Printing inks with CW lasers

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Abstract: Laser-induced forward transfer (LIFT) printing is a technique with a great future as an alternative to the inkjet printing since it is not limited by the viscosity and size of the printing particles as inkjet. Even so, the use of expensive pulsed lasers could hamper its development. The use of continuous lasers can be an alternative since they are used industrially, and their cost is lower. In this work, different continuous LIFT printing conditions are studied by changing the thickness of the donor layer, the scanning speed and the laser power. A minimum of 0.5 Ω/sq is obtained and optimal printing conditions are determined for the 3 studied parameters.

I. INTRODUCTION

In the last years, new techniques for printing electronic devices have been developed because of the increasing demand from industry to manufacture in different conditions than traditional, especially on new substrates other than silicon wafers [1]. For example, wearable electronics has exceptional applications on portable and stretchable human-interactive sensors and shows us the need of printing on materials which can provides these properties [2].

Moreover, traditional printing methods, such as roto-gravure, use rolls and screens. In roto-gravure the image that you want to print is engraved on a cylinder, so that its surface is full of cells containing the ink to transfer and their size depend on the amount of ink you want to transfer; this structure allows printing with different colour intensities [3]. This type of processes is adequate for long runs and repetitive patterns, but not for short runs and customized production. In this way, digital printing is researched and techniques like inkjet-printing looks like a good solution [1].

Widely used on graphic arts, inkjet printing was the first method used to digitally print electronic circuits. For this purpose, it had to be adapted for printing new electronic inks and it is currently the most important method in this field, allowing a good deposition of many kinds of inks. These inks are formed by a solution of metallic, dielectric or dyes nanoparticles [1]. Despite this, inkjet-printing technique is limited by the ink viscosity (for a certain printing head just a few values of viscosities allow the flow of the ink trough it) and the size of the dissolved particles (for a certain size of the output nozzle, printable particles are limited to 1/100th of its diameter) [4]. All these requirements represent a huge printable materials limitation.

Laser-induced forward transfer (LIFT) is another digital method that emerged as an alternative to inkjet printing [5]. With the inkjet-printing limitations in mind, LIFT seemed to be able to get better results because it is based on a different physical phenomenon (does not based on a flowing ink through a nozzle). This technique consists on printing a material dissolved in an ink by ejecting it from a surface, which only acts as a support, to another surface. For this, a layer of the ink, called donor layer, is placed on a transparent substrate through which it is illuminated with a focused laser beam to achieve the propulsion of tiny volumes of the ink. By intercepting the ejected ink with another substrate, the deposition of the ink is obtained on the surface of this.

Normally only pulsed lasers were used. In this case, it has been studied that the ejection of the material is through a jet generated by the expansion of a cavitation bubble in the donor layer caused by heating with the laser light (Figure 1a). Finally, this jet goes out of the donor film and freely propagates until the receiver substrate intercepts it. When this happens, a droplet is formed by the material ejected and generates a printed pixel [5].

Pulsed lasers are more expensive than analogous continuous wave lasers (CW) with the same power [6]. As this can be an issue for the LIFT development, CW laser LIFT is under study to try making this technique more affordable. Under these conditions, it has been seen that the dynamics of the transmission of the ink is different than the pulsed laser transmission (Figure 1b). In this case, the ejection of material is through a spray mechanism [4].

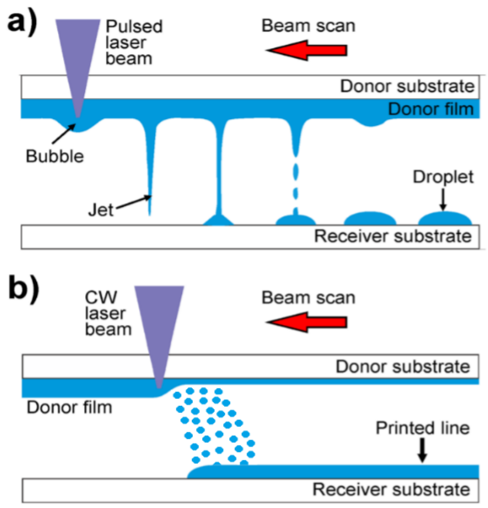

FIG. 1: Sketch of LIFT mechanisms using an ink donor layer of the printing material. (a) Pulsed laser: It shows how the laser focuses on the donor layer at points separated (determined by the repetition rate and scanning speed) and prints the material through jets. In each part of the sketch is represented the different stages of the transfer, which are laser absorption, bubble expansion, jet formation and droplet deposition (from the left to the right). (b) CW laser: It shows the operating mode of the CW LIFT that prints through the spray method continuously scanning the donor layer [4].

Also, CW LIFT is a digital technique that allows to print any type of shape just drawing it over the donor layer. In this way, it does not have the need to create screens or other elements to make the patterns (only the laser is needed). So, the non-use of elements such as rolls and the use of continuous lasers (widely used in the industry for marking,

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cutting, engraving, etc. [6]) makes CW LIFT a relatively low-cost procedure. Moreover, unlike the inkjet, as the ink is transferred from a free surface to the air it should not have restrictions on the viscosity and size of the particles that can be printed.

This work studies CW LIFT and it tries to find the best conditions for printing conductive lines changing the power supplied, the speed of the laser scanning and the thickness of the donor layer.

II. EXPERIMENTAL

A. Digital printing with laser.

The same continuous wave laser was used in all the measurements of this work. The laser in question is Baasel Lasertech, LBI-6000, a Nd:YAG laser, working at its fundamental wavelength of 1064 nm. It worked with a 1.3 mm aperture and a 100 mm focus lens. This lens is an f-theta lens that allows to focus the laser beam on any position of the focal plane with the same profile of intensities and without loss of power. It is also equipped with a system of mirrors (before the f-theta) that allows moving the beam along the plane of the substrate at different speeds. The laser beam has a Gaussian intensity profile. For this work, different LIFT printings were performed for powers between 0.5 and 6.0 W and scanning speeds between 150 and 600 mm/s. The laser was calibrated before performing the measurements with a thermopile of conversion factor of 363.7 μV/W. Changing the laser power (in the units in which laser works) and assigning its value in watts (according to the response of the thermopile) the following power values for the measurements were chosen: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0 W.

B. Sample preparation.

An ink of silver nanoparticles used in inkjet (Sigma Aldrich, ref 736481) with a density of 1.45 g/cm^3 was printed. To prepare an homogeneous ink donor layer , the ink was spread on a glass microscope slide with a blade coater. To achieve different thicknesses, the volume of ink and the height of the blade coater were changed. An estimate of its thickness was made by measuring its weight and surface and knowing its density. In total, printings for all powers previously said and 3 different thicknesses were made (10, 25 and 50 μm). The receiver substrate was also a glass microscope slide. It was separated from the donor substrate by a microscope coverslip, which is 150 μm thick and allows to ensure a close transfer of the ink. Before each printing, the receiver substrate was heated to 100 °C in an oven to achieve a better adhesion of the ink.

C. Sample printing.

The printing of straight lines was carried out and later their conductivity was analysed. For this, the receptor substrate was placed on a support. On its top, the spacers were placed and then the donor substrate with the face impregnated with ink facing the receptor substrate. The laser impinged on the non-ink part of the donor substrate and ejected the ink down to the receiver substrate. In the same microscope slide, different lines can be printed for the same donor layer, different powers and different speeds (easily controllable through the code of the program that controls the laser). It is necessary to indicate that the start of the continuous pulse of the laser is made outside the substrate to avoid possible problems generated by the peak intensity in the start of the laser beam. After printing, the donor layer cannot be used again due to the inhomogeneities generated in printing and the ink of the glass slide is cleaned. The printed slide was put in an oven at 55 °C for drying about half an hour and then it was cured at 200 °C for one hour.

D. Sample characterization.

The characterization of the samples (measurement of the dimensions and photos of the lines) was made by means of an optical microscope (Carl Zeiss, model AX10 Imager.A1) and a calliper. About the electrical characterization (resistance measurement), it was made with a multimeter (Aim-TTi, model 1906) through the two-point method.

III. RESULTS AND DISCUSSION

The first experiments done were the printing of 9 different samples divided into trios according to the thickness of the donor layer. In turn, the three samples of each thickness were differentiated by the speed of laser printing and, simultaneously, each individual sample was composed of nine printed pairs of lines, where each pair was printed at a different power. With this set of printed lines under different printing conditions, it was expected to find the different influence of each parameter on the LIFT printing.

Although the physical parameter measured was the resistance, the sheet resistance is going to be represented since it allows to compare between the different samples by eliminating the influence of the geometric factor of the resistance measure for a planar sample. This is calculated with formula (1).

$$R_s = R\frac{W}{L} = \frac{\rho}{t} \qquad (1)$$

where R is the resistance, ρ is the resistivity, W is the width, L is the length and t is the thickness of a line.

Each value of sheet resistance has its own error bars and as the laser parameters are controlled by computer they are taken with no error.

Any of the samples printed with a donor layer of 10 μm were conductive.

For the 25 μm thick samples, resistance measurements were only obtained for the higher speed samples (400 and 600 mm/s). The influence of the power can be studied representing the sheet resistance in front of power, for a determined scanning speed (Figure 2). The minimum sheet resistance (≈ 1.5 Ω/sq) is obtained for powers between 1.0 and 1.6 W and it increases for small and large values. The influence of the thickness of the donor layer can be observed by comparing these values with those of the sample of 50 μm at the same printing speed (Figure 3).

A similar dependence of the sheet resistance with the power can be observed but there is a decrease in all resistance values. Now, the zone of low sheet resistances seems to cover a greater range of powers and the minimum (≈1 Ω/sq) is around 1 W. From this, it can be said that the increase in thickness favours the printing and generates lines with less resistance.

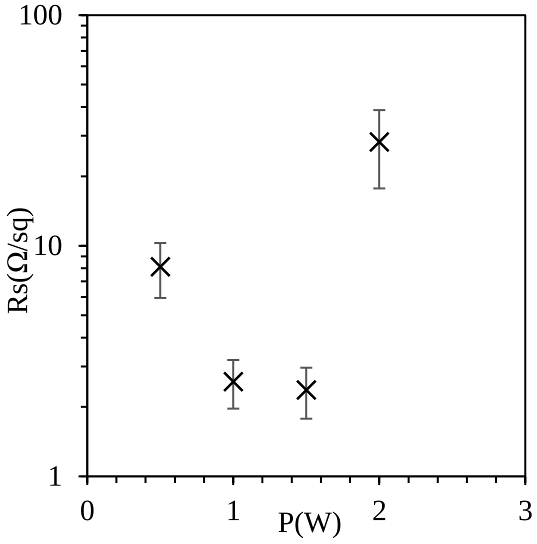

FIG. 2: Plot of measured values of sheet resistance for the sample of 25 μm of donor layer and 600 mm/s as a function of the laser power.

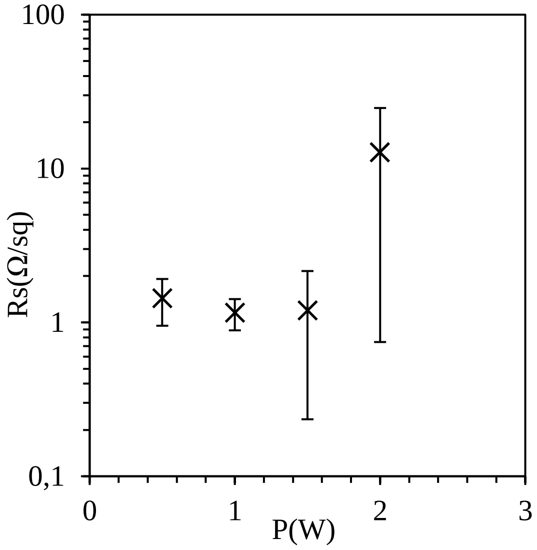

FIG. 3: Plot of measured values of sheet resistance for the sample of 50 μm of donor layer and 600 mm/s as a function of the laser power.

This coincides with the printing of non-conductive lines with donor layers of 10 μm. This result can be expected because if the donor layer is thicker, a greater transfer of material occurs. As the material is ejected through the spraying mechanism, a greater transfer of material provides a better continuity of the deposition (areas without deposition are avoided) and a lower sheet resistance of the printed lines. Moreover, a greater transfer of material allows a higher thickness of printed lines that decreases the sheet resistance as can be observed from formula (1). The influence of the speed can be observed comparing the values of this last sample (Figure 3) with the corresponding one at lower speed (Figure 4).

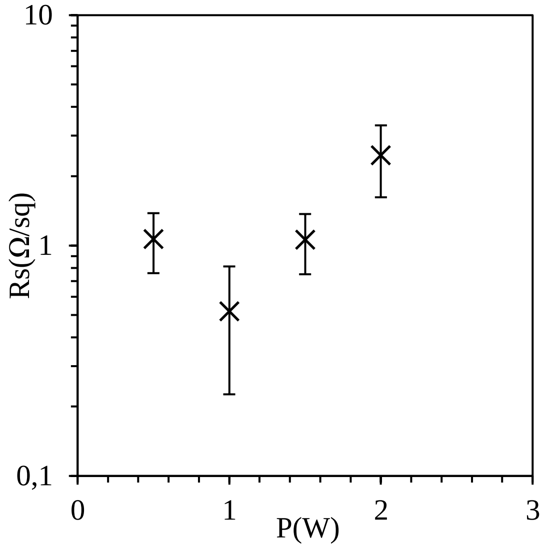

FIG. 4: Plot of measured values of sheet resistance for the sample of 50 μm of donor layer and 400 mm/s as a function of the laser power.

It can be observed that this sample has the same dependence with the power as the other two. In comparison with Figure 3, it reaches slightly lower values, it has the minimum sheet resistance in 0.5 Ω/sq around 1 W and the zone of low resistance is shorter. To better observe the dependence of the sheet resistance with the printing speed, the sheet resistances of all the samples of maximum donor thickness have been represented (Figure 5).

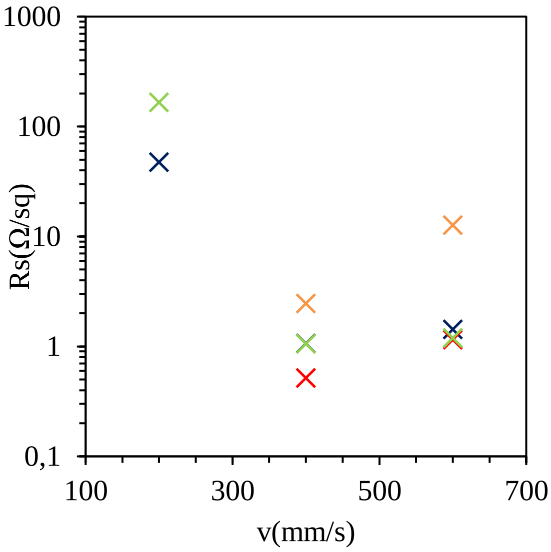

FIG. 5: Plot of measured values of sheet resistance for the 3 samples of 50 μm of donor layer as a function of the laser velocity. Each colour represents one power: blue is 0.5 W, red is 1.0 W, green is 1.5 W and yellow is 2.0 W. It should be noted that for the sample of 200 mm/s only measured resistances for 0.5 and 1.5 W. In principle, the 1 W line would have to give a lower or intermediate value to the previous two. It can be caused by an occasional bad printing (like some defect in the donor layer). The error bars are not drawn to avoid superposition of the data, but these would be the same as in Figure 3 for the 600 mm/s points and Figure 4 for the 400 mm/s points. The 200 mm/s points also have their own error.

On this graph, a minimum sheet resistance around 400 mm/s can be determined. In the same representation for the samples of 25 μm in thickness, a similar trend can be observed, but the minimum is shifted to higher speeds. This result makes sense because a thicker layer needs greater energy input to boil the ink, to produce its ejection [1], and a greater energy input is achieved with a lower scanning speed (because the energy supplied is the product of the laser power by the exposure time). This also explains that at high speeds non-conductive lines are printed (the energy is insufficient to boil the entire thickness of ink and little ink is transferred). However, the increase in sheet resistance for low speeds can be explained by the capillary effect, which produces an ink flow from hot to cold zones depending on the temperature gradient between these zones [1]. This is because at low velocity a lot of energy is accumulated and increases a lot the temperature of the ejection zone. This generates a large gradient between irradiated and non-irradiated zones and the ejection zone is emptied before boiling, making smaller the ink ejection (same effect as if the layer was thinner). Therefore, the optimal printing speed for a given thickness of the donor layer can be found.

So far, it has been seen that a thicker donor layer allows better printing and that both the power and speed have an interval where sheet resistance is minimum. Although these results can seem coherent results, it was observed that the conductive lines were on the same zone of the substrate in all the samples. Because of this, the repetitiveness of the printing was questioned and, consequently, the dependence of the resistance with the power. To solve this, it was though if the printing could depend on the area and, to determine this, different experiments were performed.

The first was to print 9 pairs of identical lines, in the same way that was printed for different powers, to compare if the sheet resistance of a same line could change along the positions (Figure 6). The line that had given lower resistances in the previous samples was chosen for this experiment.

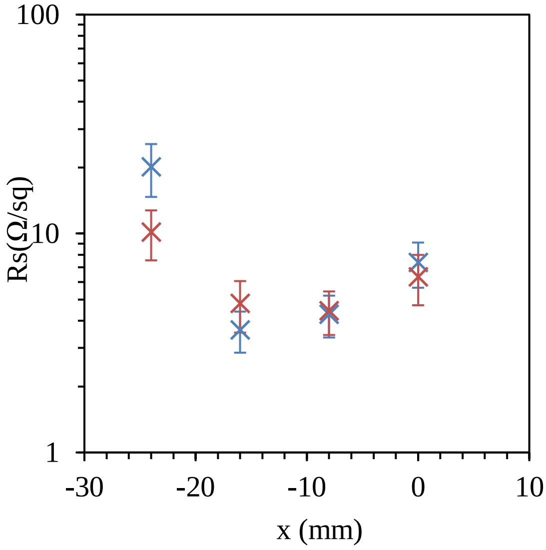

FIG. 6: Plot of measured values of sheet resistance for 2 samples of 40 μm of donor layer, 1 W and 400 mm/s as a function of the position on the substrate according to the coordinates of the laser movement.

Although the resistance of the original line has not been reached (this may be because the donor layers are approximately 40 μm instead of 50 μm), the same dependence as with the power can be observed. This experiment allows to say that the dependence found with the power was affected by the irregularity of the printing area.

This was an unexpected result (since the laser lens system should avoid differences of the laser along the plane of the substrate) and its origin was unknown. To know what the cause was, different experiments were performed. The power of the laser was measured with a thermopile in different zones over the substrate and some lines were engraved on a photographic plate, but did not seem that the power, the shape or the size of the beam changed enough to generate the differences. Also, the received power through a common substrate was measured to evaluate the effect of the reflection of the beam, but it also did not change.

With this short analysis could not find out what the origin was, but a deeper study is far from the objectives of this work. What is clear is that this problem limits the area of good printing and therefore it had to been devised a good way to measure the sheet resistance as a function of the power. This consists of repeatedly printing of a single line changing manually the position of the sample and the power of the laser after each printing. That is, all the powers (the same 9 powers as those of the first experiments) are printed at the same position concerning the laser to avoid scanning over the substrate and it always print in the same good area (Figure 7).

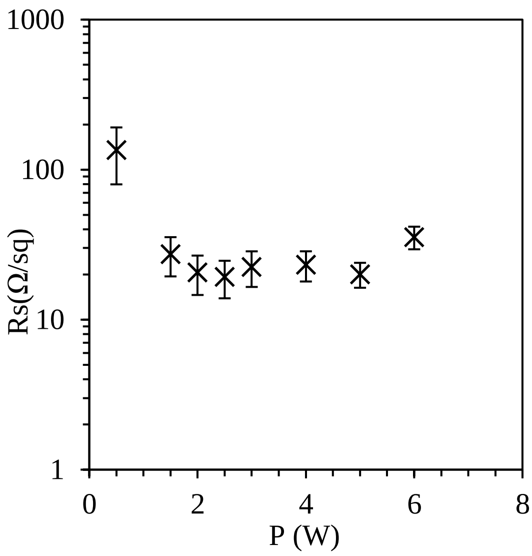

FIG. 7: Plot of measured values of sheet resistance for a sample of 25 μm of donor layer and 400 mm/s as a function of the laser power.

It can be seen a zone of constant low resistance, for a wide range of powers, and a rise for lower (<1W) and higher (>6W) powers. This is a result consistent with the theoretical phenomenon that describes the ejection of the ink. On the one hand, it is needed the boiling of the ink to form the bubbles that eject the material [1]. This explains that at low powers the sheet resistance increases because little energy is supplied, and the amount of material transferred is small. On the other hand, there is the capillarity effect, already explained in the text, which explains that at very high powers the sheet resistance increases because the ejection zone of the material is emptied before boiling and the ejection of the ink is smaller.

Despite this, an increase in the resistance values of all powers can be observed. This is due to the different printing method used on this last sample. Because of the donor layer is adhered to the lower face of the donor substrate, it ends up precipitating to the receiving substrate if printing time is large (this form drops on the receiving substrate and the donor layer becomes non-homogeneous). Because of moving the laser manually and changing the power between the printing of each line, total printing time changed from 2 to 30 s, approximately, causing the appearance of the problems previously explained. To solve this, it was decided to print on an unheated receiver substrate (since the heat radiated causes the ink to become less viscous) and optimize the process to reduce the printing time.

As receiver substrate is not hot, the ink does not instantly dry on touching it and the ink can flow into sideways, causing a decrease in thickness and an increase in sheet resistance (formula (1)). This phenomenon can be observed with the optical microscope (Figure 8).

(a)

(b)

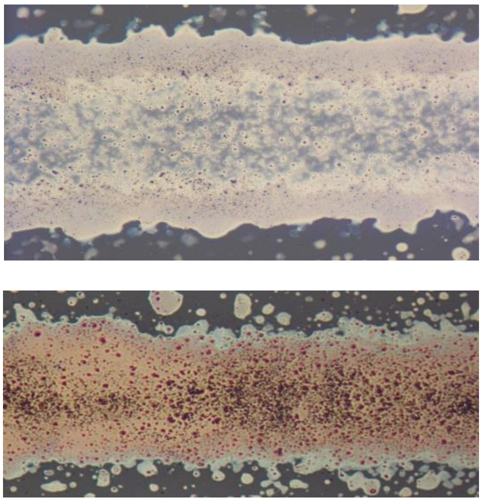

FIG. 8: Images taken with the optical microscope for a sample lines of Fig. 7 (a) and Fig. 3 (b). It can be observed how the edge of the line is abrupt when the substrate is hot and there is an area beyond the middle zone (impact zone), when is not hot, due to ink flowing.

IV. CONCLUSIONS

- In the studied range of thicknesses, the greater the thickness of the donor layer the lesser the sheet resistance of printed lines (caused by the greater continuity of the deposition of the ink and the greater thickness of lines).
- A conductive path with a minimum value of 0.5 Ω/sq has been printed with a 50 μm of donor layer at 1 W and 400 mm/s.
- It has been determined that there is a minimum of resistance at intermediate scanning speeds and its value depends on the thickness of the donor layer. For a thickness of 50 μm the minimum is around 400 mm/s.
- Regarding the power, it has been observed that there is a range of intermediate powers in which the resistance of the lines is approximately equal and small, and that grows a lot for higher (capillarity) and lower values (not enough power for boiling). For a 25 μm donor layer is between 1 and 6 W but can be expected that this tendency will be repeated under the other conditions.
- Furthermore, for getting a better printing, the substrate must be heated to ensure the instant drying of the ink.
- Therefore, to print under optimal conditions, the receiving substrate must be heated (approx. 100ºC), a sufficiently thick donor layer must be prepared (approx. 50 μm) and printed at intermediate speeds and powers, between 350 and 450 mm/s and 2 and 5 W, respectively.

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