Laser forward transfer of conductive inks

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Abstract: One of the most used inks in printed electronics is silver paste, which is extensively used in screen printed circuits. In this work the feasibility of Laser-Induced Forward Transfer (LIFT) technique was investigated for transferring screen printing silver paste. It was possible to print several droplets at different laser pulse energies for a certain donor-acceptor gap. After that, two studies were carried out: the analysis of the deposited droplets and the characterization of the dynamics of the material transfer. An approximately linear trend in the radius-energy dependence was observed, and thicknesses of the printed droplets were of the order of a few microns. The transfer dynamics was characterized by means of a time-resolved imaging method, showing three different stages on the bubble evolution: bubble expansion, bubble burst and bubble retraction. Jet formation never took place as it happens in low-viscosity inks. Results in both experiments were conclusive and consistent with each other.

I. INTRODUCTION

Laser-Induced Forward Transfer (LIFT) is a direct-write laser technique which has been demonstrated to be feasible and which is capable of transferring a wide variety of liquid inks without altering their properties: from inorganic materials as conductive inks [1], to organic materials such as polymers or biomaterials such as DNA [2]. The LIFT technique consists on using a laser pulse focused on a donor film which absorption leads to the ejection of a small amount of material onto an acceptor substrate. As shown in Fig.1, the donor substrate, which is transparent to laser radiation, is coated with a film of the material to transfer and the acceptor substrate is placed at a conveniently short distance. The absorption of the laser pulse energy induces the formation of a bubble as a result of the vaporization of the material, which pushes the non-vaporized part of the donor film towards the acceptor substrate, where the material is deposited [3]. Besides, there is also the possibility to transfer the liquid upwards, inverting the donor and the acceptor positions [1].

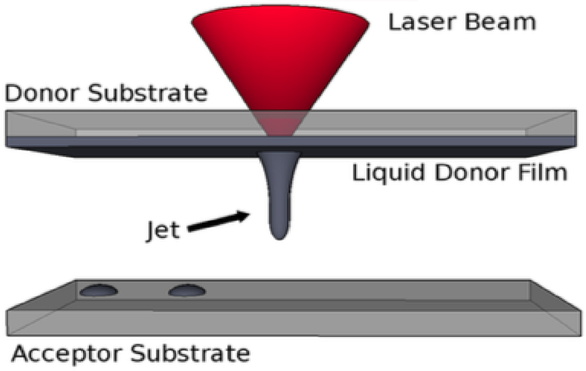

FIG. 1: Principle of operation of the LIFT technique.

LIFT is not the most extended technique to transfer materials; for instance, inkjet printing is a much more accessible technique and it has become industrially and commercially widespread [4]. However, inkjet printing presents some drawbacks, like printing high viscosity liquids, nozzle clogging or head contamination issues [5]. The advantages of LIFT over inkjet printing are notable in several instances, considering that it is possible to print a wider range of viscosities, with higher resolution and in the absence of clogging problems. The feasibility of this technique has been proved through many investigations which have analysed the influence of different parameters such as laser fluence [6], beam diameter [7] or material viscosity [8].

In the printed electronics field, there is another important technology to take into consideration: screen printing. This technique uses a mesh, which contains the pattern intended to be printed, to transfer the ink onto a substrate [9], so it does not present limitations concerning viscosity. It is important to point out that one of the most used inks in printed electronics is silver paste, since all electrical contacts are made of this material. The silver paste used in screen printing for electronics applications is usually a high viscosity ink with high conductivity, due to the large concentration of metal content, which makes this ink very suitable for the fabrication of electronic devices. However, the fact that each stencil must be fabricated specifically for each pattern is a weak point of the technique because it is time consuming and expensive. That could be improved if LIFT were used with the screen printing silver paste, since in contrast to screen printing, LIFT is a digital technique (this implies a rapid transition between the pattern design and its final obtaining). Therefore, there is an important interest in bringing LIFT to the industrial level given that it could reduce the cost of the printed electronic devices.

The aim of this work is to prove the feasibility of LIFT to print screen printing silver paste. This is carried out through two complementary studies: the analysis of the deposited droplets and the characterization of the dynamics of the transfer process by a time-resolved imaging method.

II. EXPERIMENTAL

The experiments were performed using a pulsed Nd:YAG laser with a 355 nm wavelength, a pulse duration of about 10ns and a beam diameter of approximately 6.8 μm. The donor and acceptor substrates were 25x75 mm^2 microscope glass slides. The ink used was a silver screen printing paste from Electra d'Or (ED 3000) with a viscosity of about 50 Pa·s. The donor sample was prepared settling an adhesive tape of a thickness of 50 μm onto a clean slide and removing a rectangular portion of the tape. The ink was deposited on the slide and it was

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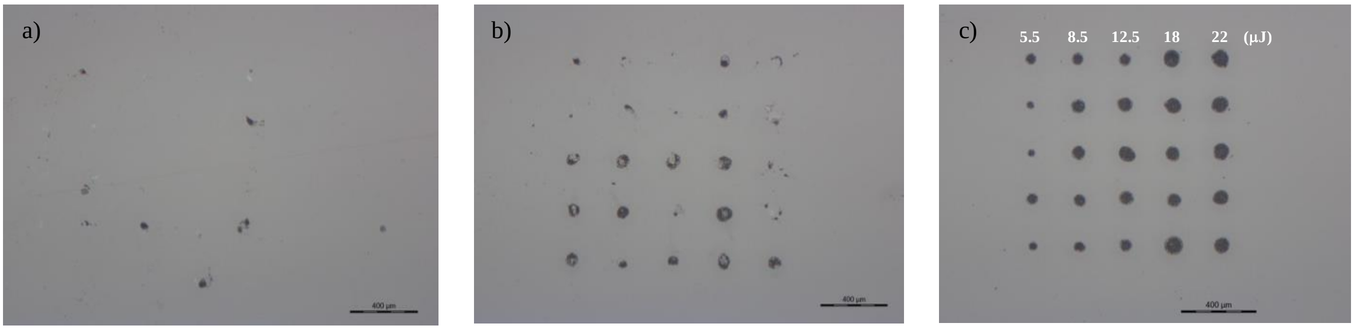

FIG. 2: Optical microscopy images of the droplets deposited by LIFT. Each matrix corresponds to a different gap distance: a) 100 μm, b) 50 μm and c) 10 μm. For matrixes a) and c) the laser pulse energy was increased from left to write from 4.5 μJ to 23 μJ approximately. For matrix b) the laser pulse energy was kept at higher values that varied between 15 μJ and 21 μJ due to the laser instability. Average energy values for each column are indicated in image c).

spread using a blade coater, so that the film of the material remained delimited into the area where there was no adhesive tape. Using this system, a film of a thickness of approximately 40 μm was systematically obtained every time. Afterwards, the sample was inverted and placed over the acceptor using spacers of different thicknesses (100 μm, 50 μm and 1200 μm) depending on the experiment. Eventually, the whole structure was placed on a computer controlled translation platform, focusing the laser on the donor film.

Together with this setup, another one was used to get the time-resolved images, which consisted of a light source (red LED), a CCD camera and a pulse generator. A microscope objective was aligned with the LED and the camera, ensuring that it was possible to observe the liquid ejection at grazing incidence with the donor layer. Besides, the LED pulse, which was about 100 ns, was synchronized with the laser pulse at a controlled delay using a pulse generator. Thus, it was possible to set the moment when the image was taken after the laser pulse reached the donor film. Then the camera was simultaneously triggered in order to capture the LED flash and obtain an image of the transfer process.

III. RESULTS AND DISCUSSION

The experiments that were carried out to prove the feasibility of LIFT for transferring screen printing silver paste were based on the systematic variation of two main parameters: the laser pulse energy and the gap distance between the donor and acceptor substrates. Once the best conditions to obtain printed droplets were found out, it was interesting to carry out a study of its shape and, otherwise, analyse the dynamics of the liquid ejection.

A. Droplet Printing

In order to check if it was possible to print silver paste droplets, a sample with a 100 μm gap between the donor and acceptor substrate was prepared first. Laser pulses were sent arranged in an array setting different energies for each column. Although the excitation of the laser lamp remained constant at each column, the laser pulse energy varied from one pulse to another due to the laser instability, obtaining a wide amount of energy values for each array. In Fig.2a, the energies varied from approximately 4.5 μJ the lowest to 23 μJ the highest. However, the result was unsatisfactory since no droplets were printed.

Therefore, the experiment was repeated diminishing the gap up to 50 μm and the results showed that there was just material transfer at high energies, but the droplets were not well defined either (Fig.2b). Finally, the experiment was carried out again placing the slides in contact, so that it existed a gap of around 10 μm between the film and the acceptor substrate (the meniscus of the liquid within the rectangular pool prevented contact between donor film and acceptor substrate). The results regarding this setup were satisfactory. As shown in Fig.2c, an array of non-overlapping droplets was obtained. The energy of the laser pulse was varied from low values around 4.5 μJ for the first column to values around 23 μJ for the last column. Besides, it is possible to observe that the radius also increases with energy, from 20 μm at low energies to 50 μm at the highest. In addition, another array was printed reproducing the same method with the same donor sample, in order to acquire a greater number of droplets.

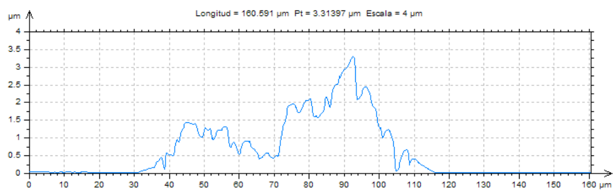

FIG. 3: Confocal microscopy profile of one droplet printed at an average laser pulse energy value (about 14 μJ).

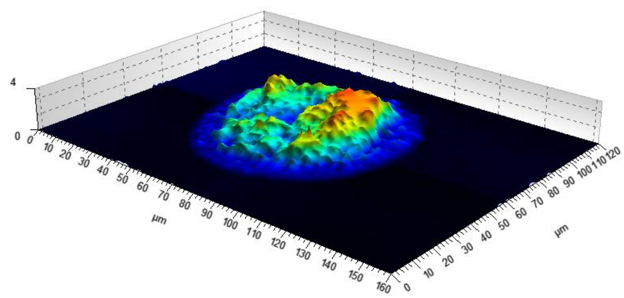

FIG. 4: Confocal microscopy 3D image of one droplet printed at an average laser pulse energy value (about 14 μJ).

A confocal microscope was used in order to obtain more information about the droplets shape once the solvent was dried out. Fig.3 shows the droplet profile for an average energy of about 14 μJ, yet the profile was similar for all the other ones, as well as the 3D representation in Fig.4. In Fig.5a it can be appreciated that from energies around 7 μJ onwards, the relation between the radius and the laser pulse energy follows an approximately linear trend. Besides, if the deposited volume is represented instead of the radius (Fig.5b), it is shown that the relation is practically linear for the whole energy range. Moreover, in Fig.5c it can be observed that the volume grows linearly with the base area, which means that the average thickness of the droplets is fairly constant with a value around 1.3 μm. Still, the real profile of the droplets has not a constant thickness and it has peaks that reach up to roughly 4 μm. It is interesting to note that the obtained thicknesses are of the order of a few microns, unlike inkjet printing, where they are about a few hundreds of nanometres [5]. As a consequence, the resulting electrical resistance of a printed line with LIFT will be lower than with inkjet printing, given that the transversal section of the line will be larger and the resistance value is given by:

$$R = \rho \frac{l}{A}$$

a) b) c)

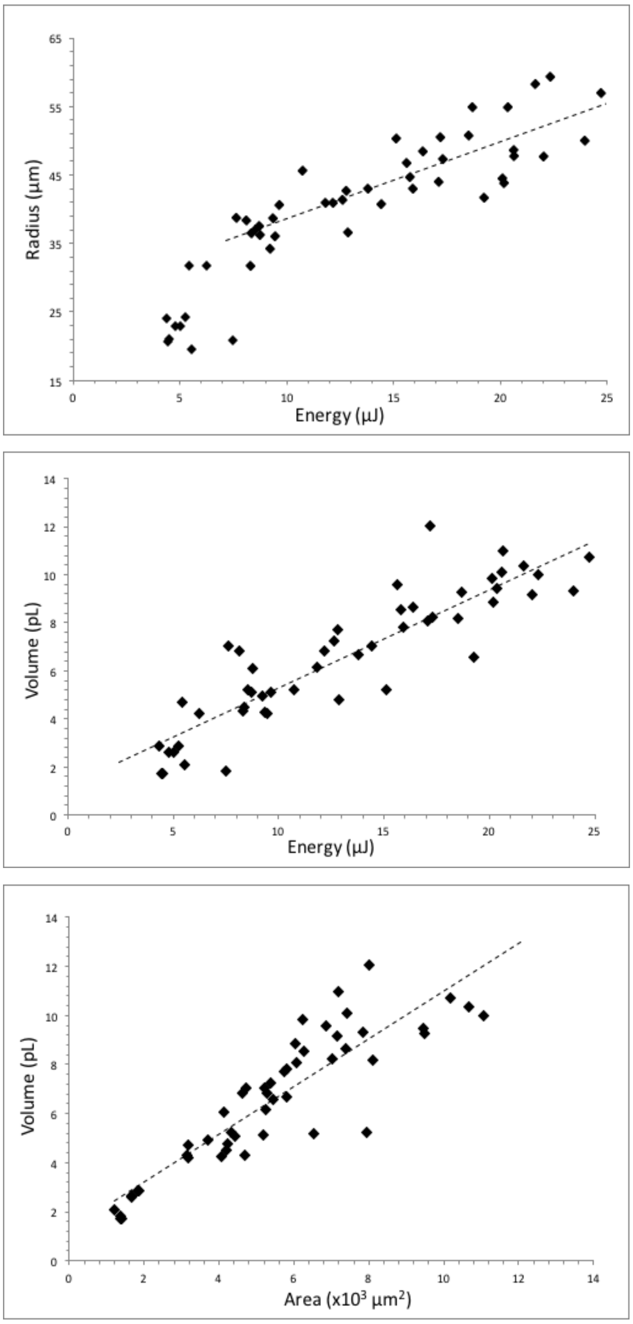

FIG. 5: Plots of the deposited droplets radius (a) and volume (b) versus laser pulse energy and droplets volume versus area (c). The dashed line corresponds to a linear fit.

B. Ink Ejection Dynamics

The analysis of the dynamics of the bubble evolution permitted to understand the liquid ejection dynamics and give an explanation concerning the results of the first experiment (Fig.2). The experiment that was carried out to study the silver paste ejection dynamics was based on the repeatability of the phenomenon of study. According to the experimental setup detailed in section II, the procedure consisted on taking several snapshots of the evolution of the bubble with different time delays from the beginning of the transfer process. After that, by ordering all the images in time, a stop-action movie of the phenomenon was acquired, thus making the analysis of the dynamics possible.

By means of the pulse generator, the laser pulse was used as the start time of image acquisition by activating the LED and the camera in turn. The LED pulse, which length was about 100 ns, lightened the sample after a precise time delay from the emitted laser pulse. Thus, since the camera exposure time (500 μs) was much larger than the LED pulse, the picture exposure time was actually determined by the LED pulse length.

This procedure was repeated several times for many laser pulses and different time delays. Besides, the sample was moved after each pulse, so that the material transfer would take place at a fresh position in the donor film each time. The displacement of the sample could be done by using a computer-controlled xyz translation stage.

The first study that was carried out was focused on observing the general dynamics of the silver paste transfer. Different snapshot sequences were obtained for three representative pulse energies (7 μJ, 14 μJ and 20 μJ approximately) in order to examine the behaviour of the bubble evolution in each case. In Fig.6, the corresponding time-resolved images are shown. The acceptor slide cannot be seen in the image because the gap distance between donor and acceptor surfaces is about 1200 μm, out of the field of view. This configuration allows to clearly observe the paste ejection dynamics. It is possible to identify three different stages during the bubble evolution: bubble expansion, bubble burst and bubble retraction. It is interesting to point out that in any case a jet formation takes place as it happens in liquid inks [3]. That fact will be key to explain why silver paste transfer does not take place for certain gap distances between the donor and acceptor substrates.

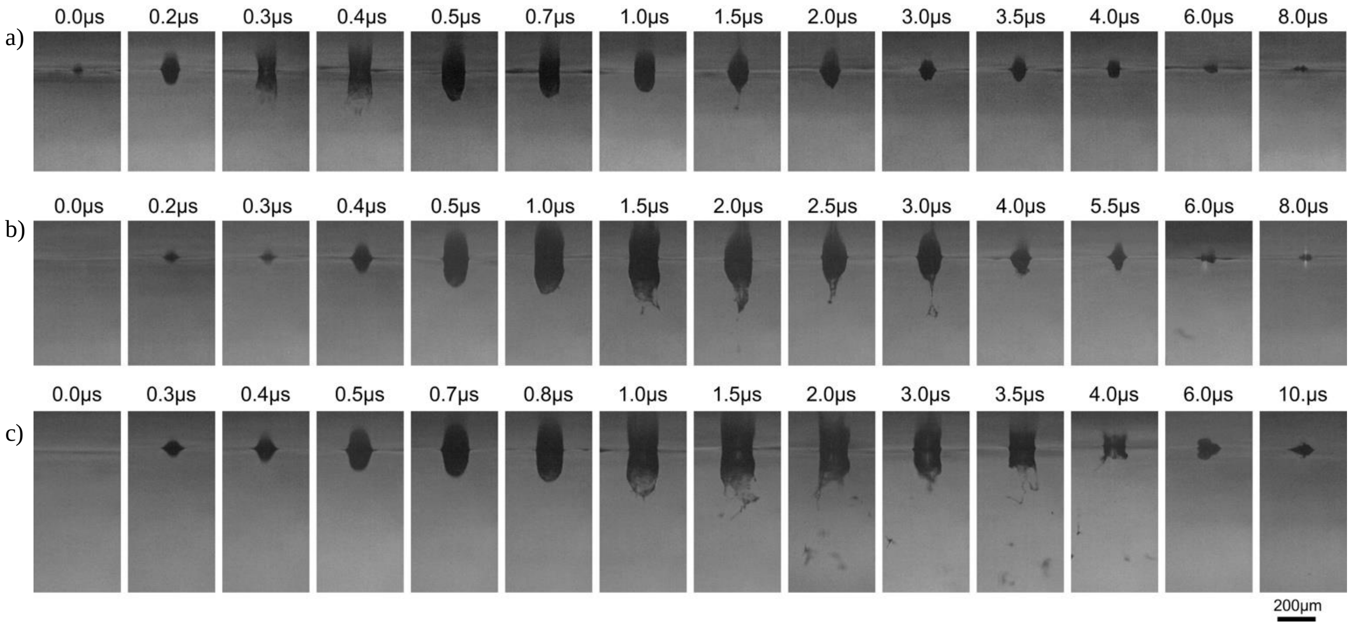

FIG. 6: Sequences of time-resolved images of the bubble evolution for different laser pulse energy values. The corresponding energies to each sequence are (a) 7 µJ, (b) 14 µJ and (c) 20 µJ. Numbers over the images indicate the time delay between the laser pulse and the caption of each image.

As it is noticeable in Fig.6, the evolution of the bubble is different depending on the laser pulse energy. The bubble burst is stronger when the energy rises, as well as the duration of the evolution is longer. It takes more time for the bubble to expand and recoil, given that the inner pressure generated by the absorption of the laser pulse in the ink layer is higher when the laser pulse energy increases. As it can be noticed in Fig.6a, the maximum expansion takes place around 0,5 µs, unlike Fig.6b and Fig.6c, where it occurs around 1.5 µs. In Fig.6c (20 µJ), the material spattering due to the bubble explosion is more significant than for lower laser pulse energies. Besides, the radius of the bubbles also increases for higher energies.

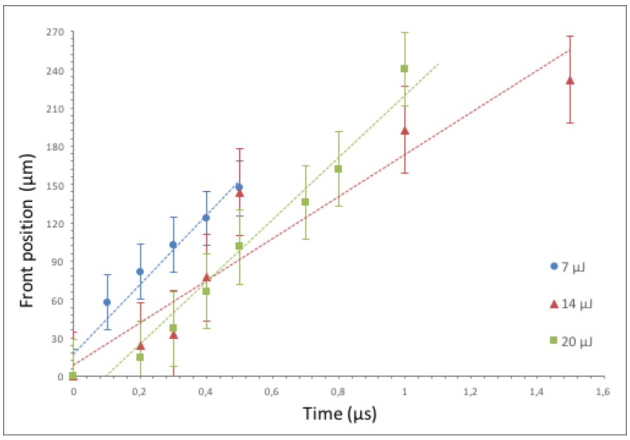

FIG. 7: Temporal evolution of the front position for each laser pulse energy value. The corresponding front velocities are approximately 270 m/s, 165 m/s and 245 m/s for 7 µJ, 14 µJ and 20 µJ respectively.

In Fig.7, the position of the bubble is represented versus time using the time-resolved images. It can be observed that for higher energies the bubble reaches a distance up to nearly 240 µm. The front velocity of the bubble for each laser pulse energy value is obtained from the slope of the linear trend. The highest velocity of the liquid ejection (270 m/s approximately) corresponds to the lowest energy value (7 µJ); however, the lowest velocity (165 m/s) corresponds to the 14 µJ laser pulse, not to the highest energy laser pulse (20 µJ) as it could be expected. Due to the bubble burst effect, noticeable in Fig.6c, it was difficult to delimit the bubble length with precision. Hence, this results can be inconclusive concerning the relation between the front velocity and the laser pulse energy.

After this general observation of the silver paste ejection dynamics, another time-resolved image sequence was obtained (Fig.8). In this case, the gap between the donor and acceptor substrates was diminished up to 250 µm and medium laser pulse energies about 15 µJ were used. The aim was to analyse the deposition of the material onto the acceptor substrate, but the problem was that if the gap was smaller than 250 µm it was very difficult to obtain snapshots where the bubble was visible due to the lack of light.

Images in Fig.8 show that there is no material transfer onto the acceptor slide for a gap distance of 250 µm. As it is also shown in Fig.6, there is practically no ejection of material throughout the whole liquid ejection evolution process. This fact means that the material transfer cannot take place unless the bubble reaches the surface below.

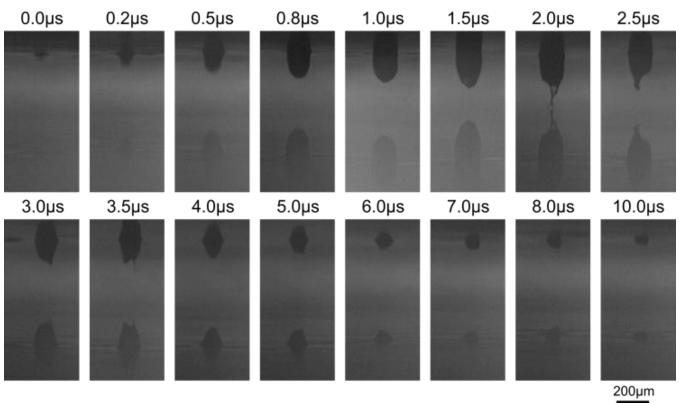

FIG. 8: Sequence of time-resolved images for the bubble evolution. Donor acceptor gap distance of 250 µm and laser energy pulse about 15 µJ.

In view of these results, an explanation regarding the first experiment can be given (Fig.2). When the gap between the donor and acceptor substrates is too large to enable the proper contact between the bubble and the acceptor slide there is no transfer of material (Fig.2a). Yet, there are some remaining traces of ink onto the slide. These can be consequence of the small amount of ejected ink during the bubble burst (which can be appreciated in Fig.6) or slight contacts between the material and the substrate. In Fig.2b, where the gap was diminished up to 50 μm and just higher laser energy pulses were used, it can be noted that most of the droplets printed have a hole at the centre. This can be attributed to an effect of the bubble explosion (Fig.6c), in which the ink is disposed in a circular ring shape leaving the centre contactless. In Fig.2c, the gap is small enough (10 μm) to enable a full contact of the bubble with the acceptor substrate. In this case, given that the proximity between the donor and acceptor slides makes the material transfer feasible, the droplets are properly printed along the whole range of laser pulse energies.

IV. CONCLUSIONS

In this work, the feasibility of laser-induced forward transfer for high viscosity inks was demonstrated, in particular for a screen printing silver paste.

It was possible to print several droplets with different laser pulse energies for a gap of 10 μm between donor and acceptor substrates. For larger gaps (50 μm and 100 μm), droplets could not be printed. The study of the printed droplet that was carried out showed that, for laser pulse energies from 7 μJ onwards, the radius presented an approximately linear growth with the pulse energy. Moreover, clearly linear trends in the volume-energy and volume-area dependences were observed. The average thickness of the printed droplets was around 1.3 μm, unlike inkjet printing, where they are about a hundreds of nanometres thick. Hence, the electrical resistance of a line printed with LIFT will be lower than a line printed with inkjet printing.

Time-resolved images sequences were obtained to perform an analysis of the liquid ejection dynamics. This study revealed that, during the bubble evolution, jet formation never occurred. Instead of this, it could be observed that the dynamics of the material transfer took place in three stages: bubble expansion, bubble burst and bubble retraction. This fact is the key to give an explanation to the absence of material transfer for larger gaps. Given that there was practically no ejection of material during the entire process, material transfer could not happen unless the bubble reached the acceptor slide.

As far as the front velocity study is concerned, the results were inconclusive. A deeper study should be carried out taking into consideration a larger number of samples.

This results may be interesting as the printed electronics field concerns, given that LIFT could bring many enhancements for printed electronic devices regarding cost and time expense.

Acknowledgments

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