GAS SENSORS FABRICATED BY LASER-INDUCED FORWARD TRANSFER

Alexandra PALLA PAPAVLU*, Fabio DI PIETRANTONIO**, Domenico CANNATÀ**, Massimiliano BENETTI**, Enrico VERONA**, Valentina DINCA*, Thomas LIPPERT***, Maria DINESCU*

*Lasers Department, National Institute for Lasers, Plasma and Radiation Physics, 077125 Magurele, Romania, **"O.M. Corbino" Institute of Acoustics, Italian National Research Council–CNR, Via del Fosso del Cavaliere 100, 00133 Rome, Italy, ***General Energy Research Department, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Abstract: *This work summarizes the developments in dynamic release layer (DRL) assisted LIFT of complex materials such as polymers, biomolecules, or carbon nanotubes for applications as recognizing elements in miniaturized surface acoustic wave (SAW) resonators and chemiresistor devices.*
As the functionality of such sensors depends on the applied laser source, target material, and transfer geometry, first an optimization of the process parameters is reported.
Following a morphological and structural characterization of the active material, the performance, i.e. the sensitivity, resolution, and response time of the laser-printed devices was evaluated by exposure of the sensor arrays to different toxic vapors. Different sensitivities and selectivity to the selected chemical agents i.e. dimethyl methylphosphonate, dichloromethane, dichloropentyhane, ethyl acetate, etc. have been measured thus proving the feasibility of LIFT for applications in sensors and biosensors.

Keywords: *laser-induced forward transfer, surface acoustic wave, sensors, chemiresistors*

1. INTRODUCTION

Environmental monitoring due to air pollution is a problem of current interest both for the industry, i.e. automotive (detection of polluting gases from cars) as well as for many research groups. Since sensors are the main components in products and systems used to detect volatile organic compounds (VOCs) in air, there are always new and innovative sensor technologies emerging. Several key requirements for sensors include sensitivity, the minimum concentration of target gases they can detect, response speed, reversibility, energy consumption, and fabrication costs [1].

A wide variety of natural occurring substances (such as cells, enzymes, receptors, and antibodies) are commonly used as sensing elements in sensor technology. Besides these biological materials, polymers and carbon nanotubes (CNTs) are used as active materials in gas sensors.

Polymers are used as recognition elements in sensor structures, due to their wide range of capabilities [2]:

1. Polymers can collect and concentrate vapor molecules on sensor surfaces by reversible sorption.

2. They can be applied on device surfaces as thin adherent films.

3. Their chemical selectivity is determined by the chemical structure, which can be varied easily through synthetic design.

4. They can yield sensors with rapid, reversible, and reproducible responses.

5. Diverse sets of polymers can be assembled rationally for sensor arrays.

In addition to polymers, single walled carbon nanotubes (SWCNT) are promising chemical sensing materials, due to their hollow structure, one-dimensional nanoscale morphology, and high specific surface area that benefits physical adsorption or chemical reaction with target molecules for signal transformations with higher efficiency and speed [3,4].

The applicability of devices based on polymer or SWCNT systems has been limited by the complexity associated with the device fabrication. An interesting alternative to conventional printing techniques is laser-induced forward transfer (LIFT). LIFT is free from clogging problems, which are characteristic for inkjet printing, and avoids the use of expensive photolithographic masks. LIFT presents also a higher potential for integration than another possible deposition methods, e.g. microspotting.

This techniques is versatile and allows printing a wide class of materials i.e. inorganic inks and pastes, metals, oxides, polymers and biological materials in solid or liquid phase [5-15]. In LIFT the material of interest is transferred by the laser beam from a transparent support (donor substrate) onto an appropriate substrate (receiver). For improving the process efficiency and reducing the risk of damaging the layer to be transferred, the donor substrate can be previously coated with a polymeric layer, which is called sacrificial dynamic release layer (DRL) [16-18].

The aim of this work is to contribute to the study of applying a clean and versatile fabrication method, i.e. DRL-LIFT of polymers and SWCNT based sensors for gas detection.

The microstructure of the active material in a gas sensor is a key parameter influencing the sensitivity of the material [19]. Therefore, the morphology and structure of the transferred pixels is established. This work is complemented by measuring the response to different gas exposure. Based on the requirements of National Institute for Occupational Safety and Health (NIOSH), a test range of 10-200 ppm of gas was considered in this work.

2. EXPERIMENTAL

2.1 Laser-induced forward transfer

The LIFT setup used in this work consists of the pulsed UV XeCl laser beam (308 nm emission wavelength, 30 ns pulse length, 1 Hz repetition rate) which is guided and imaged with an optical system onto the donor substrate to transfer micropixels from the donor substrate to the receiving surface [1, 20]. The laser fluence is varied from 100 mJ/cm^2 to 700 mJ/cm^2. A computer-controlled *xyz* translation stage allows the displacement of both donor and receptor substrates with respect to the laser beam. The donor and the receiver are kept in contact while the laser irradiates the donor from the backside. For each laser pulse single micropixels are obtained. All experiments were performed under ambient pressure at room temperature. A scheme of the LIFT setup is shown in Figure 1.
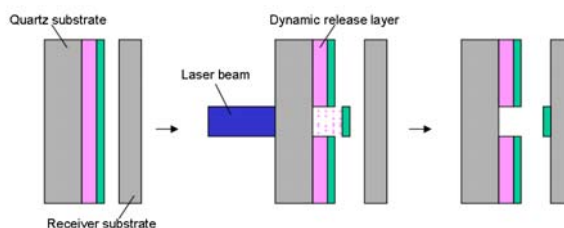

Figure 1. Scheme of the LIFT setup.

2.2 Donor and receiving substrates

The donor substrates are prepared by spin coating the triazene polymer (TP) (with a thickness of 60 nm, 100 nm, and 300 nm) onto fused silica plates (area 5 cm^2, thickness 1 mm) and then spin coating the materials to transfer: polymers and carbon nanotubes. The TP is synthesized as described by Nagel *et al.* in [16] and is then prepared by spin coating from a solution in chlorobenzene and

"HENRI COANDA"
AIR FORCE ACADEMY
ROMANIA

"GENERAL M.R. STEFANIK"
ARMED FORCES ACADEMY
SLOVAK REPUBLIC

INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER
AFASES 2014
Brasov, 22-24 May 2014

cyclohexanone (1:1, w/w). TP is chosen as DRL layer, due to the fact that the emission wavelength of the laser used in this work matches the absorption maxima of the TP.

The chemoselective polymers, polyepichlorhydrine (PECH), polyisobutylene (PIB), polyethilenimine (PEI), poly(styrene-co-maleic acid) (PScMA), and hydroxypropylmethyl cellulose (HPMC) are chosen to be deposited by laser based methods as chemical interactive membranes on surface acoustic wave (SAW) resonators due to their ability to specifically and selectively identify target gases.

As previously reported in [1, 20] the first step in the sensor array production process is to deposit the five polymers as individual thin films onto the same substrate plate by matrix-assisted pulsed laser evaporation (MAPLE). The aim is to create multi-ribbon targets, which would allow single step transfer (by LIFT) of multiple polymer layers onto different sensors arranged in a matrix.

Single walled carbon nanotubes (SWCNT, HiPco) are purchased from Nanointegris (as a dry powder) and used without further purification.

In order to obtain SWCNT thin films, 10 mg CNT are dispersed in water (15 ml) containing the nonionic surfactant Triton X (100 mg), and the dispersion is bath sonicated for 40 min. The dispersion is then spin coated onto TP coated fused silica plates under different conditions i.e. rotation speed 1500 – 2500, ramp of 1000 – 2000 rpm, and spin coating duration of 30 s and 60 s. In order to remove any trace of solvent from the donor films, the spin coated SWCNT were then left to dry on a hot plate for 2 hours at 50 °C. In Figure 2 an atomic force microscopy (AFM) image of the SWCNT donor film deposited onto a TP film is shown.
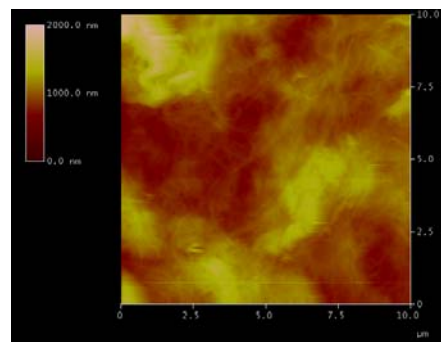

Figure 2. Atomic force microscopy image of a SWCNT donor film.

As receiver substrates, either SAW resonators (for polymer deposition) or chemiresistor structures are used.

2.3 Morphological and structural investigation

The deposited features as well as the target prior to ablation are investigated by optical microscopy. The images are acquired with an Axiovert 200 Microscope coupled to a Carl Zeiss AxioCam MRm camera.

Raman microscopy is used to check for any chemical changes in the structure of the SWCNT prior and after their deposition by LIFT. The Raman spectra of SWCNT are recorded on a Labram confocal Raman microscopy system from Jobin Yvon. The 633 nm line from a HeNe laser is used as an excitation source for the Raman spectra. The laser power at the sample surface is typically 20 mW. For each measurement, the exposure time and the accumulation were 20 s and 5 times, respectively. Raman spectra are collected over the range of 200–3000 cm^{-1}. All spectra are recorded at room temperature.

2.4 Sensitivity tests

In order to test the SAW sensor arrays, a custom sealed chamber equipped with electronic oscillators, one for each SAW resonator, is designed. The sensor arrays, composed of five polymer coated sensors and one reference device (uncoated devices), fabricated on the same quartz substrate, are placed inside the sealed chamber and connected to the conditioning electronic circuits. In order to obtain different concentrations of VOCs in N_2, the sensor array was exposed to a total flux of 1000 sccm, controlled by two flow meters: the main for the gas carrier (N_2) and the second for the analyte. The vapor concentrations are obtained fluxing N_2 in the liquid analyte by using a bubbler. The oscillation of the reference sensors is measured and the influence of humidity, temperature, pressure, etc. in the oscillation frequency is quantified by using the reference SAW devices. This information is subtracted from the measurement of the polymer coated sensors, allowing thus a precise measurement.

In order to carry out the sensitivity tests, the SWCNT pixels are transferred onto Pt electrodes. They are then mounted on a holder and electrically contacted with Ag paste. Resistance is monitored continuously with time by a computer controlled setup using a Keithley 2400 source meter. The holder is placed in a closed chamber with a constant gas supply and the baseline resistance is monitored. In order to test the sensors for their gas detection ability, different ammonia concentrations were introduced in the test chamber using a chromatography syringe. Once the sensor reached saturation, the test chamber is purged with N_2 gas until the signal recovers the original baseline value.

3. RESULTS & DISCUSSION

3.1 Polymer SAW sensors

The SAW sensors consist either of 2-port SAW resonators obtained by two IDTs arranged between reflecting gratings and operating at approximately 392 MHz or solidly mounted resonators (SMRs) operating at approximately 2 GHz [1, 20].

As reported previously [1, 20-22], the performances of the SAW sensors are mainly affected by the physical properties of the polymer coatings. Therefore in the process of applying polymer layers onto SAW devices by LIFT, parameters such as i) the laser fluence applied for the transfer, ii) the thickness of the polymer layer, iii) the laser wavelength, or iii) transfer with DRL and without DRL, are of paramount importance.

Optical microscopy images of continuous, debris free and with regular edges polymer pixels transferred onto the resonating cavity of SAW devices at laser fluences between 400 and 500 mJ/cm^2 is shown in Fig. 3 a)-f). The red square in Figure 3 a indicates the active area of the SAW sensor.

As shown in [1, 20-22], the laser fluence plays an important role in obtaining regular, debris free polymer coatings. As the image reveals (Figure 3), only between 400 and 500 mJ/cm^2 the transfer is clean and well defined. Below 400 mJ/cm^2, the polymer doesn't reach the surface of the SAW device, or only debris from the polymer reaches the SAW surface, most probably due to the limited available mechanical force from the DRL decomposition. In contrast, at too high laser fluences, debris from polymer, and destroyed IDTs are noticed.
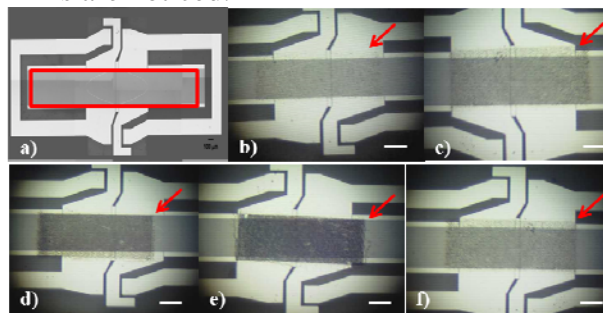

Figure 3. a) Reference SAW sensor; SAW sensor coated with b) PSCMA polymer; c) PEI polymer; d) PECH polymer; e) HPMC polymer; f) PIB polymer. The polymers are transferred at different laser fluences (from 400 to 500 mJ/cm^2). The scale bar is 100 µm.

Similarly, polymer pixels are LIFT printed onto SMR devices. The transfer is carried out in contact between the donor and the receiver substrate, as it was shown previously that the transfer across a gap is not possible [23] at ambient conditions.

"HENRI COANDA"
AIR FORCE ACADEMY
ROMANIA

"GENERAL M.R. STEFANIK"
ARMED FORCES ACADEMY
SLOVAK REPUBLIC

INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER
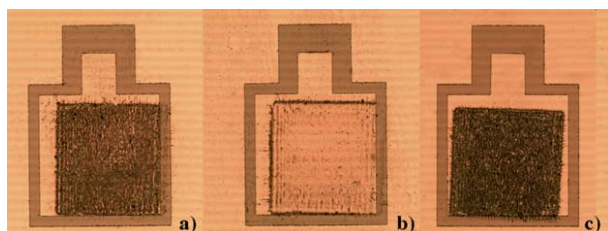AFASES 2014
Brasov, 22-24 May 2014

Figure 4. Optical microscopy images of SMR devices coated with PEI, PECH, AND PIB polymers deposited at a) 400 mJ/cm^2 laser fluence (adopted from Ref. 20)

Furthermore it is shown that not only the polymer pixels are regularly transferred onto the active area of sensor devices, but the sensors are functional after LIFT. In Figure 5 the response curves for three different polymers upon exposure to different concentration of dimethyl methylphosphonate (DMMP), i.e. from 2.5 to 40 ppm, are shown.
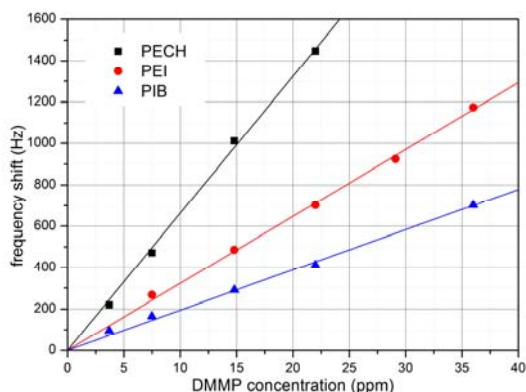

Figure 5. Response curves for PECH, PEI, and PIB sensors upon exposure to different concentration of DMMP. (adopted from Ref. 1)

The response curves for the three polymers (PECH, PEI, and PIB) to DMMP, DCM, and EtOAc show a linear behaviour in the tested concentration ranges. For PIB, a sensitivity of 19.45 Hz/ppm is obtained with a calculated detection limit of 0.51 ppm. In the case of PEI, the sensitivity and the detection limit of the sensor are, 32.34 Hz/ppm and 0.3 ppm, respectively. Finally, for the PECH a sensitivity of 66.23 Hz/ppm and a detection limit of 0.15 ppm are achieved. For all the sensors, the detection limit is calculated considering a maximum noise level of 10 Hz. As expected, the response curve behaviours of the three sensors demonstrate that PECH has a higher sensitivity to DMMP vapour than PIB and PEI [24].

3.2 Chemiresistors based on single walled carbon nanotubes

The investigation of LIFT aiming applications such as the fabrication of chemiresistor sensors requires a systematic variation of different process parameters and an analysis of the resulting morphological and chemical features of the transferred materials.

As shown previously in [25] the triazene polymer thickness is an important parameter for obtaining a regular, "clean" transfer. TP as DRL absorbs the laser radiation and subsequently decomposes into gaseous fragments which are used to transform the energy into required mechanical push. Therefore, the transfer of SWCNT with 300 and 100 nm TP release layer are investigated. It has been seen in [25] that for 300 nm TP layers and all applied conditions never results in a transfer of uniformly distributed pixels, i.e. never a CNT array, on the receiver substrate. Thus only 100 nm TP layer thicknesses are used.

Another important parameter which is investigated is the transfer of SWCNT onto different flexible substrates, appropriate in the fabrication of intelligent clothing. An optical microscopy image of SWCNT transferred by LIFT onto different flexile substrates is shown in Figure 6. As it can be seen in Figure 6, it is possible to achieve a relatively "clean" transfer, i.e. pixels with well-defined contours onto all the substrates investigated.
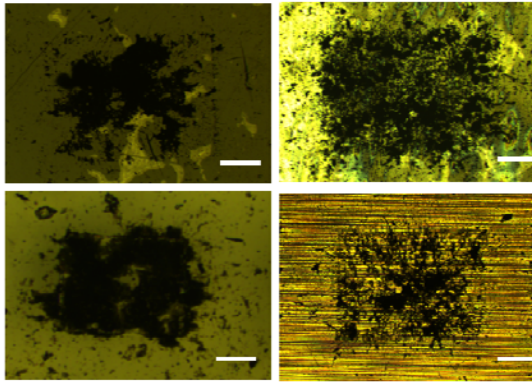
Figure 6. Optical microscopy images of SWCNT deposited onto flexible substrates (from left to right and top to bottom): Kapton, polystyrene, PDMS, Al foil. Scale bar is 100 µm.

In addition, for the fabrication of a chemiresistor sensor it is important to control the laser fluence. The laser fluence is varied over a broad range, i.e. from conditions insufficient to break the donor layer to high irradiation fluences ($0.1 - 1$ J/cm^2), in order to optimize the shape of the transferred pixels without any chemical modification of the SWCNTs. The optimum laser fluence values are found in the range 200-400 mJ/cm^2.

The transferred pixels are investigated from a structural point of view to check for possible heat damage after the transfer. The Raman spectra of the SWCNTs onto the receiver substrate are shown in Figure 7.
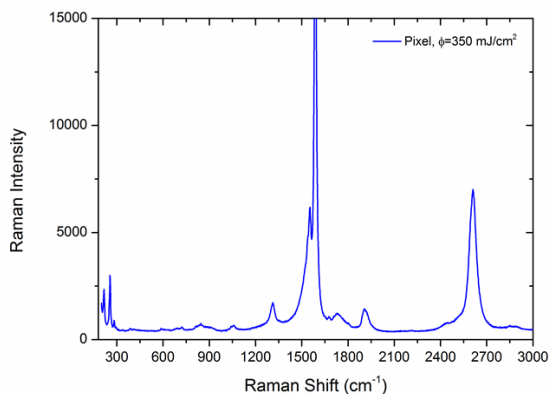

Figure 7. Raman spectra of a SWCNT pixel transferred at 350 mJ/cm^2.

The Raman spectra presents the typical Raman bands of SWCNTs: weak bands located between 100 and 300 cm^{-1} attributed to the radial breathing mode (RBM); the peak near 1330 cm^{-1} (D-band) indicates disorder in the graphitic layer of the CNTs; while the peak near 1580 cm^{-1} (G-band) is due to the tangential modes of the graphitic planes in the

CNTs. This indicates that after LIFT the SWCNT do not suffer any decomposition, and can be therefore further used in sensors applications.

The last step in order to determine the sensing ability of the SWCNT transferred by LIFT is to carry out measurements with ppm concentrations of ammonia (an electron-withdrawing vapor). In Figure 8 an example of a typical sensor response to 100 ppm ammonia is shown (adopted from Ref. 25).
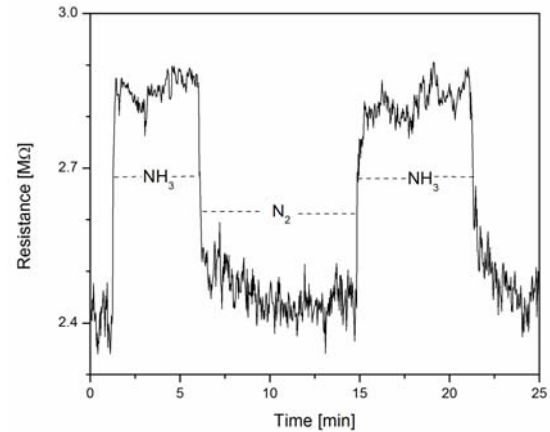

Figure 8. Sensor response upon exposure to 100 ppm of ammonia. (adopted from Ref. 25)

The LIFT-ed sensors show a repeatable response and recovery. The resistance increases sharply in the first minute, then the response begins to saturate in the next 10 minutes. The test chamber is then purged using N$_2$ gas and a spontaneous signal recovery is observed. The resistance spontaneously recovers up to 80 % of its signal response within the first $1 - 2$ minutes from the removal of the ammonia vapors. This behavior of these sensors can therefore be explained in terms of p-type characteristics.

3. CONCLUSIONS & ACKNOWLEDGMENT

The results shown above clearly reveal that laser-induced forward transfer is a suitable technique to fabricate functional SAW sensors and chemiresistors. The deposition parameters were optimized in order to minimize scattering, diffraction and attenuation of the SAWs. In addition, single walled carbon nanotube were successfully (with no structural

"HENRI COANDA"
AIR FORCE ACADEMY
ROMANIA

"GENERAL M.R. STEFANIK"
ARMED FORCES ACADEMY
SLOVAK REPUBLIC

INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER
AFASES 2014
Brasov, 22-24 May 2014

damage) transferred by LIFT onto metal electrodes to fabricate chemiresistor sensors.

REFERENCES

1. Di Pietrantonio F., Benetti M., Cannatà D., Verona E., Palla-Papavlu A., V. Dinca, M. Dinescu, T. Mattle, Lippert T., Volatile toxic compound detection by surface acoustic wave sensor arrays coated with chemoselective polymers deposited by laser induced forward transfer: application to sarin, *Sens. Actuators B* 174: 158-167 (2012).

2. Porter T. L., Eastman M. P., Pace D. L., Bradley M., Sensor based on piezoresistive microcantilever technology, *Sens. Actuators A*, 88(1), 45-51 (2001).

3. Wu Z., Chen Z., Du X., Logan J.M., Sippel J., Nikolou M., Kamaras K., Reynolds J.R., Tanner D.B., Hebard A.F., Rinzler A. G., Transparent conducting nanotube film, *Science* 305, 1273-1276 (2004).

4. Garrett M.P., Ivanov I.N., Gerhardt R.A., Puretzky A.A., Geohegan D.B., Separation of junction and bundle resistance in single wall carbon nanotube percolation networks by impedance spectroscopy, *Appl. Phys. Lett. 97,* 163105 (2010).

5. Shaw-Stewart J.R.H., Mattle T., Lippert T.K., Nagel M., Nuesch F.A., Wokaun, The fabrication of small molecule organic light-emitting diode pixels by laser-induced forward transfer, *J. Appl. Phys.* 113, 043104 (2013).

6. Palla Papavlu A., Patrascioiu A., Di Pietrantonio F., Fernadez-Pradas J.M., Cannata D., Benetti M., D'Auria S., Verona E., Serra P., Preparation of surface acoustic wave odor sensors by laser-induced forward transfer, *Sens. Actuators B* 192, 369–377 (2014).

7. Rapp L., Serein-Spirau F., Lère-Porte J.-P., Alloncle A.P., Delaporte P., Fages F., Videlot-Ackermann C., Laser Printing of Air-Stable High Performing Organic Thin Film Transistors, *Org. Electron.* 13, 2035–2041 (2012).

8. Palla-Papavlu A., Córdoba C., Patrascioiu A., Fernández-Pradas J.M., Morenza J.L., Serra P., Deposition and characterization of lines printed through laser-induced forward transfer, *Appl. Phys. A* 110, 751–755 (2013).

9. Hopp B., Smausz T., Kresz N., Barna N., Bor Z., Kolozsvári L., Chrisey D.B., Szabó A., Nógrádi A., Survival and proliferative ability of various living cell types after laser-induced forward transfer, *Tissue Eng.* 11(11–12), 1817–1823 (2005).

10. Palla Papavlu A., Dinca V., Paraico I., Moldovan A., Shaw-Stewart J., Schneider C.W., Kovacs E., Lippert T., Dinescu M., *J. Appl. Phys. 108 033111 (2010).*

11. Arnold C.B., Serra P., Piqué A., Laser direct-write of complex materials, *Mater. Res. Soc. Bull.* 32, 23–31 (2007).

12. Serra P., Colina M., Fernández-Pradas J.M., Sevilla L., Morenza J.L., DNA deposition through laser-induced forward transfer, *Appl. Phys. Lett.* 85 (9), 1639-1641 (2004).

13. Fardel R., Nagel M., Nüesch F., Lippert T., Wokaun A., Fabrication of organic light-emitting diode pixels by laser-assisted forward transfer, *Appl. Phys. Lett.* 91, 061103 (2007).

14. Chang-Jian S.K., Ho J.R., Cheng J.-W.J., Sung C.K., Fabrication of carbon nanotube field emission cathodes in patterns by a laser transfer method, *Nanotechnology* 17: 1184-1187 (2006).

15. Boutopoulos C., Pandis C., Giannakopoulos K., Pissis P., Zergioti I., Polymer/carbon nanotube composite patterns via laser induced forward transfer, *Appl. Phys. Lett.* 96, 041104 (2010).

16. Nagel M., Fardel R., Feurer P., Häberli M., Nüesch F.A., Lippert T., Wokaun A., Aryltriazene photopolymer thin films as sacrificial release layers for laser-assisted forward transfer systems: Study of photoablative decomposition and transfer behaviour", *Appl. Phys. A* 92, 781–789 (2008).

17. Lippert T., Laser applications of polymers, *Adv. Polym. Sci.* 168, 51–246 (2004).

18. Kattamis N.T., Purnick P.E., Weiss R., Arnold C.B., Thick-film laser induced forward transfer for deposition of thermally and mechanically delicate materials, *Appl. Phys. Lett.* 91, 171120 (2007).

19. Franke M.E., Koplin T.J., Simon U., Metal and metal oxide nanoparticles in chemiresistors: does the nanoscale matter?, *Small* 2, 36-50 (2006).

20. Cannatà D., Benetti M., Di Pietrantonio F., Verona E., Palla-Papavlu A., Dinca V., Dinescu M., Lippert T., Nerve agent simulant detection by solidly mounted resonators (SMRs) polymer coated using laser induced forward transfer (LIFT) technique, *Sens. Actuators B* 173, 32–39 (2012).

21. Dinca V., Palla Papavlu A., Matei A., Luculescu C., Dinescu M., Lippert T., Di Pietrantonio F., Cannata D., Benetti M., Verona E., A comparative study of DRL-LIFT and LIFT on integrated polyisobutylene polymer matrices, Appl. Phys. A 101:429-434 (2010).

22. Dinca V., Palla Papavlu A., Shaw-Stewart J., Dinescu M., Lippert T., Di Pietrantonio F., Cannata D., Benetti M., Verona E., Polymer pixel enhancement by laser induced forward transfer for sensor applications, *Appl. Phys. A* 101(3): 559-565 (2010).

23. Palla-Papavlu A., Dinca V., Luculescu C., Shaw-Stewart J., Nagel M., Lippert T., Dinescu M., Laser induced forward transfer of soft materials, *J. Opt.* 12, 124014 (2010).

24. Ballantine D.S., Rose S.L., Grate J.W., Wohltjen H., Correlation of surface acoustic wave device coating responses with solubility properties and chemical structure using pattern recognition, *Anal. Chem.* 58 (1986).

25. Palla Papavlu A., Dinescu M., Wokaun A., Lippert T., Laser-induced forward transfer of single walled carbon nanotubes, accepted for publication in *Applied Physics A* (2014).