Femtosecond Laser Processing of Soft Materials

Steffen BAUDACH, Jorg KRUGER, and Wolfgang KAUTEK Laboratory for Thin Film Technology
Federal Institute for Materials Research and Testing Unter den Eichen 87, D-12205 Berlin, Germany

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Ablation of polymer films such as polyimide, polycarbonate, polyethylenterephthalate, polytetrafluoroethylene and polymethylmethacrylate were investigated with a Ti:sapphire laser system (150 fs, 800 nm). The single pulse threshold increased from 1.0 Jcm-2 of polyimide to 2.6 Jcm-2 of polymethylmethacrylate. This correlates with the increase of the optical band gap suggesting a multi-photon absorption mechanism. All polymers show incubation effects. A stronger incubation could be found for polycarbonate, polyethylenterephthalate, and polymethylmethacrylate in contrast to the "inert" polymers polyimide and polytetrafluoroethylene due to irre-versible chemical alterations. All polymers except polyimide exhibited melting and the generation of vapour yielding swelling. Polyimide only sublimates and/or degrades. Ripples parallel to the electric field vector were generated with linear polarization of repeated laser pulses whereas circular polarization resulted in nanostructure arrays of the order of 100 nm.

Key Words: Femtosecond pulse laser, Laser processing, Polymer ablation, Nanostructures

1. Introduction

Applications of polymer films e.g. in electronic or medical
technologies require the microstructuring on uneven substrates.
This cannot be achieved by conventional photolithography which
only functions on completely flat supporting materials. Ultra-
violet short-pulse lasers (excimer, 4ƒÖ Nd: YAG) have been widely
used for such purposes.1) However, when high precision is re-

quired and substrates are extremely fragile and thermally sensi-
tive, the very low heat effect by sub-picosecond laser pulses can
avoid this micromachining problem. A solution to charring of
circuitry boards, particularly when cutting through copper, may
be cold drilling with UV ns-lasers or NIR fs-lasers. Lasers may
be effective on high-glass-transition substrates such as
polytetrafluoroethylene, polyimides, and polyesters. There is a
good chance that laser drillers in these applications will replace
mechanical tools.
Ablation experiments on various polymer films such as
polyimide (PI), polycarbonate (PC), polyethylenterephthalate
(PET, amorphous and crystalline), polytetrafluoroethylene
(PTFE) and polymethylmethacrylate (PMMA) were performed
with a Ti:sapphire laser system (150 fs, 800 nm) and are re-
viewed in this paper.2-5)

2. Experimental

A Ti: sapphire laser system (Spectra Physics, Tsunami and Spit-
fire) delivering 150-fs pulses of energies up to 0.8 mJ at ƒÉ=800
nm wavelength was used for the ablation experiments. The pulse
duration ƒÑ was measured with a scanning autocorrelator (APE,
PulseScope). The repetition rate of the laser pulses was limited

to 2 Hz. The pulse energy was changed with a combination of a
half-wave plate and a linear polarizer and could be determined
with a pyroelectric detector (BESTEC, PM 200).
Bursts of pulses with a predefined number (N) could be se-
lected with a pulse picker. The linear polarization at the laser
output could be changed to a circular one by means of a zero-
order quarter-wave plate. The laser pulses were directly focused
on the target (angle of incidence 0•‹) with an f=60 mm or an f=
25 mm focusing length lens in air, respectively. The target could
be moved with a motorised x-y-z-translation stage (LOT).
Different polymer foils (250 ƒÊm thick) like polyimide (PI),

polycarbonate (PC), polyethylenterephthalate (PET, amorphous
and crystalline), polytetrafluoroethylene (PTFE) and

polymethylmethacrylate (PMMA) were investigated (all from
Goodfellow Cambridge Ltd, Huntington). The respective poly-
mer units are depicted in Fig. 1 and a list of relevant physico-
chemical properties are listed in Table 1.
After laser treatment of the samples, the diameters D of the
ablation craters and the depth of the laser-induced cavities were
measured by means of an optical microscope (Reichert-Jung,
Polyvar). Scanning electron micrographs were obtained on a
scanning electron microscope (SEM, Hitachi S-4100) equipped
with a cold-field electron emission cathode at an accelerating
voltage of 10 kV.

3. Results and Discussion

Pulse laser illumination of polymers creates various material
modifications up to ablation. In general, the maximum laser
fluence F has to exceed a certain threshold value to cause an
irreversible change at the sample surface. Fig.2 depicts the

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Fig. 1 Polymer units of polyimide (PI), polycarbonate (PC), polyethylenterephthalate (PET), and polymethyl-
methacrylate (PMMA).

squared diameters D2 of the modified areas on polyimide in de-

pendence on F in a semi-logarithmic plot for two different fo-cusing conditions of the pulses. For laser pulses with a Gaussian spatial beam profile, D2 and F are related by6)

(1)

Fig. 2 Squared diameters D2 of the modified areas of
polyimide in dependence on the maximum laser
fluence F for circularly polarized laser pulses. ƒÑ=
150 fs, ƒÉ=800 nm. Solid symbols: focusing with f
=25 mm lens, right axis. Hollow symbols: focusing
with f=60 mm lens, left axis.

with the 1/e2 Gaussian beam radius ƒÖ0=27 ƒÊm (f=60 mm) and ƒÖ0 =8ƒÊm (f=25 mm). The determination of ƒÖ0 and the rela-
tion between ƒÖ0 and F has been described in detail.2-5) The ex-
trapolation of the curves to D2=0 result in the identification of
modification or ablation thresholds Fth. It can be clearly stated
that the modification thresholds Fth do not depend on the focus-
ing conditions of a fs-laser treatment and that Fth is influenced
by the number of pulses per spot N due to incubation effects. In
the past, a phenomenological model describing a relation be-
tween the single pulse threshold Fth(1) and the multi-pulse thresh-
old Fth(N) in the form

(2)

Table 1 Physico-chemical polymer properties. a-PET: amorphous polyethylenterephthalate, c-PET: crystalline poly-
ethylenterephthalate, a-PTFE: amorphous polytetrafluoroethylene. Tm: Melting Temperature, Tg: Glass Temperature,
•¢ Hm: Melting Enthalpy, Tb: Boiling Temperature, •¢Hv: Vaporization Enthalpy, ƒÏ: Mass Density, cp: Specific Heat,
k: Thermal Conductivity, ƒ¿: Absorption Coefficient, nD: Refractive Index, WA: Water Absorption (>24h), OC: Oxygen
Content (23•Ž).

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with a material-dependent incubation parameter ƒÌ was estab-
lished for highly absorbing materials like metals and nanosec-
ond pulse laser structuring.7) ƒÌ=1 means that no incubation
effect is observable. It could be shown that the applicability of
this model can be extended down to the femtosecond scale for
metals8) and even for polymers.3) This is demonstrated in Fig.3
for polycarbonate (PC) and polyimide (PI). A calculation yields
ƒÌ =0.74 (PC) and ƒÌ=0.87 (PI), respectively. A summary of all
Fth(N) and ƒÌ values of the polymers under investigation is given

in Table 2.

The polarization state of the laser light with repetitive pulses
shows a strong influence on the micro- and nanomorphology of
the machining result. This is illustrated for polyimide in Fig.4
and 5. Singular pulses and a limited number of pulses per spot
(N<5) with different polarization states (linear, circular) result
in the same irregular surface pattern.2) For N>5, however, this
behaviour changes significantly. For linear polarization, 50
pulses per spot generated an ablation crater (Fig. 4a) with highly
oriented ripples at the bottom (Fig. 4b). The ripples exhibit a

period comparable to the laser wavelength and their orientation
was always parallel to the electric field vector. This was con-
firmed by a rotation of the sample with respect to the beam axis.
Circular light polarization, on the other hand, caused a radial
orientation of the ripples with a period of 0.8 ƒÊm (Fig. 5a). Addi-
tionally, the morphology changed to an array of cones in the
nanometer range (Fig. 5b). Nanostructure array formation in
polyimide could also be observed under nanosecond pulse laser
irradiation.9)
The fs-laser-induced structures on polyimide can be explained
by the fact that this polymer shows practically no melting but
sublimates paralleled with degradation (Table 1). It shows the

Fig. 3 Multi-pulse incubation behaviour of polycarbonate
(•¡) and polyimide (•›). Accumulated laser fluence
N•~F(N) vs. number of laser pulses per spot N. ƒÑ=
150 fs, ƒÉ=800 nm.

Table 2 Modification thresholds Fth(N) and incubation pa-
rameters ƒÌ.

(a)

(b)

Fig. 4 Femtosecond-pulse laser ablation of polyimide in air.
ƒÑ =150 fs, ƒÉ=800 nm, F=1.3 Jcm-2, N=50, linear

polarization. (a) Total aspect, (b) detail.

(a)

(b)

Fig. 5 Femtosecond-pulse laser ablation of polyimide in air.
ƒÑ =150 fs
, ƒÉ=800 nm, F=1.3 Jcm-2, N=50, circular
polarization. (a) Total aspect, (b) detail.

smallest optical gap and the highest refractive index nD of all
materials under study. The comparatively high refractive index
supports beam refraction and the above described ripple forma-
tion.
In contrast to polyimide, polycarbonate, polymethylmethacry-
late, and polytetrafluorethylene exhibit higher optical bandgaps

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and can melt before they vaporize (Table 1). Accordingly, the ablation behaviour deviates from that of polyimide. Both poly-carbonate (Fig. 6a) and polymethylmethacrylate (Fig. 7a) show an increase of volume after a single pulse in a fluence range of more than 2 Jcm-2 above the modification threshold. This is due to the formation of systems consisting of three phases, liquid (melt) and gaseous in addition to solid. Partial gasification led to bubbles in the melt phase, which were frozen after resolidification of the liquid phase. The vaporisation may rely on degradation such as the bond breaking between oxygen bridges and carbonyl groups. This conclusion was also drawn for analogous results at PMMA after nanosecond laser treatment at 308 nm.10) The integrated volume of PMMA increased almost linearly with F.3) A flattop surface profile was reached at 3.3 Jcm-2 and material removal started in the central spot region at >4.8 Jcm-2. Repeated pulses removed the spongy volume and a crater was formed (Fig. 6b, c and Fig. 7b, c).
The single pulse threshold increased from Fth(1)=1.0 Jcm-2 of PI to 2.6 cm-2 of PMMA (Table 2). This trend goes along with the increase of the optical band gap. This suggests that a multi-photon absorption plays a crucial role. The smaller the band gap the less photons are needed to overcome it.11,12) That

(a)

(b)

(c)

Fig. 6 Femtosecond-pulse laser ablation of polymethyl-
methacrylate in air. ƒÑ=150 fs, ƒÉ=800 nm, F=3.0
Jcm-2, linear polarization. (a) N=1, (b) N=5, (c) N =100
.

means that the probability of absorption becomes greater for ma-
terials like PI and PET in comparison to PC, PTFE and PMMA
(Table 1).

The behaviour of the incubation parameters ƒÌ deviates from
that of Fth(1) in respect to the band gap. A stronger incubation
was observed for PET, PC, and PMMA in contrast to the "inert"

polymers PI and PTFE. The ester bonds in PC, PET and PMMA
show much less stability than e. g. the CO-N or ether bridges in PI towards repeated laser pulsing.

4. Conclusions

Cavities could be generated on polyimide, polycarbonate,
polyethylenterephthalate, polytetrafluoroethylene and
polymethylmethacrylate with smaller diameters than the quasi-
Gaussian 1/e2 diameter of the beam. Diameters D changed sig-
nificantly during the first 50-60 pulses. The ablation rates per

pulse were of the order of<1 ƒÊm.
The single pulse threshold increased from 1.0 Jcm-2 of PI to
2.6 cm-2 of PMMA. This trend goes along with the increase of
the optical band gap suggesting a multi-photon absorption mecha-
nism.

(a)

(b)

(c)

Fig. 7 Femtosecond-pulse laser ablation of polycarbonate
in air. ƒÑ=150 fs, ƒÉ=800 nm, F=3.0 Jcm-2, linear
polarization. (a) N=1, (b) N=5, (c) N=100.

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Incubation effects were observed for all polymers, i. e. Fth de-
creased with the number of pulses N. A stronger incubation was
observed for PET, PC, and PMMA in contrast to the "inert" poly-
mers PI and PTFE. The ester bonds in PC, PET and PMMA
show much less stability than e.g. the CO-N or ether bridges in
PI towards repeated laser pulsing.
All polymers except PI showed melting together with the gen-
eration of volatile substances yielding small bubble holes and
swelling. PI does not melt and swell because it only sublimates
and/or degrades. The remaining material forms periodical sur-
face structures. Linear polarization of repeated laser pulses
caused ripples parallel to the electric field vector. Circular po-
larization resulted in nanostructure arrays of the order of•`100

nm.

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