray energy deposited (fluence, dose). The ablation structure profiles formed at the different distances from the source are compared in Fig. 4. The fit of a d^{-2} function to the measured dependence of the ablation depth (often called etch depth) on r is shown in Fig. 5. The results clearly show a d^{-2} character of ablation efficiency dependence on the distance from the source.

Higher laser pulse energy generates stronger emission of soft x-rays, which is able to ablate polymers efficiently. But only a part of the x-ray spectra efficiently ablates the polymers due to different attenuation lengths in polymers, which determine the applied irradiation dose, see Fig. 6. One can expect soft x-rays with an attenuation length shorter than about 1 μm to be most effective. The use of air as a buffer gas to slow down ions emitted from plasma results in attenuation of $\sim$ 20 eV radiation, nevertheless photons with energy higher than 200 eV pass through the air layer without any significant attenuation, as Fig. 6 shows. Since the fit of $\alpha + \beta \mathrm{d}^{-2}$ to the measured distance dependence of the ablation depth gives $\alpha > 0$, one can suppose that the efficiency of $\sim$ 20 eV radiation is not primary to the ablation process studied under this conditions. The participation of $\sim$ 20 eV radiation in the ablation process decreases with increasing distance, due to absorption of this radiation in air. The fitted positive value of the α parameter may also indicate the occurrence of transport of the polymer induced by a secondary mechanism.

An argument testifying to an x-ray ablation mechanism based on radiation-induced polymer chain scissions is the presence of certain structures, usually centered in the irradiated regions or

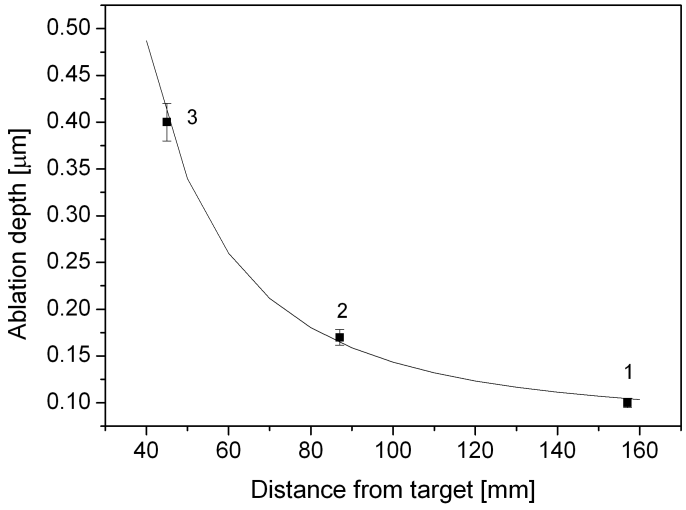

Fig. 5. Dependence of ablation depth on distance of sample from target for laser-produced plasma (scattered line) and its best fit to the function $\alpha + \beta d^{-2}$ (solid line).

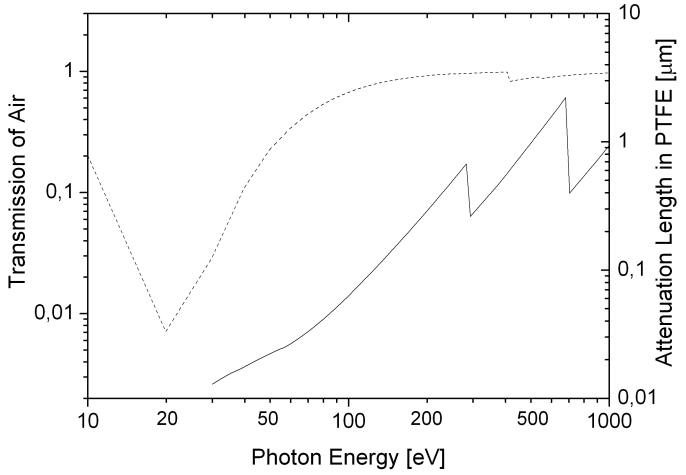

Fig. 6. X-ray attenuation length in PTFE (full line) and transmission of x-rays by a 157 mm thick, 44 Pa air layer (dotted line) versus photon energy.

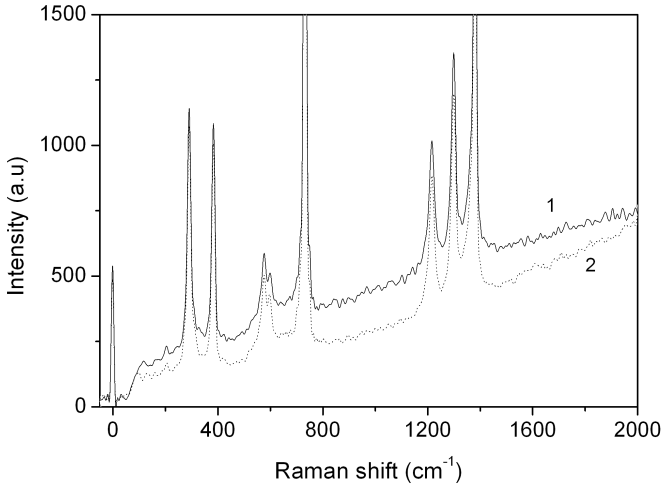

Fig. 7. Raman spectra of PTFE sample irradiated through a nickel mesh by soft x-ray radiation emitted by a molybdenum plasma. 1–unirradiated surface. 2–irradiated surface.

arising near mask-sample contacts, which exhibit hydrodynamic character. Although they are not so well developed with PTFE samples as with PMMA or PET [3-5], they can be seen in Fig. 4. We suppose that they are relics of hydrodynamic transport, from the irradiated square wells into the vacuum, of a "fluid" formed from the polymer chains undergoing multiple radiation scissions and being suddenly heated by the intense soft x-ray radiation.

The Raman spectra presented in Fig. 7 were recorded in unirradiated (spectrum 1) and irradiated (spectrum 2) areas of the PTFE sample surface. When we compare these two curves, we do not see any difference between the ablated square well bottom and undamaged material. This fact supports the mechanism of the ablation processes considering an efficient hydrodynamic transport of almost all the fragmented material into the vacuum. The Raman spectra confirm the absence of any traces of PTFE carbonization products, thus testifying to a different mechanism for soft x-ray ablation of PTFE compared to conventional polymer ablation by lasers with much longer wavelengths.

4 Conclusions

It has been demonstrated that the operating conditions of this source can be optimized to provide enough soft x-ray radiation, emitted in subnanosecond pulses, to ablate PTFE samples, even when they are located at a relatively long distance (157 mm) from the source. Polymer layers with a thickness of several hundred nanometers were ablated by a single shot, under optimum irradiation conditions. The results presented support a model of x-ray ablation based on the

assumption of radiation-induced scissions of the polymer chains, leading to formation of low-molecular fragments that blow off into the gaseous phase.

Reduction of the soft x-ray fluence by increasing the plasma-sample distance results in a dramatic decrease of ablation efficiency. The use of air as an x-ray filter makes estimation of the contribution of 20 eV radiation to the ablation process possible through comparison to ablation of PTFE in vacuum. Comparing ablation depth profiles, we can determine the spatial dependence of x-ray intensity in comparison to an assumed d^{-2} decrease in the intensity far away from the plasma.

Acknowledgement: This work was funded by the Czech Ministry of Education within the framework of the programs INGO (Grant LA055) and National Research Centers (Grant LN00-A100). The authors appreciate very much the support given by the staff of the PALS facility, Prague and Dr. D. Chvostová and Dr. V. Vorlíček from Institute of Physics, AS CR.

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