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Printing of silver conductive lines through laser-induced forward transfer

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ABSTRACT

The generation of conductive lines from liquid inks through laser-induced forward transfer (LIFT) is achieved by printing a sequence of overlapping droplets. This procedure, however, is not free from drawbacks: the formation of continuous lines is often accompanied with undesired scalloping or bulging. In this work we present an innovative method consisting in the deposition of conductive ink through LIFT inside fluidic guides produced by laser ablation. The aim of the approach is that the guides confine the liquid within them so that the most common defects can be prevented. The production of guides through laser ablation followed by LIFT of ink inside them has proved that it is possible to find conditions in which the total confinement of liquid within the guides is achieved with good uniformity all along the line. This proves the feasibility of the proposed approach for printing continuous lines free from scalloping and bulging with excellent definition.

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1. Introduction

Laser induced forward transfer (LIFT) is a direct writing technique which has been shown to be capable of printing a wide variety of materials. Though LIFT was originally applied to transfer materials from thin solid films [1,2], it was later demonstrated that the technique also allowed the transfer of materials in the liquid phase [3,4]. In fact, the LIFT of liquids operates in a similar way to inkjet printing: the material of interest is dissolved or dispersed as an ink, the ink is transferred, and following solvent removal the material remains adhered to the substrate as a pixel [5]. LIFT presents, however, remarkable advantages over inkjet printing. On one hand, it is free from clogging issues, since there is no need for a nozzle in order to print the liquid and the good spatial resolution of the technique is provided by the high focusing power of the laser beam. On the other hand, LIFT allows the user to work with a substantially broader range of inks, with few limitations concerning the viscosity or rheology of the liquid to be printed.

http://dx.doi.org/10.1016/j.apsusc.2015.11.248 0169-4332/© 2015 Elsevier B.V. All rights reserved. The principle of operation of LIFT has been described in detail previously [5]. Briefly, a pulsed laser beam is focused on a thin film of the donor ink, which itself is coated upon a substrate transparent to the laser radiation, the donor substrate. Under the action of a laser pulse, a tiny fraction of liquid is transferred from the donor ink film to the acceptor substrate, usually placed at a short distance from the donor one (between tens of microns to few millimeters). Typically, the printing outcome of a single laser pulse is a circular droplet, the size of which depends on the focusing conditions, laser pulse energy and the wetting properties of the acceptor substrate [6–9]. Using LIFT, a diverse range of materials including inorganic inks, polymers, biomolecules and living cells have been successfully printed [10–16].

The mechanisms of liquid ejection and droplet formation during LIFT have been investigated in detail [6–9,17–19] with the aim of optimizing the performance of the printing technique. The realization of patterns with geometries more complex than simple droplet arrays raise challenges greater than those associated with single droplet formation. When printing lines, for example, factors such as droplet coalescence and capillary flow within the printed line play an essential role in determining the printed line stability [20]. In practice, the formation of stable and continuous lines free from defects like scalloping or bulging is not a trivial task [20–24]. This is true not only for LIFT, but for other commonly employed

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printing techniques such as inkjet printing [25]. In a previous work [26] we proposed a printing procedure for conductive inks which mitigated a number of the problems. However, the proposed method was time consuming and the resulting degree of definition was not as good as desired, with some residual scalloping remaining.

In this work, we present an alternative approach for printing which achieves continuous lines free from bulging and scalloping in a very reproducible and controlled way. The technique consists of printing conductive inks through LIFT inside previously patterned laser ablated fluidic guides. The obtained results demonstrate excellent definition and uniformity. Furthermore, and in spite that the feasibility of the approach is demonstrated for a silver conductive ink, it can be easily extrapolated to liquids of very different nature.

2. Experimental setup

The experiments were performed using an Amplitude Systemes Yb:KYW laser with a wavelength of 1027 nm, a pulse duration of 450 fs and a Gaussian beam intensity profile. A microscope objective of 50× with a working distance of 13 mm and a numerical aperture of 0.55 was used to focus the laser radiation onto the sample. A CCD camera placed coaxial to the laser beam axis allowed controlling the position of the laser beam focus on the sample. Glass substrates coated with a 1 µm thick hydrophobic cross-linked polymer layer were used as acceptor substrates. The polymer layer was selectively removed through laser ablation in order to generate the fluidic guides and these were later filled with printed ink through LIFT. In order to achieve a good confinement of the ink inside the guides it was necessary that the polymer were substantially more hydrophobic than the glass substrate. The hydrophobicity of the polymer was achieved through the use of a fluorosurfactant additive. This combination of polymer layer/glass was chosen for convenience (the aim of the work is to prove the feasibility of the proposed printing approach), but it is anticipated that a wide range of other combinations would be possible, provided that both layer and substrate have a sufficient difference in surface energy.

The fluidic guides were produced by laser ablation using a pulse energy of 75 nJ and laser spots with a diameter of 2 µm, which corresponded to a laser fluence of about 2.4 J/cm². The production of a single fluidic guide was achieved by scanning the surface of the acceptor substrate at a speed of 1 mm/s and a laser repetition rate of 2 kHz. This resulted in a shift of 0.5 µm between consecutive overlapping laser spots. The generated debris during the laser ablation process was removed by using an air flow over the treated area.

Once the fluidic guides were produced the ink was deposited into the channels by means of LIFT. The laser pulse energy during printing was 600 nJ and the laser spot diameter $12 \,\mu m$ (a laser spot diameter larger than that used in the production of the fluidic guides was achieved by changing the distance between the objective and the sample): this resulted in a laser fluence of 530 mJ/cm^2 . In these conditions the printed droplet diameter on the glass substrate was about 180 µm. In spite that much smaller diameters can be obtained through conventional LIFT [27], the printing conditions required to achieve such small droplets are very sensitive to nonuniformities in the thickness of the donor film. Since the purpose of this work is to prove the feasibility of the proposed approach and not yet to optimize its resolution, we chose to work in the most favorable conditions for the test: printing relatively large droplets, which does not compromise the reproducibility of the printing process.

А commercially available Ag nanoparticle ink from Sigma-Aldrich[®] was used in all the LIFT experiments. The particle size was smaller than 50 nm and the solid content was around 30-35%. The donor films were prepared by blade coating thin layers of ink with a thickness between 20 and 30 µm on glass microscope slides. The gap between the donor and acceptor substrates (160 μ m) was maintained through the use of cover slips as spacers. Although it is common that LIFT experiments use a sacrificial absorbing layer, in the presented experiments this was not needed because the Ag ink itself absorbs the laser radiation at this wavelength. The printed lines, once dried, were laser cured by means of a CW Nd:YAG laser (Baasel LBI 6000, 1064 nm wavelength, 1.2 W output power and a Gaussian intensity profile) operating at a scan speed of 2 mm/s with an irradiance of about 12 kW/cm². At the end of the process the conductivity of the lines was measured and compared with the expected value for the ink.

3. Results and discussion

The common printing procedure for the generation of lines consists in depositing consecutive overlapping droplets. Fig. 1 displays the outcome of such an experiment corresponding to silver ink printed on a glass substrate. In that experiment different overlaps were tested with the aim of finding the conditions leading to the formation of stable continuous lines free from defects. The shifts between adjacent droplets (Δx) in Fig. 1 corresponded to the center to center distance and ranged from 160 to 25 µm. The first two shifts ($\Delta x = 160$ and $120 \,\mu$ m) result in non-overlapping droplets with diameters around 80 µm. When the shift becomes equal or smaller than the droplet diameter ($\Delta x \le 80 \,\mu$ m), the droplets coalesce, resulting first in dashed lines ($\Delta x = 80-72 \,\mu m$) and for even smaller shifts ($\Delta x \le 56 \,\mu$ m) continuous lines. However, in these last cases bulges are always present, mostly at the beginning of the line and occasionally in the middle. This defect can be highly detrimental in electronic circuits since it can easily lead to unwanted short-circuits between adjacent lines. It is clear, therefore, that the objective is not fulfilled: no continuous lines free from defects are obtained in such a straightforward way.



Fig. 1. Optical microscopy image of lines printed with different shifts between adjacent droplets (Δx , measured from center to center) decreasing from left to right.

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