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Ablation of poly(methyl methacrylate) induced by focused 21.2-nm laser radiation

M. Bittner, L. Juha, M. Kozlová, J. Krása, V. Létal, Z. Otčenášek, J. Polan, A. R. Präg[*], R. Sobierajski[a], M. Stupka, and B. Rus

Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, CZ-18221 Prague 8, Czech Republic
[a]Faculty of Physics, Warsaw University of Technology, Pl. Politechniki 1, PL-00-661 Warsaw, Poland

Abstract. Ne-like Zn laser driven by Prague Asterix Laser System (PALS) provides short pulses of radiation in the soft x-ray region (λ = 21.2 nm, τ < 100 ps). The soft x-ray beam was focused by a spherical Mo/Si multilayer mirror to a surface of poly(methyl methacrylate) sample, causing efficient ablation of the irradiated material. To our best knowledge, it is the first observation of material ablation induced by laser working in the soft x-ray region, i.e. λ < 30 nm. Ablation craters were analyzed with atomic force microscopy (AFM). Obtained ablation characteristics were compared with that calculated by the simulation code XUV-ABLATOR. UV-VIS spectra of photon emission from the irradiated surfaces were measured.

Introduction. Laser ablation is efficient removal of material from a surface irradiated by an intense laser beam [1]. Due to its potential use in surface micro-patterning, ablation has attracted attention from beginning of laser era. Among lasers used to material ablation, UV lasers are often used because of their reduced penetration depth and ability to induce ablation with reduction of thermal damages. It is given evidently that photochemical decomposition plays an important role at the shorter wavelengths. Recent ablation studies at the shortest wavelengths in the VUV region were conducted with F_2 excimer lasers (157 nm [2,3]) and radiation generated by four-wave-sum-frequency mixing of a frequency-doubled Nd:YAG laser (125 nm [4]). Laser sources have recently become operational at even shorter wavelengths, in the extreme ultraviolet (XUV, λ<100 nm) and soft x-ray (λ<30 nm) regions. Both plasma-based lasers [5] as well as free electron lasers (FEL) [6] reached the spectral regions. The XUV lasers have been used to induce materials ablation in [7-10]. These sources have potential to become unique tools in the field of nano-patterning of solids due to ablative imprint of features having dimensions comparable to their wavelength. A key advantage of the XUV and soft x-ray lasers for fabrication of nanostructures is unique combination of extraordinarily short wavelength, coherence, and high peak power. Results of first experiments with ablation of poly(methyl methacrylate) - PMMA induced by focused 21.2-nm radiation of Ne-like Zn laser are presented in this contribution. PMMA represents a material of first choice in our project because its ablation has been extensively studied with conventional, UV-VIS-NIR lasers [1-4,11], XUV laser [7-9], and incoherent XUV/x-ray sources [12,13]. To our best knowledge, this is the first observation of PMMA ablation induced by laser working in the soft x-ray region, i.e. λ < 30 nm.

[*]*corresponding and presenting author*: Fax: +420-2-868 90265, E-mail: praeg@fzu.cz

Experimental. The PMMA samples, in the present study irradiated by focused soft-x-ray laser beam, were 500-nm thick layers of 495K PMMA deposited on 5-mm x 5-mm 315-μm thick silicon chips, purchased from Silson (UK). Samples were irradiated by focused Ne-like Zn laser driven by Prague Asterix Laser System (PALS), see Fig.1 - right. For more details about Ne-like Zn laser see [14,15]. The output pulses have a wavelength of 21.2 nm, time duration less then 100 ps, divergence

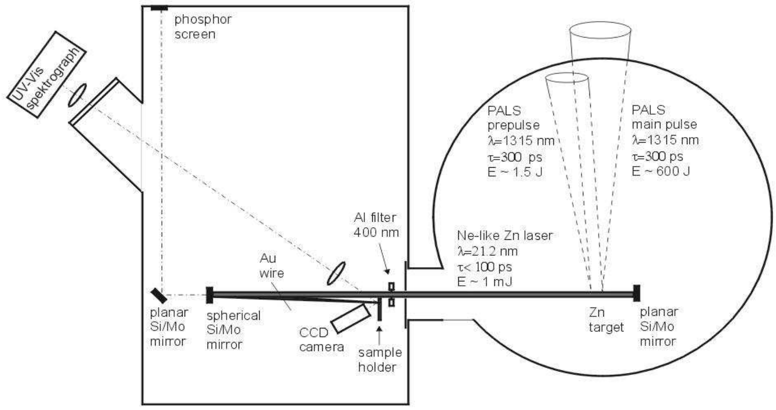


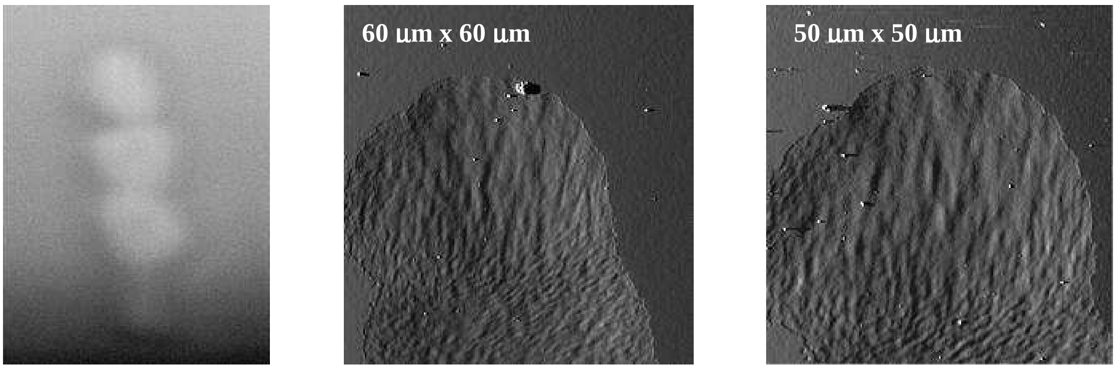
Figure 1. Top-view scheme of PALS vacuum chambers: Ne-like Zn laser was operated in spherical (right) chamber; ablation experiments were conducted in cylindrical (left)

of about 5 mrad and energy from ~ 100 μJ to 1 mJ. Ne-like Zn laser beam entered inwards the cylindrical PALS chamber (see Fig. 1 - left) through the aperture and the removable 400-nm thick aluminium filter. Thus it was partly delivered of intense but incoherent radiation emitted from zinc plasma in a direction of laser axis. Transmission of the Al filter is about 50% for 21.2-nm radiation and nearly zero for all wavelengths above 80 nm. Incoherent sub-80-nm radiation was suppressed by selective reflectivity of Si/Mo multilayer mirrors which is high (R~30%) enough only for narrow interval around 21.2 nm. Nearly-on-axis focusing setup was realized. The spherical mirror was turned about 3^{O} with respect to the axis of incoming beam in the horizontal plane of experiment. The focus was observed by the CCD camera, and by the UV-VIS spectrometer (MS257, Oriel) equipped with the sensitive detector (istar ICCD, ANDOR). Spot size and intensity of the focused laser on a sample surface was varied due to sample movement along the beam axis. Focus position was found when a size of light-emitting spot on the surface of luminescent Ce:YAG crystal was minimized. Footprint of the unfocused beam was observed at the Al-covered phosphor screen by CCD camera when the spherical Si/Mo mirror was removed. Relying on a good output stability [15] of the soft x-ray laser we may expect that several hundreds of μJ were during the ablation experiments in a single 21.2-nm pulse at the entrance of the cylindrical chamber. Ablation craters on PMMA were analyzed by AFM microscope in tapping mode (D3100 NanoScope Dimension controlled by NanoScope IV Control Station; Veeco, CA). Depths of ablation craters can be compared with the results of computer code XUV-ABLATOR. ABLATOR [16,17] is thermo-mechanical one-dimensional hydrodynamic code developed for simulation of ablation induced by broadband keV radiation. It was modified for a simulation of material ablation induced by XUV radiation with attenuation length typically much shorter then attenuation length of x-rays. Radiation-chemical degradation of PMMA to MMA or CO_2 is partly considered in XUV-ABLATOR code besides much higher surface temperature.

Results and discussion. Well-developed craters were found at surfaces of PMMA irradiated by focused 21.2-nm laser radiation. Figure 2 shows the craters ablated by one laser pulse filtered by 400 nm thick Al foil. It is clear that the ablation of PMMA was really due to the soft x-ray laser. Broader divergence of incoherent radiation leads to larger affected area then crater ablated by soft x-ray beam. Figure 3-a shows edge of the crater ablated by two partially overlapping unfiltered pulses. It is clearly visible that crater edge remains sharp and a surface relief of the craters remains similar to that created with the filtered radiation. Therefore an influence of the incoherent radiation seems to be negligible. Ablation depth determined from crater profile is 420 nm. It means that ablation rate is under given irradiation conditions equal to 210 nm/pulse. On the other hand the ablation rate simulated by XUV-ABLATOR is by factor two higher than that observed [17].

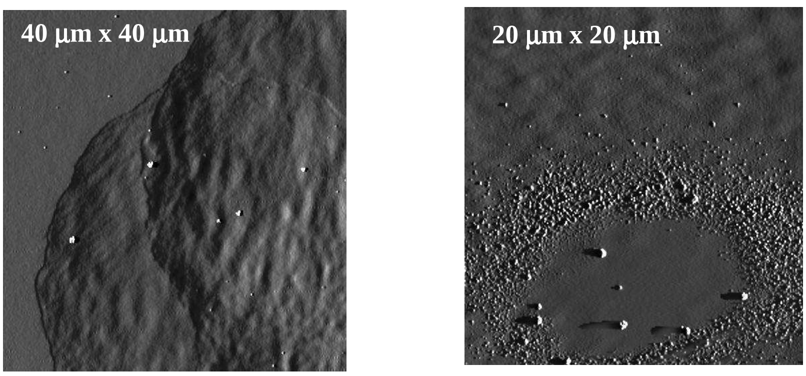
All observed craters are composed from three or four components clearly visible in Fig. 2-a. Micrometer-scale modulations seen in figures 2-b, 2-c, and 3-a are also very similar. We can conclude that the surface topography of the craters records spatial non-uniformity of the focused soft x-ray laser. If we assume that observed modulations are not caused by imperfections of focusing mirror, ablation of PMMA is able to image directly wavefront perturbations of unfocused laser beam. Figure 3-b is an AFM image of the bottom of crater ablated by three partially overlapping unfiltered pulses. Ring of very small features, likely Si droplets, is observed in the point where the depth of crater (about 600 nm) is higher than thickness of PMMA layer (500 nm).

UV-VIS emission spectra of PMMA are shown in Fig.4-a. The spectrum emitted from hot zinc plasma was identified between 350 nm and 600 nm. It spectrum appeared and disappeared according to presence or absence of aluminium filter. A red band with a maximum at 680 nm was found emitted by PMMA surface. Not always this emission was observed. It seems that emission disappears when ablated surface is irradiated by another pulse in the same position. Moreover shape and position of the red band did not change when attenuated or full soft x-ray beams were used. There are three possible explanations of the red emission at the moment. It could originate from unknown molecular species adsorbed on the surfaces of PMMA. This would explain an absence of the red band when craters were ablated on the same place by another pulse. Other possibility is that we are looking at a specific emission from a periphery of x-ray laser-produced plasma. Very cold



a) **b)** **c)**

Figure 2. PMMA ablated by single pulse of 21.2-nm laser filtered by 400-nm Al foil
a) optical micrograph, b) and c) amplitude images from AFM-tapping mode



a) **b)**

Figure 3. Craters ablated in PMMA by unfiltered pulses of 21.2-nm laser
a) edge of crater ablated by 2 pulses b) bottom of crater ablated by 3 pulses

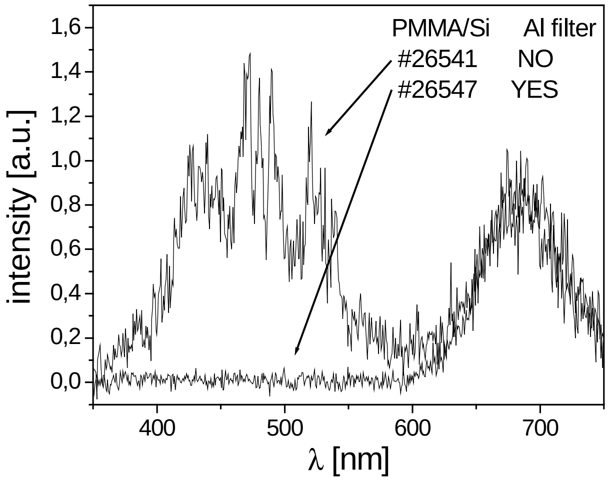


Figure 4. UV-VIS spectra emitted from PMMA surface irradiated by intense 21.2-nm radiation.

plasma with a density close to solid matter should exist in initial phase of soft x-ray ablation due to high energy of absorbed photons (58.5 eV) decomposing and photoionizing of irradiated material. Another explanation might be offered by an efficient photoionization occurring in the irradiated material. The observed red emission could come from a radiative recombination of the charge carriers generated in the material photo-ionized and partly molten by intense 21.2-nm radiation. An origin of the observed visible emission remains open question.

Conclusions. Efficient ablation of PMMA was induced by focused 21.2-nm laser radiation. Ablated surface testifies to micrometer-sized spatial non-uniformity's of focused beam. Thus PMMA ablation represents a promising method for spatially resolved radiometry of soft x-ray laser beams. The quality of ablated surface is very good (sharp edges, no bubbles, no material expansion, etc.) indicating radiation-chemical polymer decomposition as main x-ray ablation mechanisms.

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