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Ablation experiments on polyimide with femtosecond laser pulses

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Abstract. Some applications of polymer films require the microstructuring of partly uneven substrates. This cannot be achieved by conventional photolithography, usually performed with ultraviolet short-pulse lasers (excimer, fourth harmonic Nd:YAG). When processing thermally sensitive or undoped polymers with low optical absorption, the use of femtosecond laser pulses can improve the ablation precision, also reducing the heat-affected zone. Therefore, a Ti:sapphire laser system was employed to perform ablation experiments on polyimide (PI). The irradiated areas were evaluated by means of optical and scanning electron microscopy. Highly oriented ripple structures, which are related to the polarization state of the laser pulses, were observed in the cavities. The relationship between the ablation threshold fluence and the number of laser pulses applied to the same spot is described in accordance with an incubation model.

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Polyimide (PI) plays an important role in many industrial applications because of its highly adaptable properties and good thermal stability. For applications, e.g. in the electronics industry, processing of PI with high precision is needed, which can be performed with lasers. In the past, several polymers have been studied extensively with respect to ns- and fs-laser machining [1–3]. The ablation threshold fluence for fs-laser ablation is reduced compared to the application of ns-laser pulses of the same wavelength [1]. It has also been demonstrated, that transparent polymers can be laser processed with ultrashort laser pulses. This indicates that nonlinear absorption [2] and/or incubation effects play an important role. The exact ablation mechanism is still under discussion. In this paper we present ablation results of PI-foils.

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1 Experimental

A commercial Ti:sapphire laser system (Spectra Physics) with a wavelength of 800 nm and pulse energies up to 750 μJ was used for ablation experiments in air. The laser pulses were applied to the front side of the targets by the direct focusing technique, using plano-convex lenses with focal lengths f of 60 mm and 25.4 mm. Pulse durations of 150 fs were determined by a scanning autocorrelator (APE, PulseScope). The laser radiation was linearly polarized and could be changed to circular polarization by using a zero-order quarter-wave plate. The pulse energies were measured by a pyroelectric detector (BESTEC, PM 200). Polymer foils (PI (Kapton), Goodfellow, thickness 250 μm, absorption coefficient $\alpha(\lambda = 800\,\text{nm}) \approx 23\,\text{cm}^{-1}$) were mounted perpendicularly to the laser beam on a motorized x-y-z translation stage. A repetition rate of 2 Hz was chosen.

The irradiated areas were investigated by means of an optical microscope (Reichert-Jung, Polyvar) and a scanning electron microscope (SEM, Hitachi S-4100).

2 Results and discussion

Pulse laser illumination of polymers creates various material modifications up to ablation [3]. In general, the maximum laser fluence ϕ_0 must exceed a certain threshold value to cause an irreversible change in the surface. This modification threshold fluence ϕ_{th} depends essentially on the material and the number of laser pulses N applied to the same spot. It can be determined from the lateral extent of the laser-generated surface modifications processed with different laser fluences. For laser pulses with a Gaussian spatial beam profile, the maximum laser fluence ϕ_0 on the sample surface and the diameter D of the modified area are related by [4]

$$D^2 = 2\omega_0^2 \ln\left(\frac{\phi_0}{\phi_{\text{th}}}\right), \quad (1)$$

with ω_0 being the $1/e^2$ beam radius. The maximum laser fluence ϕ_0 can be obtained from the Gaussian beam radius and

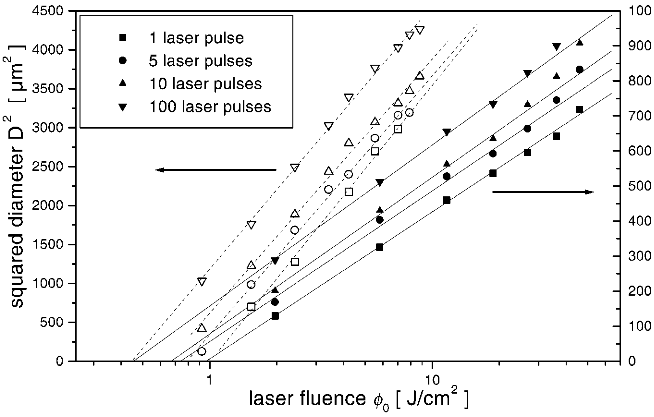


Fig. 1. The squared diameters D^2 of the modified areas versus the maximum laser fluence ϕ_0 for circularly polarized laser pulses. ($\tau = 150$ fs, $\lambda = 800$ nm; *solid symbols*: $f = 25.4$ mm, right y-axis; *open symbols*: $f = 60$ mm, left *y*-axis)

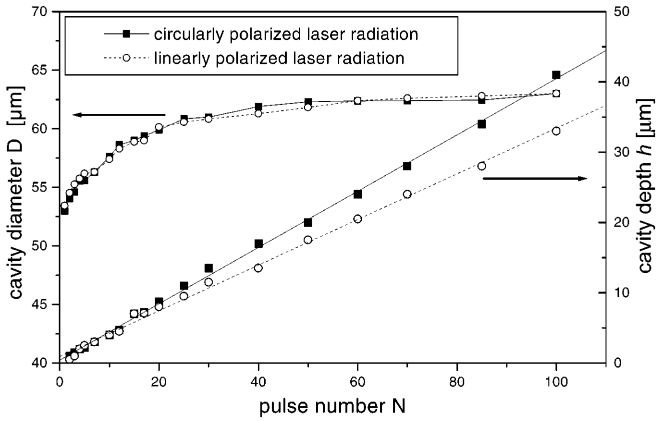


Fig. 2. The depths h and the diameters D of laser-generated cavities for linearly and circularly polarized laser pulses depending on the number of applied laser pulses N ($\tau = 150$ fs, $\lambda = 800$ nm, $\phi_0 = 1.3$ J/cm^2, $f = 60$ mm)

the measured pulse energy E_{pulse} by

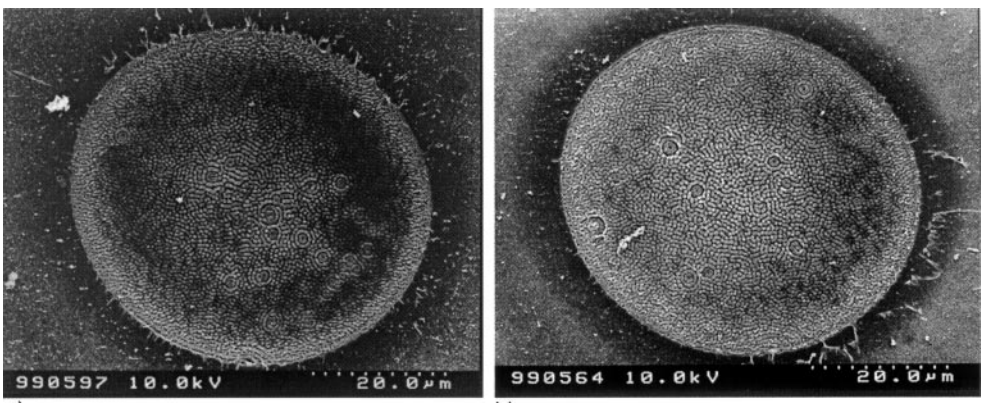
$$\phi_0 = \frac{2E_{\text{pulse}}}{\pi\omega_0^2}. \qquad (2)$$

In order to estimate the beam radius ω_0 a graph (not shown here) depicting the squared diameter D^2 as a function of the logarithm of the pulse energy E_{pulse} can be used due to the linear relation between E_{pulse} and ϕ_0 (1, 2). The slope of a linear fit according to (1) yields the Gaussian beam radius ω_0. A value of $\omega_0 = 8$ µm was found for the focal length $f = 25.4$ mm and $\omega_0 = 27$ µm for $f = 60$ mm. With the known beam radii the laser fluence ϕ_0 in front of the surface can be calculated from (2). Figure 1 shows the squared diameter D^2 of the modified areas versus the laser fluence ϕ_0 for circularly polarized pulses with a duration of 150 fs. By extrapolation of the fits to $D^2 = 0$, the modification threshold fluence ϕ_{th} can be determined. This threshold decreases for an increasing number of laser pulses. Values between $\phi_{\text{th}}(1) = 1.0$ J/cm^2 for single pulse modification and $\phi_{\text{th}}(100) = 0.5$ J/cm^2 for 100 applied laser pulses were observed (Fig. 1). Experiments with different focal lengths result in the same modification threshold fluences. This might be expected, owing to the nonexisting plasma shielding for fs-laser ablation [5]. The same threshold fluences were also observed for linearly polarized pulses.

For further investigations the pulse number N was systematically varied for both polarization states. In each series the pulse number was increased from $N = 1$ to $N = 100$ at a fixed laser fluence of $\phi_0 = 1.3$ J/cm^2. Figure 2 shows the diameter D and the depth h of the modified areas versus the number of laser pulses N. The diameters are the same for both polarizations. D changes significantly during the first 30 laser pulses. For $N > 30$ the diameters are nearly constant.

The cavity depth h increases for circular polarization, indicating a higher ablation rate compared with linear polarization. Average ablation depths per pulse d of 0.40 µm (circular polarization) and 0.32 µm (linear polarization) were obtained at the same laser fluence (slope of the linear fits in Fig. 2).

Inspection of the laser-generated cavities in PI shows the formation of periodic surface structures that depend on the polarization state of the laser beam. For a small number of applied laser pulses ($N < 5$) with a fluence above the single pulse modification threshold, the surface shows an irregular pattern (see Fig. 3a,b; $\phi_0 = 1.3$ J/cm^2). No significant differences were observed in the patterns by using linearly or circularly polarized laser pulses. With an increasing number of applied laser pulses ($N > 5$), different behaviors were seen for the two polarization states. Figure 4a shows an SEM picture of a cavity generated with $N = 50$ pulses of linearly polarized radiation. At the bottom of the crater highly oriented ripples with a period of ~ 0.8 µm were observed (comparable to the



a) b)

Fig. 3a,b. SEM pictures of the modified PI surface after irradiation with **a** linearly and **b** circularly polarized laser pulses ($N = 3$, $\tau = 150$ fs, $\lambda = 800$ nm, $\phi_0 = 1.3$ J/cm^2, $f = 60$ mm). No significant differences were observed

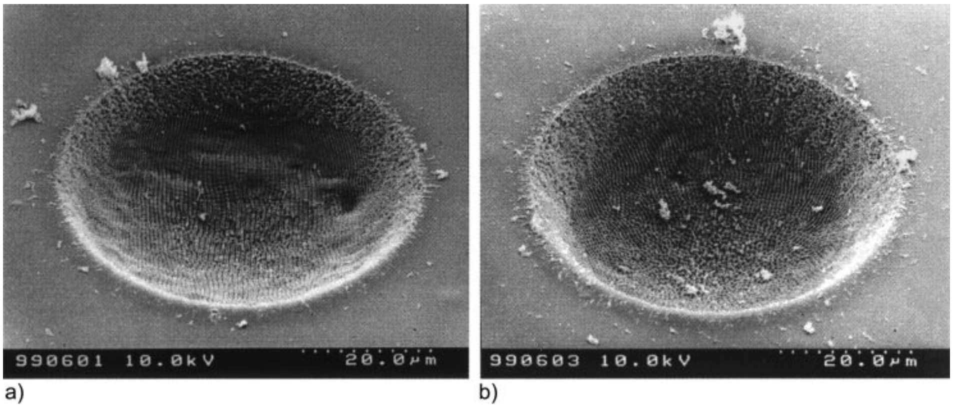


Fig. 4a,b. SEM pictures of the irradiated areas, obtained with 50 laser pulses: **a** linear polarization (vector of electric field is parallel to the periodic structure); **b** circular polarization of the laser pulses ($\tau = 150$ fs, $\lambda = 800$ nm, $\phi_0 = 1.3\,\mathrm{J/cm^2}$, $f = 60$ mm, visual angle 60°). The structures formed show the same period in both cases, but differ in direction

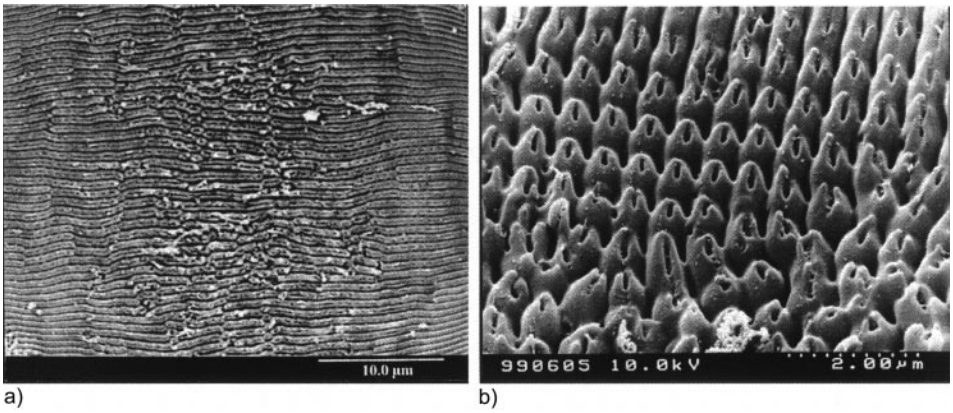


Fig. 5a,b. SEM picture of the central part of Fig. 4a and Fig. 4b in greater detail: **a** linear polarization and **b** circular polarization. The formation of small grooves and holes can be noticed in the parallel (**a**) and cone structures (**b**)

laser wavelength). The ripple orientation was always parallel to the vector of the electric field. This was verified by rotating the sample in steps of 20° around the beam axis. In the outer region the ripples are very smooth and straight. In the centre of the hole each ripple splits into two parts, showing a small groove in the middle (see Fig. 5a). The wall of the cavity has a rough appearance without ripples. No significant material redeposition in the surroundings of the ablated areas was observed. The correspondence between the ripple period and the laser wavelength is well known, but for the observed direction we obtained different results from those published for PI in [6] and from other materials like metals and ceramics [7]. Ripples parallel to the electric field vector have also been reported for fused silica [8].

In the case of circularly polarized light, the ripple pattern is radially oriented (Fig. 4b). A weak formation of separated domains can be observed, which are distinguished by slightly different ripple orientations. The ripples have the same period as those shown in Fig. 4a. The morphology changes to an array of small cones (depicted in Fig. 5b) towards the centre of the cavity bottom. At the top of each cone a small hole can be seen. A cone formation in PI has previously been observed at different wavelengths [9, 10], and has been explained by shielding and diffraction effects induced by impurities in the sample. The exact mechanism is not clear, but we assume a similar explanation with respect to the structures in Fig. 4b and Fig. 5b.

For an empirical description of the incubation behavior, i.e. the dependence of the modification threshold fluence on the number of applied laser pulses, an accumulation model has been introduced for ns-laser pulse irradiation of highly absorbing materials such as metals [11]. It yields a relation between the single pulse threshold fluence $\phi_{\mathrm{th}}(1)$ and the threshold fluence $\phi_{\mathrm{th}}(N)$ for applying N laser pulses to the same spot by

$$\phi_{\mathrm{th}}\,(N) = \phi_{\mathrm{th}}\,(1)\,N^{\xi-1}, \tag{3}$$

which is also valid for fs-laser pulses [12, 13] and ceramic materials [7]. The exponent ξ characterizes the degree of incubation. A value of $\xi = 1$ indicates that the ablation thresh-

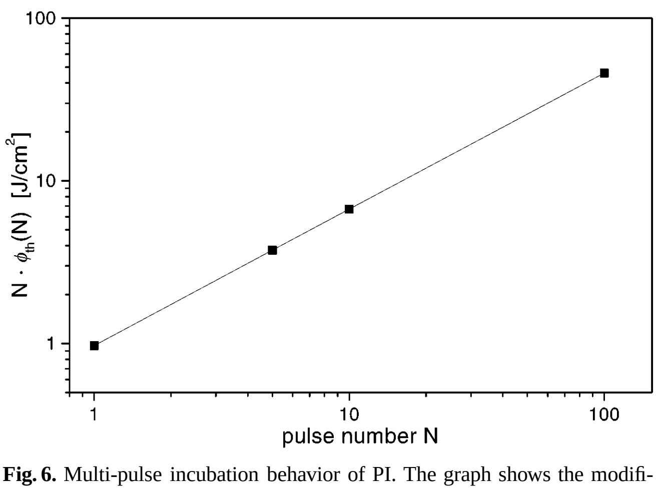


Fig. 6. Multi-pulse incubation behavior of PI. The graph shows the modification threshold fluence $\phi_{\mathrm{th}}(N)$ multiplied by the number of applied laser pulses N versus N in a double-logarithmic plot (see (3)). The slope yields the incubation exponent ξ

old does not change with the pulse number N. It is interesting to note that the determined modification thresholds for PI are in good agreement with this model (Fig. 6). An incubation exponent of $\xi = 0.87$ can be deduced from the slope of the fit in Fig. 6. The validity of (3) was also checked for other polymers (PC, PMMA [14]) The value of the incubation exponent for PI differs from the estimated ones for PC and PMMA ($\xi \approx 0.7$) and is comparable to those of metals [12, 13]. This implies that (3) describes the threshold behavior of different materials in a general way.

3 Conclusion

In this paper we report on ablation experiments on PI foils with ultrashort laser pulses (150 fs) in air. It was observed that circularly polarized radiation enhances the average ablation depth per pulse by a factor of 1.3. The surface morphology depends on the polarization state of the laser pulses. The modification threshold fluences were determined for different pulse numbers ($N = 1...100$). Values between $1.0\,\mathrm{J/cm^2}$ for single-pulse laser ablation and $0.5\,\mathrm{J/cm^2}$ for the application of 100 laser pulses were observed. The surface modification threshold for multi-pulse irradiation could be described in accordance with an incubation model.

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