Femtosecond-Laser-Assisted Wet Chemical Etching of Polymer Materials

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ABSTRACT: Polymers are modified by femtosecond-(fs)-IR-laser irradiation under various process parameters. Several sorts of thermoplastic polymer are employed: polymethylmethacrylate (PMMA), fluorinated PMMA, poly-N-methyl methacrylimide (PMMI), polystyrol, polycarbonate, polyimide, and polyethylene. After the fs-laser-induced modification process, the irradiated area is developed by an aqueous solution of a solvent agent (n-hexane, benzene, and methylisobutylketone). The surface topography of the fs-laser-irradiated area is characterized by stylus-profilometry before and after the development procedure. Some preliminary explanations are given about the solution mechanism of the fs-laser-irradiated polymer region. The experimental results are relevant for the fabrication of three-dimensional (3D)-structures in the volume of a transparent polymer material by fs-laser irradiation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1229–1238, 2006

Key words: surface; laser ablation; microstructuring; modification; solution properties

INTRODUCTION

Nanosecond-(ns)-UV-excimer lasers are often employed for microstructuring of the surface of polymer materials by laser ablation.[1–2] But by this method, it is not possible to fabricate three-dimensional (3D)-structures like channels inside the volume of a transparent polymer substrate due to its strong material absorption at the surface layers of the polymer substrate. In contrast to the ns-UV-laser irradiation, transparent polymer materials can be easily processed inside the substrate volume by femtosecond-(fs)-IR-laser irradiation. The focus of the fs-laser beam is positioned inside the polymer substrate volume. In the focus zone, the laser power becomes very high and the polymer material gets modified due to nonlinear effects like multiphoton-absorption.[3–4] It is expected that the fs-laser-assisted modification process yields the formation of small polymer defragmentation products. However in the substrate volume, ablation is difficult to be induced by laser radiation because no material can be removed from inside the polymer substrate.

In this study, another approach is proposed to fabricate 3D-structures in a transparent polymer substrate by a novel fs-laser-assisted wet chemical etching procedure. It is expected that the solubility of the polymer substrate in the fs-laser-irradiated area is enhanced by the fs-laser light due to the formation of small polymer defragmentation products. This process is called modification process. Thus after the fs-laser irradiation the modified area can be solved by a suited solution agent and so a 3D structure can be realized. The subsequent chemical treatment of the fs-laser-irradiated and -modified area is called development. Both the laser-assisted modification and the subsequent development are called laser-assisted wet chemical etching process. However, most polymer materials are strongly swollen by the common solution agents, and so it is not possible to generate fine 3D-structures by this method. Besides in this context, ablation is considered as an undesired and negative side effect, because the formation of volatile matters in the bulk of polymer material causes serious damage inside the polymer substrate. Consequently, it is necessary to find a polymer material that becomes modified and soluble, but not ablated by fs-IR-laser radiation, and to find out the best combination between a polymer material and a solution agent as well as the optimum process parameters by which no swelling occurs during development. For this purpose, fs-IR-irradiation and solution experiments are done at the surface of different polymer substrates: the substrate surface of several polymer samples are irradiated by fs-IR-laser radiation, and thereafter, solution tests are performed. The principal aim of the experiments is the
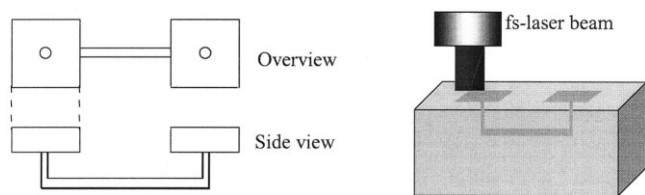
Figure 1 Schematic illustration of a simple 3D structure with an opening connected to the substrate surface[5].

Figure 2 Experimental set-up of the fs-IR-laser illumination facility with scanning unit of the sample holder (xyz-stage).

modification of the polymer material becoming more soluble without any ablation occurring and also matching the requirements of nonswelling during development, thus the microstructure should be bordered by sharp edges after the etching process, especially after the development. Later, the results of the preliminary experiments are used for the fabrication of sharply edged 3D-structures inside the substrate volume with an opening connected to the surface (Fig. 1).[5] Finally, such a very simple 3D-microstructure sample is presented in this article.
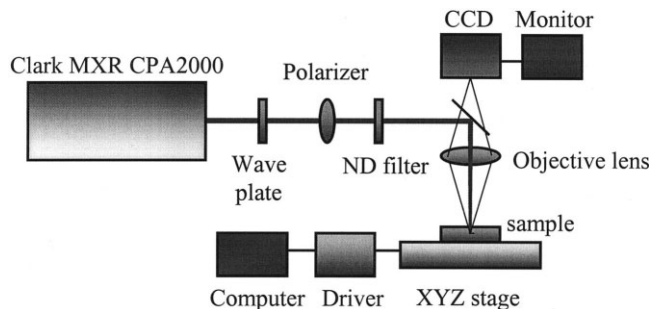
The experiments are analogous to the ones performed by Masuda et al. and by Cheng et al.,[5–7] but instead of costly photosensitive glass (Foturan) and noxious hydrofluoric acid an inexpensive polymer material and a nonhazardous solvent agent are employed. The principal aim of this work is to find out the optimum material combination.

Several papers are published about the fs-laser-assisted proceeing of nonfluorinated polymethylmethacrylate (PMMA).[8–13] However, there are only few reports about other polymeric materials treated by fs-laser irradiation.[14–15] The fs-laser-assisted wet chemical etching of transparent polymers permits the manufacturing of 3D-structures like microfluidic channels inside the substrate bulk. Thus, by combination with optical microstructures like waveguides or gratings, the realization of a microfluidic chip with integrated optical elements for diagnostic purposes (e.g., fluorescence spectroscopy) becomes possible.

Experimental set-up

The following sorts of polymers are employed for the irradiation experiments: PMMA, fluorinated PMMA, poly-*N*-methyl methacrylimide (PMMI), polystyrol (PS), polycarbonate (PC), polyimide (PI), and polyethylene (PE). All polymer sorts are thermoplastics with different polarity characteristics (Table I). The polymer samples have a rectangular shape and the substrate surfaces are polished. As a fs-laser source, a fiber laser of the type Clark-MXR CPA 2000 is employed featured by the following technical specifications (Fig. 2): pulse duration, 150 fs; central wavelength, 775 nm; maximum single pulse energy, 800 μJ; and maximum repetition rate, 1 kHz. The laser pulse energy is adjusted by an attenuator. The fs-laser beam is focused by an optical micro-objective with a numerical aperture NA of 0.35 yielding a focus diameter $d_{\text{focus}} = 1.22\ \lambda/\text{NA} = 1.22 \times 775\ \text{nm}/0.46 \approx 2.05\ \mu\text{m}$. By a CCD camera system, the focus of the fs-laser beam can be positioned directly on the planar surface of the polymer substrate. The polymer sample is fixed on a substrate holder that is located on a xyz stage, and so the polymer sample can be moved in all three directions. By the right choice of the pulse energy and by focusing the fs-laser beam directly on the polymer surface, the right movement (translational movement in x-direction with a speed of 20 μm/s) yields a strip area in which the polymer surface is modified.

After the fs-laser irradiation, the modified area is solved by an aqueous solvent agent. Several solvent agents with different polarity are chosen (Table II): pure *n*-hexane as a nonpolar solvent agent, pure benzene as a minor polar solvent agent, and a 5% aqueous solution of methylisobutylketone (MIBK) as a polar solvent agent. Higher concentrations of the aqueous MIBK solution as well as aqueous ethanol and isopropanol solutions with any concentrations yield dissatisfactory results because of their aggressive impact on the sample surface and huge swelling of the polymer material. Methanol was not taken into consideration

TABLE I
Polarity of the Thermoplastic Polymers Used in the Laser-Assisted Wet Etching Experiments

Thermoplastic polymers	Polarity
PMMA	+
FluorinatedA PMMA	+
PMMI	+
PS	o
PC	+
PI	+
PE	−

+, highly polar; o, slightly polar; and −, nonpolar.

Solvent agent	Polarity
n-Hexane	−
Benzene	o
5% aqueous solution of MIBK	+

+, highly polar; o, slightly polar; and −, nonpolar.

because of its toxicity. MIBK was chosen as a sample polar solvent agent because it is a well-known solvent agent for polymers.[16–18]

The development process is quite simple: the laser-irradiated polymeric sample is inserted into a glass box filled by the solvent agent, and then the glass box is put in an ultrasonic bath. The development process takes place at room temperature ($T = 20°C$). Preliminary experiments have shown that already after 0.5 min, the results of the experimental development procedure do not change any more, but the bath takes 10 min to guarantee the complete removal of the residues. After the development, the sample was rinsed by distilled water.

The groove depth in the fs-laser etched area of the polymer substrate is measured in dependence on the laser pulse power by a commercially available stylus-profilometer (KLA tencor α-step 200) before and after the development. By this method, it is possible to examine the laser-irradiated polymer solution and swelling properties. Other measurement techniques like AFM are more precise but not featured with a sufficient measurement range. Before the actual depth measurements start, some preliminary experiments are performed to find out the optimum measurement

parameters like scanning velocity. A lower velocity than 400 μm/s does not change the results significantly. A sample groove depth measurement is shown in Figure 3.

The quality of the processed polymer surface is also examined by Optical Light Microscopy (OLM).

RESULTS AND DISCUSSION

Polymethylmethacrylate

The ablation groove depth of nonfluorinated PMMA strongly depends on the laser pulse power [Fig. 4(a)]. Below a threshold pulse power of 0.21 mW, no material removal can be detected. Above 0.21 mW, the groove depth strongly increases until a saturation level is attained at a laser pulse power of 0.6 mW.

After development by a 5% aqueous MIBK solution, the groove structure retains its width ($\approx 15\mu$m measured by stylus-profilometer), while the groove depth increases [Figs. 4(a) and 5]. The MIBK treatment yields a relatively smooth and sharp structure as observed by the optical light microscope (Fig. 5). In both cases before and after development, both curves are similar to an Arrhenius plot. Besides, between 0.21 and 0.3 mW there exists a laser pulse power region in which only little ablation takes place, but the fs-irradiated polymer material gets highly modified and well soluble, and so the groove depth is strongly enhanced by the development with MIBK [Fig. 4(a)]. So this polymer seems to be suitable for the generation of 3D-structures in a transparent polymer substrate by the fs-laser-assisted wet chemical etching process described earlier. After development by benzene, the groove structure of the PMMA sample is swelling
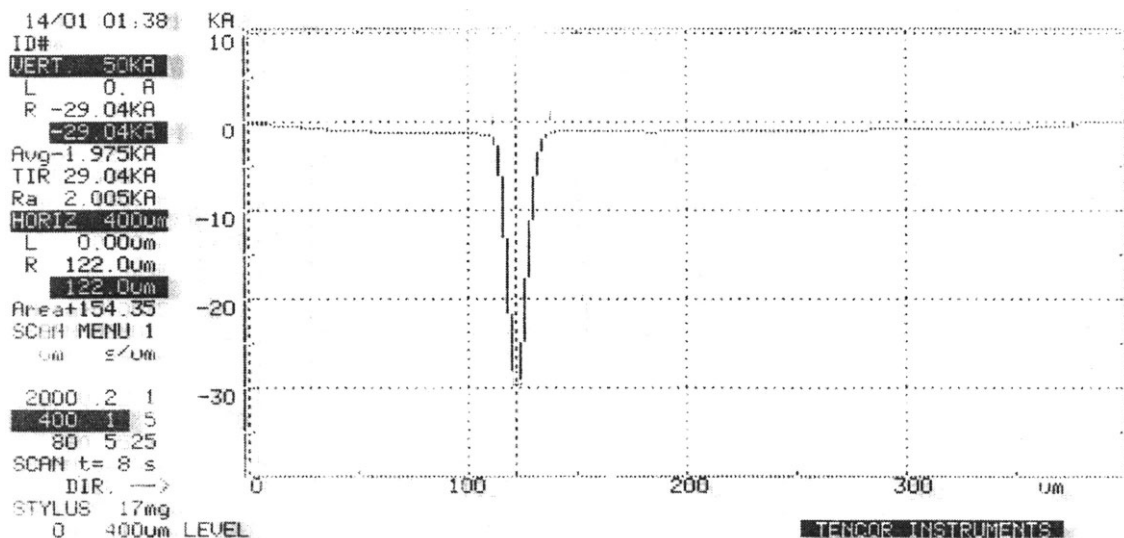
Figure 3 sample groove depth measurement done by stylus profilometer (sample: fs-irradiated PC developed by MIBK).

(a)

(b)
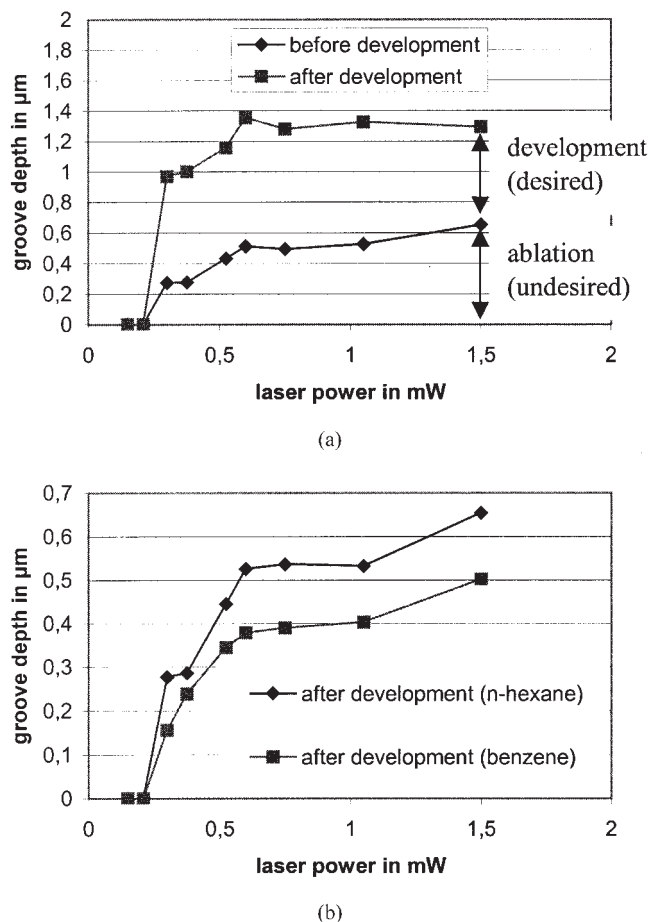
Figure 4 (a) Ablation and etching depth curves of nonfluorinated PMMA drawn against the fs-laser pulse power before and after the development by MIBK; ablation is an undesired effect, while development is a desired effect. (b) Etching curves of nonfluorinated PMMA drawn against the fs-laser pulse power after the development by benzene and n-hexane.

[Fig. 4(b)]. The groove depth is diminished because the tip of the stylus is hindered from completely entering the groove structure by its swollen edges. No

significant change of the ablation groove depth occurs in the development by n-hexane [Fig. 4(b)]. Thus, both solvent agents benzene and n-hexane are not suited for the formation of 3D-structures in PMMA.
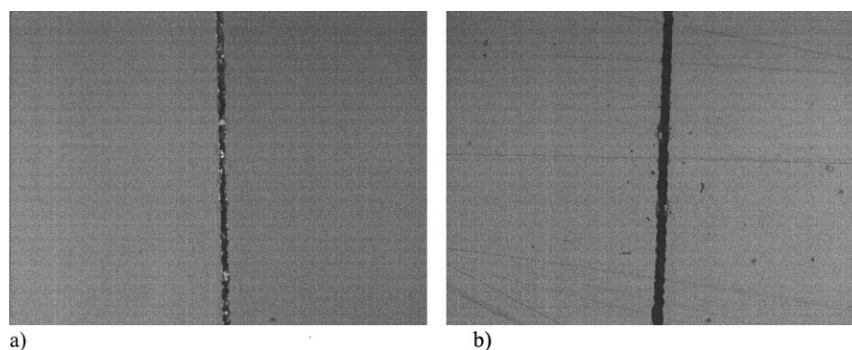
The results of all development experiments are summarized in Table III.

During fs-laser irradiation, the atomic bondings of the organic polymer molecules are excited vibrationally or rotationally due to single photon absorption or they are shifted to a higher electronical energy states due to multiphoton absorption followed by a rapid conversion of photon energy into vibrational or rotational energy. Both kinds of absorption lead to considerable heating of the polymer material in the irradiated zone, triggering a photothermal modification and ablation process. Generally, a photothermal process is an activated process subject to Arrhenius Law[19]:

$$k_r(T) = k_{r,0} \exp\left(\Delta E_{act}/RT\right) \quad (1)$$

with k_r as the velocity constant of the chemical reaction, $k_{r,0}$ as a proportional factor, ΔE_{act} as the molar activation energy, R as the molar gas constant, and T as the thermodynamical temperature. It can be assumed that the product yield of the chemical reaction is proportional to the velocity constant. An activated process is always featured by a threshold, explaining the Arrhenius-like plot of the etching depth in dependence on the laser pulse power before and after development.

By laser irradiation of PMMA, not only radical degradation products are formed but also polar defragmentation species are generated.[20] It is well-known that polar polymer materials are well soluble in polar solvent agent, while nonpolar polymers are well soluble in nonpolar solvent agent. Swelling occurs if a minor polar thermoplastic polymer is treated by a polar or a nonpolar solvent agent and if a polar or nonpolar thermoplastic polymer is developed by a

a)

b)

Figure 5 Optical light microscope image of the groove in nonfluorinated PMMA (a) before and (b) after development by MIBK.

TABLE III
Results of the Development Experiments. Several Combinations Between fs-Laser Irradiated
**Polymers and Solvent Agents with Different Polarities were Investigated**

Polymer	Solution agent		
	Aqueous MIBK	Benzene	*n*-Hexane
PMMA	+ [Figs. 4(a) and 5]	o [Fig. 4(b)]	− [Fig. 4(b)]
fluorinated PMMA	− (Figs. 6 and 7)	−	−
PMMI	+ (low power); o (high power) (Fig. 8)	o	−
PS	o (Fig. 9)	o	
PC	+ (low power); o (high power) (Fig. 10)		−
PI	+ (Figs. 11 and 12)	o	−
PE	−	o	+ (Fig. 14)

+, well soluble; o, swellable, slightly or nonsoluble; and −, nonswellable and nonsoluble. Low power < 1 mW and high power > 1 mW.

minor polar solvent agent.[21] This can explain why the fs-laser-irradiated PMMA material is well solved by MIBK, which is a highly polar solvent agent, while the fs-laser-irradiated PMMA material is not well-soluble by the other solvent agents. By solving almost the entire polymeric defragmentation residues, the depth of the groove increases and the structure appears to be smoother and sharper. In this case, the development by MIBK has a "cleaning"-effect on the fs-laser ablated zone of the PMMA sample surface. After the development, the sample shows groove structures featured by relatively sharp edges as observed by OLM, but their quality is not as high as the quality of the fluorinated PMMA or the PI samples discussed later.

Fluorinated PMMA

The groove depth of fluorinated PMMA is drawn against the pulse laser pulse power (Fig. 6). The groove depth increases with increasing laser pulse power. Up to a laser pulse power of 0.6 mW, the average groove depth increase is nonuniform. At a laser pulse power more than 0.6 mW, the increase of the groove depth becomes steady.
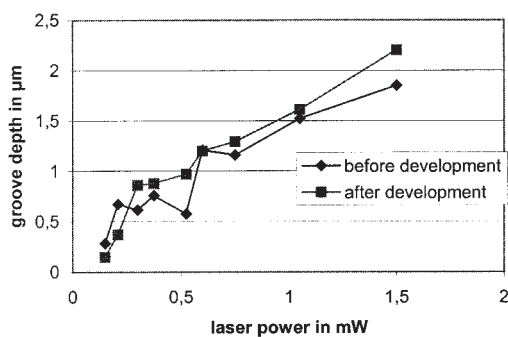

Figure 6 Ablation and etching depth curves of fluorinated PMMA drawn against the fs-laser pulse power before and after the development by MIBK.

After the development by an aqueous 5% MIBK solution, the groove depth curve appears to be a little more uniform than before the development, but the groove depth has not increased significantly and both curves are not very clearly distinct from one another (Fig. 6). This is also confirmed by the OLM pictures of the groove taken before and after development (Fig. 7): no significant difference can be observed between both pictures. Sharp structures can be observed (Fig. 7). After the development by pure benzene and pure *n*-hexane also no significant change can be observed.

As the development effect has no strong effect on the groove depth, no laser pulse power region exists in which the fluorinated PMMA polymer material gets modified and well-soluble by fs-laser irradiation without any ablation effects occurring. Consequently, the polymer is not suited for the generation of 3D microstructures in a transparent polymer substrate by the fs-laser-assisted wet chemical etching process.

Generally, fluorinated polymers are thermally more stable than their hydrogenated homologues due to the fact that the C—F bonding energy is the highest known in organic chemistry. Also, the size and electrical charge of the fluorine atoms compared with the hydrogen ones are higher, and so the molecular mobility is confined and the electrostatic interactions between adjacent atom groups is increased, yielding a stiffer and more rigid molecular structure. Thus, both the high C—F bonding energy as well as the size and charge number of the fluorine atom contributes to a higher glass transition and degradation temperature as well as to a diminished solubility. This explains why fluorinated PMMA is more temperature-resistant and less soluble than nonfluorinated PMMA. Consequently, the amount of soluble polymeric defragmentation products caused by a photothermal degradation process is also significantly reduced. Thus, the subsequent development by MIBK has only a little effect on the groove depth.
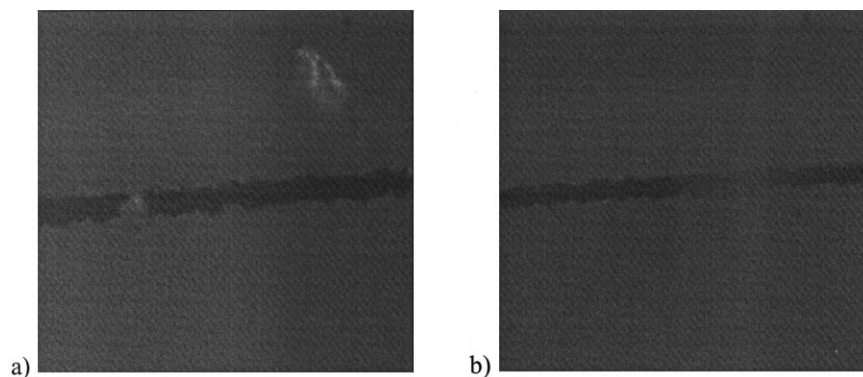
Figure 7　Optical light microscope image of the groove in fluorinated PMMA (a) before and (b) after development by MIBK.

Poly-*n*-methyl methacrylimide

The dependence of the groove depth on the laser pulse power is shown in Figure 8. The groove depth increases with increasing laser pulse power.

After development by a 5% aqueous MIBK solution, the measured depth of the groove generated by a laser pulse power less than 1 mW is increased, while at a laser pulse power above 1 mW, the situation is quite opposite. Also, after the development with benzene, a swelling effect is observed similar to PMMA. Fs-laser-irradiated PMMI cannot be developed by *n*-hexane.

PMMI has a similar chemical structure to PMMA and so it can be expected that during fs-laser irradiation similar fs-laser-induced defragmentation reactions occur[20]: radical as well as polarised defragmentation species are produced. These defragmentation species are resolved by the aqueous MIBK solution, resulting in a rise of the groove depth in the laser pulse power range below 1 mW. But at a laser pulse power above 1 mW, the swelling of the polymer material prevails over the solution process, indicating that the defragmentation products of PMMI are not as well soluble by MIBK as the defragmentation products of nonfluorinated PMMA. The similar chemical struc-

ture of PMMI also explains the similar solubility behavior to PMMA concerning benzene and *n*-hexane.

Polystyrol

The groove depth dependence on the laser pulse power is shown in Figure 9. The groove depth increases with increasing laser pulse power.

Development experiments of the fs-laser-irradiated zone by a 5% aqueous MIBK solution and by benzene yield such a swelling and so it was totally impossible to do any stylus-profilometry measurements. No development experiments have been performed with *n*-hexane for technical reasons.

Polystyrene is expected to absorb fs-IR-laser irradiation by multiphoton absorption and so it is assumed to be degraded by fs-IR-laser irradiadion in a similar way as in the case of ns-UV-laser irradiation. The benzene ring is photolytically activated and destroyed, yielding two highly polarized carbonyl groups.[2,22–24] But not all benzene rings are defragmented and so it retains a nonnegligible rest of almost nonpolar benzene rings. So the fs-laser-irradiated area of the polymer surface has a polar as well as a nonpolar character because of the existing carbonyl groups and benzene-rings. The highly polar water and
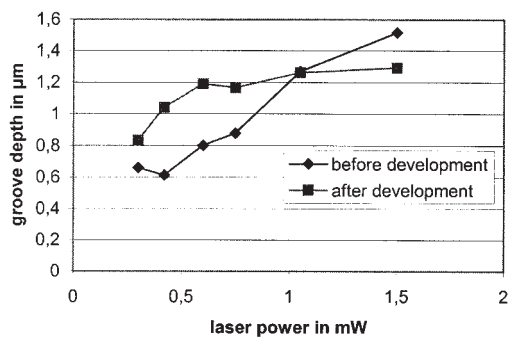
Figure 8　Ablation and etching depth curve of PMMI drawn against the fs-laser pulse power before and after the development by MIBK.
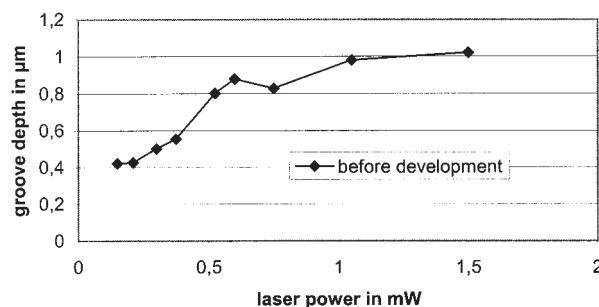
Figure 9　Etching depth curve of PS drawn against the fs-laser pulse power before the development by MIBK.
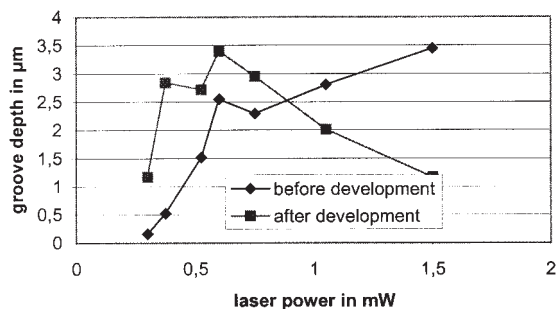
Figure 10 Ablation and etching depth curves of PC drawn against the fs-laser pulse power before and after the development by MIBK.

MIBK molecules associate with the polar carbonyl-groups tending to remove the polar defragmentation products away by a solvation process (the almost non-polar benzene rings are not surrounded by the polar solvent molecules). But the defragmentation products are hindered from being removed by the stable, sterically bulk, and immobile benzene rings affiliated with the still existing polymer molecule, and so no material removal occurs. Instead, the whole process results in a huge swelling of the treated polymer.

Polycarbonate

The groove depth of PC is measured in dependence on the laser pulse power (Fig. 10). The groove depth increases with increasing laser pulse power. Up to a laser pulse power of 0.6 mW, the groove depth increase is very strong in comparison to the other polymer materials, and so very high groove depths and rates are attained. At a laser pulse power more than 0.6 mW, the groove depth increase is quite moderate.

After development by a 5% aqueous MIBK solution, the groove depth decreases in the range of laser pulse power larger than 0.6 mW (Fig. 10). However, at a laser pulse power below 0.5 mW, the material removal by development strongly prevails over the material removal by ablation. Development experiments with *n*-hexane yield no significant change of the groove depth. For technical reasons, no development experiments are done with benezene.

PC is known to be ablated very well by UV-laser radiation[1,2,25–26] due to its benzene ring in the polymer main chain. The incident UV-photons are photolytically absorbed by the benzene rings, yielding a cleavage of the ring structure and, consequently, of the main chain. It could be expected that the same situation occurs in the case of fs-IR-laser irradiation. The incident photons are assumed to be absorbed photolytically by a multiphoton absorption process also resulting in the same defragmentation mechanism of the polymer chain.

Analogous to PS, the destruction of the benzene ring results in the formation of highly polar carbonyl-groups and a small, but a nonnegligible amount of almost nonpolar benzene rings remains. Thus, the same swelling effect occurs, but not in such a degree as it is the case of PS, and thus at low laser pulse power, the fs-IR-laser-irradiated polymeric material is solved by the polar solvent agent. But by a high laser pulse power, the remaining functional groups become totally defragmented, eventually reducing the polarity in the fs-IR-laser-irradiated area of the polymer. Thus, the polar solution effect is diminished and the swelling effect now dominates. In contrast to PS, in the case of PC the benzene ring is located in the polymer main chain. By the destruction of the benzene ring the polymer main chain is also destroyed. This has a reducing effect on the immobilization of the polar defragmentation products, as described in case of PS, and thus also on the swelling effect, but this explain the higher material removal of PC at the same laser power in comparison to PS (Fig. 9 and Fig. 10).

Polyimide

The groove depth of PI is drawn against the laser pulse power (Fig. 11). Below 0.375 mW, no ablation occurs, also no material removal after development can be observed. At 0.375 mW in the laser-irradiated zone, polymer material is removed by development, although no ablation takes place. In the range of low laser pulse power between 0.42 mW and 0.525 mW, the groove depth increases very strongly with increasing laser pulse power (threshold). At a laser pulse power more than 1.05 mW the groove depth increases very slowly with increasing laser pulse power. After development by a 5% aqueous MIBK solution, the groove depth is increased to higher depth values (Fig. 11), but the groove width remains constant ($\approx$ 14.5 μm). The groove edges of the structure before and
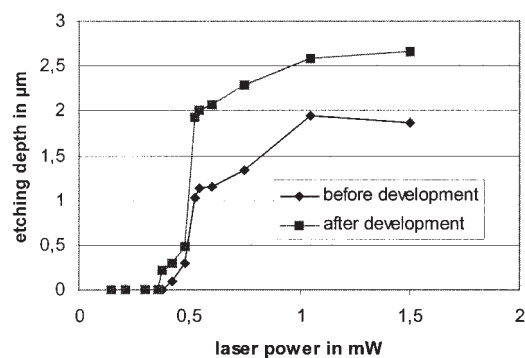
Figure 11 Ablation and etching depth curves of PI drawn against the fs-laser pulse power before and after the development by MIBK.
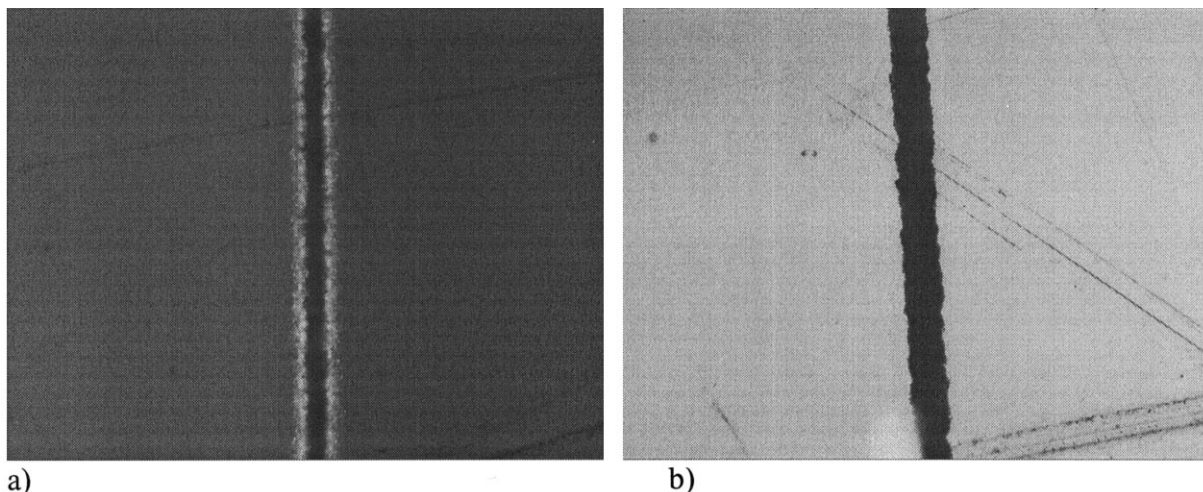
Figure 12 Optical light microscope image of the etched groove in PI (a) before and (b) after development by MIBK.

especially after the development seem to be very accurate as observed by OLM (Fig. 12). Development by benzene only results in a swelling of the fs-IR-laser-irradiated polymer material, while development by n-hexane yields no change in the groove depth.

A simple 3D-structure was directly written into the volume of a PI substrate by a focused fs-laser (process parameters: laser pulse power, 0.68 mW; scanning speed, 20 μm/s; depth of the structure, 100 μm; and length of the structure, 4 mm). A schematic illustration of the microstructure is given in Figure 1. Afterwards the structure was developed by MIBK solution. The OLM picture of the 3D-structure shows a straightforward linear channel (diameter: 3 μm) in the depth of 100 μm below the surface (Fig. 13). The focus position of the OLM is set at the channel structure. In the surrounding of the channel, the polymeric material appears to be shortly melted by thermal loading.

Inside a very narrow laser pulse power range around 0.375 mW, PI gets modified and thus well soluble without any ablation occurring: so it can be concluded that this polymer is suited for the generation of 3D-structures in a transparent polymer substrate by the fs-laser-assisted wet chemical etching process.

The fs-laser-induced defragmentation mechanism of PI is assumed to be similar to the one of PC as both polymers contain benzene rings in the polymer main chain.[25–26] But the fs-laser-irradiated zones of PI are developed very well by the aqueous MIBK solution without any material left in the laser-irradiated area, indicating a high solubility of the fs-laser treated polymer material. This can be explained as follows. All the nonpolar benzene rings in the polymer main chain are destroyed by fs-laser irradiation, yielding the destruction of the polymeric main chain and a great amount of polar carbonyl groups, and so almost no nonpolar benzene rings remain hindering the solution process.

Summarizing PI appears to be the most suited polymer for the generation of microstructures at the substrate surface by the fs-laser-assisted wet chemical etching process, especially in the laser pulse power range around 0.375 mW in which PI gets modified and soluble, but not ablated.

Polyethylene

The ablation groove depth of PE is investigated in dependence on the irradiation parameters (Fig. 14). The groove depth increases with increasing laser pulse power. Up to a laser pulse power of 0.75 mW, the groove depth increases strongly. At a laser pulse
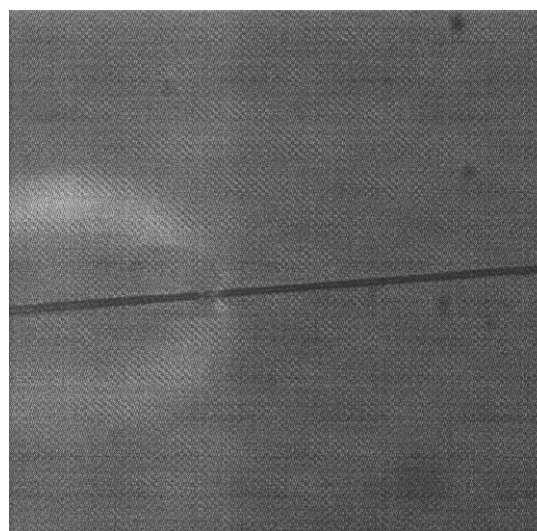
Figure 13 OLM image of a simple 3D-structure inside the volume of a PI substrate after development; depth of the structure below the surface is 100 μm and the schematic illustration of this 3D-structure is shown in Figure 1.
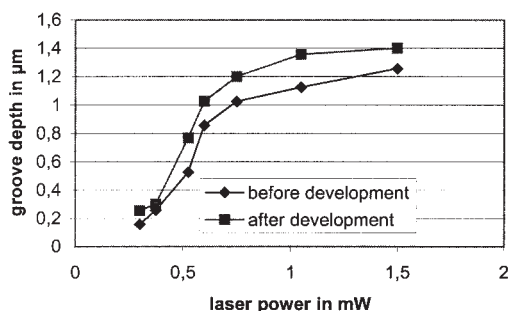
Figure 14 Ablation and etching depth curves of PE drawn against the fs-laser pulse power before and after the development by *n*-hexane.

power more than 0.75 mW, the increase of the groove depth is moderate.

After development by pure *n*-hexane, the groove depth slightly increases (Fig. 14). Development experiments by benzene show a slight swelling and development experiments by aqueous MIBK solution yields no significant change of the groove depth.

PE is a nonpolar polymer consisting only of methylene groups (nonpolar C—C and C—H-bondings). It can be expected that by fs-IR-laser irradiation, nonpolar molecular defragments are produced. As generally unpolar polymers are well-solved by unpolar solvent agents, the groove depth is increased by the development with *n*-hexane.

Solution mechanism

The development experiments confirm that polar thermoplastics are well-solved by polar solvent agents (e.g., PMMA by MIBK) and nonpolar thermoplastics are solved by nonpolar solvent agents (e.g., PE by *n*-hexane).[21] But nonpolar thermoplastics are not solved by polar solvent agents (e.g., PE by MIBK) and polar thermoplastics are not solved by nonpolar solvent agents (e.g., PMMA by *n*-hexane). Besides minor polar thermoplastics are swelled by polar and nonpolar solvent agents (e.g., PS by MIBK and *n*-hexane) and minor polar solvent agents are swelling polar and nonpolar thermoplastics (e.g., PMMA and PE by benzene). A significant contrast exists between nonpolar thermoplastics/solvent agents and minor polar thermoplastics/solvent agent, e.g., nonpolar polymers are not solved by polar solvent agents, but minor polar thermoplastics are already swelled by the same polar solvent agent. Contrary, minor nonpolar thermoplastics/solvent agents do not differ significantly from a polar thermoplastics/solvent agents concerning their solubility behavior, e.g., a polar thermoplastics is not solved by nonpolar solvent agents, also a minor nonpolar thermoplastics is not solved by the same nonpolar solvent agent without any swelling occurring. Obviously, it can be concluded from this nonsymmetric solubility behavior that the polar solution mechanism differs strongly from the nonpolar solution mechanism. Obviously, the polar solution mechanism has a hindering effect on the nonpolar solution mechanism, while the nonpolar solution mechanism does not affect the polar solution mechanism in any way. This could be explained as follows. Associates are formed by the polar molecules (thermoplastic polymer or solvent agent) due to the attractive Coulomb interaction. So an activation energy is required for the dissociation of such associative molecular complexes that cannot be provided by a nonpolar solution process. On the other hand, the mingling of two polar components (e.g., thermoplastic polymer and solvent agent) due to attractive Coulomb interaction is not hindered by a nonpolar surrounding.

But some exceptions exist. Fluorine and aromatic thermoplastic polymers are very difficult to be solved due to the relatively big size of the fluorine atom (e.g., fluorinated PMMA in any solvent agent) and to the sterically bulk and immobile benzene rings of aromatic polymers (e.g., PS in MIBK). Both groups are hampering the solution process.

CONCLUSIONS

The surface of all employed transparent polymers can be processed by fs-IR-laser radiation with PMMA and PI showing the best results. Especially PI, but also nonfluorinated PMMA can be sufficiently well developed by MIBK without any swelling effects occurring, and so they are the most suited polymers for the generation of 3D-microstructures in the substrate volume of a transparent polymer by the fs-laser-assisted wet chemical etching process.

Nonfluorinated PMMA seems to be a good candidate for such application because material removal by development strongly prevails over the material removal by the ablation process. Also, PI seems to be another good candidate for the same application: although ablation is not negligible, the edges of the structures are very sharp and accurate after the development process has taken place. Although ablation is negligible in the case of PC at low laser pulse power, the swelling of the polymer material is unclear. Fluorinated PMMA is not suited for this purpose because the polymer material gets ablated by fs-laser irradiation with only a minor development effect on the groove depth occurring, although structures of high quality are obtained.

References

1. Jain, K. Excimer Laser Lithography; SPIE Press: Washington, 1990.
2. Duley, W. W. UV-Lasers: Effects and Applications in Materials Science; Cambridge University Press: Cambridge, 1996; p 154.
3. Baudach, S.; Bonse, J.; Krüger, J.; Kautek, W. Appl Surf Sci 2000,154–155, 555.
4. von der Linde, D.; Sokolowski-Tinten K.; Bialkowski, J. Appl Surf Sci 1997, 109, 1.
5. Cheng, Y.; Sugioka, K.; Masuda, M.; Toyoda, K.; Kawachi, M.; Shihoyama, K.; Midorikawa, K. RIKEN Review 2003, 50, 101.
6. Cheng, Y.; Sugioka, K.; Midorikawa, K.; Masuda, M.; Toyoda, K.; Kawachi, M.; Shihoyama, K. Opt Lett 2003, 28, 1.
7. Masuda, M.; Sugioka, K.; Cheng, Y.; Aoki, N.; Kawachi, M.; Shihoyama, K.; Toyoda, K.; Helvajian, H.; Midorikawa, K. Appl Phys A 2003, 76, 857.
8. Jones, D.; Scully, P. J.; Jaroszynski, D. A. Proc ICALEO'02 2002, 4, 2999.
9. Scully, P. J.; Jones, D.; Jaroszynski, D. A. J Opt A: Pure Appl Opt 2003, 5, S92.
10. Zoubir, A.; Lopez, C.; Richardson, M.; Richardson, K. Opt Lett 2004, 29, 1840.
11. Yamada, K.; Ishizuka, T.; Watanabe, W.; Itoh, K. Opt Express 2002, 10, 1173.
12. Ohta, K.; Kamata, M.; Obara, M. In Proceedings of Commercial and Biomedical Applications of Ultrafast Lasers IV; SPIE, 2004; Vol. 5340, p 172.
13. Kamata, M., Ohta, K., Obara, M. Proc 5th CLEO/Pacific Rim'03 2003, 2, 690.
14. Klein-Wiele, J.-H., Bekesi, J.; Ihlemann, J.; Simon, P. Proceedings of ILATA'03; SPIE, 2004; Vol. 5399, p 139.
15. Klein-Wiele, J.-H., Simon, P. Proceedings of LPM'03; SPIE, 2003; Vol. 5063, p 445.
16. Novembre, A. E.; Masakowski, L. M.; Hartney, M. A.; Polym Engineer Sci 1986, 26, 1158.
17. Merchant, D. F.; Scully, P. J.; Schmitt, N. F. Sens Actuators 1999, 76, 365.
18. Wong, Y. M.; Scully, P. J.; Kadim, H. J.; Alexiou, V.; Bartlett, R. J. J Opt A: Pure Appl Opt 2003, 5, S51.
19. Dyer, P. E. Appl Phys 2003, A77, 167.
20. Wochnowski, C.; Metev, S.; Sepold, G.; Appl Surf Sci 2000, 154–155, 706.
21. http://www.fbv.fh-frankfurt.de/mhwww/KKC-Vorlesung/5Qualitaet.htm
22. Rabek, J. F. Photodegradation of Polymers; Springer: Berlin, 1996; p 82.
23. Peeling, J.; Clark, D. T. Polym Degrad Stab 1980–1981, 3, 97.
24. Weir, N. A. Polym Degrad Stab 1982, 4, 143.
25. Srinivasan, R. Appl Phys 1993, A56, 417.
26. Rubahn, H.-G. Laseranwendung in der Oberflächenphysik und Materialbearbeitung, Teubner Verlag: Stuttgart, 1996; p 100.