ALT 12
Advanced Laser Technologies
2 – 6 September 2012, Thun, Switzerland

ALT 12
c/o Bern University of Applied Sciences
Engineering and Information Technology
Pestalozzistrasse 20, CH-3400 Burgdorf
info@alt12.org, www.alt12.org
0041 (0) 34 426 42 06

LASER MICROPRINTING OF TRANSPARENT AND WEAKLY ABSORBING SOLUTIONS

Authors:

P. Serra, A. Patrascioiu, A. Palla-Papavlu, J.M. Fernández-Pradas, J.L. Morenza

DOI: 10.12684/alt.1.51

Corresponding author: P. Serra

e-mail: pserra@ub.edu

Laser Microprinting of Transparent and Weakly Absorbing Solutions

P. Serra, A. Patrascioiu, A. Palla-Papavlu, J.M. Fernández-Pradas, J.L. Morenza

Departament de Física Aplicada i Òptica, Universitat de Barcelona,
Martí i Franquès 1, E08028-Barcelona, Spain

Abstract

A laser-based technique for printing transparent and weakly absorbing liquids is developed. Its principle of operation relies in the tight focusing of short laser pulses inside the liquid and close to its free surface, in such a way that the laser radiation is absorbed in a tiny volume around the beam waist, with practically no absorption in any other location along the beam path. If the absorbed energy overcomes the optical breakdown threshold, a cavitation bubble is generated, and its expansion results in the propulsion of a small fraction of liquid which can be collected on a substrate, leading to the printing of a microdroplet for each laser pulse. The technique does not require the preparation of the liquid in thin film form, and its forward mode of operation imposes no restriction concerning the optical properties of the substrate. We demonstrate that the technique is capable of printing microdroplets with good resolution, reproducibility and control, and analyze the influence of the main process parameters. The mechanisms of liquid printing are also investigated: time-resolved imaging provides a clear picture of the dynamics of liquid transfer which allows understanding the main features observed in the printed droplets.

Introduction

Direct printing is an adequate approach for micropatterning in applications requiring a high degree of flexibility [1]. The most representative example of a direct printing technique is inkjet printing, which allows depositing materials that have been dissolved or suspended in a liquid: droplets are formed when the 'ink' is forced through a small nozzle [2]. However, nozzle clogging constitutes a serious limiting factor when high resolution is desired [3].

Laser-induced forward transfer (LIFT) of liquids has appeared as an interesting alternative to inkjet printing [4]. In LIFT, droplets are deposited through liquid transfer from a donor film to a receptor substrate by means of the action of a laser pulse. In this case no nozzle is required to limit the dimensions of the droplets: these are determined by the diameter of the focused laser beam, and by the thickness of the film, typically of a few microns [5].

Many of the solutions containing materials of interest in technological applications are transparent to the most conventional laser radiations. This problem has been solved through the intercalation of a solid laser absorbing layer between the donor liquid film and its transparent supporting substrate [6]. In this way, materials such sensitive as polymers [7], DNA [8, 9], proteins [10], or even living cells [11, 12] have been deposited without alteration of their functional properties.

The main drawback of LIFT is, however, the preparation of the liquid film. In general it is hard obtaining reproducible thin films with thickness uniformity along their whole area, and good stability: liquid films tend to shrink, even if the surface tension is low, and evaporation becomes significant due to their large surface to volume ratio. Furthermore, the preparation of a liquid film requires of good wettability, which is usually achieved through addition of surfactants to the ink; however, this is detrimental for the deposition of droplets with very small diameters. Finally, it has to be considered that the film preparation not only constitutes an additional step in the printing process, but also increases the risk of contamination.

In this work we develop a technique for the laser printing of transparent liquids which does not require the preparation of any film: the liquid is directly printed from the reservoir containing it. In this way it is possible to deposit well-defined uniform microdroplets with very high reproducibility.

Experimental

The principle of operation of the laser forward printing technique relies on the highly localized absorption of strongly focused ultrashort laser pulses in the close proximity of the free surface of the liquid contained in a reservoir. This results in the generation of a cavitation bubble underneath the free surface of the liquid. Once generated, the cavitation bubble expands, displacing the liquid around it. Then, a fraction of the liquid is propelled away, and collected onto a substrate. Provided that both the depth of the bubble and its pressure are the adequate ones, it can be expected that the liquid will be deposited on the substrate in the form of a well-defined droplet. For this to occur, both the laser pulse energy and focusing depth should be

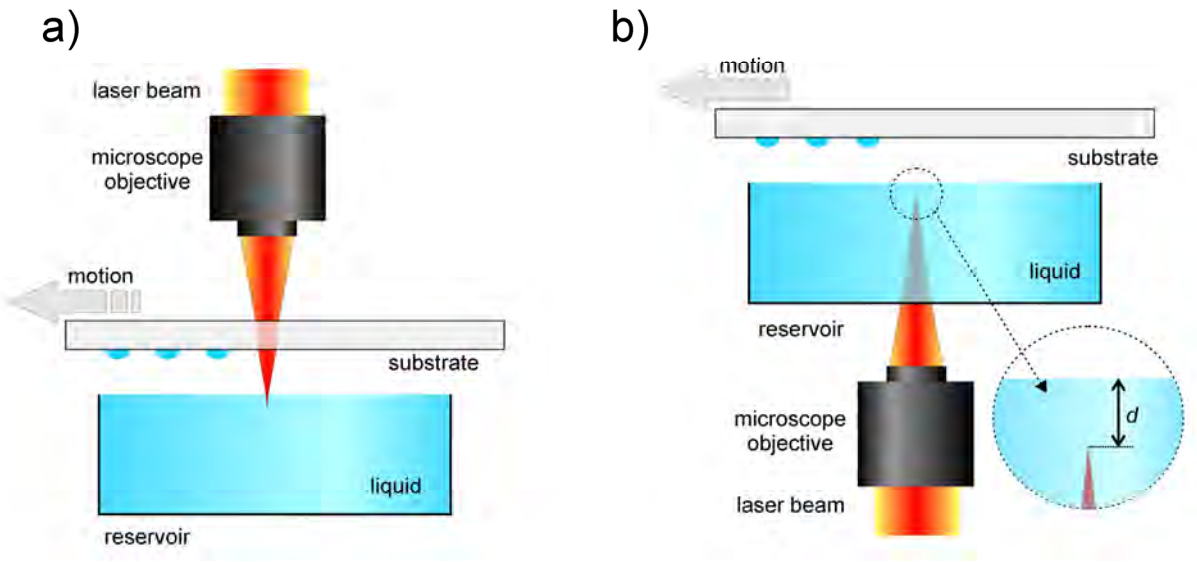

Figure 1
Principle of operation of the film-free laser printing technique in both a) backward and b) forward configuration.

properly adjusted in order to allow liquid transfer devoid of splashing.

Printing microdroplets of transparent or weakly absorbing liquids following the previously described principle of operation is possible through any of the two configurations (backward and forward) schematized in Figure 1. In this technique, each droplet results from a single laser pulse, and the generation of micropatterns can be achieved through the translation of the substrate respect to the laser beam.

The experiments were carried out using a diode pumped Yb:KYW femtosecond laser (1027 nm wavelength, 450 fs pulse duration, 1 mJ maximum pulse energy, 1 kHz repetition rate). The laser radiation was focused through a microscope objective (50×, NA 0.55) with a long working distance of 13 mm. A high numerical aperture provides the strong focusing that, in addition to femtosecond laser radiation, allows achieving the extremely localized absorption of the laser pulse energy in the focal volume. The substrates were commercial poly-L-lysine coated microscope slides, and they were located on a computer-controlled xyz translation stage, which motion was synchronized with laser pulse firing. The liquid reservoir was a 100 µL cylindrical plastic container, held in an independent z translation stage. Patterning was achieved by translating the substrate in the x and y directions after each laser pulse. Moreover, material deposition could be in-situ controlled through a CCD camera. In all the experiments the separation between the liquid free surface and the substrate was around 500 µm.

Two solutions consisting of mouse and rabbit immunoglobulin G (IgG, Sigma Aldrich) both dissolved at a concentration of 0.05 µg/µL in a solution of phosphate buffered saline (PBS) with glycerol (20% v/v), were used to test the feasibility of the technique for sensitive materials printing through the preparation of microarrays containing spots of both proteins. Once the drops were dried, the slides were blocked with 3% (w/v) BSA (bovine serum albumin, Sigma Aldrich) in PBS for 30 min at room temperature, washed three times with 0.1% (v/v) Tween-20 (Sigma Aldrich) in PBS, and then incubated for 30 min at room temperature with Cy5-conjugated secondary antibodies against mouse IgG (Jackson Immunoresearch) and Cy3-conjugated secondary antibodies against rabbit IgG (Amersham biosciences). Afterwards, the slides were washed consecutively with 0.1% (v/v) Tween-20 in PBS for three times, water, and 96% (v/v) ethanol. Finally, the microarrays were analyzed through a fluorescence scanner operating at 543 nm and 635 nm to excite Cy3 and Cy5, respectively. In all cases, optical microscopy was used to characterize the morphology of the microdroplets immediately after deposition.

Time-resolved imaging was carried out with a strobe lamp (18 ns pulse duration) at grazing incidence respect to the liquid free surface. The light emitted by the lamp was collected by a 2 Mp CCD camera coupled to a magnification system consisting of a microscope objective (15 ×, 0.32 NA) and a teleobjective with a focal length of 100 mm. A liquid solution consisting in a mixture of water and glycerol at 20% (v/v) was used for the time-resolved experiments.

Results and discussion

In transparent aqueous solutions and for femtosecond laser pulses focused just beneath the liquid free-surface, non-linear radiation absorption occurs in the tiny focal volume through multiphoton and avalanche ionization. This results in the formation of a highly-excited and highly-

confined plasma. For such short laser pulses, there is practically no conduction of heat to the surroundings of the interaction region. Plasma expansion originates a cavitation bubble in the liquid, which further expansion displaces some liquid beyond the free surface. The amount and morphology of deposited material will depend on the relative position of the focal volume with respect to the liquid free surface: it is possible to find a range of focusing depths that in either of the two available configurations leads to the generation of well-defined droplets on the receiving substrate.

High-resolution printing

The reproducibility of the technique in droplet printing is demonstrated through the preparation of microarrays of well-defined and regular droplets (Figures 2a and 2c). It can be observed that all the droplets are uniform, with a circular contour, and present a diameter of around 40 µm. Such high reproducibility demonstrates that the technique allows overcoming the drawbacks associated with the lack of uniformity and stability of the liquid film inherent to LIFT. Moreover, the in-situ control of the deposition process through the CCD camera facilitates finding the adequate printing conditions through the simultaneous adjustment of both pulse energy and focusing depth. This allows obtaining very small droplets in an easy and flexible way. These results demonstrate that this new printing technique indeed makes possible printing droplets with high resolution and reproducibility in a really user-friendly way, making unnecessary the use of printing heads or the previous preparation of the liquid in thin-film form [13, 14]. In fact, liquids can be spotted from practically any container, like the wells of a microtiter plate, which in addition minimizes the risk of contamination.

Biomolecule deposition is tested as a functionality proof-of-concept. Both mouse and rabbit IgG solutions are used for such a purpose. Each of the two microarrays presented in Figure 2a and 2c, corresponds to a different solution: the microarray in Figure 2a correspond to mouse IgG, and the microarray in Figure 2c to rabbit IgG. The fluorescence image of the same microarrays obtained after the immunoassay (Figures 2b and 2d) reveals the specific binding of each tagged anti-IgG

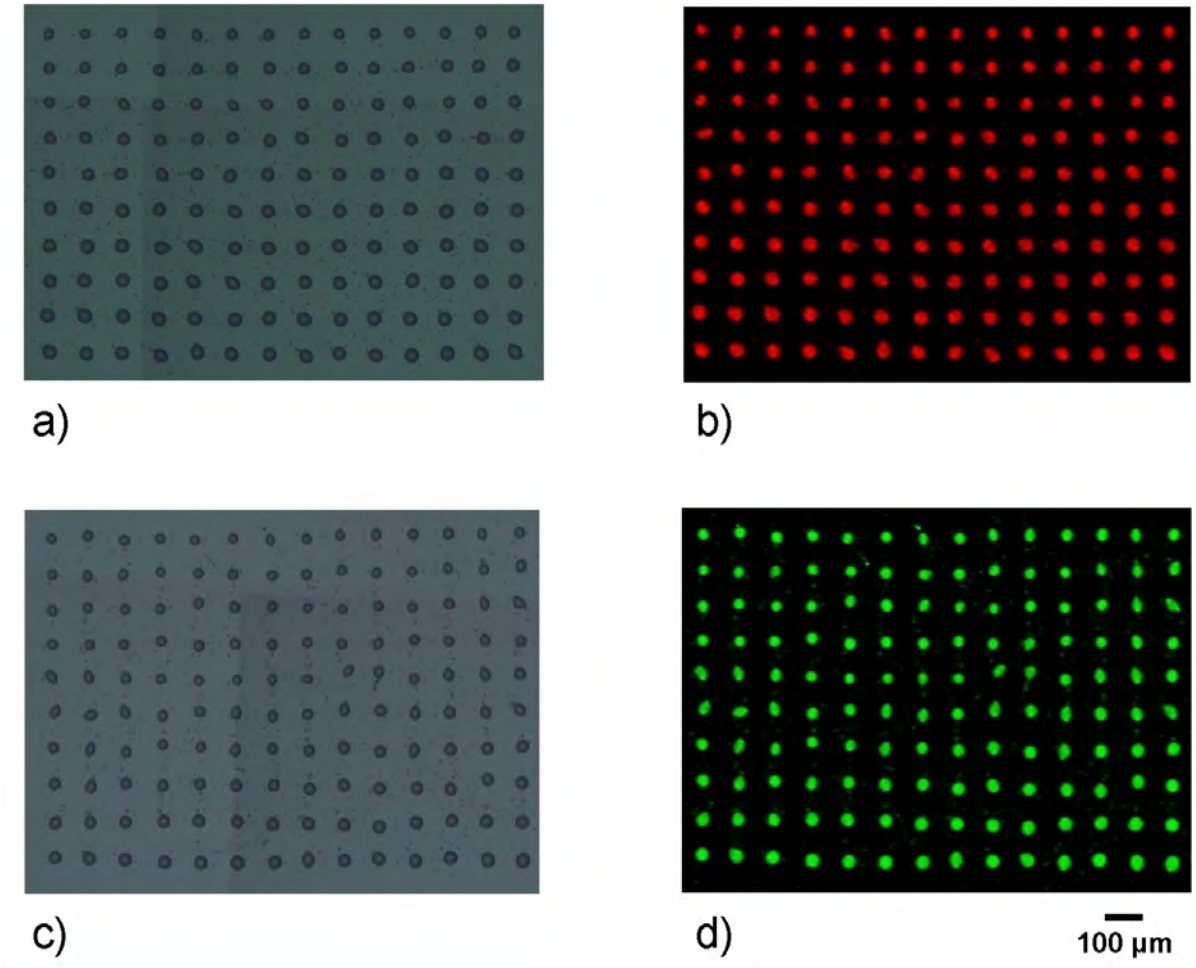

Figure 2
a) Optical microscopy image of the mouse IgG microarray; b) Fluorescence image of the array after conjugation with Cy5-conjugated mouse anti-IgG. c) Optical microscopy image of the rabbit IgG microarray; d) Fluorescence image of the array after conjugation with Cy3-conjugated rabbit anti-IgG. Laser intensity is 10^{14} W/cm^2.

to its complementary with an intensity level that can be detected with a conventional scanner. This result validates the proof-of-concept set forth above.

Printing dynamics

Time-resolved imaging helps to reveal the precise mechanisms responsible for material transfer during the laser printing of transparent and weakly absorbing liquids. With the purpose of elucidating those mechanisms series of images are acquired at conditions leading to the formation of well-defined sessile droplets.

A series of images obtained at a laser pulse intensity of about 5×10^{14} W/cm^2, is presented in Figure 3. In the analysis of the images it must be taken into account that the liquid free surface reflects quite well the incoming light; so, all the observed features are accompanied by their mirror images. The action of the laser pulse results in the formation of a conical protrusion in the liquid surface. The protrusion grows fast, and after a few μs after the laser pulse a thin needle-like jet originates from its pole. The jet develops while the protrusion collapses, and keeps on advancing with an estimated speed of about 20 m/s. At about 22 μs a second protrusion appears. The preferential growth along the axial direction of this second protrusion, with little lateral expansion, indicates that it would be better qualified as a jet. This second jet progresses together with the first one, at an initial speed estimated to be of around 5 m/s. At about 150 μs the first jet breaks up, being the fragments projected along the vertical direction, while the second jet keeps on advancing. At about 200 μs its shape changes dramatically: its central part progressively thins, developing a neck, while the tip becomes spherical. At about 380 μs the neck pinches off, emitting a spherical droplet, which flies away the liquid free surface, leaving behind a liquid thread which at 500 μs suffers a second pinch-off. The emitted liquid finally coalesces in flight, becoming a second flying droplet.

The results of these experiments clearly reveal that, although presenting common features, the mechanisms of liquid transfer in the new laser printing technique are quite more complex than those corresponding to LIFT [15-17]. Thus, further

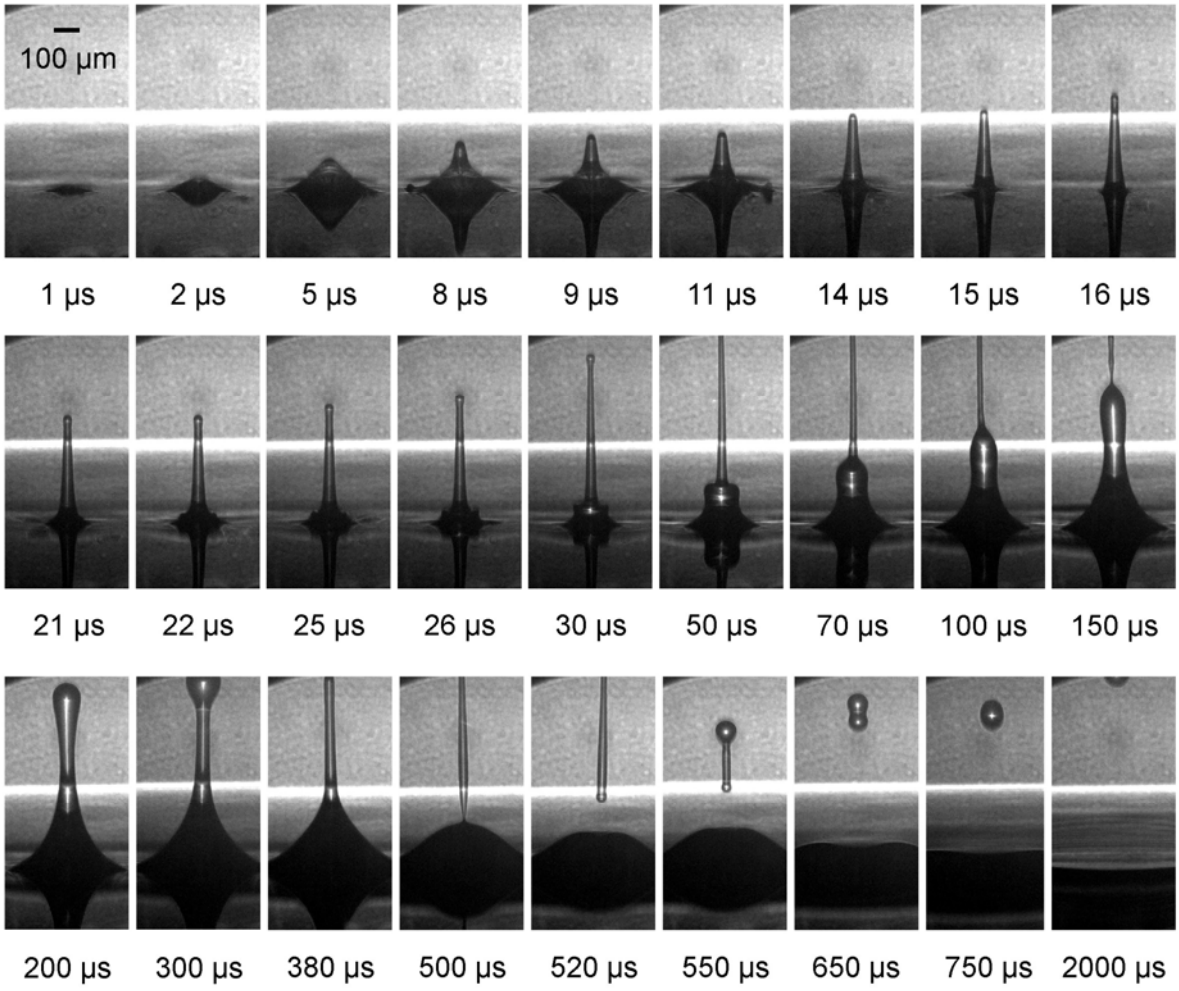

Figure 3
Series of time-resolved images of liquid ejection during the laser backward transfer of a water and glycerol solution. Delay time after the laser pulse is indicated in the bottom of each image.

investigations will be worth in order to better understand the surprising dynamics encountered during laser printing experiments.

Conclusion

The laser-based technique developed in this work allows printing microdroplets of transparent and weakly absorbing liquids without the constraint of preparing the liquids in thin film form, and making possible the localized deposition of sensitive materials such as biomolecules. The printing mechanism is mediated by the formation of liquid jets which result from the dynamics undergone by a cavitation bubble generated close to the liquid free surface through the subsurface focusing of a laser pulse. Such dynamics proceeds through the ejection of a first long and thin jet during bubble expansion, and through the formation of a second shorter and thicker jet, both emerging from the liquid free surface.

Acknowledgment

This work is funded by MCI of the Spanish Government (Projects MAT2010-15905 and CSD2008-00023), by the European Commission (ICT: e-LIFT, Grant Agreement No. 247868), and Fondo Europeo de Desarrollo Regional (FEDER).

References

[1] K.K.B. Hon, L. Li and I.M. Hutchings (2008), Direct writing technology - Advances and developments, CIRP Annals-Manufacturing Technology, 57, 601-620

[2] H. Sirringhaus and T. Shimoda (2003), Inkjet printing of functional materials, MRS Bulletin, 28, 802-806

[3] P. Calvert (2001), Inkjet printing for materials and devices, Chemistry of Materials, 13, 3299-3305

[4] C.B. Arnold, P. Serra and A. Piqué (2007), Laser direct-write of complex materials, MRS Bulletin, 32, 23-31

[5] M. Colina, M. Duocastella, J.M. Fernández-Pradas, P. Serra and J.L. Morenza (2006), Laser-induced forward transfer of liquids: Study of the droplet ejection process, Journal of Applied Physics, 99, 084909-1/7

[6] J.M. Fernández-Pradas, M. Colina, P. Serra, J. Domínguez and J.L. Morenza (2004), Laser-induced forward transfer of biomolecules, Thin Solid Films, 453-454, 27-30

[7] C. Boutopoulos, V. Tsouti, D. Goustouridis, S. Chatzandroulis and I. Zergioti (2008), Liquid phase direct laser printing of polymers for chemical sensing applications, Applied Physics Letters, 93, 191109-1/3

[8] P. Serra, M. Colina, J.M. Fernández-Pradas, L. Sevilla and J.L. Morenza (2004), Preparation of functional DNA microarrays through laser-induced forward transfer, Applied Physics Letters, 85, 1639-1641

[9] M. Colina, P. Serra, J.M. Fernández-Pradas, L. Sevilla and J.L. Morenza (2005), DNA deposition through laser induced forward transfer, Biosensensors and Bioelectronics, 20, 1638-1642

[10] J.A. Barron, H.D. Young, D.D. Dlott, M.M. Darfler, D.B. Krizman and B.R. Ringeisen (2005), Printing of protein microarrays via a capillary-free fluid jetting mechanism, Proteomics, 5, 4138-4144

[11] B. Hopp, T. Smausz, N. Kresz, N. Barna, Z. Bor, L. Kolzsvári, D. Chrisey, A. Szabó and A. Nógrádi (2005), Survival and proliferative ability of various living cell types after laser-induced forward transfer, Tissue Engineering, 11, 1817-1823

[12] N.T. Kattamis, P.E. Purnick, R. Weiss and C.B. Arnold (2007), Thick film laser induced forward transfer for deposition of thermally and mechanically sensitive materials, Applied Physics Letters, 91, 171120-1/3

[13] M. Duocastella, J.M. Fernández-Pradas, J.L. Morenza, D. Zafra and P. Serra (2010), Novel laser printing technique for miniaturized biosensors preparation, Sensors and Actuators B: Chemical, 145, 596-600

[14] M. Duocastella, A. Patrascioiu, J.M. Fernández-Pradas, J.L. Morenza and P. Serra (2010), Film-free laser forward printing of transparent and weakly absorbing liquids, Optics Express, 18, 21815-21825

[15] M. Duocastella, J.M. Fernández-Pradas, P. Serra and J.L. Morenza (2008), Jet formation in the laser forward transfer of liquids, Applied Physics A, 93, 453-456

[16] M. Duocastella, J.M. Fernández-Pradas, J.L. Morenza and P. Serra (2009), Time-resolved imaging of the laser forward transfer of liquids, Journal of Applied Physics, 106, 084907-1/7

[17] M. Duocastella, J.M. Fernández-Pradas, J.L. Morenza and P. Serra (2010), Sessile droplet formation in the laser-induced forward transfer of liquids: a time-resolved imaging study, Thin Solid Films, 518, 5321-5325