

Laser-Induced Forward Transfer: An Approach to Single-Step Polymer Microsensor Fabrication

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Laser-induced forward transfer (LIFT) using a triazene polymer as dynamic release layer was used for the transfer of polyethyleneimine (PEI) pixels for microsensors applications. A XeCl laser was used to transfer the PEI pixels from a thin film coated onto the triazene layer. The PEI films were either in direct contact with the receiver or a gap was maintained between the donor film and the receiver. An optimization of the process was carried out by changing the laser fluences, the ratio between the thickness of the PEI and of the triazene layer, and the transfer distance. Well-defined, regular PEI pixels were obtained on the receiver. The morphology of the patterns was characterized using optical microscopy and scanning electron microscopy (SEM). The transfer onto surface acoustic wave (SAW) devices suggests that LIFT is a promising technique for the fabrication of microsensors with polymers as active layer.

Keywords: Laser-Induced Forward Transfer, PEI, SAW.

1. INTRODUCTION

The precise positioning of polymeric compounds is an essential part for their use in technological applications. The development of laser techniques for transferring different materials in a controlled and direct manner on solid surfaces has attracted much attention during the last years for various applications.^{1–7} For example, a rapid deposition and patterning by Laser Induced Forward Transfer (LIFT) in a clean environment of high T_c superconducting thin films has applicability for micro- and opto-electronic applications.⁸ Also, the possibility of transferring liquids through LIFT revealed that this technique could be applied to the deposition of organic and biological compounds in solution,^{9–12} and it was demonstrated that LIFT could be used to successfully transfer proteins^{10–12} or DNA.¹³

LIFT assisted by a release layer or by a dynamic release layer (DRL) has already been used for printing micron-sized patterns or features of a wide range of materials in solid or liquid/viscous state.^{14–17} For example, LIFT and triazene polymers as release layer were successfully applied to transfer sensitive materials such as organic light emitting diode pixels,¹⁴ living cells¹⁵ and nanocrystal quantum dots¹⁶ as well as for transferring pixels from thin metallic films.¹⁷ The transfer of polymer patterns has an increased interest due to their application in chemical or bio-sensors. One attractive polymer in this field is polyethyleneimine (PEI) which has a variety of applications, e.g., chemical sensing, due to its reactivity with hydrazine based compounds, but also in the biomedical field, due to its capability as transfection enhancer.

In this study, the laser printing of PEI using a dynamic release layer is analyzed, where the optimal parameters for obtaining well defined pixels of a transferred polymer are established. Preliminary studies on the characteristics of

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PEI pixels obtained by LIFT for microfabrication sensors are also described.

2. EXPERIMENTAL DETAILS

The transfer was achieved using a single pulse from a XeCl excimer laser (Compex, Lambda Physik, 308 nm, 30 ns). A square mask with an aperture of 2 mm was applied to utilise a homogeneous part of the beam, which was focused by a lens onto the backside of the donor film with a demagnification of 4, giving a spot size of 500 μm . The donor and the receiver substrates were placed perpendicular to the beam in close contact ($<1 \mu\text{m}$) or with a gap defined by a spacer (up to 100 μm) on a motorized translation stage.

The computer-controlled system allows creating a matrix of pixels for each sample, where the pulse energy is varied. The profile of the transferred patterns was measured by profilometry (Ambios XP-1 profilometer). The images were taken by an optical microscope (Zeiss Axio-plan) coupled with a digital camera (Leica DC500) and/or by a scanning electron microscopy (SEM). A pixel matrix was created from the polymers film by varying the fluence for each line to establish the optimum parameters for a clean transfer. All transfer experiments were performed in air. The transfer experiments were performed at low (up to 400 mJ cm^{-2}) and high fluences (up to 800 mJ cm^{-2}) to investigate the influence of the fluence range on the transfer. An additional triazene polymer layer, acting as dynamic release layer or sacrificial layer, was introduced to avoid laser induced degradation of the PEI.

The multilayer donor films were prepared by coating successively fused silica substrates with the triazene polymer and the transfer material, i.e., PEI. Films of the triazene polymer were prepared by spin coating from solutions of the triazene polymer in chlorobenzene/cyclohexanone (1:1, w/w) with final film thicknesses of 0 to 250 nm. Polyethylenimine (PEI, 1.5 to 5 wt% in ethanol) was spin-coated on top of the triazene layer and thin films with thicknesses from 100 nm to 300 nm were obtained. The exact thickness of the films was determined by a surface profiler (Dektak 8000). The depth of the ablated craters from the target, as well as the height of each transferred pixel was measured with the surface profiler.

The receiver substrates were glass plates cleaned by sonication and SAW devices fabricated in two different configurations, i.e., resonator and delay line. Optical microscopy and SEM were used to analyze the morphology of the deposited pixels.

3. RESULTS AND DISCUSSION

The transfer of polymer patterns has practical interests, for instance as sensitive layer on various devices for sensors

applications. The influence of the laser fluence in relation with the thickness of the target material on the transfer is discussed first. Constant layer thicknesses of 150 nm of PEI on top of a 200 nm thick triazene polymer layer were selected for the experiments related to the influence of the laser fluence on the transferred pixels. All applied fluences were investigated at least three times. The observation from optical microscopy images reveal that a clean transfer can be achieved for a quite narrow window of fluences. An overview of the donor (up) and receiver substrates (down) after the transfer is presented in Figure 1 for fluence values for which the transfer is clean and well defined. Transfer without any type of debris or splashes around the pixels was achieved between 590 mJ cm^{-2} and 800 mJ cm^{-2} . In the case of high fluence, the material is removed from the irradiated spot (Fig. 1(a)), and the material is transferred as polymer pixel that can be found intact on the receiver (Fig. 1(c)). By decreasing the laser fluence (590 mJ cm^{-2}), the delamination is still observed on the donor surface, and the square edges are clearly cut-out (Fig. 1(b)), while the pixels keep a regular shape, but with a different surface aspect and with missing part inside the pixel (Fig. 1(d)). The transferred materials changes in aspect and even more non-continuous regions appear inside the pixels (Fig. 2) for fluence values in the range of 450–300 mJ cm^{-2} .

By decreasing the fluence to values below 300 mJ cm^{-2} , the transfer is becoming less regular (Fig. 3 left column) and at very low values, below 200 mJ cm^{-2} , no transfer occurs anymore (Fig. 3 right column). This is very different to the transfer metals or liquids where much lower fluences are required.^{8,9,14}

The thickness of the triazene polymer is important, because together with the applied fluence, it determines the amount of released gas and the remaining thickness of non-ablated triazene polymer.^{14,17} The transfer of PEI was therefore investigated with different triazene polymer layer thicknesses (from 0 to 250 nm) while keeping the PEI layer thickness unchanged. For all the samples, the fluence at which a complete detachment of the polymer pixel occurs was determined by visual inspection of the donor substrates. These detaching fluences depend strongly on the triazene polymer layer thickness.¹⁷

A clean transfer was only achieved with a layer of triazene polymer which is thicker than the thickness of PEI whereas all thinner triazene polymer films did not yield any satisfactory results. Some examples can be seen in Figure 3. The arrow indicates the decrease of the laser fluence (from maxim value of 300 mJ cm^{-2} to minim value of 100 mJ cm^{-2}). One important effect is clearly visible: for thinner layers of TP and thicker PEI films, the amount of triazene polymer becomes too small to provide the force needed to overcome the mechanical resistance of the polymer, i.e., to "cut" a PEI pixel from the film. The detaching

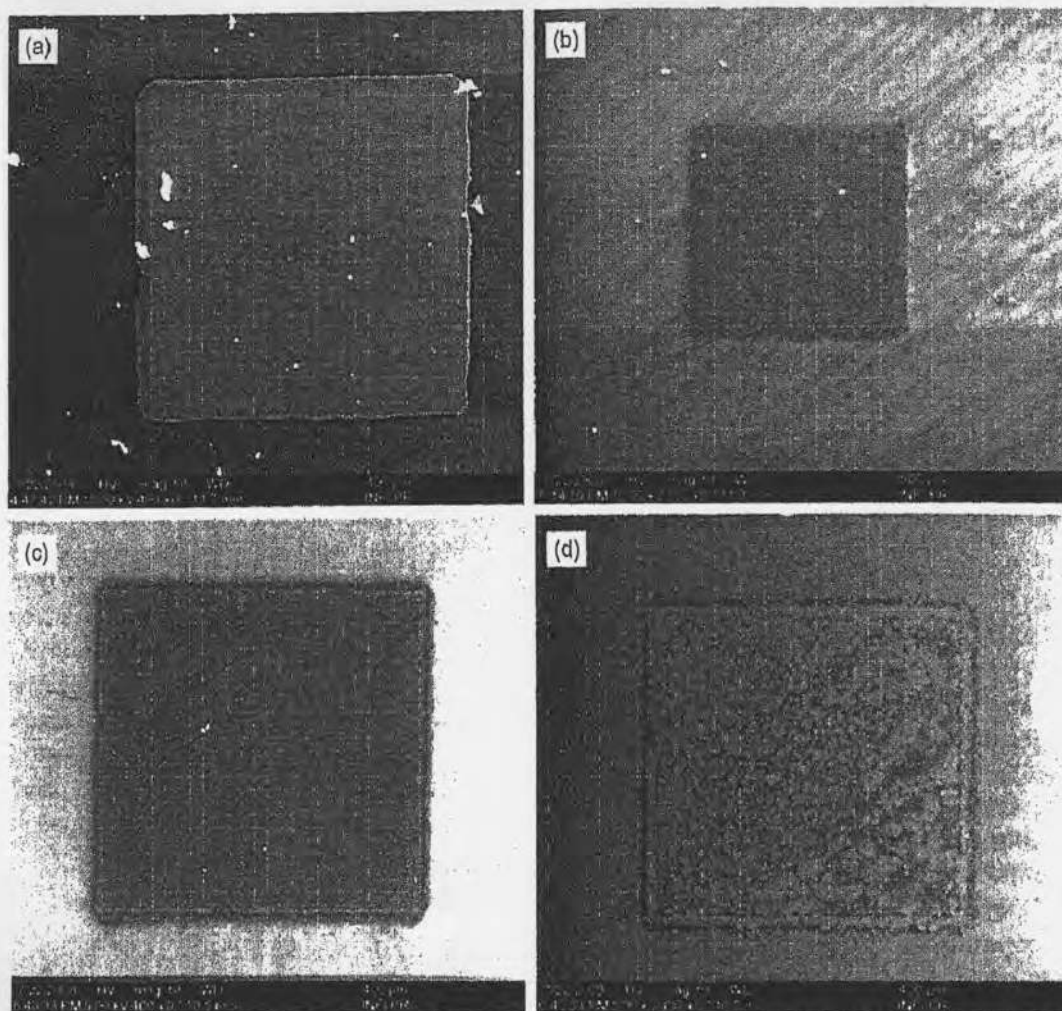


Fig. 1. SEM images of the irradiated spot for fluences of 800 mJ cm^{-2} (a) and 675 mJ cm^{-2} (b) and the corresponding PEI pixels (c and d) transferred on glass.

is therefore not complete and a deformation of the polymer induced by the pressure from the TP decomposition is observed. One part of the polymers sticks on the receiving substrates (Fig. 3 bottom) but the major part of the pixel remains on the target due to the limited available mechanical force (pressure). Some edges consist of teared out film that do not adhere to the receiver substrate. In these cases the pixel does not break into pieces but the pixel edges are folded during the transfer.

When the same thickness of the triazene polymer and PEI was used, an improvement of the surface of the pixel is observed but better results are obtained by increasing the thickness of the triazene polymer which is larger than the thickness of the PEI layer.

Homogeneous deposits with well-defined edges are obtained as well in this case for high fluences ($700\text{--}800 \text{ mJ cm}^{-2}$), (Fig. 4(a)) while for lower fluences, particles or debris appear around the deposits. The debris observed for the pixels obtained at 550 mJ cm^{-2} is not easy to remove with a soft air blow as shown in Figure 4(b). An optimal transfer can be achieved by using a layer of the triazene polymer that exceeds the thickness of the polymeric

layer, whereas thinner films require lower fluences for the transfer.

Another important observation is related to the fact that the receiving substrates should be in close contact for a controlled transfer. The optical microscopy images reveal that for any successfully used before conditions, no well defined pixels were obtained for the transfer across a gap. This can be explained by the fact that the shockwave formed is reflected when it reaches the receiver surface, and destroys the material.

Initial tests for transferring polymers on transducers have also been performed.

The main parameters that have to be controlled for the successful transfer on the active area of the sensor are: the thickness, the homogeneity and the area of the film coating. It is critical to obtain a high homogeneity of the coating in order to minimize scattering and diffraction of the SAWs. In addition to the coating thickness that affects the SAW phase velocity and the insertion losses, it is important that the impact of the polymer should not destroy the interdigital transducers (IDTs) of the device.

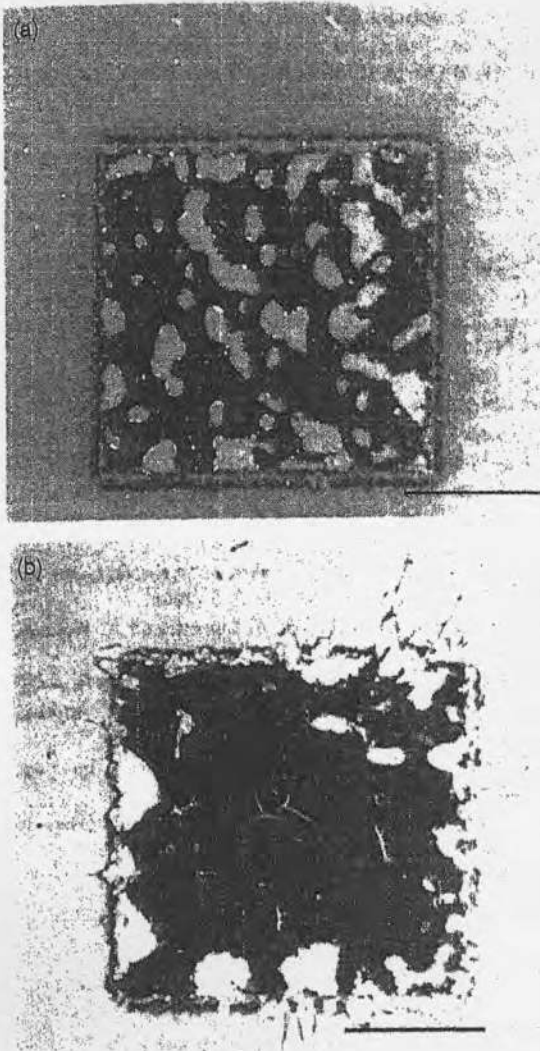


Fig. 2. SEM images of PEI pixels on glass obtained with fluences of (a) 450 mJ cm^{-2} and (b) 300 mJ cm^{-2} . The scale bar is $200 \mu\text{m}$.

Values corresponding to the insertion losses for two fluences employed for transfer are shown in Figure 5. The PEI pixel was transferred to specific areas of interest without destroying it (Fig. 5, insertion). It was observed that for high fluences (800 mJ cm^{-2}) the IDTs are easily destroyed either by the shock wave or by the high velocity impact of the flyer on the IDT surface. For example, for fluences smaller than 700 mJ cm^{-2} , reasonable changes in the insertion losses are obtained.

The choice of the sensor polymer layer was guided by the final goal of our LIFT method, which is to transfer pixels of chemoselective polymers for fabricating chemoselective sensors. The transfer of various polymer pixels without altering the properties of the transferred materials is critical in order to assess the relevance of this technique for the microfabrication of sensors. Further investigations will be carried out to determine the sensitivity of the device to hydrazine based compounds and for various gases.

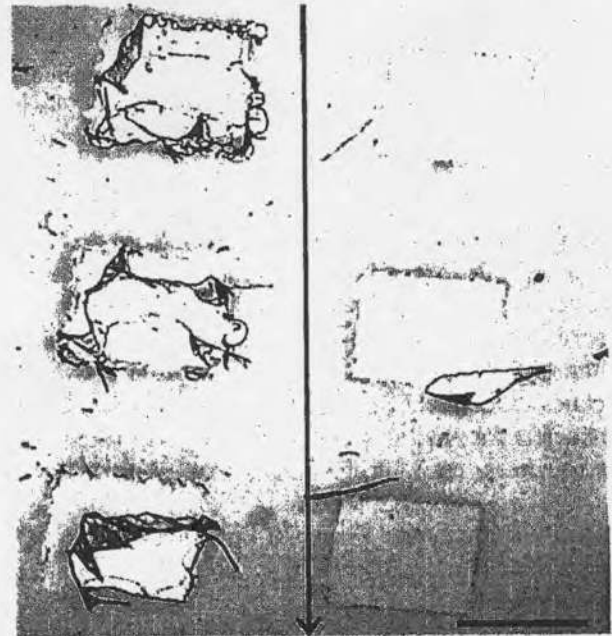


Fig. 3. Optical microscope images of PEI pixels transferred on glass for fluences lower than 300 mJ cm^{-2} (left column) and lower than 200 mJ cm^{-2} (right column). The scale bar is $500 \mu\text{m}$.

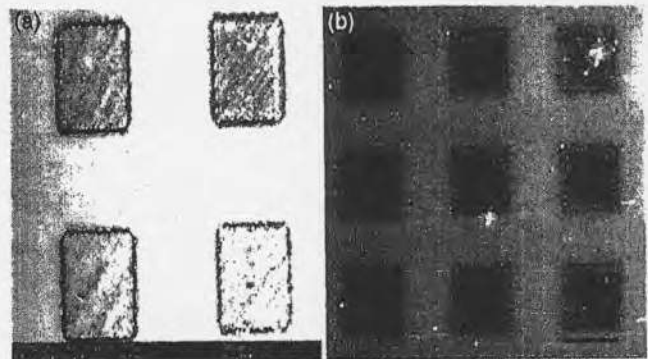


Fig. 4. SEM images of PEI pixels array transferred on glass for fluences of 800 mJ cm^{-2} (a) and 550 J cm^{-2} (b).

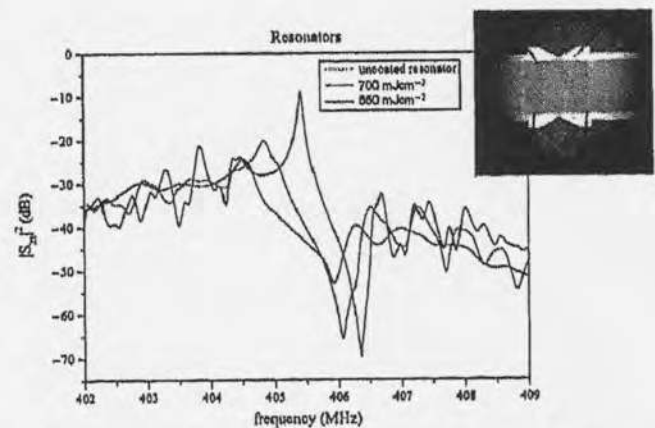


Fig. 5. Changes in insertion losses graph in the cases of the transfer with two different fluences and PEI polymer pixels transferred on IDT surface (insertion).

RESEARCH ARTICLE

4. CONCLUSIONS

The laser-induced forward transfer is strongly influenced by the process parameters and only a narrow operating window can be applied for a successful transfer. There is a minimal thickness of the dynamic release layer, i.e., the triazene polymer, required to benefit fully of the advantages offered by a dynamic release layer. SEM and optical microscope image analyses on the deposited films show that continuous, hole free pixels are obtained for specific experimental conditions. Both, the laser fluence as well as the total target thickness and the relation between the thicknesses of the PEI to the triazene polymer, are key parameters for obtaining continuous polymer pixels with a low roughness on SAW devices.

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References and Notes

1. F. J. Adrian, J. Bohandy, B. F. Kim, A. N. Jette, and P. Thompson, *J. Vac. Sci. Technol. B* 5, 1490 (1987).
2. C. Arnold, P. Serra, and A. Pique, *MRS Bull.* 32, 23 (2007).
3. I. Zergioti, S. Mailis, N. Vainos, C. Fotakis, S. Chen, and C. Grigoropoulos, *Appl. Surf. Sci.* 601, 127 (1998).
4. B. Hopp, T. Smausz, N. Kresz, N. Barna, Zs. Bor, L. Kolozsvári, D. B. Chrisey, Szabó, and A. Nógrádi, *Tissue Eng.* 11, 1817 (2005).
5. D. Banks, P. Grivas, C. Mills, J. D. Eason, and I. Zergioti, *J. Appl. Phys. Lett.* 89, 193107 (2006).
6. I. Zergioti, A. Karaiskou, D. G. Papazoglou, C. Fotakis, M. Kapsetaki, and D. Kafetzopoulos, *Appl. Phys. Lett.* 86, 163902 (2005).
7. J. A. Barron, B. R. Ringeisen, H. Kim, B. J. Spargo, and D. B. Chrisey, *Thin Solid Films* 453–454, 383 (2004).
8. E. Fogarassy, C. Fuchs, F. Kerherve, G. Hauchecome, and I. Perrière, *J. Mater. Res.* 4, 1082 (1989).
9. V. Dinca, M. Farsari, D. Kafetzopoulos, A. Popescu, M. Dinescu, and C. Fotakis, *Thin Solid Films* 18, 6504 (2008).
10. D. B. Chrisey, A. Piqué, R. A. McGill, J. S. Horwitz, B. R. Ringeisen, D. M. Bubb, and P. K. Wu, *Chem. Rev.* 103, 553 (2003).
11. P. Serra, J. M. Fernández-Pradas, F. X. Berthet, M. Colina, J. Elvira, and J. L. Morenza, *Appl. Phys. A: Mater. Sci. Process.* 79, 949 (2004).
12. B. R. Ringeisen, D. B. Chrisey, A. Piqué, H. D. Young, R. Modi, M. Bucaro, J. Jones-Meehan, and B. J. Spargo, *Biomaterials* 23, 161 (2002).
13. A. Karaiskou, I. Zergioti, C. Fotakis, M. Kapsetaki, and D. Kafetzopoulos, *Appl. Surf. Sci.* 208–209, 245 (2003).
14. R. Fardel, M. Nagel, F. Nuesch, T. Lippert, and A. Wokaun, *Appl. Phys. Lett.* 91, 061103 (2007).
15. A. Dorniswamy, R. Namynn, T. Lippert, and L. Urech, A. Wokaun, M. Nagel, B. Hopp, M. Dinescu, R. Modi, R. Auyeung, and D. Chrisey, *Appl. Surf. Sci.* 252, 4743 (2006).
16. J. Xu, J. Liu, D. Cui, M. Gerhold, A. Y. Wang, M. Nagel, and T. Lippert, *Nanotechnology* 18, 025403 (2007).
17. R. Fardel, M. Nagel, F. Nuesch, T. Lippert, and A. Wokaun, *Appl. Surf. Sci.* 254, 1322 (2007).