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Short-wavelength ablation of polymers in the high-fluence regime

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Abstract

Short-wavelength ablation of poly(1,4-phenylene ether-ether-sulfone) (PPEES) and poly(methyl methacrylate) (PMMA) was investigated using extreme ultraviolet (XUV) and soft x-ray (SXR) radiation from plasma-based sources. The initial experiment was performed with a 10 Hz desktop capillary-discharge XUV laser lasing at 46.9 nm. The XUV laser beam was focused onto the sample by a spherical mirror coated with a Si/Sc multilayer. The same materials were irradiated with 13.5 nm radiation emitted by plasmas produced by focusing an optical laser beam onto a xenon gas-puff target. A Schwarzschild focusing optics coated with a Mo/Si multilayer was installed at the source to achieve energy densities exceeding 0.1 J cm^{-2} in the tight focus. The existing experimental system at the Laser Laboratorium Göttingen was upgraded by implementing a 1.2 J driving laser. An increase of the SXR fluence was secured by improving the alignment technique.

Keywords: extreme ultraviolet, soft x-ray, ablation, polymers

(Some figures may appear in color only in the online journal)

1. Introduction

Detailed investigations of short-wavelength ablation using various plasma-based extreme ultraviolet/soft x-ray (XUV/SXR) sources represent relatively recent [1–5] but rapidly growing research activity. Mechanisms and characteristics of the XUV/SXR ablation may, especially in molecular solids, differ dramatically from the ablation induced by conventional, long-wavelength (i.e. UV/Vis/IR) lasers. It follows from the fact that each XUV/SXR photon carries enough energy to break any chemical bond in an irradiated material. Therefore, the XUV/SXR ablation of organic polymers is initiated by photo-induced polymer chain scissions. Then, material erosion occurs due to the formation of volatile products in polymer radiolysis and they evaporate from the irradiated surface into the vacuum. The chain decomposition process can, in principle, compete with the cross-linking of polymer molecules, which acts against the material erosion. Both processes may influence the efficiency and quality of micro-structuring of a polymer material. Although the initiation of the polymer erosion is basically non-thermal, the ablation should be affected by a thermalized portion of the absorbed energy in the high-fluence regime. A phenomenological model of the XUV/SXR-induced ablation/desorption is given in [6].

This work tests two plasma-based sources providing nanosecond pulses of short-wavelength radiation to ablate poly(1,4-phenylene ether-ether-sulfone) (PPEES) in comparison with poly(methyl methacrylate) (PMMA) chosen as a reference material.

The compact capillary-discharge XUV laser (the capillary-discharge laser (CDL) source [7, 8]) developed at Colorado State University and operated in Prague provides pulses of monochromatic 46.9 nm radiation while the laser-produced plasma (LPP) source (the Laser Laboratorium

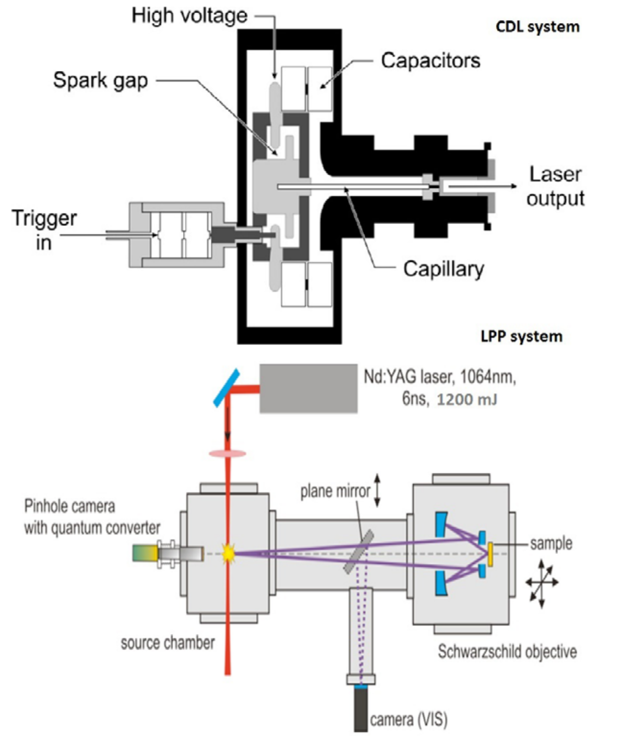

Figure 1. Experimental systems: scheme of the CDL system operated in Prague [7] (top) and scheme of the LPP system operated at LLG in Göttingen [5] (bottom).

Göttingen (LLG) source [9, 10]) located in Göttingen emits SXR radiation with wavelengths centered at 13.5 nm.

The effect of single and multiple pulse exposure of the target materials was analyzed. Damage patterns were first inspected using a Nomarski (DIC) microscope. The ablation rates for various XUV/SXR fluences and damaged morphologies were determined using a surface profiler based on white light interferometry.

2. Materials and methods

The ablation experiment has been performed in LLG with PMMA as a reference material and, with the same setup, a target material. The material chosen as the target to be tested is PPEES (see www.sigmaaldrich.com/catalog/product/aldrich/440965?lang=en&region=CZ).

This polymer has physical properties similar to those of PMMA, but a higher radiation resistance was expected. Because of the presence of π electrons in PPEES molecules, it is more difficult to ablate PPEES but offers the possibility to have a better defined (likely smoother) ablated area and shallower crater. Thanks to this property, PPEES is a promising candidate for high-precision surface patterning.

The PPEES target has been prepared by applying a spin coating on a monocrystalline silicon substrate. A small puddle containing a certain volume of 0.1 M solution of the polymer in chloroform was deposited on the center of the substrate and then the substrate was spun at high speed (about 3000 rpm). Then the solution is uniformly spread on the substrate and the solvent evaporated leaving a thin film of resin on the substrate.

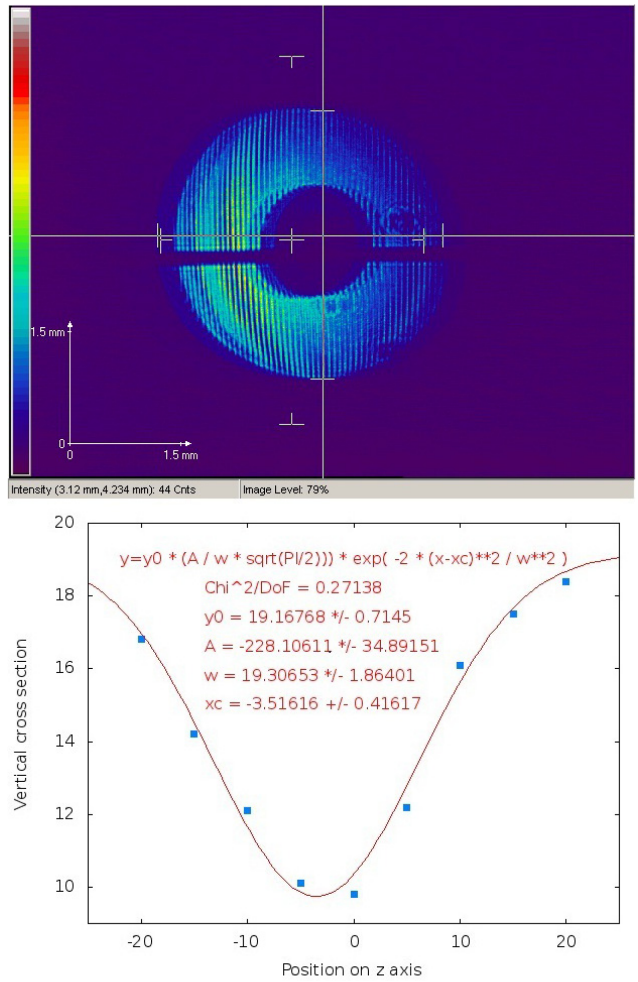

Figure 2. Evaluation of the focal position using the LLG source at a wavelength of 13.5 nm: Ronchi test result (top) and Gaussian fit (bottom).

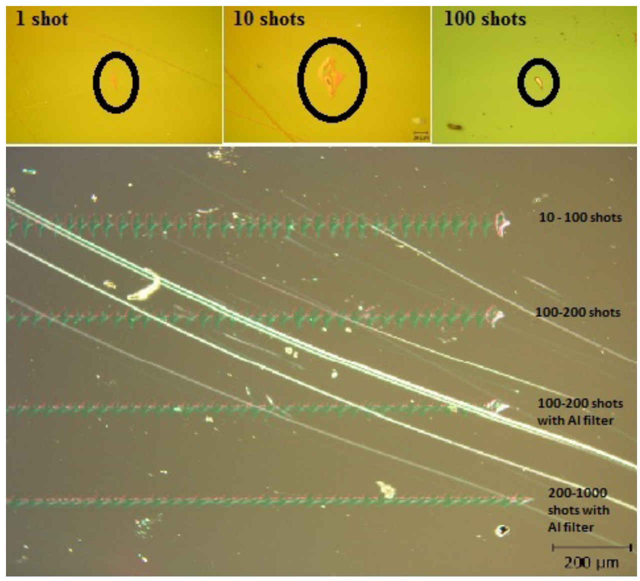

Figure 3. Capillary discharge laser at a wavelength of 46.9 nm: caustic measurement wavelength 46.9 nm (bottom) and ablation measurement (top). The shape of the crater is almost the same along the line of the caustic. Looking at the image on the right it can be seen that the annular form is preserved although, augmenting the number of shots, its dimension increases.

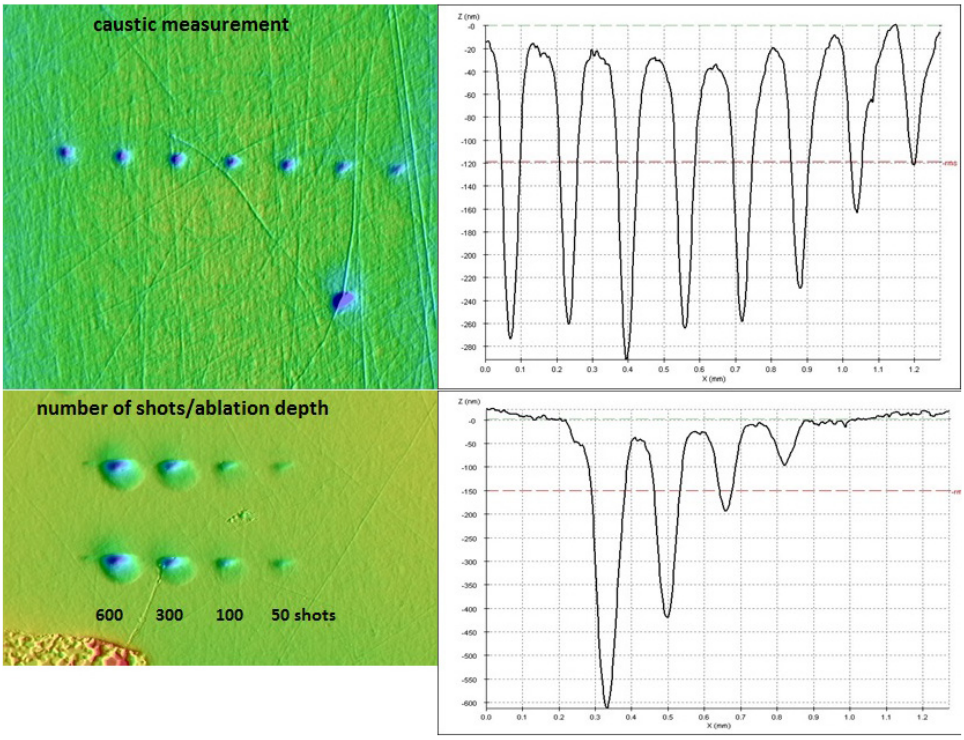

Figure 4. LLG source at a wavelength of 13.5 nm: example of caustic (top) and dependence of ablation depth on number of shots (bottom) measurement on PMMA.

The target prepared has been used to study an XUV ablation process in Prague. Ablation experiments have also been performed after implementing the existing experimental system at LLG in Göttingen.

The capillary-discharge Ne-like Ar XUV laser [7] installed and operated in Prague (see figure 1) was used for the initial experiments demonstrating the possibility to ablate PPEES by intense XUV radiation. Its characteristics are a wavelength of 46.9 nm, a pulse length of 1.5 ns (FWHM), a maximum pulse energy around 10 μJ, a repetition rate of 5 Hz—typical and 12 Hz—maximum, a capillary lifetime of (2–3)$\times 10^4$ pulses and a current of $\sim$21 kA. The capillary is Al_2O_3 (inner diameter: 3.2 mm; length: 210 mm), Ar filled (50 Pa). A spherical multilayer Sc/Si mirror with a focal length of 0.25 m has been used for focusing the CDL beam. The mirror was designed and manufactured to have maximum reflectivity at 46.9 nm and at a 6° angle between the incident and reflected beams [8].

The second experimental system, built and operated at LLG, is shown in figure 1 as well. A new driving laser with the following characteristics has been installed for the present experiment: a wavelength of 1064 nm, a pulse length of 7 ns, jitter $<$1 ns, divergence $<$0.5 mrad (Gaussian profile at far field), an energy stability of $<$1% for 90% of pulses and the maximum pulse energy of 1.2 J (i.e. two times larger than that used by Barkusky *et al* [5] in earlier experiments).

A Schwarzschild focusing optics [5] with Mo/Si multilayer coating was installed at the source to generate a focal spot with energy densities exceeding 0.1 J cm^{-2}.

An increase of energy fluence is needed to reach an efficient ablation mode, and can be obtained by the alignment technique. The laser beam has been aligned by means of a lens and, after that, the plasma was centered under the nozzle. To align the Schwarzschild objective, a Ronchi test [11] and Gaussian fit were performed (figure 2).

Once the focal position was indicated, a caustic ablation test [12] was performed on the reference target (PMMA) and after indicating the new focal position, a PPEES target was placed in the holder and exposed to radiation emitted by plasmas created in the 10 bar Xe gas target. After analyzing the caustic curve, an ablation test has been performed varying the number of shots in the tight focus position.

3. Results

The preliminary measurements performed in Prague with the 46.9 nm laser demonstrated the possibility to ablate the PPEES by XUV radiation, i.e. at longer wavelengths that are more strongly absorbed by the irradiated material than the 13.5 nm radiation. Taking the density of PPEES equal to 1.24 g cm^{-3} [13] and its elemental composition being $C_{18}SO_4H_{12}$ (figure 1), we get an attenuation length of the XUV laser radiation in PPEES of approx. 20 nm (see http://henke.lbl.gov/optical_constants/filter2.html). The short attenuation length results in a high-energy density in the near surface region.

The following picture (figure 3) shows that the crater structure is stable with varying number of shots; therefore a well-defined, well-developed ablated area can be achieved. Indeed it can be seen that the annular form is preserved, although, augmenting the number of shots, its dimension increases. Small differences between the craters obtained are due to the redeposition of the material along the crater shape and, for a number of shots equal to or superior to 100, from the damage of the silicon substrate.

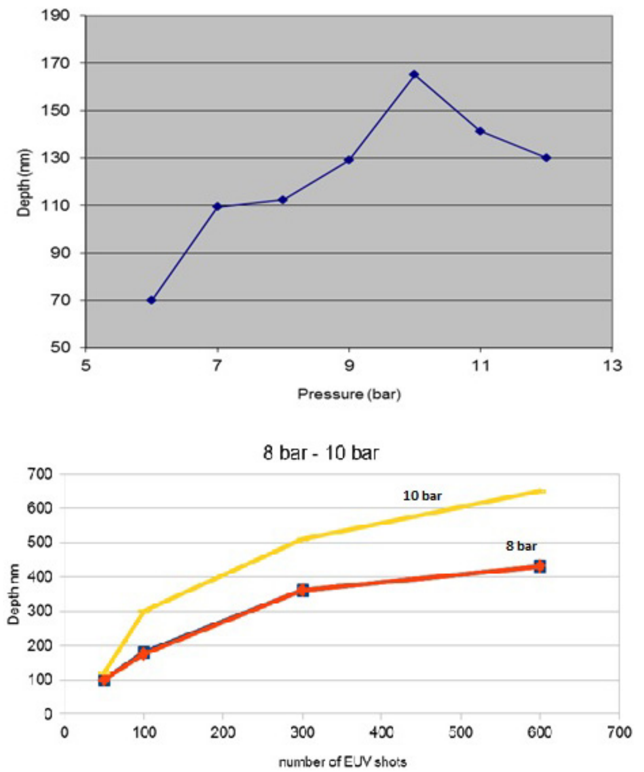

Figure 5. Evaluation of the dependence on the pressure: ablation depth in PMMA as a function of the gas pressure (top) and PMMA ablation depth as a function of the number of SXR shots from the LLG source operated at gas pressure of 8 and 10 bar (bottom). These values were analyzed because 8 bar was the value used by Barkusky *et al* [5] and 10 bar is the higher value that can be reached before the re-absorbing process becomes dominant and for this reason this is the value selected for the current ablation test experiment.

The caustic measurements on PMMA have been performed at LLG to test the stability of the system and to find an optimum focal position (figure 4).

A measurement of the ablation depth as a function of the number of shots on PMMA has been performed obtaining reproducible results (figure 4).

A measurement of the depth variation as a function of the gas pressure was performed. The pressure at which the maximum depth is obtained is 10 bar and the efficiency of the system increases with pressure until the re-absorbing process of EUV light inside Xe gas becomes dominant (figure 5).

The effect of the fluence on the ablation depth has also been investigated. Two cases were considered (8 bar, 87 mJ cm^{-2} and 10 bar, 127 mJ cm^{-2}), and the obtained result is shown in figure 5.

After finding the focal position and the optimum gas pressure (10 bar), an ablation test was performed on the PPEES sample. Ablation was not observed for fluences up to 127 mJ cm^{-2}, which means that the energy fluence was below the ablation threshold of PPEES. Therefore, we should increase the output energy of the LLG source and focus its SXR emission onto a smaller spot to reach the SXR ablation threshold of PPEES.

4. Conclusions

The possibility to obtain a well-developed ablation crater in PPEES has been demonstrated with the 46.9 nm capillary-discharge XUV laser. This is in good agreement with the earlier results [14–16] of ablation experiments conducted with different materials irradiated with intense XUV radiation, which is very strongly absorbed by solids.

The more penetrating 13.5 nm radiation (its attenuation length in PPEES is about 215 nm (see http://henke.lbl.gov/optical_constants/filter2.html)) was not able to ablate the PPEES material, although PMMA was ablated quite effectively under these irradiation conditions. Higher radiation stability of PPEES is expected because of the presence of π electrons in PPEES molecules in contrast to less radiation resistant structures such as PMMA or PBS [17].

An attenuation length prolonged at the shorter wavelength is likely to be responsible for the difference in response of PPEES to radiation from the CDL source and the LLG source.

Acknowledgments

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