

Polymer pixel enhancement by laser-induced forward transfer for sensor applications

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Abstract This paper presents polymer pixel printing for applications in chemoselective sensors where nanosecond laser direct transfer methods, with a triazene polymer (TP) acting as a Dynamic Release Layer (DRL), are used. A systematic study of laser fluence, donor film morphology and both single- and multiple-pixel deposition were optimized with the final goal to obtain continuous pixels of sensitive polymers, polyethylenimine (PEI) and polyisobutylene (PIB), on SAW surfaces. Morphology characterization after the laser transfer has been performed by Optical Microscopy and Scanning Electron Microscopy (SEM). The responses of the coated transducers were measured after deposition with different laser fluences and it was found that a fluence under 625 mJ/cm^2 was required in order to prevent damage of the interdigital transducers (IDT) of the sensor devices. The sensitivity of the polymer coated devices to acetone concentrations gives an indication that LIFT can be used for printing sensitive polymer pixels onto transducer devices.

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1 Introduction

The demand for flexible technologies that are good for manufacturing chemical sensors for the detection of air-borne species has rapidly increased in recent years. The need for portable, low-cost and easily deployable chemical and biological sensors has become even more urgent due to increased counter terrorism operations. The new sensor generation has to meet specific requirements i.e. to respond to low concentrations of potentially harmful chemical agents, considerably lower than those immediately dangerous to life and health: discriminate between chemical warfare agents and other chemicals in the environment, and to identify them in the presence of other harmful chemical agents.

Sensors based on electro-acoustic detection techniques, exploiting the propagation of either Surface Acoustic Waves (SAW) or Bulk Acoustic Waves (BAW), use oxidic/metallic membranes or nanostructures as active layers. These constitute a very sensitive class of sensors, appropriate for fulfilling the stringent requirements needed for counter terrorism biological and chemical sensors outlined above [1].

Recent advances in SAW devices and micro-machined cantilever structures in conjunction with the use of both organic and inorganic active layers such as porous metallic oxides, polymers or metal-porphyrins have created gas sensors with improved performances. The sensitivity of such sensors can be very high, up to 1 picogram (10–12 g) and, moreover, it is nonionic and nonspecific. They can directly measure the mass of each chemical compound absorbed into or adsorbed onto a sensitive membrane [2].

The recent advances in laser processing of polymeric materials mean that laser-processing techniques are very suitable for the latest microstructuring applications. Laser methods are clean, versatile and flexible and the resolution attainable meets even the most advanced requirements

for sensor (and hybrid electronics) machining. In addition, new emerging laser deposition techniques as matrix assisted pulsed laser evaporation-direct write (MAPLE-DW) [3] and laser-induced forward transfer (LIFT) [4] allow good control of the deposition of laterally resolved polymeric structures (“pixels”) onto wafer.

By using different types of pixels made of polymers with different functionalities, an array of sensors can be built. The use of polymers sensitive to different gases has emerged as a new solution for the fabrication of chemical sensors both because of their high degree of sensitivity and because of the large range of different functionalities that they offer [5].

Until now it has been almost impossible to obtain pixels with the conventional coating methods. Polymers, with their inherently high molecular weights are not sufficiently volatile and thermally stable for dry evaporation-deposition procedures. Wet deposition techniques are not appropriate because solvent often remains in the polymer films [6]. To avoid decomposition of these sensitive macromolecular materials or to prevent one from having an undefined amount of solvent in the film, only “mild” and “solvent-free” coating technologies should be used to obtain thin-film polymeric layers.

This study proposes a new approach to polymer pixel deposition problem based on the use of SAW structures for chemical sensors by the deposition of polymers as active and sensitive membranes using a mild, “solvent-free” or “dry” material transfer technique called dynamic release layer assisted laser-induced forward transfer (DRL-LIFT) [7].

In our case, the sacrificial DRL is a triazene polymer (TP) designed to absorb the laser radiation and decompose into small, gaseous, molecular fragments that propel the material to be transferred and reduce the risk of damaging the polymer pixel [8].

2 Materials and methods

2.1 Patterning system

Transfer was achieved using single pulses from both a XeCl excimer laser (Compex, Lambda Physik, 308 nm, 30 ns pulse length, 1 Hz repetition rate), and a “Surelite II” pulsed Nd:YAG laser (Continuum Company, 266 nm wavelength, 5 ns pulse duration, 1 Hz repetition rate). The laser beam passed through a square mask with a variable aperture, which was used to utilize a homogeneous part of the beam. The laser beam was focused by a lens onto the backside of the donor film giving spot sizes of $200\ \mu\text{m} \times 200\ \mu\text{m}$, $250\ \mu\text{m} \times 1\ \text{mm}$ and $800\ \mu\text{m} \times 2\ \text{mm}$. The donor and the receiver substrates were placed in close contact onto a motorized translation stage.

2.2 Donor films

Multilayer donor films were prepared and used as LIFT targets, otherwise known as donor substrates. All of the donor substrates consisted of a TP spin coated onto fused silica plates. The transfer materials were then coated on top of the TP. The TP was synthesized as described by Nagel et al. in [9]. Polyethylenimine (PEI) and polyisobutylene (PIB) were used as sensitive materials and coated on top of the TP by two approaches: spin coating and matrix assisted pulsed laser evaporation (MAPLE).

2.2.1 Spin coating experiments

Solutions of Triazene (2% dissolved in a mixture of chlorobenzene and cyclohexanone (1:1 w/w)) PEI (1.5% dissolved in ethanol) and PIB (1.5% dissolved in toluene) were made to be used in the preparation of thin films by spin coating. The experiments were carried out using a spin coater with dispenser (SCS P6708). The process involves depositing a small volume of solution through a $0.45\ \mu\text{m}$ filter onto the center of the substrate and then spinning the substrate for 60 s at speeds of 2000 rpm with a ramp of 1000 rpm/s. The films were dried after deposition overnight at room temperature. The final film thickness was determined by profilometer measurements (Veeco Dektak 8 Profilometer).

2.2.2 MAPLE experiments

MAPLE is a deposition method suited for the deposition of thin films with controllable morphology and uniformity [10]. Briefly, the technique involves diluting the material of interest in a volatile, non interacting matrix or solvent (0.1–5 wt%) freezing the mixture to create a solid target/system. When the system is irradiated by a laser beam, the solvent evaporates whereas the guest molecules are collected on a substrate [10, 11].

In this study, the beam from a pulsed Nd:YAG laser was focused onto the frozen polymer targets (1.5 wt%) (two different experiments). The laser fluences ranged from $0.1\ \text{J}/\text{cm}^2$ – $0.5\ \text{J}/\text{cm}^2$. The substrates were fused silica plates pre-coated with TP and which were placed at a distance of 4 cm from the frozen system. The number of pulses was varied from 6000 to 20000 pulses in order to vary the thickness of the deposited thin polymer films. To have uniform evaporation, the target was rotated during the experiments. In order to control the temperature of the target during deposition two thermocouples were placed at two different positions of the target holder. The background pressure between 7×10^{-5} and 2×10^{-4} mbar was obtained with a Pfeiffer-Balzars TPU 170 turbo molecular pump ($170\ \text{L s}^{-1}$).

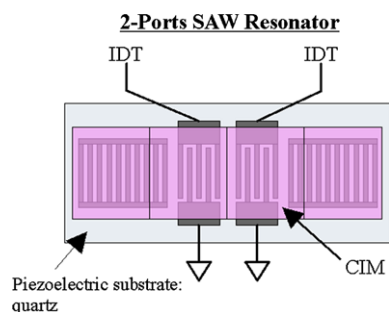


Fig. 1 Schematic representation of SAW resonator coated by a chemically interactive membrane (CIM)

2.3 Receiver substrates

Both 1 inch \times 1 inch glass slides cleaned prior the transfers, and standard 2-port SAW resonators operating at approximately 405.4 MHz were used as receiver substrates. The interdigital transducers are shaped with a Gaussian apodization in order to minimize spurious transverse modes, with a wavelength of 8 μm (I) finger overlap of 800 μm (W) with cavity length of 1140 μm .

For the fabrication of the SAW devices, the structures were formed on a quartz substrate and the pattern was obtained by a lithographic process using poly(methyl methacrylate) (PMMA) as resist and deep UV radiation, in order to obtain a high resolution.

The electrodes consisted of Al films grown by radio frequency reactive magnetron sputtering technique from a 99.999% pure Al target in an Ar atmosphere (thickness 100 nm). Finally, a lift-off process is used to obtain the interdigital transducers (IDT) with different features.

2.4 Gas sensing measurements

SAW devices are largely used to measure physical parameters, such as force, acceleration, pressure, electric and magnetic fields, etc., or chemical and biochemical values, such as gas, vapor or ion concentrations in both gaseous and liquid environments [12–14]. When a SAW resonator is coated by a proper chemically interactive membrane (CIM) (Fig. 1), adsorption and desorption of the analyte from the membrane give rise to changes in the CIM's properties (mass density, elastic, viscoelastic and electric properties), which are detected as shifts in the resonant frequency of the SAW resonator.

The coated area represents the active area of the device. SAW sensors have been tested upon exposure to concentrations of acetone using the Network Analyzer. The test devices are placed in a sealed chamber where the total flow is set to 150 sccm. Three flow meters were used: two for the gas carrier (N_2) and the other for the analyte. The responses are obtained by fluxing N_2 in liquid analyte such as acetone. The response curves were obtained at 20°C.

3 Results and discussions

The aim of this study is to optimize printing active polymer pixels onto SAW devices for chemical sensors. To achieve this goal a parametric study was carried out. The effects of the laser fluence, donor films thickness and morphology and both single-pixel and multipixel transfer were investigated to obtain continuous pixels of sensitive polymers on SAW surfaces.

3.1 The influence of laser fluence

The laser fluence is an important parameter that requires careful control in order to obtain a regular, debris free transfer. The data in this section were obtained for films of 100 nm TP layers coated with 50 nm of both PEI and PIB. The laser fluence was varied over a broad range, i.e. from sufficient conditions to eject the donor films up to high irradiation (300–800 mJ/cm^2) in order to optimize the shape of the transferred pixels without any structural modification of the polymer material.

As a first step the threshold fluence for the removal and transfer of the polymer material with the 308 XeCl laser is 300 mJ/cm^2 whilst for the 266 nm laser system it is 375 mJ/cm^2 . The pixels shown in Fig. 2 are obtained for PIB, for different laser fluences with the 266 nm laser system (Fig. 2a) and with the 308 nm laser system (Fig. 2b).

For the excimer laser systems, below the threshold fluence there can only be seen the edges of the ablation spot which are visible probably due to slightly higher beam intensity at the edge. For the 266 nm laser system using the same fluencies as for the 308 nm laser system, there is only a small quantity of material transferred below the threshold fluence, and for higher values the morphology looks different compared with that obtained with the 308 nm laser system. This can be best explained by the difference in the profiles of the laser beam in the two cases described. The XeCl excimer laser delivers a large, rectangular, top hat beam whilst the applied fourth harmonic of Nd:YAG laser has a poor spatial homogeneity of the beam intensity. This fact and the higher absorption of the polymer at 308 nm represent explanation for the differences observed in the transferred pixel morphology.

Even though the fluences used to transfer the polymeric materials are much above the fluence needed to vaporize the TP layer (which occurs at 50 mJ/cm^2 for a 100 nm thick TP layer), the fluence of 325 mJ/cm^2 was still too low to result in a clean transfer of the polymeric layer. The fact that the fluence needed to ablate the TP layer has a very low value is an advantage because it is therefore very probable that no contamination of the transferred polymer pixels with debris from the ablation of the TP will be observed.

Only above 400 mJ/cm^2 is obtained a clean transfer i.e. pixels with a well-defined contour are obtained. The high

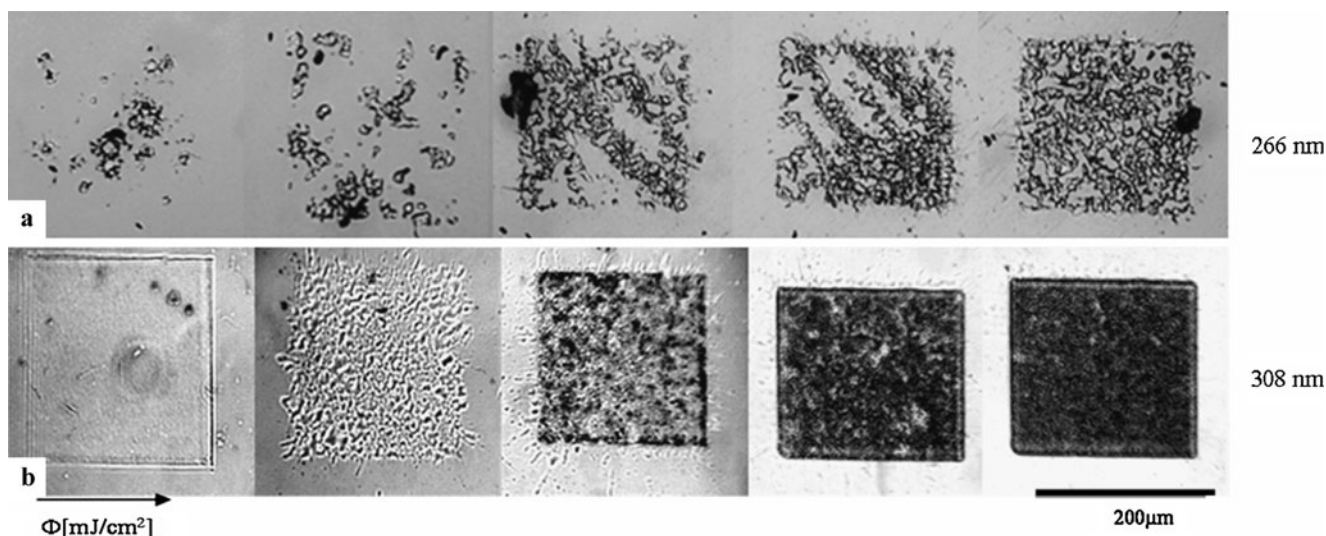


Fig. 2 Optical microscopy images of PEI pixels transferred by LIFT onto glass by 266 nm (a) and 308 nm (b), at different fluences. From left to right: 300 mJ/cm², 325 mJ/cm², 375 mJ/cm², 400 mJ/cm², 450 mJ/cm²

value of the fluence necessary for a complete transfer is explained by the nature of the materials to be transferred; polymers deform plastically and they require stronger propulsion to be detached from the target than for more brittle materials.

When higher fluences are applied (in the range of 700 mJ/cm²) the collision speed of the flyer with the substrate might damage not only the polymer pixel, but also the receiver substrate [16].

Similar results are obtained for the PEI polymer, but due to its higher stiffness value (characterized by a tensile strength of 105 MPa for PEI whilst for PIB is up to 50 MPa), the fluence needed to achieve a removal of the polymer was lower, namely 250 mJ/cm² for the 308 nm laser system and 300 mJ/cm² for the 266 nm laser system. This observation corresponds with previous results related to the use of different fluence value for laser transfer of the same thickness of materials with different properties [15].

All the results discussed above are for experiments where the targets used were prepared by MAPLE. For the experiments using targets prepared by spin coating, similar results related to the fluence values are obtained. The main difference observed for the transferred pixels is related to the influence of the target surface morphology and is discussed in the next section.

It would be interesting to compare the laser fluences required to transfer polymer pixels of different thicknesses but for our application the transferred polymer pixels should have a thickness of about 50 nm and therefore only these thicknesses are analyzed in detail.

Moreover, previous studies [16] have shown that a separation distance between the donor and the receiver substrates results in damage of the transferred material, therefore these

transfer experiments were carried out in close contact between the donor and the receiver.

3.2 Influence of donor substrate morphology

The thickness and morphology of the donor substrate can affect the functionality of the devices significantly. The phase SAW velocity and insertion losses are both dependent on the pixel thickness applied on the active area of the device [16]. SAW scattering and diffraction can be minimized with a less rough active surface. This aspect involves a high donor substrate surface smoothness. The requirements for the donor substrate are therefore a relatively thin film; that is, more importantly, a film uniform in thickness, and it should have a low surface roughness.

The two methods (spin coating and MAPLE) used to obtain the donor substrates resulted in morphology differences. The relationship between the donor substrate morphology and the morphology of the transferred pixels can be seen in the Fig. 3. Ripple defects occurred with spin coating of the polymers (Fig. 3a and b). The ripple peaks, marked in the images with arrows are radial oriented and the periodicity is of the order of tens of microns range. Their occurrence is thought to arise due to evaporation driven surface tension effects [17].

For the MAPLE-prepared donor substrates, no ripples were observed (Fig. 3d and e). The chemical structure of the polymers was preserved after the deposition, as confirmed in our previous studies using FTIR measurements [18]. The coating smoothness as well as their effects upon the phase SAW velocity and insertion losses will be discussed later.

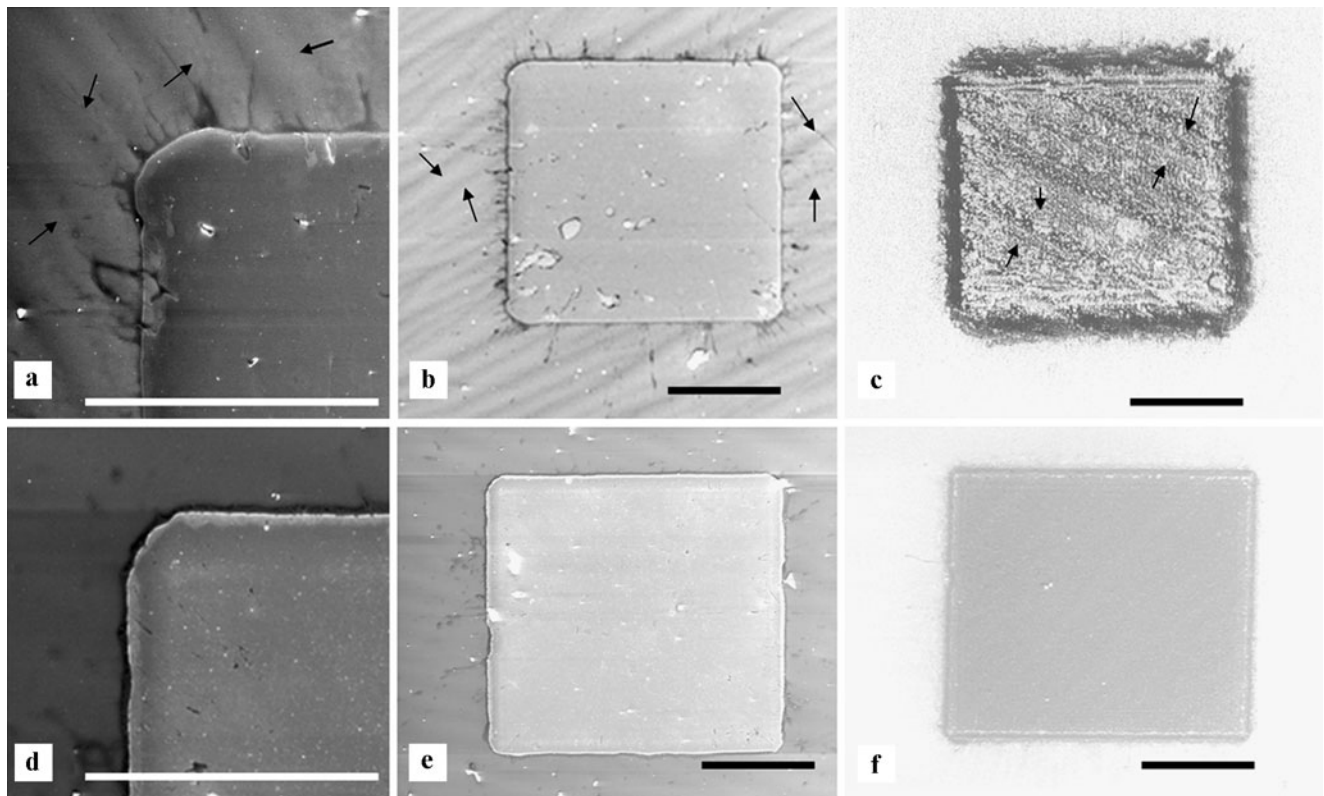
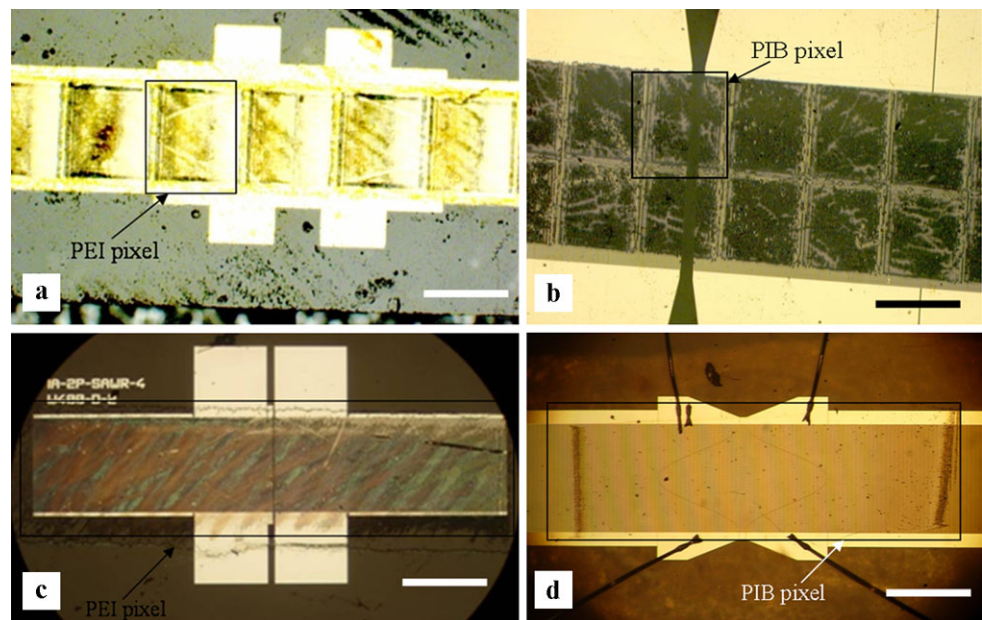


Fig. 3 SEM images of the craters within the donor substrates obtained by spin coating (**a**-close up and **b**) and MAPLE (**d**-close up and **e**) and the corresponding pixels (**c** and **f**). The presence of ripples onto target

obtained by spin coating and the pixel transferred is marked by arrows. The laser fluence was 450 mJ/cm^2 . Scale bar is $200 \mu\text{m}$. The substrates used are glass

Fig. 4 Optical images of PEI (**a**) and PIB (**b**) multiple pixels transferred on the IDTs at 450 mJ/cm^2 laser fluence; optical images of single PEI polymer pixel (**c**) from a target obtained by spin coating and optical images of single PIB polymer pixel (**d**) (450 mJ/cm^2) from a target obtained by MAPLE. Scale bar is $400 \mu\text{m}$



3.3 Single-pixel devices versus multipixel devices

For the 2-port SAW resonators, multiple pixels were transferred onto the interdigital transducers (IDTs); that is, onto the acoustic resonating cavity of the devices (Fig. 4).

For a preliminary set of depositions at high fluences (above 500 mJ/cm^2), the resonator performances were strongly lowered by the polymer coatings. The magnitude of the frequency responses expressed as the scattering parameter (S_{21}) for the polymer coated devices are shown in

Fig. 5 Frequency responses of multiple pixels coated resonators (a) and of an uncoated resonator (b)

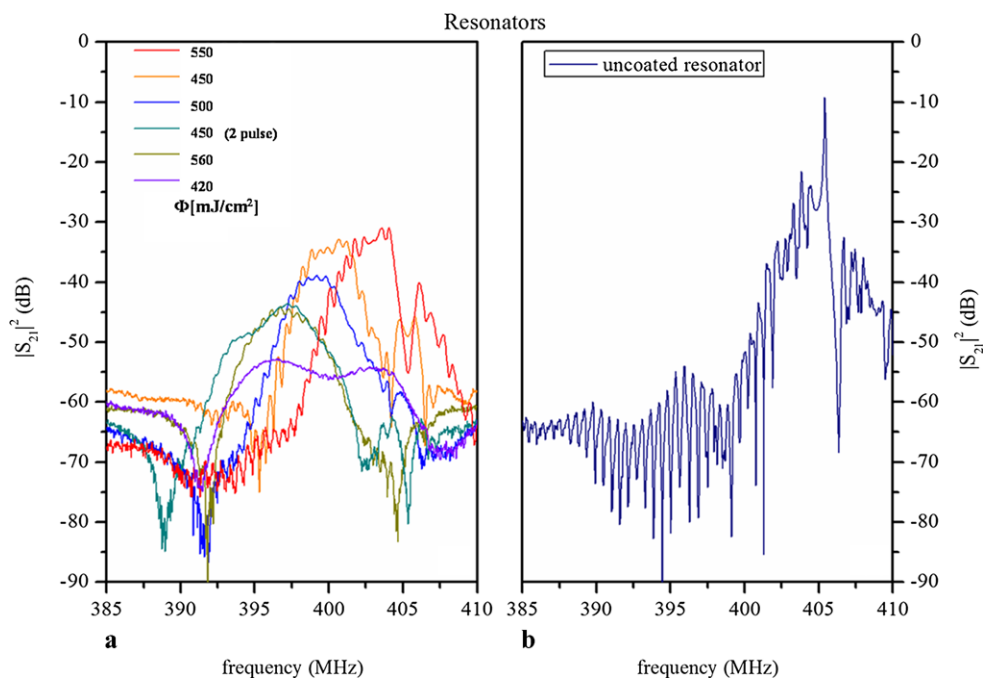


Fig. 6 Single-pixel polymer (PIB) based device response to acetone. The fluence used to transfer the pixel was $450 \text{ mJ}/\text{cm}^2$

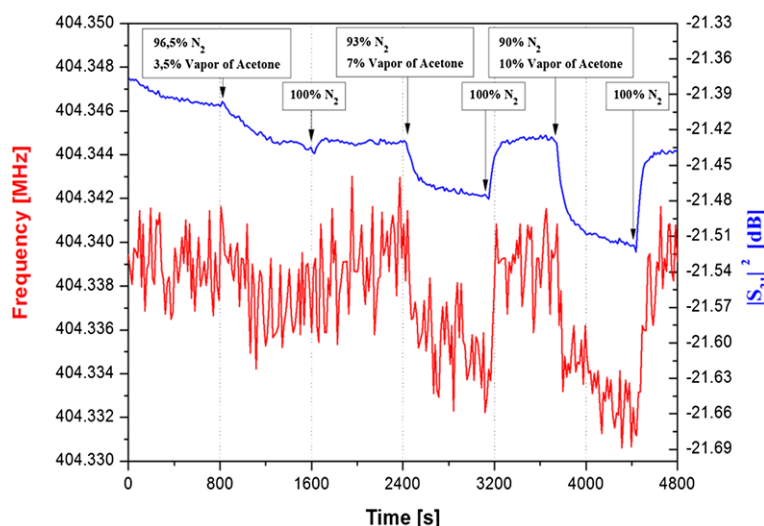


Fig. 5a, while in Fig. 5b the response of an uncoated device is presented. Even for values of fluences ($420\text{--}500 \text{ mJ}/\text{cm}^2$) for which well-defined and smooth pixels are obtained, it is observed that the resonant peak seen in the uncoated device is not present. These devices are therefore non-functional. This can be explained by the inhomogeneous cover of the active area of the SAW device. The overlapping and high surface roughness of the multipixel polymer surface (for low value of the fluence cases) are the main factors causing inhomogeneous covering of the devices. For this reason, single pulses were applied to transfer single pixels with sizes corresponding to the active area of the device (Fig. 5c and d).

It was observed that the devices on which one pixel was transferred with lower fluences ($300\text{--}400 \text{ mJ}/\text{cm}^2$) are non-

functional due to the high roughness and incomplete coverage of its active area. The maximum applied fluence should be less than $500 \text{ mJ}/\text{cm}^2$ and functional devices were obtained for fluence values of 400 up to $500 \text{ mJ}/\text{cm}^2$.

For these devices, the resonant peak seen in the uncoated device is observed (figure not shown). For higher fluences ($>625 \text{ mJ}/\text{cm}^2$) the aluminum metallization of the IDTs is easily damaged. Exposure of PIB coated device to a nitrogen flux containing from 3.5% to 10% acetone results in changes in the resonant frequency and the corresponding insertion losses. The reversible response to the different acetone concentrations is shown in Fig. 6. These preliminary measurements give an indication that LIFT can be used for printing sensitive polymer pixels onto transducer devices.

4 Conclusions

The LIFT method has been successfully used to print polymer pixels as active and sensitive membranes onto SAW structures for chemical sensors applications. The main parameter that has to be controlled in order to minimize scattering and diffraction of the SAWs is surface roughness of the polymer area coating. SEM and optical microscopy pictures revealed more uniform polymer coverage of the substrate surface deposited by MAPLE compared with spin coating. Additionally, it is critical not to damage the IDT, so laser fluence is an important variable to control.

Promising results for detecting non-polar organics like acetone were obtained by using single polyisobutylene pixel transferred by LIFT onto active area of the device. Future work will involve printing of different types of pixels, i.e. polymers with different functionality onto a sensor matrix, which will enable the production of sensor arrays.

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References

1. S.J. Ippolito, A. Trinchì, D.A. Powell, W. Wlodarski, Acoustic wave gas and vapor sensors, in *Solid State Gas Sensing* (Springer, Berlin, 2008), pp. 1–44. doi:[10.1007/978-0-387-09665-0](https://doi.org/10.1007/978-0-387-09665-0)
2. G. Guan, B. Liu, Z. Wang, Z. Zhang, *Sensors* **8**, 8291–8320 (2008). doi:[10.3390/s8128291](https://doi.org/10.3390/s8128291)
3. D.B. Chrisey, *Science* **289**, 879–881 (2000)
4. A. Klini, A. Mourka, V. Dinca, C. Fotakis, F. Claeysens, *Appl. Phys. A Mater. Sci. Process.* **87**(1), 17–22 (2007)
5. H. Bai, G. Shi, *Sensors* **7**, 267–307 (2007)
6. T. Lippert, *Adv. Polym. Sci.* **168**, 51–246 (2004)
7. M. Nagel, R. Hany, T. Lippert, M. Molberg, F.A. Nüesch, D. Rentsch, *Macromol. Chem. Phys.* **208**(3), 277–286 (2004)
8. L. Urech, T. Lippert, *Laser Ablation and its Applications*, vol. 129 (Springer, Berlin, 2007), pp. 281–297
9. M. Nagel, R. Fardel, P. Feurer, M. Häberli, F. Nüesch, T.K. Lippert, A. Wokaun, *Appl. Phys. A* **92**(4), 781–789 (2008)
10. D.B. Chrisey, A. Piqué, R.A. McGill, J.S. Horwitz, B.R. Ringeisen, D.M. Bubb, P.K. Wu, *Chem. Rev.* **103**, 553–576 (2003)
11. A. Purice, J. Schou, P. Kingshott, M. Dinescu, *Chem. Phys. Lett.* **435**, 350–353 (2007)
12. D.S. Ballatine, R.M. White, S.J. Martin, A.J. Ricco, E.T. Zellers, G.C. Frye, H. Wohltjen, *Acoustic Wave Sensors* (Academic Press, San Diego, 1997), Sect. 4.2.1
13. F. Josse, F. Bender, R.W. Cernosek, *Anal. Chem.* **73**, 5937–5944 (2001)
14. S.J. Martin, G.C. Frye, J.J. Spates, M.A. Butler, *IEEE Ultrason. Proc.* **2**, 423–434 (1996)
15. R. Fardel, M. Nagel, F. Nüesch, T. Lippert, A. Wokaun, *Appl. Surf. Sci.* **254**, 1322–1326 (2007)
16. V. Dinca, R. Fardel, F. Di Pietrantonio, D. Cannatà, M. Benetti, E. Verona, A. Palla-Papavlu, M. Dinescu, T. Lippert, *Sens. Lett.* **8**, 436–440 (2010). doi:[10.1166/sl.2010.1291](https://doi.org/10.1166/sl.2010.1291)
17. D.P. Birnie III, D.M. Kaz, D.J. Taylor, *J. Sol-Gel Sci. Technol.* **49**, 233–237 (2009)
18. A. Palla-Papavlu, C. Constantinescu, V. Dinca, A. Matei, A. Moldovan, B. Mitu, M. Dinescu, *Sens. Lett.* **8**(3), 502–506 (2010). doi:[10.1166/sl.2010.1302](https://doi.org/10.1166/sl.2010.1302)