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Laser structuring of thin layers for flexible electronics by a shock wave-induced delamination process

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Abstract

The defect-free laser-assisted structuring of thin films on flexible substrates is a challenge for laser methods. However, solving this problem exhibits an outstanding potential for a pioneering development of flexible electronics. Thereby, the laser-assisted delamination method has a great application potential. At the delamination process: the localized removal of the layer is induced by a shock wave which is produced by a laser ablation process on the rear side of the substrate. In this study, the thin-film patterning process is investigated for different polymer substrates dependent on the material and laser parameters using a KrF excimer laser. The resultant structures were studied by optical microscopy and white light interferometry (WLI). The delamination process was tested at different samples (indium tin oxide (ITO) on polyethylene terephthalate (PET), epoxy-based negative photoresist (SU8) on polyimide (PI) and indium tin oxide/copper indium gallium selenide/molybdenum (ITO/CIGS/Mo) on PI.

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Keywords: Laser-induced delamination process; laser structuring; flexible substrate; thin layer etching

1. Introduction

Flexible electronics is a growing market and the development of new cost-effective manufacturing is necessary. Laser-based fabrication techniques exhibit an outstanding potential for the fast and easy structuring of thin layers especially on flexible substrates. However, the direct ablation process of thermally sensitive thin films like organic semiconductors for photovoltaic and light-emitting diodes (OLEDS) as well as compound semiconductors like CIGS

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is very difficult to perform without damage the sensitive thin films, for example due to thermal effects, ripples formation, and debris deposition processes [1]. Some studies show that also at ultrashort pulse laser irradiation (ps to fs) defects can occur in sensitive systems [1].

Indirect laser methods making use of mechanical effects of laser irradiation like laser-induced shock waves can be applied for thin-film structuring. This approach is a very interesting method with a big application potential due to the weak thermal effects into the thin-layer system and is called SWIFD (shock wave-induced film delamination) according to Ref. [2]. At SWIFD, the shock wave is induced by a laser-induced ablation process on the back side of the substrate. The laser-induced delamination process is studied for thin-film patterning, e.g. for CIGS solar cells [2]. Laser-induced mechanical delamination processes of thin films are known and can be discussed in relation to thermal-induced stress effects [3]. Although a direct laser ablation at the rear side of the substrate is mainly a thermal effect thermal-induced modifications of the thin layers on the front side of the flexible substrates induced by the laser irradiation of the rear side of the substrate can be excluded. Furthermore, the formation as well as the propagation of laser-induced shock waves in solids is well known [4]. Special attention is given to the interaction of shock waves at surfaces and interfaces. For example, the laser-induced shock wave-generation technique can be applied for measuring the adhesion of thin films [5]. Besides the structuring the laser-induced shock waves can also be used for the transfer of layer systems. This method is called laser-induced forward transfer (LIFT) [6-8] whereas at the SWIFD method the shock wave formation process is spatially separated from the delaminated material. In this study, the SWIFD-induced structuring at different thin layers on flexible polymer substrates was studied.

2. Experimental set-up

(a) (b)

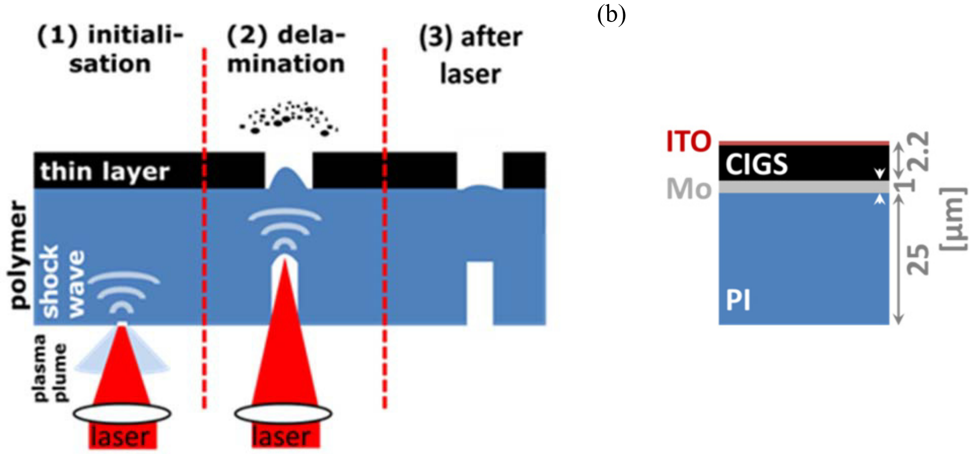


Fig. 1. (a) Schematic illustration of the laser shock wave-induced delamination process:

(1) Initialisation: The irradiation of the back side of the polymer induced an ablation process and a shock wave formation inside of the polymer.
(2) The shock wave and the deformation of the polymer surface induced a cracking and delamination of the thin layer where in some cases a thinning of the polymer substrate is necessary.
(3) Besides the delamination of the thin layer also a modification of the back side of the polymer surface can be found due to the elastoplastic deformation of the substrate.

(b) Sketched setting of the CIGS solar cell.

The schematic illustration in Fig. 1 shows the experimental set-up together with the studied delamination process for thin-film patterning. The delamination process is caused by a shock wave that is induced by the rear side laser ablation of the polymer substrate (see Fig. 1 (a)). The irradiation of the rear side of the polymer foil at sufficient high laser fluences results in a laser ablation process and a shock wave formation inside of the polymer (see Fig. 1 (a) (1)). However, at thick polymer foils and strong sticking layers on the front side of the polymer the first laser-induced shock wave is not sufficient to induce the delamination process. In these cases a multi pulses laser-induced thinning of the polymer foil is necessary (see Fig. 1 (a) (2)) and the shock wave and the deformation of the back side of the polymer surface induced a cracking and, finally, a delamination of the thin layer (see chapter 3).

After the laser treatment, besides the delamination of the thin layer also a modification of the back side of the polymer surface can be found due to the elastoplastic deformation of the substrate (see Fig. 1 (a) (3)). Further information about the delamination process can be found in [2]. The samples under investigation comprise a polymer substrate that can be ablated by UV laser photons and a thin film (stack) on the front side. In this study we tested the delamination process at different thin film/polymer substrate combinations: 800 nm indium tin oxide (ITO) on 110 µm polyethylene terephthalate (PET), 1.2 µm epoxy-based negative photoresist (SU8) on 25 µm polyimide (PI) and indium tin oxide/copper indium gallium selenide ($d_{ITO} + d_{CIGS} = 2.2$ µm)/1 µm molybdenum (ITO/CIGS/Mo) on 25 µm polyimide (PI) (see Fig. 1 (b)). A KrF excimer laser with a wavelength of $\lambda = 248$ nm, a pulse duration of $\Delta t_p = 25$ ns, and a repetition rate of $f = 10$ Hz was used for irradiation sample areas of 50 x 100 µm² (at CIGS solar cell irradiation: 100 x 100 µm²) with a laser fluence Φ up to 45 J/cm². No confining material was applied in this study. The resultant structures were analysed by optical microscopy. Furthermore, the pattern height and the surface morphology were analysed with white light interferometry.

3. Results and discussion

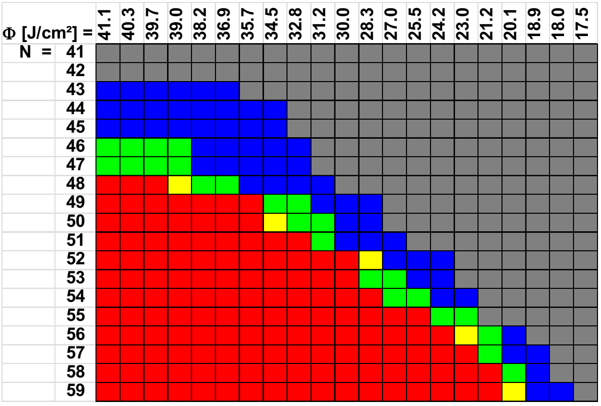
3.1. ITO on PET

As first system a commercial ITO on PET was tested where the ITO layer should be removed by a shock wave-induced laser ablation process on the rear side of the PET. First of all, the ablation of the PET substrate was studied. In Fig. 2 (b) the ablation rate – laser fluence dependency is shown. The ablation rate $\Delta z^{\#}$ increases almost linearly with increasing laser fluence and the dependency can be analytically described by $\Delta z^{\#} = 0.0219$ µm/(J/cm²) * Φ + 1.44 µm. Furthermore, the ablation of the PET substrate induced a shock wave into the substrate where the ablation-induced pressure can be estimated by Mora and Ballard [9, 10] where the estimated ablation pressure p is dependent on the laser fluence Φ and the $p(\Phi)$ dependency is summarized in Fig. 2 (b) (blue line).

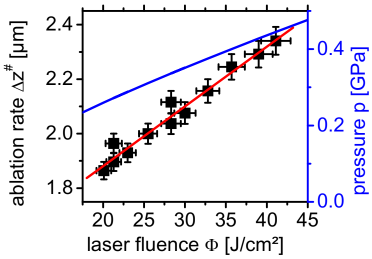
The irradiation of the back side of the PET results in the modification of the front side of the ITO-covered PET where the modification is dependent on the laser parameters. Typical modifications of the ITO film are: crack formation without delamination, cracks with partial delamination and removal of ITO flakes from the PET. In Fig. 2 (a) the particular surface modification dependent on the laser parameters (laser fluence Φ and number of laser pulses N) are colour-coded summarized (grey: no modification of the surface; blue: cracking of the ITO; green: delamination of the ITO; yellow: delamination of the ITO with a low front side surface damage of the PET substrate; red: full penetration of the of the PET). The parameter window (*green region*) for the shock wave-induced removal of the ITO is very small.

An exemplary optical microscopic and WLI image in the *green region* (delamination of the ITO) is presented in Fig. 2 (c) (ii) and (iii) at $\Phi = (41.1 \pm 1.9)$ J/cm² and N = 47 and an exemplary optical microscopic image of the ITO surface in the *blue region* (cracking of the ITO) is presented in Fig. 2 (c) (i) at $\Phi = (41.1 \pm 1.9)$ J/cm² and N = 45. Especially the WLI image of the *green region* example presented that the laser process results in a partial delamination of the ITO and in a deformation of the surface (see line profile: black line Fig. 2 (c) (ii)).

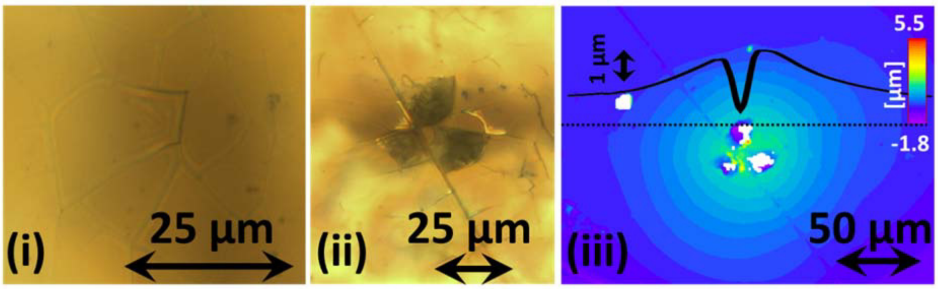
Based on the measuring of the ablation depth on the PET the results suggest that the successful delamination of the ITO requires a distinct thinning of the substrate down to a residual substrate thickness of 4 µm at high laser fluences where the required residual substrate thickness decreases with decreasing laser fluence. This effect can be explained by the decreasing of the laser-induced ablation pressure by decreasing laser fluence (see Fig. 2 (b) blue line). The very small required residual substrate thickness explains the very small parameter window.



(a)



(b)



(c)

Fig. 2. (a) (left) Summary of the irradiation results of the 800 nm ITO on 110 µm PET (grey: no effect on the front side; blue: cracking of the ITO layer, no delamination; green: delamination of the ITO; yellow: delamination of the ITO with a very low front side surface damage of the PET substrate; red: full penetration of the PET);
(b) Ablation rate – laser fluence dependency (red line: linear approximation of the dependency $\Delta z^{\#} = 0.0219$ µm/(J/cm²) * Φ + 1.44 µm and blue line: estimated laser irradiation-induced ablation pressure dependent on the laser fluence using the model from Mora and Ballard [9, 10]);
(c) Optical microscopic image (i) at N = 45 and (ii) at N = 47 at $\Phi = (41.1 \pm 1.9)$ J/cm² and (iii) WLI image and line profile at N = 47 and $\Phi = 41.1$ J/cm² (white colour: non-measurable region).

The small parameter window and the partial and randomly distributed delamination of ITO on PET demonstrated that the laser-induced shock wave-assisted delamination process is only limited suitable for a technological application.

3.2. SU8 on PI

As second system SU8 on PI was studied. In agreement with the analyses of the ITO/PET system the resultant modifications of the SU8/PI system were colour-coded summarized in Fig. 3 (a) (grey: no effect on the front side; blue: cracking of the ITO layer, no delamination; turquoise: instable region: cracking and unspecific delamination; green: delamination of the SU8; yellow: delamination of the SU8 with a very low front side surface damage of the PI substrate; red: full penetration of the PI).

In contrast to the ITO/PET system a larger process window (*green region*) was found. Furthermore, in agreement with the ITO/PET system also the ablation depth on the back side of the PI substrate was analysed. In Fig. 3 (b) the ablation rate – laser fluence dependency is shown. The ablation rate of the PI is almost similar to the ablation rate of the PET and in agreement with the PET results the PI ablation rate increases with increasing laser fluence. Because both substrates are polymers with a similar ablation and plasma formation process the generated shock waves should bear a similar strength. In a good approximation the estimated pressure – laser fluence dependency for the PET (see Fig. 2 b (blue line)) is almost equal to the p(Φ) dependency of the PI. Therefore, the differences in the thin-film material delamination patterning cannot be explained by the shock wave strength so that material properties of the film or interface characteristics have to be considered for discussion.

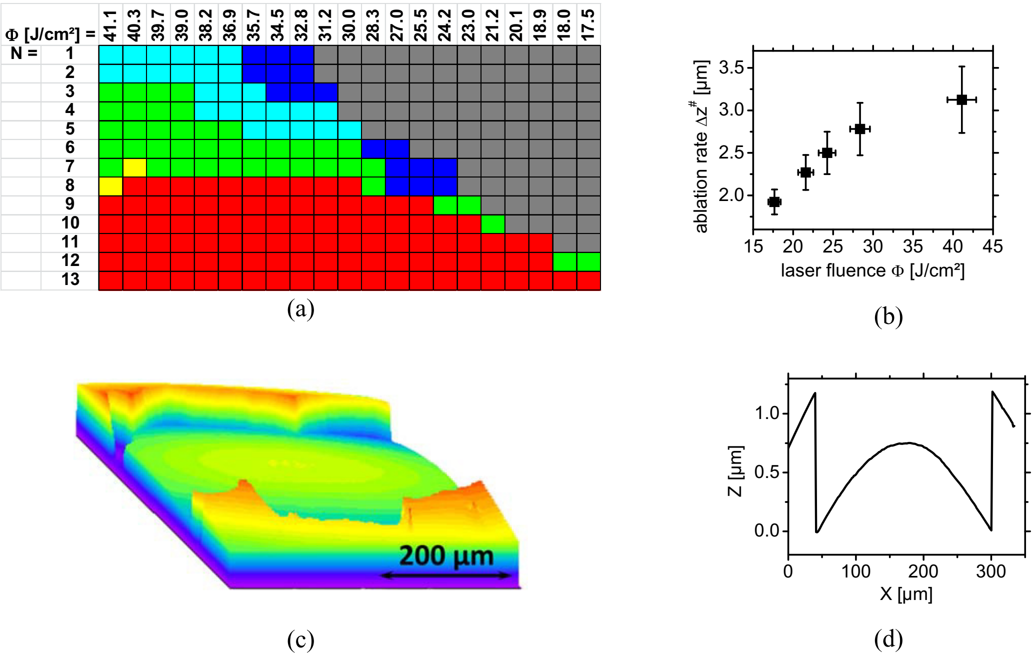


Fig. 3. (a) Summary of the irradiation results of the 1.2 µm SU8 on 25 µm PI (grey: no effect on the front side; blue: cracking of the ITO layer, no delamination; turquoise: instable region: cracking and unspecific delamination; green: delamination of the ITO; yellow: delamination of the ITO with a very low front side surface damage of the PET substrate; red: full penetration of the PET);
(b) Ablation rate – laser fluence dependency;
(c) WLI image of a delaminated region (for the laser irradiation a scanning of a line was used) with Φ = (41.1 ± 1.9) J/cm², N ≈ 5;
(d) Line profile (from Fig. 3 c).

The large process window in contrast to the ITO/PET system can be explained by a large residual substrate thickness, only a small thinning of the substrate is necessary for a successful structuring.

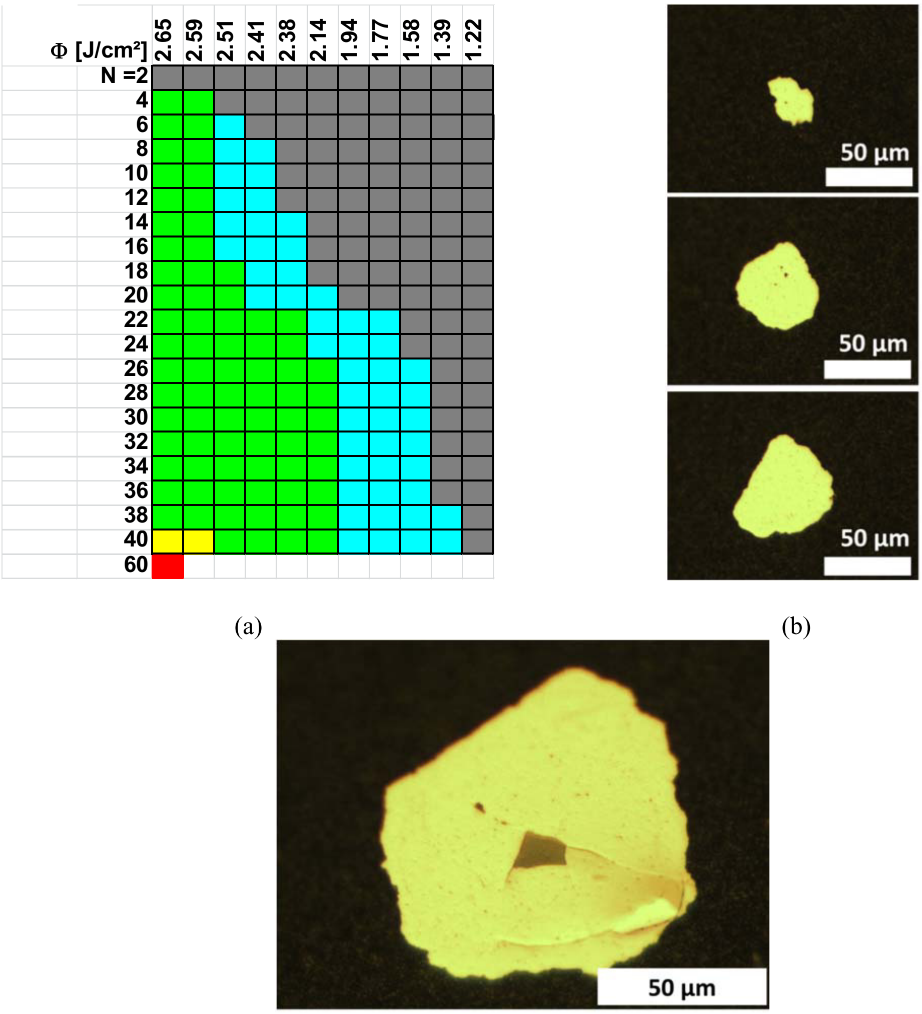
Based on the ablation depth analyses, a maximum required residual substrate thickness of ~ 20 µm can be estimated.

Furthermore, a more detailed analysis of the delaminated area dependent on the laser parameters presents a clear trend: the delaminated area increases with increasing laser fluence and increasing number of laser pulses. The large parameter window allows the easy structuring of the SU8 on PI. In Fig. 3 (c) the resultant morphology of a structured SU8 induced by a laser scribe on the PI back side ($\Phi = (41.1 \pm 1.9)$ J/cm², $N \approx 5$) is presented. The delamination process allows the well-defined structuring of the SU8 with a well-defined vertical breaking edge (see Fig. 3 (d)).The lateral precision of the edge is moderate and the width of the structured trench presents a variation of smaller than 30% (minimum-to-maximum width value to average width).

Furthermore, the analyses of the surface morphology of the patterns after the irradiation present a remaining bending of the substrate in the field of the laser spot (see Fig. 3 (d)).

The large parameter window and the well-defined delamination process demonstrated that the laser-induced shock wave-assisted delamination process is suitable for the structuring of SU8 on PI.

3.3. CIGS on PI



(c)

Fig. 4. (a) Summary of the irradiation results of the CIGS solar cells on PI (grey: no effect on the front side; turquoise: instable region: unspecific delamination; green: delamination of the CIGS including the ITO front contact; yellow: delamination of the CIGS with damage (cracking and partial delamination) of the molybdenum back contact; red: full penetration of the PI);
(b) Optical microscopic image of the laser-treated CIGS solar cell at $\Phi = (2.65 \pm 0.12)$ J/cm² and at N = 4, 6 and 8 (from top to bottom) (dark region: non-modified CIGS solar cell, bright region: uncovered molybdenum back contact);
(c) Optical microscopic image of the laser-treated CIGS solar cell at $\Phi = (2.65 \pm 0.12)$ J/cm² and at N = 40.

As third system a CIGS solar cell (ITO/CIGS/MO) on PI was studied. In agreement with the other systems the resultant modifications at the CIGS system were colour-coded summarized in Fig. 4 (a) (grey: no effect on the front side; turquoise: instable region: unspecific delamination process; green: delamination of the CIGS including the ITO front contact; yellow: delamination of the CIGS with a damage (cracking or delamination) of the Mo back contact; red: full penetration of the PI).

The results presented that the shock wave-structuring method allows a very easy delamination of the CIGS including the ITO from the Mo back contact due to the very large process window (*green region* Fig. 4 (a)). This allows, for example, the easy and fast production of well-defined trenches in the CIGS solar cell (see [2]) and in contrast to a direct ablation process [11, 12] no thermal effects, like melting, can be found on the edges.

In contrast to the ITO/PET and SU8/PI systems a distinct smaller laser fluence and smaller ablation pressure are necessary for a successful structuring of the CIGS solar cell material, respectively. This effect can be most likely explained by the weak sticking of the CIGS in the Mo back contact.

Furthermore, in agreement with the SU8/PI results also the results of the CIGS delamination presented that the delaminated area increased with increasing number of laser pulses (see Fig. 4 b) and increasing laser fluences.

Besides the CIGS delamination, the laser treatment at a high number of laser pulses (large thinning of the PI substrate) and a high laser fluence induced a cracking and partial delamination of the molybdenum back contact (see Fig. 4 (c)). These results suggest that besides the CIGS delamination the laser treatment also allows the structuring of the Mo back contact.

The demonstrated very large parameter window and the well-defined delamination process allow the easy and selective delamination of the CIGS material including the ITO front contact from the Mo back contact. Furthermore, at a high number of laser pulses and high laser fluence also a delamination of the Mo from the PI substrate is possible.

The very different results regarding the laser fluence and the extension of the process window cannot be discussed with different ablation pressures and, therefore, different strengths of the shock waves. More likely the thin-film properties as well as the interface characteristics influence the measured effects. At least two effects have to be considered for delamination: (i) the mechanical stability of the film that is important for crack formation in the film near the laser spot edges and (ii) the adhesion of the film to the substrate. In general it is well known that metal oxide films stick very well, resist films stick sufficiently for performing the lithography, and CIGS films having a limited adhesion to the molybdenum allow the patterning by mechanical tools. Besides the shock wave also the surface bending and the bending-induced stress into thin layers play an important role for the cracking and delamination effect of the thin layers on the front side of the flexible substrates.

4. Conclusion and outlook

The laser-induced shock wave structuring of thin layers on flexible substrates was studied. Different systems such as ITO/PET, SU8/PI as well as CIGS solar cell/PI were studied experimentally. The presented method allows the fast structuring of thin layers without thermal modification of the thin film [2] where the analysed systems are different suitable for a technological application of the studied method:

ITO on PET limited suitable
SU8 on PI suitable
CIGS solar cell on PI suitable

The results presented that the method allows a very well vertical precision structuring of the thin layer with a well-defined breaking edge (e.g. see Fig. 3 d). However, the lateral precision is limited (e.g. see Fig. 3 c). The lateral precision can be most likely improved using a structured master positioned on top of the thin layer. Increasing the laser-induced pressure by confinement conditions, like water on the back side of the flexible substrate, can most likely improve the structuring results and increase the area of applications.

Furthermore, the experimental results presented that the laser treatment process induced a plastic deformation of the front side of the polymer foil. This effect can be most likely controlled by the variation of the laser beam profile and will allow a fast mask-free surface morphology modification, e.g. for MEMS applications.

Acknowledgement

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