Laser-induced forward Transfer: a Direct-writing Technique for Biosensors Preparation

Pere SERRA[*], Juan Marcos FERNÁNDEZ-PRADAS[*], Mónica COLINA[*], Martí DUOCASTELLA[*], Jorge DOMÍNGUEZ[**] and José Luis MORENZA[*]

[*]*Universitat de Barcelona, Departament de Física Aplicada i Òptica, Martí i Franquès 1, E-08028 Barcelona, Spain*
[**]*IRBB-Barcelona Science Park, Universitat de Barcelona, Josep Samitier 1, E-08028 Barcelona, Spain*

The focusing power of lasers make them adequate tools for patterning applications that require high levels of spatial resolution. Laser-induced forward transfer (LIFT) is a direct-writing technique allowing the deposition of tiny amounts of material from a donor thin film through the action of a pulsed laser beam. Although LIFT was originally developed to operate with solid films, it has been demonstrated that deposition is also viable from liquid films. In this case the transferred material is not vaporized; rather, a small amount of liquid is directly ejected from the film to the receptor substrate, where it deposits in the form of a microdroplet. This makes LIFT adequate for biosensors preparation, since biological solutions can be transferred onto solid substrates to produce micrometric patterns of biomolecules. In this case, the liquid solvent acts as transport vector of the biomolecules. The viability of the technique has been demonstrated through the preparation of functional biosensors showing similar performances and higher scales of integration than those prepared through more conventional techniques.

DOI: 10.2961/jlmn.2006.03.0017
Keywords: Laser direct-write, LIFT, biosensors, microarrays, biomolecules, DNA, proteins

1. Introduction

The development of new and versatile technologies for the preparation of biosensors is becoming an expanding field of research due to the multiple applications of these devices in areas of such interest as genomics, proteomics or biomedical diagnostics. The principle of operation of a biosensor is always based on the specificity of a biological molecule to only bind to its perfect complementary or to catalyze a determined chemical reaction; the occurrence of one of these phenomena is usually detected by electrical or optical means. Thus, all the biosensors production technologies must offer reliable strategies to deposit and immobilize biological molecules onto solid substrates. Furthermore, the need for parallel detection of thousands of different biomolecules in genomics and proteomics applications, or the availability of body implanted sensors for *in-situ* diagnostics and control of chronic pathologies, impose the additional requirement of miniaturization to all these technologies.

Pattern-transfer techniques, like photolithography, have been successfully applied to the preparation of miniaturized biosensors. This kind of techniques, due to its parallel production method, is ideal for large-scale fabrication of identical units. However, the high cost and long production times of the required molds and masks make them inappropriate for more customized needs or rapid prototyping applications. In these cases, direct-write techniques, thanks to their versatility and low cost, appear to be the most convenient alternative.

The most conventional direct-writing techniques for miniaturized biosensors preparation are ink-jet printing and dip-pen microspotting [1,2], which allow for the deposition of small droplets of biomolecules-containing solutions onto planar solid substrates: minimum droplet volumes in the range of 100 pL (which result in minimum spot diameters between 75 and 100 μm) can be obtained from total sample volumes between 5 and 100 μL [3]. Although such levels of spatial resolution meet the basic requirements of many present applications, higher scales of integration would be desirable. In addition, it is worth mentioning that these techniques present important drawbacks, like the difficulty of avoiding contamination issues, or clogging problems in the case of ink-jet printing, that seriously compromise their performances. The use of lasers as writing tools appears to be an interesting alternative: their high focusing power should provide higher degrees of spatial resolution and their non-contact nature should avoid major contamination problems.

Laser-induced forward transfer (LIFT) is a direct-writing technique that allows depositing tiny amounts of material from a thin film (deposited onto a transparent holder) to a receptor substrate by means of the action of a laser pulse. The technique was initially developed to transfer inorganic materials from precursor solid films [4-6], and its mechanism of operation consisted in the complete vaporization of a small portion of the film and further recondensation of the vapor onto the receptor substrate in the form of a solid dot. However, it was later shown that transfer was also possible from pastes and liquids [7, 8]. In these cases, the transfer mechanism appeared to be different. Instead of being vaporized, a small volume of paste or liquid was directly ejected from the holder under the action of a laser pulse, and the material preserved its paste or liquid nature once deposited onto the receptor substrate.

The possibility of transferring liquids allowed LIFT to be applied to the deposition of biomolecules in solution [9]. This, alongside with its high degree of spatial resolution, made LIFT an interesting alternative technique for biosensors preparation. In this context, the viability of LIFT for the deposition of biological material without loss of bioactivity has been repeatedly tested. Thus, proteins [3,10-12], DNA [13-16] and cells [17-19] have been successfully deposited. It has to be mentioned that DNA has even been deposited through LIFT without decomposition from a solid film by means of sub-ps laser pulses [20].

The research devoted to the study of LIFT for biosensors preparation has not only been focused to test its viability to deposit biomolecules. Some effort has also been directed to the understanding of the physical transfer process, so different to that corresponding to the more conventional LIFT of solid films. Thus, in the case of liquids, the transfer process has been analyzed by time-resolved CCD imaging [21-23] and also through the characterization of the material deposited under systematic variation of different technological parameters [3,15,23,24].

The difference in the transfer mechanism for the LIFT of solids and liquids has originated a certain multiplicity of names for the application of the technique to the liquids case. Indeed, the authors that first applied it to the transfer of pastes and liquids named it matrix assisted pulsed laser evaporation direct write (MAPLE-DW) [7], and other authors used the term biological laser printing (BioLP^{TM}) [3] for a variant of the technique where an absorbing layer was intercalated between the transparent holder and the liquid film. Another name recently used is laser direct-write addition (LDW+) [25]. Since all these techniques share the same operation principle, and the term LIFT makes no explicit reference to any particular transfer mechanism, we think that it is more convenient to preserve the original name and, therefore, we have adopted it in all our works.

In this work we outline the main steps followed in our research devoted to the application of LIFT to the preparation of biosensors: characterization of the transfer process, viability test of the technique for the deposition of biomolecules, and fabrication and characterization of a truly functional DNA microarray.

2. Experiment

A scheme of the method of operation of LIFT is presented in Fig. 1. A pulsed laser beam is focused by means of a microscope objective on a thin film of the solution to be transferred through a holder transparent to the laser radiation. The holder-film system has been usually named ribbon [8]. Under the action of the laser pulse, a tiny amount of liquid is transferred to the receptor substrate, which is placed parallel and at a short distance to the ribbon. Once a dot is deposited, the ribbon-receptor substrate system is displaced a pre-set distance by means of a translation stage and a new dot can be deposited. Through precise control of stage trajectory and dot overlap, any two-dimensional pattern can be produced.

It has already been mentioned that during the preparation of biosensors through LIFT, the material to be transferred (a biomolecules containing solution) is directly deposited in the liquid state. In order for the biomolecule to be immobilized onto the appropriate receptor substrate, the solvent has to be evaporated after deposition. In the case of porous substrates, like nylon, no further steps are required: the biomolecules remain intercalated between the nylon fibers. In the case of non-porous substrates, like poly-L-lysine coated glass, a UV radiation treatment of the deposited material is required after drying to covalently bond the biomolecules to the receptor substrate surface.

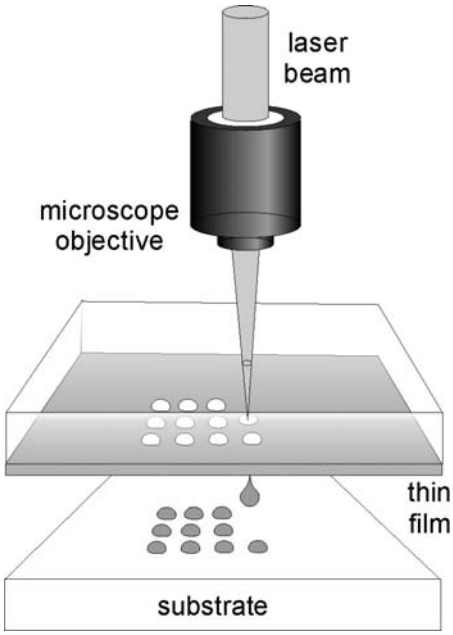

Fig. 1 Scheme of the LIFT method of operation.

Once immobilized, the biomolecules can act as sensing elements in the biosensor. It has to be pointed out that all the bioactivity characterizations included in this work correspond to fluorescence assays. In these tests, the immobilized biomolecule is submitted to a solution containing molecules of its perfect complementary tagged with a fluorochrome. The signal detected by a fluorescence scanner when the fluorochrome is excited with radiation of the appropriate wavelength reveals the positions where bonding between complementary pairs take place, that is, the positions where the biomolecules were immobilized.

The laser used in our experimental setup is a frequency tripled Nd:YAG laser (355 nm wavelength) that provides pulses of 10 ns duration at repetition rates between 1 and 20 Hz. The maximum pulse energy is about 1 mJ. However, the typical pulse energies used in all our LIFT experiments were in the range of some μJ. The beam presents an elliptical Gaussian intensity distribution. The ribbon has always consisted of a glass microscope slide coated with a Ti thin film, about 50 nm thick, and a liquid thin film of the solution to be transferred spread on it. The Ti film, which acts as laser radiation absorber, is a major requirement, since most biological solutions are transparent to the 355 nm wavelength radiation. Several methods can be used to spread the liquid film onto the slide: spin-coating, blade-coaters, etc. For liquid solutions of low enough surface tension and small operating volumes (about 1 μL), there is even no need for the use of any spreading device: the thin film is spontaneously spread once the

liquid is deposited onto the Ti coating. The sample volumes used in our experiments ranged between 0.5 and 20 µL, and the resulting liquid films presented a thickness between 1 and 15 µm. It is important to note that LIFT allows operating with sample volumes as small as 0.5 µL, since this constitutes an advantageous issue when working with scarce and expensive biological molecules. The receptor substrates have always been poli-L-lysine coated glass slides, and distances about 100 µm have been kept between these substrates and the liquid films. The laser beam is focused onto the Ti film by means of a 15× microscope objective optimized for the 355 nm radiation. The ribbon-substrate systems are placed on a xyz translation stage whose x-y motion allows the production of the pattern, and whose z displacement allows the variation of the laser beam dimensions on the sample. The resulting beam radii ranged from 10 to 100 µm.

The morphology of the transferred material is characterized by means of optical microscopy, and a fluorescence scanner operating at 543 and 635 nm exciting wavelengths is used in the bioactivity tests. Cyanine molecules (Cy3 and Cy5) are always used as fluorescence tags. Emission from Cy3 is green and emission from Cy5 is red.

3. Results and discussion

3.1 Transfer process

The study of the transfer process is not only directed to test the spatial resolution and control performances of the LIFT technique, but also to get a deeper knowledge of the involved mechanisms. A simple solution suitable to act as a solvent for biomolecules is adequate for such a purpose. In our LIFT experiments it consisted of water and glycerol (50% v/v) with a small amount of sodium dodecyl sulfate (SDS) at 2 mg/mL. These experiments, carried out at varying laser pulse energies and laser beam dimensions (Fig. 2), revealed that there exists a wide range of parameters where a single droplet is deposited per laser pulse. The dimensions of the droplet increase with pulse energy at fixed laser focusing conditions from a minimum value corresponding to a minimum energy (E_{min}) below which no transfer takes place. Both threshold energy and droplet radius decrease with laser beam dimensions, which agrees with the expectation that the more focused the laser beam is, the higher the spatial resolution of the technique. There were obtained droplets as small as 30 µm. It is important to note that the droplets are transferred from a nozzle-free surface, and that their micrometric dimensions are directly related to the characteristics of the laser beam. This makes LIFT a technique free of clogging problems. The quality of the droplets also depends on the laser pulse energy and focusing conditions. Thus, pulse energies just above the transfer threshold always produce uniform, well defined and rounded droplets, while as the energy increases, uniformity is lost and the droplets present irregular shapes. At the smallest beam dimensions, significant splashing appears at the highest energy values. This behavior can be explained in terms of the kinetic energy of the ejected material before its impact against the receptor substrate. At

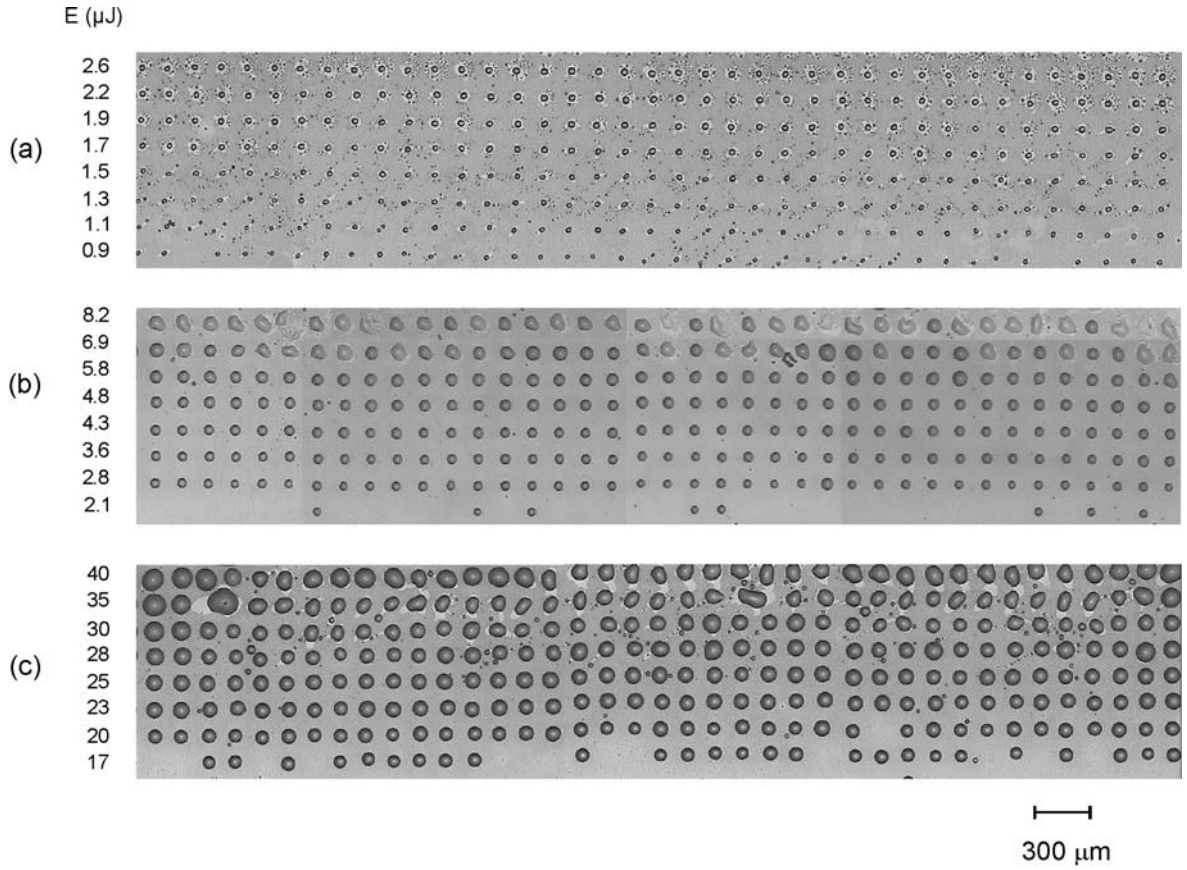

Fig. 2 Optical microscopy images of arrays of LIFT-generated droplets at different laser pulse energies and laser beam dimensions: a) $\omega_x=\omega_y=$ 11 µm, b) $\omega_x=$ 31 µm, $\omega_y=$ 25 µm, and c) $\omega_x=$ 95 µm, $\omega_y=$ 64 µm. In the elliptical Gaussian beam ω_x corresponds to the major radius and ω_y to the minor one.

pulse energies close to the transfer threshold the kinetic energy is low enough for the material to be gently deposited onto the substrate, which leads to the appearance of circular droplets. At higher energies, the spreading and recoil effects of the liquid after the impact are greater, what accounts for the loss of uniformity in the droplets [26] and, at the extreme focusing conditions, for the splashing. This last phenomenon could be due either to the breakdown of the liquid during the impact, or to its direct emission as an expanding jet [22]. In conclusion, it can be stated that the optimum working regime is that close to the transfer threshold conditions, where good quality droplets are obtained, and which dimensions can be controlled through simultaneous variation of both laser pulse energy and laser focusing conditions.

The comparison between the characteristics of the LIFT deposited droplets and the spots left by the laser beam on the Ti film (Fig. 3) reveals that the lateral dimensions of the droplets are considerably larger than those of the spots. And it is surprising to point out that there is even no need to ablate the Ti film for droplet transfer to occur. For energies close to the droplet transfer threshold there is no ablation spot on the metallic film. Only some cracks are appreciable. We suggest two possible mechanisms to explain how transfer is possible without the absorbing coating removal. The first one consists of heating without a significant ablation of the Ti film through laser radiation absorption in the metal. A small amount of liquid in contact with the hot metallic film can then be vaporized, and the resulting vapor bubble can propel liquid away the ribbon. In the second suggested mechanism, the laser heating of the Ti film would provoke the formation of a mechanical shock wave that would be responsible for the cracking of the film and the ejection of liquid material. In any case, it is important to remark that not only is there no need to ablate the Ti coating for transfer to occur, but also that these are the conditions that correspond to the optimum working regime described above.

Although the physical parameter that determines the maximum achievable spatial resolution is the droplet radius (or diameter), this is not the most adequate parameter to describe the transfer process. Once a droplet is deposited, its lateral dimensions depend strongly on the surface composition of the receptor substrate, while the transfer process is completely independent on the presence of such

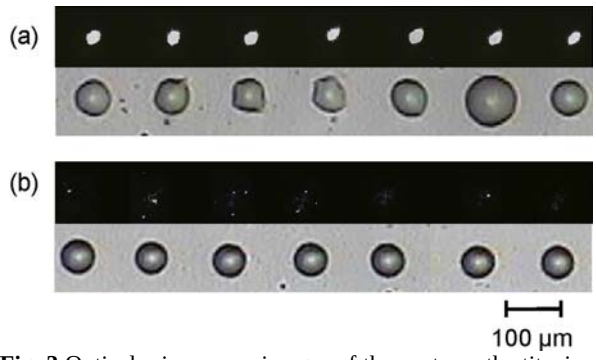

Fig. 3 Optical microscopy images of the spots on the titanium thin film (upper row) and their corresponding droplets (lower row) obtained at two different laser pulse energies: a) 4.8 µJ and b) 3.6 µJ.

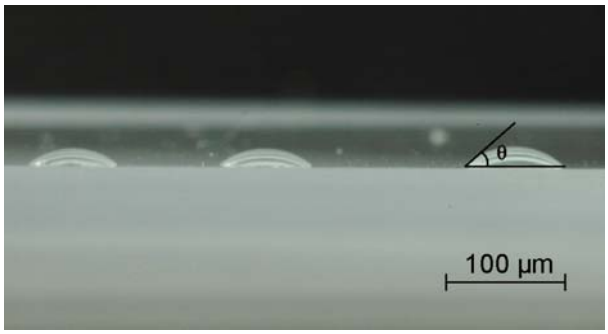

Fig. 4 Optical microscopy images at grazing incidence of three microdroplets transferred through LIFT. The angle θ corresponds to the contact angle.

a substrate. Therefore, the analysis is better carried out in terms of the droplet volume, which can be calculated from measurements of both LIFT-deposited droplets radii and contact angles (Fig. 4), measured to be about 30^o from grazing microscopy images. The as-obtained droplet volumes are in the range 1-100 pL. The quantitative study of the relationship between the transferred droplet volume and the laser pulse energy revealed a linear dependence between these parameters for all the laser focusing conditions [24]. Similar dependences have been found between the ejected droplet volume and different energy-related technological parameters during the transfer process in ink-jet printers [27,28]. The analysis also revealed the existence of an energy density threshold, $F_o = 0.13\ J/cm^2$, independent of the laser focusing conditions, that determines the amount of liquid ejected in each case. Indeed, for energies above the energy transfer threshold E_{min} the volume of the transferred droplet corresponds to the volume of the portion of liquid film intercepted by that part of the laser beam which energy density surpasses F_o (Fig. 5). This parameter F_o could be interpreted as the energy density threshold required to produce a perturbation in the liquid (vapor bubble or mechanical wave). Only if the total energy delivered by the laser pulse reached the value E_{min}, the perturbation would be able to overcome the viscous and surface tension forces of the liquid, and the droplet could be finally ejected (Fig. 5). The last important conclusion of this quantitative analysis is that the amount of vaporized solution during the LIFT process is negligible. This statement will become especially relevant in the bioactivity assays.

3.2 Viability test

The study of the transfer process showed that LIFT is an adequate technique for the deposition of liquid solutions with good spatial resolution and control. However, this is not enough to grant that LIFT is adequate for biosensors production. This should be done through demonstrating that biomolecules preserve their activity after transfer, and also that the response of a LIFT-prepared biosensor is equivalent to that of a biosensor produced through conventional techniques.

In the preceding section it was shown that during the LIFT of liquid films the transferred material always remains in the liquid state. There is no significant vaporization of the material to be deposited. This is the main characteristics of the process that makes it suitable for

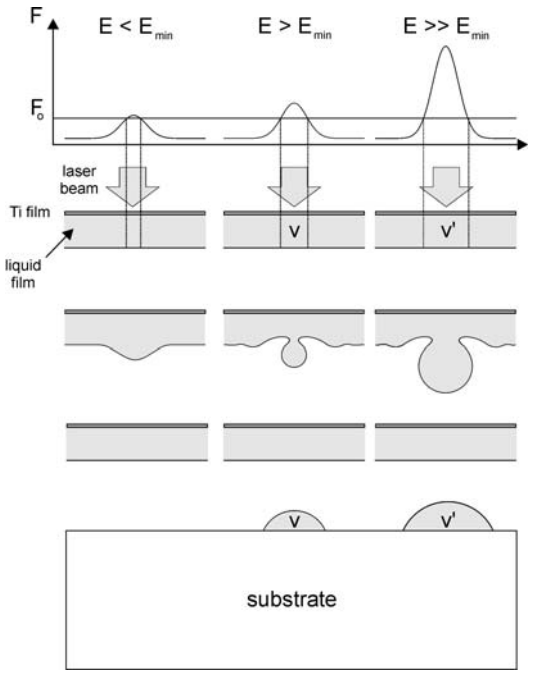

Fig. 5 Schematic representation of the ejection process during the LIFT of liquid films. The depicted Gaussian profiles correspond to the laser energy density (F) distribution. E_{min} is the laser energy threshold and F_o is the laser energy density threshold. The volumes (v and v') of the transferred droplets are indicated.

biomolecules deposition. The liquid solvent where biomolecules are immersed acts as their transport vector to the receptor substrate. This is the major difference with respect to the conventional LIFT of solid films: in this later case the deposition of biomolecules would not be possible, since the complete vaporization of the solid film would result in their decomposition and, in consequence, in the total loss of bioactivity. The results of the bioactivity test presented in Fig. 6 illustrate these aspects. They correspond to a LIFT-prepared array of droplets, obtained at different laser pulse energies, of a proteins-containing solution: human IgG in a PBS (0.01 M, pH 7.4) with 40% glycerol at a concentration of 0.05 µg/µl. The image in Fig. 6a is an optical microscopy picture of the as-deposited droplets. It can be observed that it displays the main features described in the preceding section. The image in Fig. 6b corresponds to the fluorescence scan obtained after having applied a Cy5-conjugated rabbit anti-human IgG to the protein array. The perfect correspondence between droplets and fluorescence dots indicates that, irrespective the laser pulse energy conditions, in all the cases the transferred biomolecules preserved their biological activity, since they were able to bond to their complementary pair. As a final remark, it should be also noted that it has never been observed any effect of the possible residues of Ti on the biological activity of the deposited molecules [11,13].

The viability of the LIFT technique for biosensors production was demonstrated through the preparation of a functional biosensor: a biosensor capable not only to sense a specific biomolecule with a signal level detectable with conventional means, but also to discriminate two similar but not identical biomolecules. The chosen biosensor consisted in a DNA microarray of two different human genes [15]. The microarray shown in Fig. 7a, deposited through LIFT at 20 µJ laser pulse energy, contained three different solutions with the same solvent, a buffer solution consisting in glycerol (50% in volume), dimethyl sulfoxide (25% in volume), and TrisEDTA (25% in volume). The solution deposited in columns 1, 4, and 7 contained a single strand cDNA of a human gene, the v-ets avian erythroblastosis virus E26 oncogene homolog 2 (ETS2, 2205 base pairs long). The one in columns 2, 5, and 8 contained the buffer solution alone (negative control). Finally, the one in columns 3, 6, and 9 contained another single strand cDNA of a different human gene: the mitogen-activated protein kinase 3 gene (MAPK3, 525 base pairs long). Both cDNA-containing solutions had a concentration of 250 ng/µl. After deposition, the microarray was submitted to a standard hybridization protocol with the complementary strands of the transferred DNA, each one differently tagged: ETS2 with Cy3 and MAPK3 with Cy5. The fluorescence image recorded after hybridization is presented in Fig. 7b. This result demonstrates that hybridization occurred only where DNA was deposited (no fluorescence signal was recorded in the columns corresponding to the negative control), that there was enough signal to be easily detected with a conventional fluorescence scanner and that the prepared microarray was really specific: Cy3 tagged ETS2 complementary strand only hybridized in columns 1, 4, and 7, and Cy5 tagged MAPK3 complementary strand only hybridized in columns 3, 6, and 9. These results really demonstrate that LIFT is a viable technique for biosensors preparation. Furthermore, it can be pointed out that the performance of LIFT-prepared biosensors is comparable to that of biosensors produced with other conventional techniques. Indeed, quantitative analyses of the fluorescence results corresponding to different DNA microarrays of similar morphological

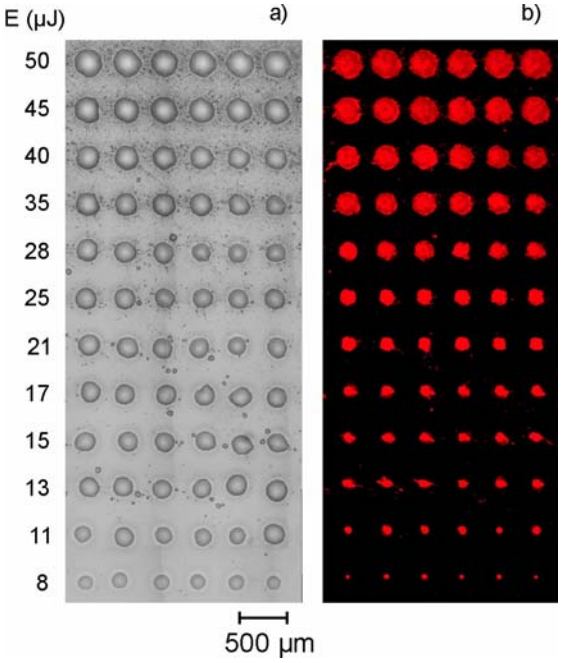

Fig. 6 Optical microscopy image of a) an array of droplets of an IgG solution obtained at different laser pulse energies, and b) its corresponding fluorescence image after application of Cy5- anti-IgG.

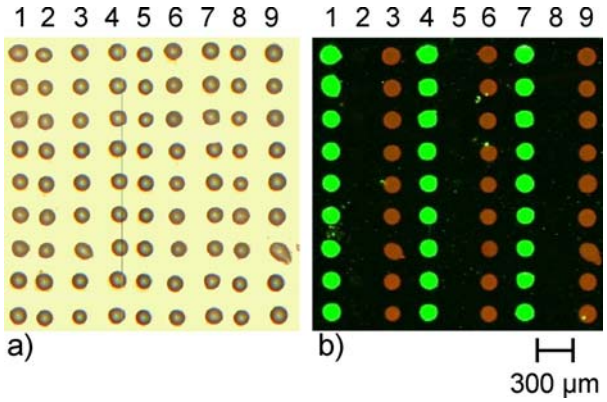

Fig. 7 Optical microscopy image of a) an array of droplets of three different solutions containing two different cDNA strands and a negative control, and b) its corresponding fluorescence image after hybridization with their complementary strands.

characteristics prepared through LIFT and through pin microspotting revealed that they present very similar both fluorescence intensity and unspecific hybridization levels [16]. That comparative study also allowed showing that the biomolecule concentration of the deposited droplets was practically identical to that of the liquid film of the ribbon, what constitutes a quantitative proof that there is no significant biomolecule damage due to the action of the laser beam during the transfer process.

4. Conclusion

The application of LIFT to material deposition from liquid films makes this technique especially suitable for miniaturized biosensors preparation, since in this way biomolecules-containing solutions can be spotted with precision onto a solid substrate where the biological molecules are immobilized for sensing.

The action of a laser pulse leads to the ejection of a small amount of liquid that is deposited onto the receptor substrate in the form of a droplet. Since the transferred material remains in the liquid state during the whole process, there is no biomolecule decomposition and, therefore, the deposited material preserves its bioactivity. The volume of the ejected droplets is determined by the dimensions of the laser beam; the high focusing power of lasers allows the obtaining of micron-sized droplets, what provides this technique with a high degree of spatial resolution. The dimensions of the deposited droplets can easily be controlled through simultaneous variation of both the laser pulse energy and laser focusing conditions.

The preparation through LIFT of a specific biosensor, a DNA microarray, has proofed the viability of the technique for such a purpose. The prepared microarray is capable, not only to sense a specific DNA strand with a signal level detectable with conventional means, but also to discriminate two different human genes, what makes it perfectly functional. In addition, the quantitative analysis of the signal provided by the microarray has demonstrated that the DNA concentration of the transferred material is equal to that of the liquid film, what proofs that there is no biomolecule damage during LIFT.

Therefore, LIFT constitutes a viable alternative to more conventional techniques for biosensors preparation, with the additional advantages of presenting higher degrees of integration, and avoiding contamination and clogging problems due to its non-contact nozzle-free nature.

Acknowledgments

This work forms part of a research program funded by MEC of the Spanish Government (Project No. MAT2004-03741), the European Regional Development Fund (FEDER) and DURSI of the Catalan Government (2005 SGR00464).

References

[1] D. Rose, in *Microarray Biochip Technology*, edited by M. Schena (Eaton Publishing, Natick, 2000), p.19
[2] T. Okamoto, T. Suzuki, and N. Yamamoto, Nat. Biotechnol. **18**, 438 (2000).
[3] J.A. Barron, H.D. Young, D.D. Dlott, M.M. Darfler, D.B. Krizman and B.R. Ringeisen, Proteomics **5**, 4138 (2005).
[4] J. Bohandy, B. F. Kim, and J. Adrian, J. Appl. Phys. **60**, 1538 (1986).
[5] E. Fogarassy, C. Fuchs, F. Kerherve, G. Hauchecorne, and J. Perriere, J. Appl. Phys. **66**, 457 (1989).
[6] Z. Kántor, and T. Szörényi, J. Appl. Phys. **78**, 2775 (1995).
[7] A. Piqué, D.B. Chrisey, R.C.Y. Auyeung, J. Fitz-Gerald, H.D. Wu, R.A. McGill, S. Lakeou, P.K. Wu, V. Nguyen, and M. Duignan, Appl. Phys. A **69**, S279 (1999).
[8] A. Piqué, R. A. McGill, D. B. Chrisey, D. Leonhardt, T. E. Mslna, B. J. Spargo, J. H. Callahan, R. W. Vachet, R. Chung, and M. A. Bucaro, Thin Solid Films. **355-356**, 536 (1999).
[9] P. K. Wu, B. R. Ringeisen, J. Callahan, M. Brooks, D. M. Bubb, H. D. Wu, A. Piqué, B. Spargo, R. A. McGill, and D. B. Chrisey, Thin Solid Films **398-399**, 607 (2001).
[10] B. R. Ringeisen, P. K. Wu, H. Kim, A. Piqué, R. Y. C. Auyeung, H. D. Young, and D. B. Chrisey, Biotechnol. Prog. **18**, 1126 (2002).
[11] P. Serra, J. M. Fernández-Pradas, F. X. Berthet, M. Colina, J. Elvira, and J. L. Morenza, Appl. Phys. A. **79**, 949 (2004).
[12] P.K. Wu, B.R. Ringeisen, D.B. Krizman, C.G. Frondoza, M. Brooks, D.M. Buba, R.C.Y. Auyeung, A. Piqué, B. Spargo, R.A. McGill and D.B. Chrisey, Rev. Sci. Instrum. **74**, 2546 (2003).
[13] J. M. Fernández-Pradas, M. Colina, P. Serra, J. Domínguez, and J. L. Morenza, Thin Solid Films **453-454**, 27 (2004).
[14] J. M. Fernández-Pradas, P. Serra, M. Colina, and J. L. Morenza, Proc. SPIE **5662**, 582 (2004).
[15] P. Serra, M. Colina, J. M. Fernández-Pradas, L. Sevilla, and J. L. Morenza, Appl. Phys. Lett. **85**, 1639 (2004).
[16] M. Colina, P. Serra, J. M. Fernández-Pradas, L. Sevilla, and J. L. Morenza, Biosens. Bioelectron. **20**, 1638 (2005).
[17] J. A Barron, B. R. Ringeinsen, H. Kim, J. Spargo, and D. B. Chrisey, Thin Solid Films. **453-454**, 383 (2004).

[18]D. B. Chrisey, A. Piqué, R. A. McGill, J. S. Horwitz, B. R. Ringeisen, D. M. Bubb, and P. K. Wu, Chem. Rev. **103**, 533 (2003).
[19]B. Hopp, T. Smausz, Zs. Antal, N. Kresz, Zs. Bor, and D. Chrisey, J. Appl. Phys. **96**, 3478 (2004).
[20]A. Karaiskou, I. Zergioti, C. Fotakis, M. Kapsetaki, and D. Kafetzopoulos, Appl. Surf. Sci. **208-209**, 245 (2003).
[21]D. Young, R. C. Y. Auyeung, A. Piqué, D. B. Chrisey, and D. Dlott, Appl. Phys. Lett. **78**, 3169 (2001).
[22]D. Young, R. C. Y. Auyeung, A. Piqué, D. B. Chrisey, and D. Dlott, Appl. Surf. Sci. **197-198**, 181 (2002).
[23]E.C. Kinzel, X. Xu, B.R. Lewis, N.M. Laurendeau, and R.P. Lucht, JLMN **1**, 74 (2006).
[24]M. Colina, M. Duocastella, J.M. Fernández-Pradas, P. Serra, and J.L. Morenza, J. Appl. Phys, **99**, 084909 (2006).
[25]C.B. Arnold, H. Kim, M. Ollinger, T.E. Sutto, and A. Piqué, Proc. SPIE **5662**, 555 (2004).
[26]D. C. D. Roux, and J. J. Cooper-White, J. Colloid Interface Sci. **277**, 424 (2004).
[27]N. Reis, C. A. Ainsley and B. Derby, J. Appl. Phys. **97**, 094903 (2005).
[28]A. Asai, T. Hara and I. Endo, Jpn. J. Appl. Phys. **26**, 1794 (1987).

(Received: May 16, 2006, Accepted: November 28, 2006)