Manufactured microlenses by polimer inkjet printing

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Abstract: In this work, we have studied the one single drop ejection of two photocurable inks, inkepo and inkormo, printed with nozzles of 21,5μm and 9μm of diameter. We have also established the process to manufacture the minimum microlens array that is possible to print with a cost-effective inkjet printer using two substrates of SiO2 (one bare and the other silanized). Theoretical predictions of the minimum velocity for the onset of breakup have been experimentally checked, and we have found 5m/s for an optimal waveform of 10.5μs of pulse length and a voltage range of 18-26 for both nozzles and both inks. We found that the minimum array has diameters of the drops of 15±1μm, with 31±1μm between the centres of the drops. This minimum array was manufactured on a SiO2 surface treated with a silane-based self-assembled monolayer.

I. INTRODUCTION

Over the years, the industry has been very interested in micro optical devices such as microcameras. Since microlenses have an excellent light collecting efficiency, they are commonly used in optoelectronic devices to improve the focusing on the sensitive areas. Some examples where these microlens arrays (MLA) are applied are charge coupled devices (CCD's), light emitting diodes (LED's) and even in detectors for medical imaging as the positron emission tomography (PET) and the endoscopes.

To manufacture the microlens arrays, there are different methods based on nanotechnologies such as nanoimprint, hot embossing, soft lithography, UV lithography, electron and ion jets and thermal processes. Contrarily to these conventional methods, inkjet printing (IJP) is a cost-efficient, low-waste (as all the deposited material is used) and low-temperature technology, and no mask is needed. Moreover, the inkjet printing is non-contact and it allows us to print drops one by one as well as to apply patterns. The IJP is PC controlled in such a way that the parameters of the pattern could be changed in real time. Hence prototypes are easily done.

In this work we have developed the methodology to deposit in a controlled way two different inks: inkepo and inkormo. Both inks had been tested in nozzles diameter of 50μm [1]. The aim of this work is to develop the deposition methodology and then, to characterize the single drops of these inks printed with the nozzles of 21.5μm and 9μm (corresponding to drop volumes of 10pl and 1pl, respectively). This paper attempts to fix the parameters to print the drop array as smaller as possible. An array of these drops would be very useful for many applications, including increasing the fill factor of single photon avalanche diodes (SPAD).

II. THEORETICAL BACKGROUND

In the IJP the drops travel in the air and along its trajectory they could breakup. This drop breakup has been widely studied [3-5] and it has been found that the Reynolds number, the Weber number and the Ohnesorge number are the most useful dimensionless physical parameters to characterize the flow.

The Weber number describes the relative importance of kinetic energy and surface energy. For a spherical drop, it can be qualitatively described as:

$$\mathrm{We} \sim \frac{\mathrm{E}_{kinetic}}{E_{Surface}} = \frac{\frac{1}{2}mv^2}{A_{drop}\,\sigma} = \frac{1}{12}\frac{\rho\, d^3\pi v^2}{d^2\pi\sigma} = \frac{1}{12}\frac{\mathrm{d}v^2\rho}{\sigma}, \quad (1)$$

$$\mathrm{We} = \frac{\mathrm{d}v^2\rho}{\sigma}, \quad (2)$$

where ρ is the density of the fluid, v is its velocity relative to the air, d is the drop diameter (which is considered the same as the nozzle) and σ is the surface tension.

Considering the Weber number and an inviscid fluid, it is possible to segregate different mechanisms of breakup [4]:

1. Vibrational breakup We ≤ 12
2. Bag breakup 12 < We ≤ 50
3. Bag-and-stamen breakup 50 < We ≤ 100
4. Sheet stripping 100 < We ≤ 350
5. Wave crest stripping followed by catastrophic breakup We > 350

These mechanisms can be synthetized in the following three regimes: for We<12 the liquid is ejected from the nozzle continuously; 12<We<50 is the drop-on-demand (DOD) regime, which is characterized by ejecting a single drop equal or bigger than the nozzle diameter; and the last one, for We>50, is the atomization regime where the fluid is ejected at high velocity, producing a dispersion like a spray.
When the viscosity is not negligible we should consider the effect of the Ohnesorge number.

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\mu}{\sqrt{\rho d\sigma}}\,, \quad (3)$$

where Re is the Reynolds number and it is defined as the ratio between the kinetic energy and the dissipated energy (viscous forces):

$$Re = \frac{\rho v d}{\mu}. \quad (4)$$

Here μ is de dynamic viscosity of the liquid drop.

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As Schmehl [5] concluded, the onset breakup of the drop occurs for Weber numbers higher than the critical one (We_c), which is given by eq. (5) for fluids with 0.1>Oh>1.

$$\mathrm{Wec} = 12(1 + 1.077\mathrm{Oh}^{1.6}), \qquad (5)$$

In the interaction with the substrate, the Young's equation determines the edge angle between the substrate and the drop:

$$\gamma_{sl} = \gamma_{sg} - \gamma_{lg} \cos\ \theta_c, \qquad (6)$$

where γ_{sl}, γ_{sg} and γ_{lg} are the solid–liquid, solid–gas, and liquid–gas interfacial energy, with γ_{lg} being the surface tension and θ_c is the edge angle with the substrate. Depending on the cleaning of the substrate and the atmospheric conditions, we can obtain different results easily.

Finally, the Bond number is useful to compare the gravitational forces and the surface tension forces. The lower is the Bond number, the more stable the drops are produced.

$$Bo = \frac{\rho g d^2}{\sigma}. \qquad (7)$$

III. EXPERIMENTAL TECHNIQUES

A. Ink and substrate properties

Photocurable inkepo and inkormo inks, based on epoxy resins (from micro resist technology GmbH, Germany), were chosen due to their high transparency at wavelengths >400nm as well as compatible properties with inkjet printing. Inkormo is a commercial ink verified by different studies [2] and inkepo is an experimental non-validated ink (see table I). After deposition, inkepo has to be baked during 10mins at 85-90ºC in order to evaporate solvents. Then, it needs UV curing to promote photo acid generation, and post-baking at 100ºC for 5 minutes to produce the cross-linking (full solidification). Whereas, inkormo only needs two steps: soft-baking at 80-90ºC for 5-15 minutes for solvent evaporation and UV curing to the cross linking. UV curing has been performed in both cases for 3 minutes 20 seconds at 2.5mW/cm2 with a LV202-E UV Exposure Unit peaking at 365nm.

	Inkepo	InkOrmo
Refractive index	1.476±0.005	1.459±0.005
Surface tension [mNm^{-1}]	35	35
Dynamic viscosity [mPa*s] at 1000^{-1} 25ºC	18±1	12±1
Exp Dynamic viscosity [mPa*s] at 0.2^{-1} 25ºC	21±1	17.2±0.5
Density [g/cm^3]at	1.162±0.002	1.135±0.003

Table I : Refractive index, dynamic viscosity and density (provided by MicroResist Technology), dynamic viscosity (experimental measurements) and density of inkepo and inkormo.

B. Surface treatment

We have used two wafers of Si coated with O-Si-O and a total thickness of 600µm: one of them is bare and the other one is silanized. The bare substrate is first cleaned with acetone and then with isopropanol. To assure any solvent is eliminated, N2 gas flow is applied. After that, the substrate is baked at 200ºC on a hotplate and then, it is cooled down to room temperature before the drop deposition.

In order to increase the hydrophobicity, the silanization process has been proved to be a successful method [1]. We have carried out the silanization process at the Nanotechnology Platform from the Barcelona Scientific Park. The substrate is first cleaned as explained above. Then, the substrate is deposited in a vacuum chamber with trichloro(1H, 1H, 2H, 2H-Perflouroctyl) silane (FOTS) to its evaporation during 1h, forming a self-assembled monolayer of silane (SAM), highly hydrophobic.

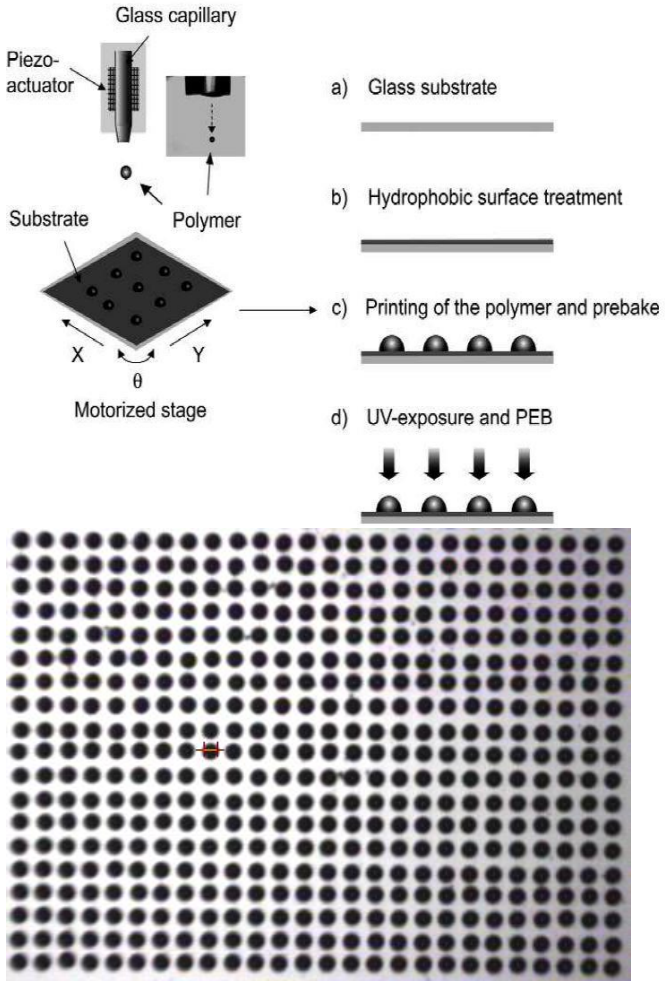

FIG. 1: Left-up (Image courtesy of MicroResist): Schematics of the IJP setup, showing the substrate freedom liberty degrees. Right-up: Schematics of the IJP process. Down: UV-exposure and post exposure bake. Bottom panel, resultant microdrop generation with 25µm of diameter.

C. Ink-jet printing

In order to eject the drops and manufacture the microlenses, we have used a piezo-actuated inkjet printer (Dimatrix 2800 series) in DOD mode with two cartridges of 1pL and 10pL, each one with 16 ejectable nozzles. The diameter of these nozzles are 21.5um and 9.0um respectively. The recommended fluids to work with Dimatrix material printer (DMP) are those which their viscosities are in range of 10-12mPas and 28-33mNm^{-1}, but it is also possible to work with 2-30mPas fluids because the nozzle is heatable until 70º. It is also possible to use a fluid with a surface

tension higher than the recommended one but it limits the performance of the process.

Before placing the inks inside of the ink cartridges, they have been filtered with a teflon 0.2μm-pore filter for 10pl ink and 0.09μm pore for 1pl. In order to avoid satellites, shown in Figure 2 (bottom panel), and to produce stable and reproducible drops it is also necessary to modify the waveform of the cartridge. The waveform is the form of signal that the computer sends to the piezoelectric actuators in order to compress the chamber and eject the fluid. Droplet velocity and tuned waveform were computed viewing the drop shape with a CCD camera coupled to a stroboscope. The drops were deposited on the substrate, placed on a movable x, y platen in a dust-free atmosphere with variable temperature.

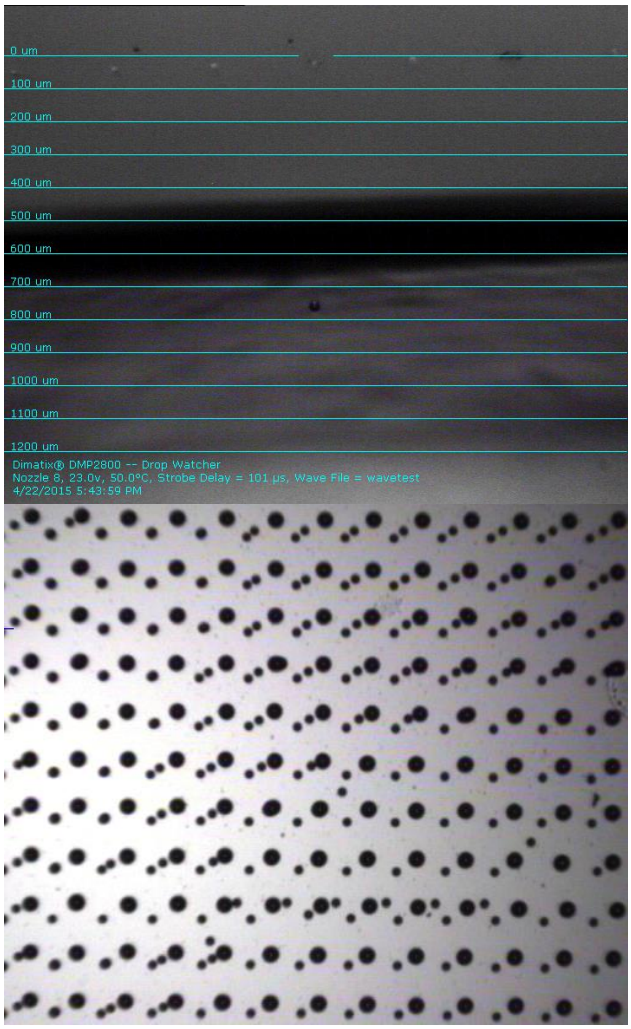

FIG. 2: Upper panel shows one single microdrop of 10pL, falling from the nozzle with 28microns of diameter seen from the drop watcher. Bottom panel shows a printed microdrops with satellites due to a bad calibration of the waveform.

D. Characterization

The drop diameter was measured with the fiducial camera and the software provided by Dimatrix and corroborated with an optical microscopy. Lens geometry (3D shape) was characterized with an interferometer (Sensofar PLu 2300). Transmission and absorption (SPECORD 205) and the dynamic viscosity with a viscometer (BROOKFIELD DV-I PRIME)

IV. RESULTS

The minimum velocity of the drop ejections have been computed using eq. (2) and eq. (5). At room temperature, the parameters that we obtain are 5.2±0.3 and 5.0±0.3 m/s for inkepo and inkormo respectively with the 10pl nozzle. In these calculations, we have used the experimental viscosity, measured with a viscometer. For 1pl the minimum velocity is 9.4±0.9 m/s for inkepo, and 8.9±0.8 m/s for inkormo.

	inkepo	inkormo
Weber critical number (10pl)	19.3±0.03	17.5±0.02
Weber critical number (1pl)	26.7±0.1	23.1±0.1
Ohnesorge number (10pl)	0.70±0.02	0.59±0.02
Ohnesorge number (1pl)	1.08±0.07	0.901±0,07

Table II: Weber critical number and Ohnesorge number calculated using the density and surface tension and nozzle diameter given by MicroResist and Dimatrix companies. The viscosity used in this calculations has been measured with a viscometer.

Theoretical predictions have been checked with both nozzles. In order to produce the optimal drop, we have to fix the voltage and the pulse length of each segment in the waveform (see Figure 3). The same waveform that was found as optimal for inkepo works well with inkormo. The piezoelectric can be easily understood: firstly, a bias voltage is applied to the pumping chamber and when voltage decreases to zero, the piezoelectric is back to a relaxed position and the chamber has its maximum volume, at this moment the fluid is pulled inside the chamber. With a voltage increment, the chamber is compressed and the drop is ejected. Optimal pulse length for our inks has been found to be 10.5 μs and voltage range of 18-26 V for 10pl nozzle at room temperature, and the same waveform can be used for 1pl nozzle at 50ºC and for both inks. As it can be seen in the Table II, the Ohnesorge number of inkepo for 1pl cartridge overcomes the Ohnesorge maxim number for the onset of breakup, and reducing the viscosity (by increasing the cartridge temperature) we could decrease the Ohnesorge number. Experimentally, the temperature was changed for the 1pl nozzle because we have reached the maximum voltage of the DMP, which is required for printing using this nozzle. The higher the voltage, the larger the velocity of the drops is. The viscosity is, essentially, a fluid friction that produces a loss of kinetic energy, thus the velocity also increases with temperature of the nozzle since the viscosity is lower for high temperatures.

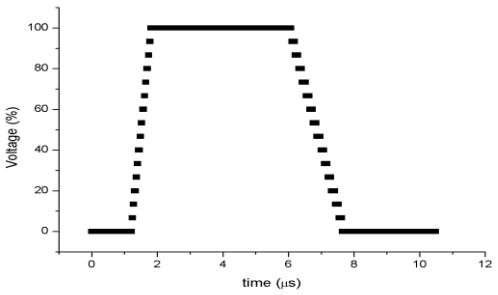

FIG. 3: Waveform of inkepo and inkormo. Y-axis presents the % over the voltage that we choose.

The velocity of the drops varies from 5.5 to 9 m/s for inkepo and from 5 to 9m/s for inkormo. Their velocities have been computed thanks to the drop watcher mode viewing with the stroboscope vision at 100 μs delay as we could see at Figure 2 (upper panel). For lower voltages than the minimum one, no drop generation occurs and for higher voltages satellites are created.

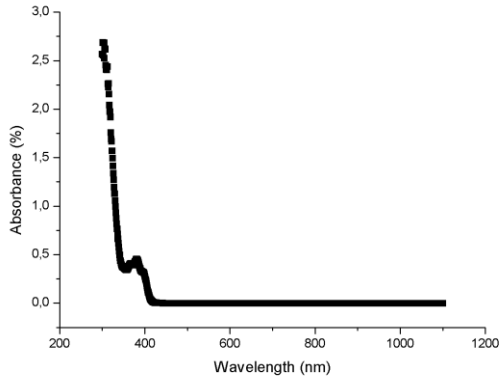

FIG. 4: Absorbance of inkormo in the range 300nm < λ < 1100nm

The light transmission of the inkormo is T>98% in the range of 410nm < λ < 1100nm and for inkepo T>97%, the absorbance is lower than the 0.01% for the same range of wavelength for both inks. As we can see, the absorbance increases for λ lower than 410nm. It happens because the inks are UV-curable. These inks have good properties to make the microlenses.

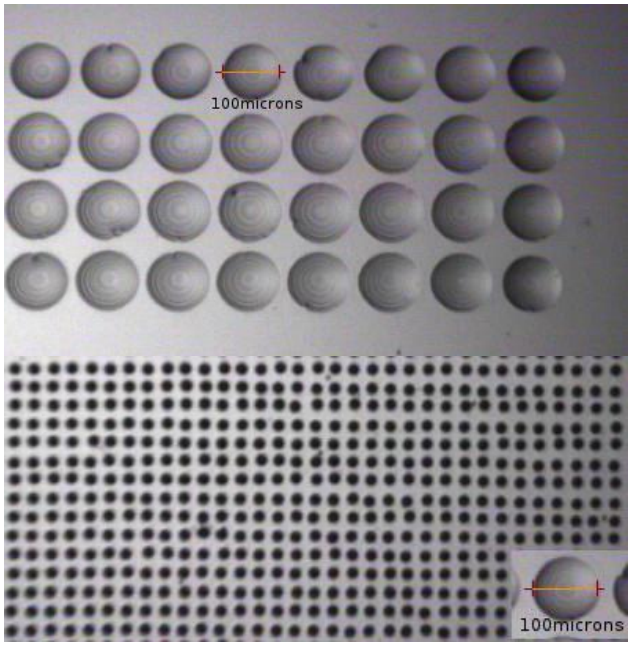

FIG. 5: Comparison between the maximum distance obtained (100μm) with 10pl cartridge drop in bare substrate and the minimum (15μm) for coated substrate with 1pl cartridge.

Different results are obtained for drop deposition. For a bare-glass substrate, the diameter of a single drop of 10pl is 100±2μm (Figure 5, upper panel) and for treated SiO2 20±2μm. In the case of the 1pl nozzle, the minimum drop diameter that has been obtained is 15±2 μm (Figure 5, bottom panel), whereas for higher velocities, larger diameters are produced. The reproducibility of the drops has been reached for the same velocity. We have obtained a minimum distance between the drops centres of 31±1μm and diameter of 15±1μm, where the error corresponds to the standard deviation. These results has been computed using the SPIP Software to analyse 30 different drop diameters and 30 distances in all directions. For lower distances, the drops gather together. Considering the accuracy of the DMP in (x,y) position, ±24μm is an accurate result, although it only works if we print all the drops using a pattern and not printing drop-by-drop.

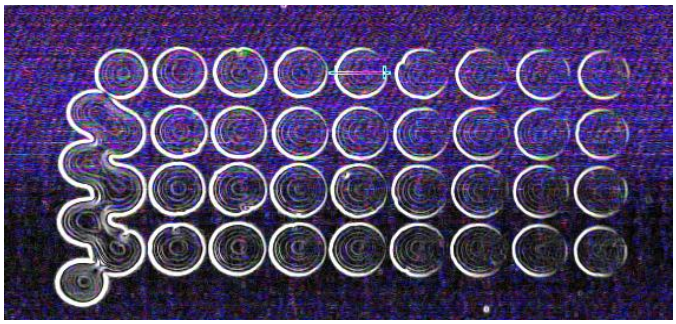

FIG. 6: Sobel filter is applied to the image taken with the drop watcher. The drops have 100μm of diameter.

For the study of their spherical shape we have applied a Sobel filter and several drops (Figure 6). We have obtained that for bare SiO2 the shape is less spherical than for the coated substrate. It has also been found that single drops present a worst spherical shape than when printing multiple drops.

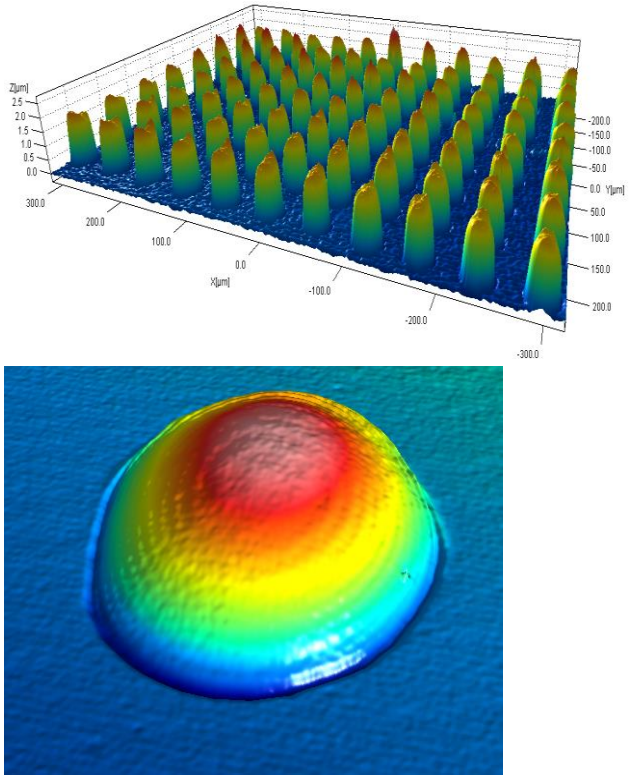

FIG. 7: In the upper panel we can see an array of microdops analysed with confocal microscope. The bottom panel shows an image of a drop analysed with confocal microscopy with 30μm diameter and 1μm of high contact angle 20º.

As a complementary study, we have analysed the 3D morphology of the printed drops using a confocal microscope. Apparently, we have found a non-expected and curious phenomenon on the lenses geometry, although it could just be an optical effect due to the fact that we have two layers of transparent materials (SiO2 and the drop). This phenomenon consist in a ring stain, also known as coffee ring effect. This effect was first explained by Deegan et al. [6]. These authors conclude that the ring stain is due to the capillary flow length. This flow causes a displacement of the particles to the perimeter of the drop, which means that the particles concentrate in the perimeter during the evaporation while the particles that are originally on the perimeter of the drop stay in it. However, Younker et al. [7] found out that the coffee ring effect is due to the shape of the particles on the inside part of the fluid. For spherical particles, the ring stain appears while this effect does not come out when ellipsoidal particles are injected. This could be a possible solution in our case to avoid coffee ring. However, the analysis of the drops using an electronic microscope in order to ensure if our drops really present coffee ring is left for further studies.

Despite that, we successed in producing one array of drops without the ring stain (Figure 7). This is because we print several drops to manufacture one single microlens, ejecting these drops with a time delay between them. This delay let the solvent to evaporate, and when the next drop is printed, it falls inside the ring stain and full it, and the same happens for the following drops.

V. CONCLUSIONS

Drop ejection of inkepo and inkormo has been possible for nozzles smaller than 50 μm. In the case of 10 pl cartridge, the drop ejection is possible at room temperature with a pulse length of 10,5μs and an amplitude of 18-26V. For the 1pl cartridge it requires the same parameters but heated at 50ºC.

Drops have been obtained with DMP in a SAM coated-SiO2 with a minimum diameter of 15±1 μm and distances of 31±1 μm between drops centres. The arrays and the single drops that we have obtained are highly reproducible.

We have found no significant discrepancies between inkepo and inkormo. They behave slightly different in the drop ejection but they interact in the same way with the substrate and can be printed following a similar procedure.

When the diameter of the drop is not a crucial parameter, thus it is not necessary to print the minimal array, it is better to use the 10pL cartridge on a treated SiO2 since the drops would have the maximum height and sphericity.

We can also propose a solution to avoid the coffee ring effect: to print one drop, cure it and later print again another drop on the top of the first one.

Two contributions are left to be included in further studies: (1) the manufacture of higher drops on the substrate, and (2) the study of the microdrops on nitride, usually used in SPADS as last layer of coating. We conclude by mentioning an open problem: is it possible to avoid the ring stain for a single drop by injecting ellipsoidal particles keeping the optical properties of the ink?

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