Ablation of organic polymers by 46.9-nm-laser radiation

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We report results of the exposure of poly(tetrafluoroethylene) -(PTFE), poly(methyl methacrylate) -(PMMA), and polyimide -(PI) to intense 46.9-nm-laser pulses of 1.2-ns-duration at fluences ranging from ~0.1 to ~10 J/cm^2. The ablation rates were found to be similar for all three materials, ~80–90 nm/pulse at 1 J/cm^2. The results suggest that the ablation of organic polymers induced by intense extreme ultraviolet laser radiation differs from that corresponding to irradiation with longer wavelengths. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1854741]

Ablation of organic polymers by optical radiation, in particular from excimer lasers, has been extensively studied.[1–3] However, polymer ablation induced by extreme ultraviolet (XUV) radiation with wavelength shorter than 100 nm is discussed in only a small number of publications. Poly (butene-1 sulphone),[4] PMMA,[5,6] poly (ethylene terephthalate),[7] and PTFE[5,8] were ablated by incoherent, nonmonochromatic XUV emission from laser-produced plasma. A Z-pinch plasma was used as an XUV source for ablation of PMMA[5] and PTFE.[5,9] Very recently PMMA was efficiently ablated by sub-100-fs pulses of 86-nm-radiation provided by a free-electron laser.[7,10] A large number of studies on direct photoetching of the organic polymers induced by XUV synchrotron radiation were also reported.[11–13] However, according to Haglund's criterion[14] this photoinduced material removal is closer to laser desorption than to laser ablation because of a low peak power of the photon beams delivered by a synchrotron radiation source.

The recent advances in compact high repetition rate XUV lasers[15] producing nanosecond pulses of monochromatic radiation with energy of several hundred micro-Joules opens the possibility to study materials ablation in a new regime. In this letter, we report on the ablation behavior of three common organic polymers: PTFE, PMMA, and PI, irradiated with an intense focused 46.9-nm-laser beam. The ablation processes induced by nanosecond pulses of 46.9-nm-laser radiation are compared with those occurring in the polymer materials irradiated with conventional longer wavelength laser sources.

The samples studied here were 1-mm-thick sheets (Goodfellow) cut into 2.0×5.0 mm^2 chips. The PTFE and PI samples were polished, while the PMMA was used directly with no additional treatment. The samples were placed into vacuum chamber where they were exposed to 1.2 ns FWHM pulses of 46.9 nm radiation from a capillary discharge Ne-like Ar laser.[15] Laser pulses with energy of ~130 μJ were focused onto the sample surfaces by a spherical Sc/Si multilayer-coated mirror[16] with measured reflectivity of ~30%. A motorized positioning system was used to translate the samples along the beam optical axis, as well as in the directions perpendicular to the beam.[17] The former motion allowed us to vary the irradiation fluence by controlling the laser spot diameter on the sample surface, while the pulse energy and duration were kept constant.

Figure 1 shows an optical micrograph of a PMMA sample exposed to three different fluences, with increasing value in the arrow direction. The six craters in each row were formed upon accumulation of 1, 2, 4, 8, 16, or 32 shots at each particular fluence. The horizontal ridges observed in the ablated spots are the result of the shadow produced by the sample holder, which blocks part of the laser beam.[17] The PTFE and PI samples were irradiated in the same way as

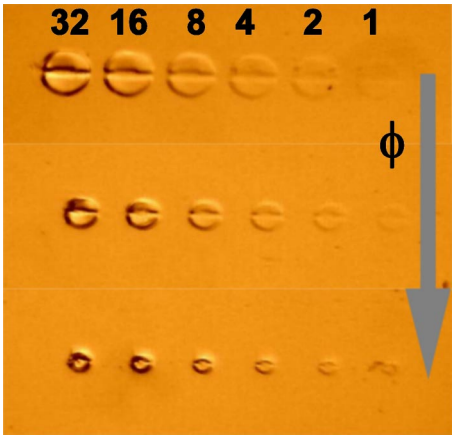

FIG. 1. (Color online) Optical micrograph of a PMMA sample irradiated with 46.9 nm light at three fluences (~1, 2, and 4.5 J/cm^2) with an increasing number of laser shots from 1 (right) to 32 (left). The fluence increases from top to bottom and the number of shots increases from the right to the left.

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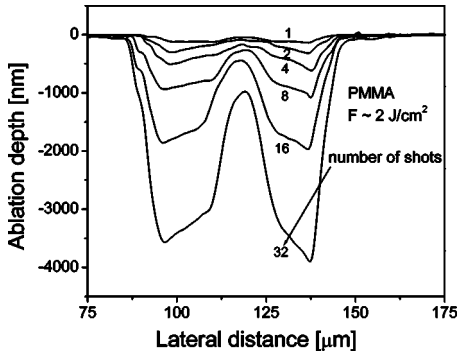

FIG. 2. Profiles of the craters ablated in PMMA by 46.9 nm laser light at a fluence of 2.0 J/cm^2.

PMMA. Cross sections of the ablated craters were measured with a profiler (Alpha Step 500) in the vertical direction crossing the ridges of the unirradiated zones. The irradiation fluence was determined from the laser pulse energy and the ablated area defined as the region where the ablation depth becomes distinguishable from the unexposed surface after the single-shot exposure.

Figure 2 shows a series of ablation profiles for PMMA created by a different number of laser shots at a fluence of 2.0 J/cm^2. The ablation rates evaluated from the measured profiles for all three polymers ablated by either 4 or 32 accumulated pulses are compared in Fig. 3. Numerous previous ablation experiments conducted with UV and VUV excimer laser pulses of nanosecond duration have shown that PTFE, PMMA, and PI differ significantly in their ablation behavior. PI and PMMA belong to groups of strongly and weakly absorbing materials in the UV region, respectively, while PTFE has the first absorption band at $\lambda < 160$ nm. Experiments[18] with even shorter-wavelength emission (157-nm-F_2 laser) have shown efficient ablation of all the polymers of our interest, but the ablation rate as well as the attenuation length, which is generally considered[3,19] to be the parameter that controls the ablation process, still differ from one polymer to another (see Table I). In contrast, the 46.9 nm results summarized in Fig. 3 and in Table I show similar ablation rates within the experimental error for PTFE, PMMA, and PI. This result can be explained by the values of the attenuation lengths for the 46.9 and 157 nm radiation (Table I). While the attenuation lengths are different in all three materials at 157 nm, they are almost the same in PMMA and PI at 46.9 nm. The absorption of 46.9 nm radiation in PTFE is stronger than in PMMA and PI. However, polymer chain scissions by high-energy photons are induced more efficiently[20] in PTFE

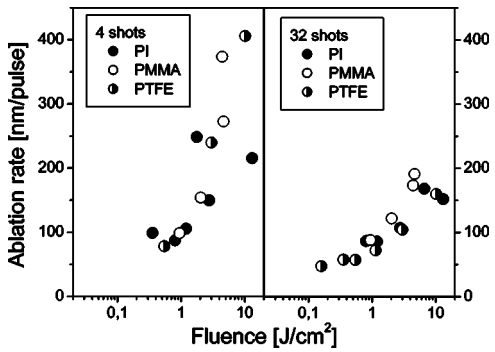

FIG. 3. Ablation rates of PTFE, PMMA, and PI irradiated by a 46.9 nm laser beam as a function of fluence.

TABLE I. Attenuation lengths and ablation rates of PTFE, PMMA, and PI irradiated by 46.9- and 157-nm light. The attenuation lengths at 46.9 nm were calculated from Ref. 26, and the ablation rates were taken from Fig. 3 for 32 laser shots. The values related to the F_2-laser irradiation ($\lambda = 157$ nm) were published in Ref. 18.

	Ablation rate (nm/pulse)		Attenuation length (nm)	
Polymer	46.9 nm ($\phi \sim 1$ J/cm^2)	157 nm ($\phi \sim 300$ mJ/cm^2)	46.9 nm	157 nm
PTFE	83	370	12	172
PMMA	87	260	19	117
PI	88	150	16	79

than in PMMA and PI. This is likely to even out the ablation rate for PTFE with other polymers. This uniformity of ablation rates could be very beneficial for using the XUV laser radiation in direct polymer nanostructuring.

Long-wavelength ablation with a laser fluence ϕ is a threshold process in which the polymer ablation rate d is controlled by a threshold fluence ϕ_{th}:[3]

$$d = 1/\alpha \ln(\phi/\phi_{th}), \tag{1}$$

where α is the absorption coefficient of the material. In contrast with the long wavelength case, at XUV wavelengths the energy of a single photon is sufficient to make a significant damage in polymers. Therefore, a question arises of whether a fluence threshold exists for ablation at 46.9 nm. It is evident from Fig. 3 that the measured ablation rates at this wavelength do not fulfill Eq. (1). The slope is varying with the fluence and there is no well-defined threshold fluence. This suggests the need for establishing a new model describing the ablation rate of polymer ablation by the XUV radiation, especially in the low fluence regime.

It has been previously reported that the quality of ablated surfaces improves as the wavelength of radiation is reduced from the visible-UV range to 157 nm[18,21] and 125 nm,[22] and that at the shortest wavelengths high quality surfaces are obtained even upon irradiation with relatively long (nanosecond) pulses. As illustrated by the AFM image in Fig. 4(a) and optical micrograph in Fig. 4(b), all structures produced in this work for the three polymers were observed to have high-quality surfaces and cleanly cut walls with very well developed sharp edges, not affected by a thermal damage. This is caused by a strong localization of the absorbed energy, i.e., both the attenuation and the thermal diffusion lengths are here very short (~10 nm; see Table I and Ref. 23). The

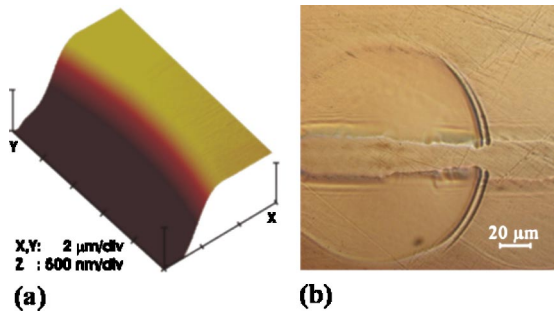

FIG. 4. (Color online) (a) AFM image of the edge of a crater ablated in PMMA by 16 accumulated 46.9 nm laser pulses at a fluence of 2.5 J/cm^2; (b) optical micrograph of the craters ablated in PI at 0.25 J/cm^2 with 32 (left) and 16 (right) laser pulses.

direct, radiation-chemical action of 26.4 eV photons on the structure of molecular solids can be partly responsible for this observation (i.e., only a portion of absorbed energy is thermalized). Experiments conducted on organic polymers with synchrotron radiation[12,24,25] and plasma-based XUV sources[5,7] indicate that the chain scissions are dominant processes in materials irradiated by short-wavelength radiation.

In summary, we have studied the ablation behavior of polymers with an XUV laser with wavelength shorter than 50 nm. The key ablation process is likely to be a radiolysis of the polymer chains by XUV photons, resulting in the formation of numerous small molecular fragments that are subsequently removed from the surface of the samples.

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