Fs-laser-induced Fabrication of Polymeric Optical and Fluidic Microstructures

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In this paper first experimental results are presented on the fabrication of integrated-optical microstructures by femtosecond-laser irradiation at the surface or in the volume of a polymeric substrate. Thereby the refractive index or the optical absorption coefficient of the polymer material is locally modified in a controllable way due to non-linear optical effects like multi-photon absorption. By this way surface relief grating structures, volume grating structures and linear waveguiding structures are generated. The surface relief gratings have diffraction efficiencies about 0.2 (first diffraction order), the diffraction efficiencies of the volume gratings are approximately smaller by one order of magnitude.
Besides experiments have been performed on the modification of the polymeric surface by fs-laser irradiation followed by subsequent development of the irradiated area by an etching liquid generating linear groove structures. By this way simple linear microstructures are generated into the polymer substrate. The results of these experiments are relevant for the fabrication of three-dimensional structures in the polymeric substrate in the future. All the gratings and the linear microstructures can be considered as basic components for the fabrication of complex micro-optical and fluidic systems in a polymeric substrate (photonic lab-on-the-chip).

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1. Introduction

Micro-optical and fluidic elements play an important role in modern microtechnology especially in biotechnology and integrated optics [1-2]. Polymers are more and more often employed as an alternative basic material for the fabrication of optical grating structures due to their inexpensiveness and easy processing [3]. Besides polymers can be treated by ns-UV-laser radiation in order to modify their optical surface properties [4] or to microstructure their surface by ablation [3]. By fs-laser radiation micro-structures can be realized not only at the surface, but also deep inside the volume of a polymer substrate without damaging the substrate surface. Thereby the fs-laser beam focus is positioned inside the substrate in order to proceed the polymeric material. Due to the short laser pulse duration, the intensity inside the laser beam focus becomes very high inducing nonlinear optical processes like multi-photon absorption. By this way the polymeric material is modified or carbonized implying a change in the refractive index (modification) or material absorption coefficient (carbonization). Thus waveguide-like structures and phase gratings can be realized by the modification of the refractive index and amplitude gratings can be generated by the periodic modulation of the material absorption coefficient. Also the solubility of the area inside the polymeric substrate is increased by fs-IR-laser irradiation so the laser-irradiated area can be removed by the development by a suitable organic solvent agent. So microfluidic channels can be generated inside the polymeric substrate which are connected to the substrate surface.
The aim of the paper is the presentation of some preliminary experimental results concerning the feasibility of a fs-laser based fabrication technique of polymeric microfluidic and –optic structures.

2. Experimental set-up

Sample material
The following sorts of polymers are employed for the irradiation experiments: Polymethylmethacrylate (PMMA), fluorinated PMMA, Poly-N-Methyl Methacrylimide (PMMI), Polycarbonate (PC), Polyimide (PI) and Polysiloxane. The polymer samples are cast and thus its surface have optical quality. The samples have a rectangular shape and the substrate surfaces are polished.

fs-IR-laser irradiation facility
A fibre laser of the type Clark-MXR CPA 2001 is employed featured by the following technical specifications (Fig. 1):

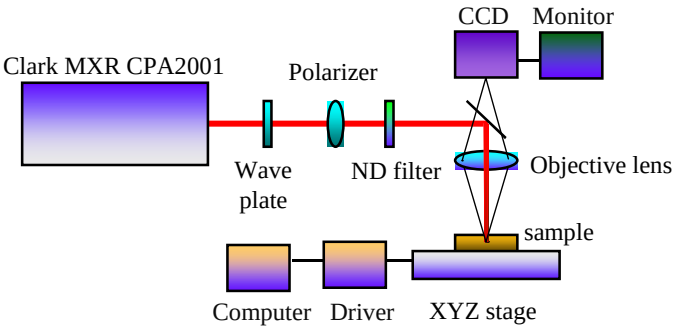
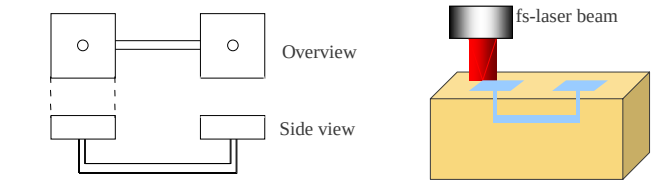


Fig. 1: *Experimental set-up of the fs-IR-laser illumination facility with the sample holder located on a xyz-stage*

pulse duration = 150 fs, central wavelength = 775 nm, maximum single pulse energy = 800 µJ, maximum repetition rate = 1 kHz. The laser pulse energy is adjusted by a ND-filter. The fs-laser beam is focused by an achromatic micro-objective with a numerical aperture NA of 0.46 yielding a focus diameter d_{focus} = 1.22 λ / NA = 1.22*775 nm / 0.46 ≈ 2.05 µm. 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 which is located on a xyz stage, so the polymer sample can be moved in all three directions. By the right choice of pulse energy the fs-laser beam directly focussed on the substrate surface initiates material ablation, while focussing inside the substrate volume causes a modification or carbonization of the polymer material.

Sample characterization

The surface topography of the fs-laser irradiated polymer substrate is investigated by a light microscope (LM) (Carl Zeiss Jenapol interphako), a stylus-profilometer (KLA tencor alpha-step 200), Scanning Electron Microscopy (SEM) (Carl-Zeiss DSM 940) and Scanning Nearfield Optical Microscopy (SNOM) (Omnicron TwinSNOM).



a) **b)**

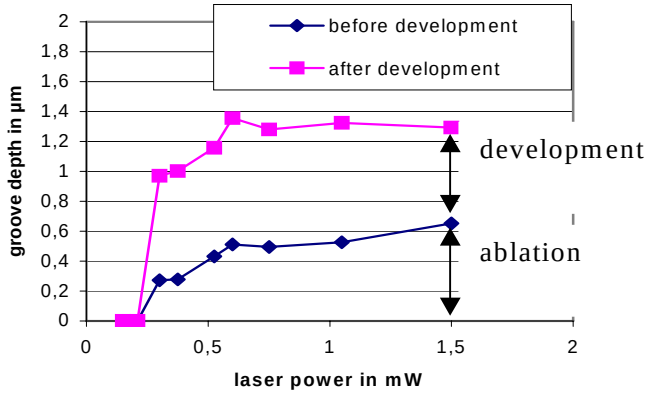
Fig. 2: *Illustration of a simple 3D micro-fluidic structure with an opening connected to the substrate surface*
a) *Schematic top and side view*
b) *fs-laser induced fabrication process*

3. Results and discussion

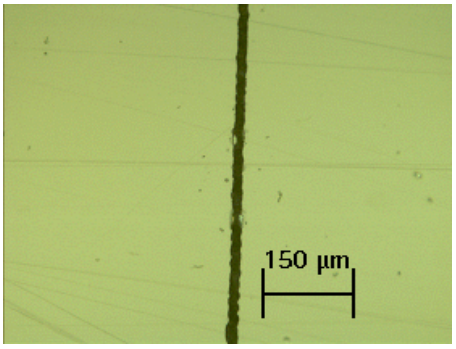
The following polymeric microstructures are generated by the fs-laser assisted processing technology: groove structures, waveguide-like structures and grating structures (volume and surface relief gratings, phase and amplitude gratings). All the microstructures are discussed in the following:

3.1 Groove structures

The aim of the experiments is to fabricate polymeric 3D-microfluid structures (Fig. 2) by the following way: the fs-laser beam is focussed inside the polymeric substrate. The polymeric material inside the laser beam focus is modified due to multi-photon processes and thus becomes soluable to several solvent agents.



a)

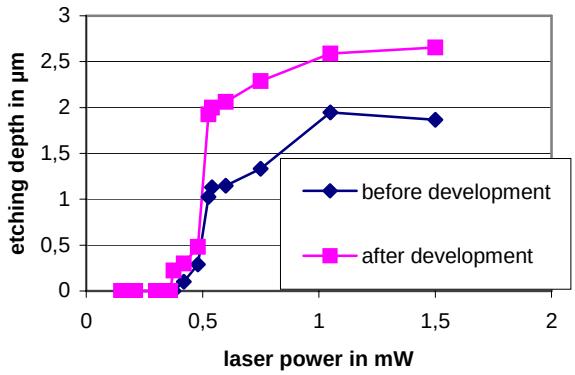


b)

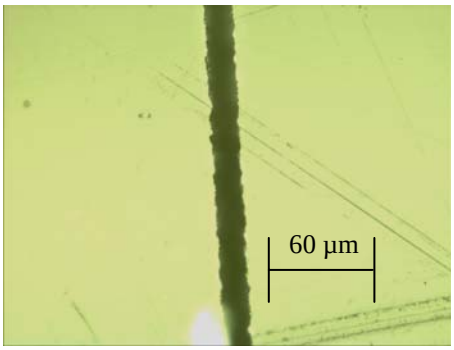
Fig. 3: *Removal of fs-laser irradiated regions of PMMA by development using MIBK*
a) *groove depth dependence on the laser power before and after development by MIBK*
b) *light microscope picture shows a sharply edged structure after development by MIBK*

In order to find the best polymeric material for this application the following preliminary solution experiments are performed: A strip-like structure at the polymeric substrate surface is modified by the fs-laser beam focussed directly onto the polymeric substrate surface (translational movement in x-direction with a speed of 20 µm/s). Then the modified area is developed by aqueous 5%- methylisobutylketone (MIBK) solution in order to test its solubility.

Several sorts of polymers were tried for these experiments with PMMA and PI showing the best results. The solubility of both PMMA and PI is strongly increased by the fs-laser induced modification process (Fig. 3 and 4). Also the polymeric surface structures are sharply edged after the development by MIBK. The groove depth are measured by stylus profilometry.



a)



b)

Fig. 4: *fabrication of 3D-microfluidic structures in PI*
a) *groove depth dependence on the laser power before and after development by MIBK*
b) *light microscope picture shows a sharply edged structure after development by MIBK*

As a demonstration sample, a simple micro-fluidic channel similar to Fig. 2 is produced inside the volume of the PI substrate. The focus of the micro-objective is positioned in a depth of 100 µm inside the polymeric substrate. The translation velocity was 20 µm/s and the laser power was 0.68 mW. The light microscopic picture shows this fluidic channel in a depth of 100 µm below the undamaged substrate surface (Fig. 5). SNOM measurements yield no destruction of the polymeric substrate surface.

3.2 Waveguide-like structures

Two waveguide-like structures W-1 and W-2 were fabricated in a PMMA substrate. The following irradiation parameters are employed: laser power = 0.175 mW, scanning speed = 200 µm/s (sample W-1) and 20 µm/s (sample W-2). Both waveguides were fabricated in a depth of 100 µm to the substrate surface.

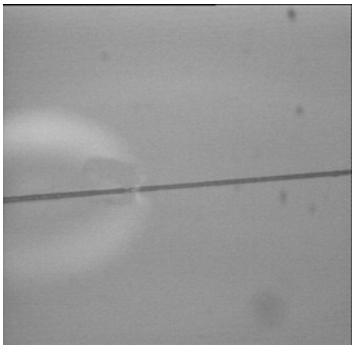


Fig. 5*:top view of a simple 3D-channel structure inside the volume of a PI substrate after development; width of the structure ≈12 µm; depth of the structure below the surface ≈100 µm; the schematic illustration of this 3D-structure is shown in Fig. 2*

The light microscope image of the first sample W-1 shows a transparent linear strip structure confined by very sharp edges (Fig. 6a). Its cross-section is rectangular, transparent, sharply-confined and it is as small as the focus diameter (approx.. 2 µm) (Fig. 6b).
Obviously the incident fs-laser irradiation induces a multi-photon photo-chemical process modifying the refractive index. The region, in which the refractive index is modified, is exactly confined to the laser-illuminated area.
No light coupling into the waveguide-like structure was possible by a circular fiber (diameter: 4 µm, monomode for red light), because the cross-sections of both waveguides are too different. So the light-guidance of this optical structure is not proven until now. The shape of the cross-section is presumably due to the mismatch between focus radius and Rayleigh length. Eventually plasma channeling also plays a relevant role. In contrast to us other working groups have used a non-achromatic micro-objective [5-8] (Fig. 1) obtaining a similar cross-section which is explained as follows: The frequency spectrum of the laser pulse is very broad due to the short pulse duration. Each wavelength has another refractive index (dispersion) and consequently corresponding to another focus length forming the rectangularly shaped focal area. A more symmetrical waveguide cross-section can be generated by the employ of a cylindrical micro-objective with another numerical aperture [5] (Fig. 1) or the usage of a slit in front of the micro-objective [6-8], thus the light in-coupling may become easier.
The light microscope image of the second sample W-2 shows a black linear strip structure. The cross-section of the sample W-2 is larger that the one of the sample W-1. Its edges are not-sharply confined and appears to be thermally stressed. In the surrounding of the carbonized center the polymer material is transparent and its refractive index seems to be modified as it is the case of the sample W-1.
Obviously in the focal area the incident fs-laser irradiation is

a) **b)**

Fig. 6: a) *topview of the integrated-optical waveguide-like structure W-1 directly written into the volume of a polymeric substrate by IR-fs-laser irradiation (scanning speed = 200 µm/s)*
b) *cross-section of the integrated-optical waveguide-like structure W-1 directly written into the volume of a polymeric substrate by IR-fs-laser irradiation (scanning speed = 200 µm/s)*

absorbed by the polymer material inducing a thermal carbonization process and thus an increase of the material absorption coefficient of the polymeric material. The laser beam intensity must surpass a threshold in order to induce the carbonization process. Otherwise the process does not take place, but only the refractive index is modified explaining the transparent refractive index modification zones in the surrounding areas. Consequently the carbonization process is an activated process which is typical for thermal processes. This can explain why the black carbonized area is larger than the focal point area, because generally activated thermal processes does not only occur in an area exactly confined to the laser-irradiated region, but also in its surrounding area due to heat conductance.
The second sample W-2 was produced by a scanning speed which is ten times less than the one of the first sample W-1, so the energy entry per time unit into the polymeric material is increased.

3.3 Grating structures

Surface relief gratings are generated by positioning the fs-

polymer material	laser power	diffraction efficiency	polymer material	laser power	diffraction efficiency
PMMA	0.3 mW	0.059	PI (developed)	0.6 mW	0.1715
PMMA fluorinated	0.3 mW	0.1	PI (developed)	0.48 mW	0.13
PMMI	0.3 mW	0.1275	Polysiloxane	0.945 mW	0.059
PC	0.3 mW	0.164	Polysiloxane	0.6 mW	0.059
PC	0.26 mW	0.1275	Polysiloxane (developed)	1.35 mW	0.11
PI	0.6 mW	0.10875	Polysiloxane (developed)	0.675 mW	0.079

a)

polymer material	laser power	diffraction efficiency	polymer material	laser power	diffraction efficiency
PMMA (depth 50µm)	0.26 mW	0.00001	PMMI	0.15 mW	0.001
PMMA (depth 100µm)	0.26 mW	0.0000325	PC	0.15 mW	0.0245
PMMA (fluorinated)	0.26 mW	0.001245	PI	0.48 mW	0.08
PMMA (fluorinated)	0.21 mW	0.00111	Polysiloxane	0.675 mW	0.12
PMMI	0.26 mW	0.039	Polysiloxane	0.54 mW	0.008
PMMI	0.21 mW	0.046			

b)

Tab.1: *Diffraction efficiencies of polymic gratings produced by fs-laser irradiation* **a)** *surface relief gratings* **b)***volume gratings*

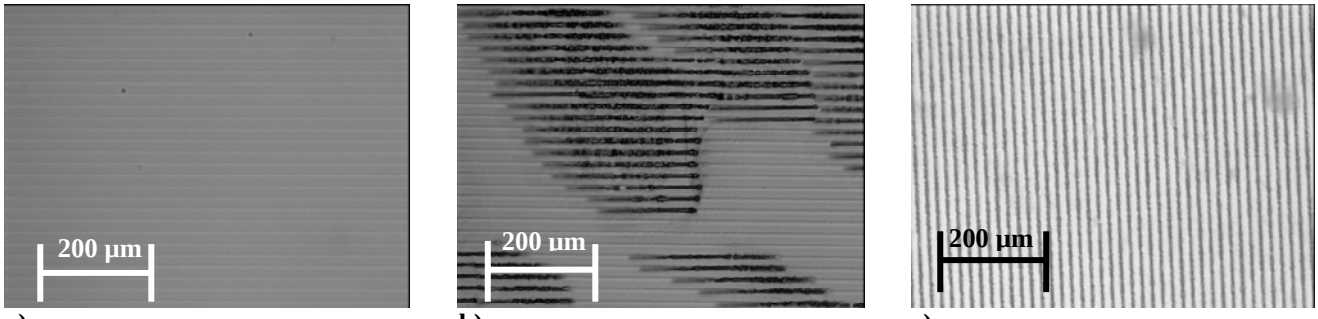
a) **b)**

Fig. 7: a) *SEM-image of a PMMA surface relief grating (p = 0.3 mW)*
b) *SEM-image of a fluorinated PMMA surface relief grating (p = 0.3 mW)*

laser beam focus directly onto the polymeric substrate surface inducing a removal of the polymeric material, while volume gratings are produced by positioning the laser focus inside the substrate volume inducing a local modification of the refractive index (phase grating) or an increase of the material absorption coefficient (amplitude grating).
The applied laser power values are given in the Tab. 1 showing the diffraction efficiencies of the grating samples.

The laser power refers to the unfocussed laser raw beam. It could be expected that the power of the laser beam focus inside the polymer substrate (volume grating generation) is strongly inferior to the power of the laser beam focus at the substrate surface (surface grating generation) due to material absorption and defocussing effects inside the substrate material. All the grating samples have a grating period of 10 µm and the grating area covers 1 mm * 1mm. The scanning speed was always 250 µm/s. The volume gratings are generated in a depth of 100 µm except for the first PMMA sample. Some surface relief grating samples (PI and Polysiloxane) are developed by an aqueous 5% MIBK (Methylisobutylketone) solution in order to increase the grating groove depth (see also Section 3.1) and so the grating amplitude and thus to amplify the diffraction efficiency.

The diffraction efficiency of the grating structures are measured by a HeNe-laser and a photodetector. The diffraction efficiency of the n-th order is calculated by the formula $\eta_n = P_n/P_{total}$ with P_n as the light power diffracted into the n-th order and P_{total} as the total light power comprising all diffraction orders including the 0-th one. By this way the material absorption is taken into consideration. The thickness of the volume grating can be approximately assumed as the double value of the focus depth (focus depth $\approx 2*\lambda/NA^2$ = $2*775/0.46^2$ = 7.33 µm). Eventually the focus depth is higher (compare Fig. 6b), but remains constant throughout the experiments. The thickness of the surface grating depends on the amplitude of the grating relief profile at the sample substrate.
The SEM images of the polymeric surface relief gratings show regularly aligned groove structures in a parallel way, where the fs-laser beam focus has removed the polymeric material from the substrate surface. The groove edges are quite rugged as seen in case of PMMA (Fig, 7a), but they



a) **b)** **c)**

Fig. 8: *volume gratings written by fs-laser irradiation in polymers (depth: 100 µm)*
a) *purely phase grating (PMMA) (p = 0.26 mW)*
b) *transistion state between phase and absorption grating (PMMA) (p = 0.26 mW)*
c) *purely absorption grating (Polysiloxane) (p = 0.675 mW)*

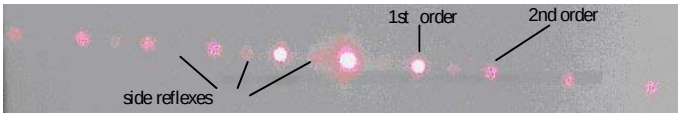
become significantly smoother by use of fluorinated PMMA (Fig. 7b). Obviously the fluorination of the polymer causes an improvement of the surface quality in the ablated area. Two sorts of volume gratings exist:at a low laser power (0.26 mW) volume phase gratings are generated (Fig. 8a) which are totally transparent and featured by a periodically refractive index modulation. The polymeric substrate surface is not damaged by the fs-laser irradiation as investigated by SNOM. At a higher laser power amplitude gratings occur which are not totally transparent, but featured by a periodically material absorption coefficient modulation. In Fig. 8b the laser power is chosen in such a way that the transition state between phase and amplitude grating occurs. The applied laser power is 0.525 mW, which is a threshold intensity: in some regions only the refractive index modification still occurs (transparent areas), while in some other regions already the thermal carbonization process takes place. A purely amplitude volume grating can be obtaind by fs-laser irradiation of aromatic polymers and Polysiloxane (Fig. 8c).

Both the surface relief and the volume grating diffract visible red light (Fig. 9), so obviously the optical structures are formed in a sufficiently accurate way.

Some other surface relief and volume gratings, consisting of several different sorts of polymer materials, are prepared under various process parameters. Their first order diffraction efficiencies are recorded (Tab. 1). The first order diffraction efficiency is defined as the mean value between the diffraction efficiencies of the first and minus first orders.

Concerning the first order diffraction efficiencies of the surface relief gratings one can generally cite the following: the aromatic polymers (PC, PI) have the highest diffraction efficiency espcially PC without development and PI after development. The polyacrylates (PMMA, PMMI) have a much lower diffraction efficiency than the aromatic ones. The diffraction efficiency of polyacrylates can be increased by fluorination, however the diffraction efficiency of fluorinated PMMA is inferior to the one of non-fluorinated PMMI, a special polyacrylate derivative. The diffraction efficiency of Polysiloxane is comparable with the one of polyacrylates. Increasing the laser power does not imply automatically an increase of the diffraction efficiency as it is the case of PC. In case of PI and Polysiloxane the diffraction efficiency remains constant. Eventually by a too high laser power thermal defragmentation process of the grating structures occur deteriorating the grating quality. However the diffraction efficiency can be increased by the development because the groove depth of the grating grids is increased (Section 3.1).

Generally the diffraction efficiencies of the volume gratings are much inferior to the ones of the surface relief gratings. Volume gratings in Polysiloxane and aromatic polymers are mostly amplitude gratings (Fig 8c) which have the highest diffraction efficiencies. However the diffraction efficiency of polyacrylates are increased by fluorination. Increasing the laser power does not imply automatically an increase of the diffraction efficiency as it is the case of PI. Analogue to the surface relief gratings a too high laser power eventually implies a thermal destruction of the volume grating.



a)

b)

Fig. 9 : *diffraction patterns of fs-laser written gratings in PMMA*
a) *surface relief grating (p = 0.3 mW)*
b) *volume grating (p = 0.26 mW, depth: 100 µm)*

4. Conclusion

It has been shown that micro-optical and –fluidic structures can be produced in polymer substrate by the fs-laser based fabrication technique. By the combination complex fluidic-optical structures can be fabricated as usually used in the biotechnology: The realization of a polymeric 3D-lab-on-a-chip with integrated optics in the near future seems to be feasible by this laser-based fabrication method. However further investigations are required to optimize the process fabrication parameters and the functional properties of such microstructures.

5. Acknowledgement

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