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Surface Modification by EUV laser Beam based on Capillary Discharge

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Abstract**—**Many applications require surface modification and micro-structuring of polymers. For these purposes is mainly used ultraviolet (UV) radiation from excimer lamps or excimer lasers. However, these sources have a decided disadvantage - degrading the polymer deep inside due to relatively big radiation penetration depth which may exceed 100 µm. In contrast, extreme ultraviolet (EUV) radiation is absorbed in a layer approximately 100 nm thick only. In this work, the radiation from a discharge-plasma EUV source (with wavelength 46.9 nm) based on a capillary discharge driver is focused with a spherical Si/Sc multilayer mirror for surface modification of PMMA sample or thin gold layer (thickness about 40 nm). It was found that the focused EUV laser beam is capable by one shot to ablate PMMA or layer of gold, even if the focus is significantly influenced by astigmatism.

Keywords**—**ablation, capillary discharge, EUV laser, surface modification

I. Introduction

ABLATION of organic polymers by extreme ultraviolet (EUV) radiation with wavelength shorter than 100 nm is discussed in a relatively small number of publications. It was shown that soft X-ray (SXR) or EUV radiation can be utilized for direct photo-etching and surface modification of materials due to very short absorption length of EUV photons in any material. Photo-etching of inorganic materials is also possible but requires higher EUV fluence in relation to polymers. Poly(butene-1-sulfone) (PBS) [1], polymethylmethacrylate (PMMA) [2]-[4] polyethylene terephthalate (PET) [5] and polytetrafluoroethylene (PTFE) [2], [6] were ablated by incoherent, nonmonochromatic EUV emission from laser-produced plasma. A Z-pinch plasma was used as an EUV source for ablation of PMMA [7]-[8] and PTFE [7]-[9]. The ablation of polymers was also obtained using EUV radiation from a free-electron laser [5] and EUV synchrotron radiation [10]-[11]. In all these cases, photons of EUV radiation have much more energy than the photons from excimer lamps or excimer lasers. Releasing of electron is caused by the absorption of such a high energy photon. In the case of polymers a single photon is capable to break many molecular bonds of a polymer chain, thereby enabling surface modifications of the sample. Some fragments of the chain can then evaporate from the polymer surface. The absorption length of EUV radiation in any materials is rather small and not exceeds approximately 100 nm. The structuring of topography of a polymer surface at micrometer and nanometer scales (e.g. by EUV radiation) can significantly affect its hydrophobicity, wettability, adsorption, adhesive and optical properties, which is of great interest for biomedical and optical industries [4].

In this work we present results of experiments connected with surface modification of organic and inorganic materials with an intense 46.9 nm EUV laser beam with and without EUV optics. At first we studied a surface modification of PMMA by unfocused EUV radiation of our Ne-like Ar^{8+} laser (with wavelength of 46.9 nm, pumped by pulse, high-current capillary discharge). It turned out that at this small fluency level the surface modification by EUV radiation is very weak; on the other hand modification by primary particles (emitted from the capillary) and by secondary ones (originating from interaction of radiation and primary particles with obstacles) is extremely strong (dominates). Therefore, a mechanical shutter was installed to avoid the particles. Simultaneously the spherical Si/Sc multilayer mirror was placed in the vacuum interaction chamber. These changes enabled us to study laser-output-pulse characteristics in visible range [12]. It was found that the far field laser beam profile with a diameter ~5 mm has an annular shape (similarly as in [13]). In case of near field the output laser beam profile with a diameter ~ 0.6 mm has an intense single peak. Furthermore, the beam profile in the region around laser beam waist was influenced by astigmatism. and following studying a surface modification by focused EUV laser beam. In consequence of possible ambiguous interpretation of these results in visible region we are obliged to look for new diagnostic tools. During the later experiments PMMA/gold-covered-PMMA samples were selected as a target for focused EUV laser beam.

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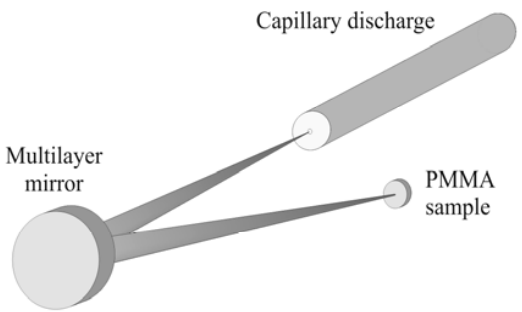

Fig. 1 Schematic presentation of experimental setup used to focus EUV laser beam

II. Experimental Apparatus

The high current flowing through the capillary results in pinching of the Ar plasma to form the hot thin plasma column along the axis. The experimental setup is shown schematically in Fig. 1. The high current pulses used for excitation of the capillary plasma are produced by a Marx generator, coupling section and pulse forming line. This water filled fast capacitor is discharged through a self-breakdown spark gap pressurized with SF_6 gas to the capillary. Significant part of the capillary discharge device is the capillary. At present we use ceramic capillaries made from alumina (Al_2O_3). The ~23 cm long capillary is directly attached to the main spark gap (having one common electrode). The gas filling and pumping part is attached to the outer end of the capillary (through the orifice in the outer electrode). The generated radiation was brought out through ∅0.8 mm orifice in the outer electrode. Typical values of argon pressure inside the capillary prior to breakdown are in the range from 10 Pa to 100 Pa. A pre-ionization current precedes the main discharge (typically it is initiated 10 μs prior to the spark gap breakdown and its current has usually amplitude ~10 A) and it is produced by an independent circuit. A detailed description of our capillary discharge driver CAPEX can be found in the early published paper [14].

A mechanical photographic shutter (with electronic actuator) was placed ~550 mm from the capillary mouth. Its position is a compromise between small beam diameter (requiring as close as possible position to the capillary mouth) and large difference of time-of-flight of light, and of particles (requiring as far as possible position from the capillary mouth). Its function can be seen in the Fig. 2.

The laser beam is focused with a spherical (R=2100 mm) Si/Sc multilayer-coated mirror which was placed in a vacuum chamber ~4200 mm from the capillary mouth. In our first experiments with detection EUV radiation in visible region footprint of the laser beam was on-line registered by a “phosphor” screen (ZnS, density 8 mg/cm2)/photographic camera assembly [12]. Nowadays, the EUV laser beam is visualized by ablation of easily ablative material (PMMA/gold-covered-PMMA samples).

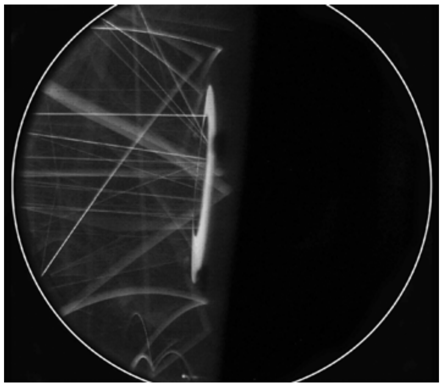

Fig. 2 A side view of the shutter – the time integrated photograph: the ring-shaped capillary light illuminates the opened shutter, the particle traces are blocked by the closed shutter.

III. Experimental Results

A. PMMA with Laser Beam without EUV Optics

At first, the unfocused EUV laser beam was used for surface modification of PMMA sample. In these experiments the target was a layer of PMMA on a Si substrate. The whole target was masked by a Ni grid (step 100x100 μm, free windows 70x70 μm) for easy identification and comparison of exposed and unexposed areas. Three types of experiments were performed that were analyzed by atomic force microscope (AFM). The sample in Fig 3 a) was illuminated by 100 capillary shots with unfiltered axial capillary radiation together with EUV radiation at 46.9 nm. It turned out that the exposed material expands, the surface is getting rough, and the border between exposed and unexposed is relatively well defined. The sample in Fig 3 b) was illuminated by 100 capillary shots with unfiltered axial capillary radiation (similarly as in the previous case), however this time the Ar pressure was little bit changed so that no lasing appeared. It turned out that if the exposed material expands then negligibly only. The boundary is relatively well defined. The sample in Fig 3 c) was illuminated by 280 capillary shots (2.8 times more than in previous cases to compensate the Al filter attenuation) with only unfocused EUV laser beam. Thin (0.4 μm) aluminum filter was placed between capillary discharge and PMMA sample to significantly reduce visible, UV, VUV and EUV radiation. Each 20 shots the Al filter was changed for a new one (to avoid the foil perforation by particle impacts). However, this sample resembles the previous one: no visible effect of illumination by coherent EUV radiation was observed. It seems that volume enlargement of PMMA sample and roughening of its surface is caused by simultaneous/quasi-simultaneous sample illumination by EUV laser beam and incoherent visible, UV, VUV, and EUV radiation. This is the result of breaking of numerous molecular bonds in a polymer chain which is enabled modifications of the PMMA sample surface.

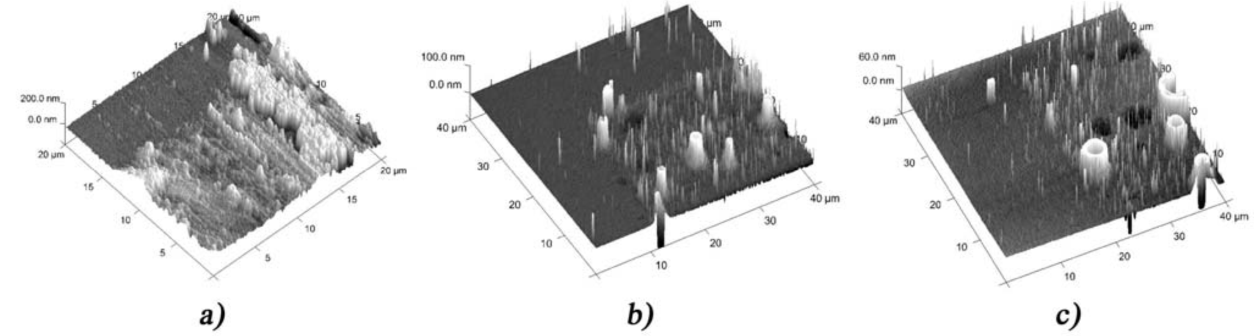

Fig. 3 Illuminated PMMA sample with: a) no Al filter, unfocused laser beam and EUV radiation, b) no Al filter, no laser beam and EUV radiation, c) Al filter, unfocused laser beam and no EUV radiation.

B. PMMA with Laser Beam with EUV Optics

Experiments with ablation of PMMA sample by focused beam of our EUV laser were performed. It turned out that the energy of our laser beam is higher than ablation threshold of PMMA (see Fig. 4). Analysis of these footprints by optical microscope between crossed polarisers shows that the sample has no residual stress caused by local heating. It seems that the ablation is not a result of thermal effects of radiation, but of quantum ones only. It was found that astigmatism of our EUV radiation is very strong, astigmatic difference being ~16 mm. Later it turned out that the distortion of focal spot is caused by distorted mirror shape.

At first, ablated PMMA samples were analysed by scanning electron microscope, but unfortunately this analysis was not successful. Therefore, the analysis of beam footprints by atomic force microscope (AFM) was performed. It was found that ablated part has on its surface more or less contrast periodic structure with period ~2.8 μm and with peak-to-peak depth ~5-10 nm. The last experiment should have answer, how grid with smaller characteristic pattern influences this surface periodic structure. Therefore, PMMA sample was ablated with EUV laser beam through Au grid (step 12.5x12.5 μm, windows 7.5x7.5 μm) by one shot (see Fig. 4 a) and five shots (see Fig. 4 b). Analysis of these laser beam footprints exposed through Au grid was realized by atomic force microscope. Single ablated window with dimensions 10x10 μm (see Fig. 4 c)) obtained by AFM microscope in 3D and 2D is shown that period of the diffraction pattern changes from ~800 nm (at the edge of window) down to ~125 nm (in the middle of the window). A clearly visible diffraction pattern (esp. at the edges) suggests that hardly any melting takes place.

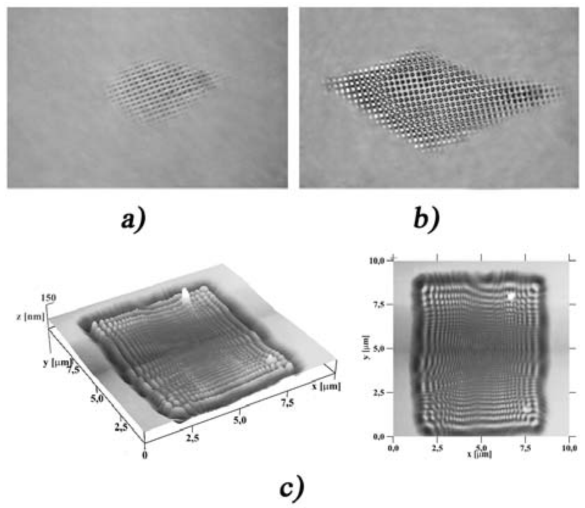

Fig. 4 PMMA samples ablated through Au grid (step 12,5x12,5 μm, windows 7,5x7,5 μm) by: a) one shot of EUV laser and b) five shots of EUV laser – microphotograph, geometrically reflected illumination; ablated single window mapped by AFM in 3D and 2D.

C. Gold Layer with Laser Beam with EUV Optics

As already mentioned, analysis of our first ablated PMMA samples by scanning electron microscope was not successful, but for this analysis the PMMA sample was covered by a thin (~40 nm) layer of gold. Already the first test shots at this layer showed that the energy of our laser is sufficient for ablation of this layer. Gold-covered-PMMA samples were analyzed by AFM microscope. Typical ablated laser beam footprint (~100 μm) at focus (~1427 mm from the mirror) is shown on the left images of Fig. 5. Laser beam footprint (~250 μm) taken far from the focus (~1450 mm from the mirror) has an annular shape similarly as in earlier experiments in visible region (see right image in Fig. 5).

Afterwards, analysis of gold-covered-PMMA samples by AFM microscope in extended modes was performed. Phase contrast on the right-top image in Figure 6 indicates that physical properties of underlying substrate are significantly different from those of the gold film. Analysis of the ablated

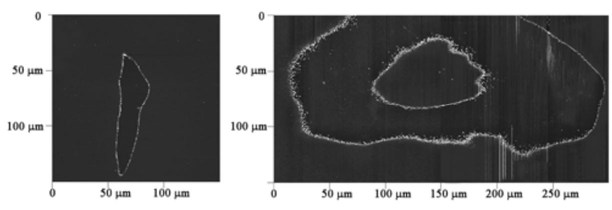

Fig. 5 Analysis of the gold-covered-PMMA by AFM microscope: Left - whole ablated laser beam footprint at focus, Right - whole ablated laser beam footprint out of focus

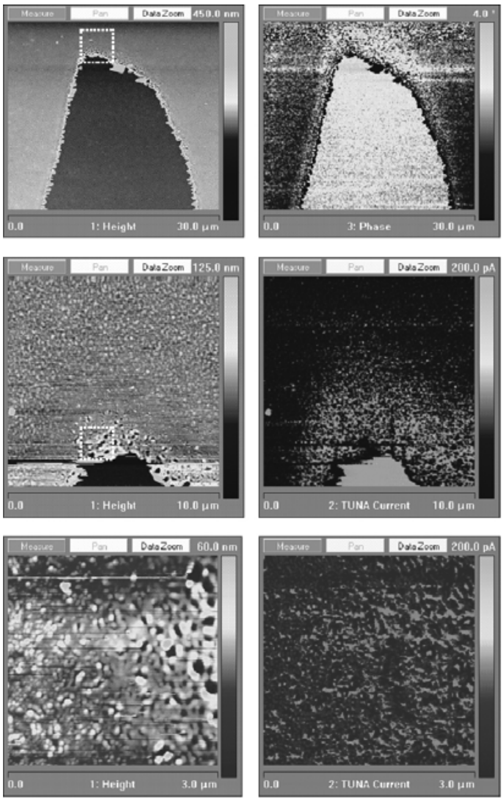

Fig. 6 Analysis of the gold-covered-PMMA by AFM microscope: Top - scaled-up edge of footprint in AFM tapping mode, height (Left) and phase (Right) images, Middle and Bottom- scaled-up edge of footprint in AFM extended TUNA mode, height (Left) and TUNA current (Right) images.

spot in AFM working in extended TUNA mode (in which local conductance was measured) (Middle and Bottom right images in Figure 6) show that the composite area, where gold is intermixed with PMMA, spreads several microns from the border of the laser spot. Any melting effects on the edge of ablated laser beam footprint are not observed. Analysis of the last results with ablation of gold-covered-PMMA confirmed our assumption that in our case the quantum ablation plays a dominant role and the thermal effects are negligible.

IV. Conclusion

Experiments with surface modification of organic and inorganic materials with an unfocused and focused 46.9 nm EUV laser beam were realized. Unfocused radiation does not ablate PMMA sample but results in volume enlargement of PMMA and in roughening of its surface. Energy of focused EUV laser is sufficient for ablation PMMA or gold-covered-PMMA samples by one shot. Analysis of ablated footprints by AFM microscope shows that key role in surface modification of PMMA/gold-covered-PMMA plays quantum effects.

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