Digital Printing of µPlasmas to Selectively Improve Wetting Behavior of Functional Inks for Printed Electronics

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Abstract

In this article we investigate the change in wetting behavior of inkjet printed materials on either hydrophilic or hydrophobic plasma treated patterns, to determine the minimum obtainable track width using selective patterned µPlasma printing. For Hexamethyl-Disiloxane (HMDSO)/N_2 plasma, a decrease in surface energy of approx. 44 mN/m was measured. This resulted in a change in contact angle for water from <10 up to 105 degrees, and from 32 up to 46 degrees for Diethyleneglycol-Dimethaclylate (DEGDMA). For both the nitrogen, air and HMDSO/N_2 plasma single pixel wide track widths of approx. 320 µm were measured at a plasma print height of 50 µm. Combining hydrophilic pretreatment of the glass substrate, by UV/Ozone or air µPlasma printing, with hydrophobic HMDSO/N_2 plasma, the smallest hydrophilic area found was in the order of 300 µm as well.

Introduction

For several decades plasmas or electrical discharges are being widely used in a variety of industrial applications. Applications range from ozone generation, pollution control, lasers, lighting, flat large area displays and surface treatment. In recent years the use of dielectric-barrier discharge (DBD) plasmas made it possible to operate plasmas at atmospheric pressure in a controlled manner, thus creating the possibility to treat materials which cannot sustain heat or vacuum [1, 2]. DBD plasmas are characterized by the presence of a di-electrical insulating layer between two metal electrodes in addition to a discharge gap [3, 4]. The wealth of electrically charged particles in plasmas, like ions, electrons and radicals can be used to modify the chemical structure of a substrate to promote or demote adhesion or wetting of materials dependent on the plasma gas composition. For instance the use of air, nitrogen or argon as plasma gas can increase the surface energy of a material, improving the wetting behavior. The use of fluoropolymers or siloxanes as precursor material to a plasma gas decreases the surface energy, worsening the wetting behavior of the substrate. For instance, hexamethyl-disiloxane (HMDSO) in a nitrogen plasma grows a very smooth layer of a nonpolar $Si\text{-}O_2$ network on the surface of the substrate, decreasing the surface energy of glass from 68 mN/m to 20-24 mN/m [5]. This results in a change in water contact angle from approx. 5-10 degrees for untreated glass to 100-120 degrees for treated glass, changing the surface from hydrophilic to hydrophobic [6-13].

The use of plasma treatment in the production of organic electronics as a means to improve the wettability of a substrate is well known [14-16]. As in most cases, plasma treatment is done over the complete surface, deposited functional materials like e.g. inkjet printed conductive inks will spread further, creating broader lines. This lowers the highest obtainable resolution of the printed pattern, which in some cases is not wanted. By selectively changing the wettability of the substrate, changing it from hydrophilic to hydrophobic and back when needed, inkjet printed line widths could potentially be controlled. Selective control of wettability using plasma or other technologies is very difficult without the use of masking [17]. However with the recent development of the µPlasma printing technology, this might be possible. µPlasma printing is able to selectively and mask less treat the surface with an atmospheric plasma using digital patterning technology similar to drop-on-demand inkjet printing [3].

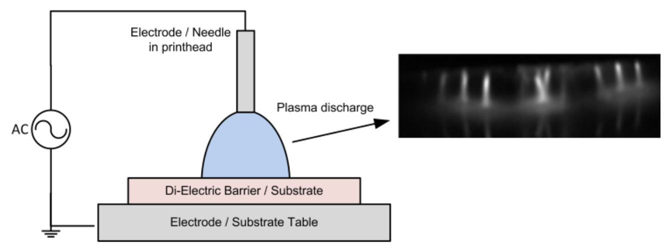

Figure 1. *DBD plasma configuration for the Innophysics POD24 µPlasma printhead. Photo on right shows multi-needle plasma discharge.*

Figure 1 shows the DBD configuration of a single needle, out of 24, in the µPlasma printhead. Each needle can be separately addressed to obtain a discharge when needed. In combination with a bitmap, patterned plasma treatment is possible. Previous research by the same authors showed for atmospheric air plasmas on different types of plastic foils, on average, an increase of 17 mN/m in surface energy after 3-5 passes (treatments). They also showed it was possible to selectively plasma treat the substrate creating areas with different wettability detectable by inkjet printing [5].

In this paper we focus on determining the minimal µPlasma print resolution using both hydrophilic and hydrophobic plasma treatments. First, we will experimentally determine the width of a single pixel wide µPlasma track using air at atmospheric pressure as plasma gas. This will increase the wetting locally, creating more hydrophilic lines compared to its surroundings on the substrate. Second we replace the air with hexamethyl-disiloxane (HMDSO) added as precursor material to nitrogen as plasma gas and print similar single pixel wide µPlasma tracks. This will decrease the wetting locally creating a more hydrophobic line compared to its surroundings on the substrate. Finally, we will combine hydrophilic and hydrophobic treatments by first treating the complete substrate with either UV/Ozone or air µPlasma making the substrate hydrophilic, followed by localized HMDSO/N_2-plasma treated areas with decreased in-between spacing.

Experimental

For the µPlasma treatments an Innophysics POD24 plasma print head was used. Inkjet printing was performed using a Dimatix Spectra SE128 print head. Both print heads were mounted in a PixDro LP50 Desktop Inkjet Printer.

As noted above, three types of experiments were performed. First, single pixel wide hydrophilic lines were air plasma printed on Polycarbonate (Goodfellow 0.125 mm) and glass slides (Thermo Scientic Menzel Gläser, 76x22x1 mm). Experimental settings for the print height and number of treatments were chosen using Design of Experiments as shown in table 1. Second, hydrophobic single pixel wide lines were printed on glass substrates. A mixture of hexamethyl-disiloxane (HMDSO) from Sigma Aldrich and nitrogen was used as plasma gas (200 ml/min, 20 vol% HMDSO saturated N_2) . Third, the glass substrate was pretreated with either UV/Ozone for 5 min. or air plasma (75 µm print height, 5 treatments) to create a hydrophilic substrate, followed by a patterned HMDSO/N_2 treatment of 10x20 mm^2 rectangles spaced at 5, 3, 2, 1, 0.5 and 0.3 mm apart. All plasma treatments were performed at 90 dpi. For the first experiment, the print height was varied according to the settings from the Design of Experiments (table 1). For the other experiments the print height was kept at 75 µm. The discharge voltage was chosen according to the print height in order to get a stable plasma (4 kV at 75 µm, 6kV at 880 µm).

After plasma treatments the substrates were inkjet printed upon to detect the changes in wetting behavior between the treated areas. Diethyleneglycol-Dimethaclylate (DEGDMA, Sigma Aldrich) with 0. 1 wt% Coumarin 153 (Sigma Aldrich) fluorescent dye was used as ink. Analysis of the samples was done using an Olympus BX60 Fluorescent microscope and image analysis software (National Instruments Vision Assistant). Contact angle measurements were performed with a Dataphysics OCA-30.

Results

First the minimal track width of a single plasma printed line was determined. Two Design of Experiments (DoE) were performed with polycarbonate and glass as substrate respectively. Figure 2 shows the results for selected microscope images at increasing print heights and number of plasma treatments for the polycarbonate substrate. In red the fluorescent inkjet printed droplets can be seen. In the plasma treated area, centered horizontally in each image, the wetting of the droplet increases causing the droplet to grow in diameter visualizing the plasma treated area.

Table 1. Experimental settings for Design of Experiments.

Parameters	Substrate	Minimum	Maximum
1: Print height Treatments	Polycarbonate	200 µm 1	880 µm 9
2: Print height Treatments	Glass	50 µm 1	280 µm 9

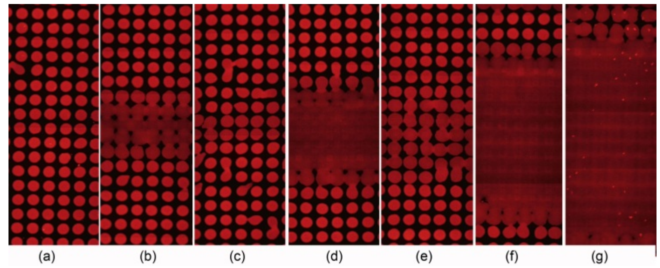

Figure 2. Fluorescent images of air plasma treated PC, inkjet printed with DEGDMA at 115 dpi for a selection of the DoE experiment. Letters correspond with the data in table 2. At the centre of each image a single pixel wide plasma line was printed

Table 2 shows the print settings for the selected pictures and the determined width of the changed wetted area. Although the plasma printed line for each image was one pixel wide, it is clearly visible that both print height and the amount of treatments have a profound influence on the width of the wetted area. The smallest width was found to be approx. 650 µm at a print height of 280 µm and 2 plasma treatments. As glass substrates showed a better distinction in droplet diameters for DEGDMA between treated and untreated areas compared to PC, the DoE was repeated on glass substrates, albeit with the minimal print height decreased to 50 µm. The results of these experiments are shown in figure 3 and table 2.

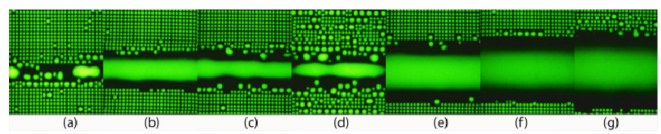

Figure 3. Fluorescent images of air plasma treated glass, inkjet printed with DEGDMA at 300 dpi for a selection of the DoE experiment. Letters correspond with the data in table 2. At the centre of each image a single pixel wide plasma line was printed

Second, the effect of adding hexamethyl-disiloxane (HMDSO) to the plasma gas (N_2) was investigated. A gas mixture of saturated HMDSO in N_2 with unsaturated N_2 in a ratio of 20:200 ml/min was continuously flushed between the glass substrate and print head.

Table 2. Single pixel line width for selected air plasma treated glass experiments from figure 2 for PC and figure 3 for glass.

Figure	2a	2b	2c	2d	2e	2f	2g
Print height (µm)	200	200	280	280	540	540	800
Treatments	1	5	2	8	1	5	8
Width (mm)	n/a	0.92	0.65	1.53	1.63	2.7	3.2
Figure	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
Print height (µm)	50	50	77	163	163	163	250
Treatments	1	5	2	1	5	9	8
Width (mm)	0.32	0.52	0.47	0.36	0.93	1.0	1.16

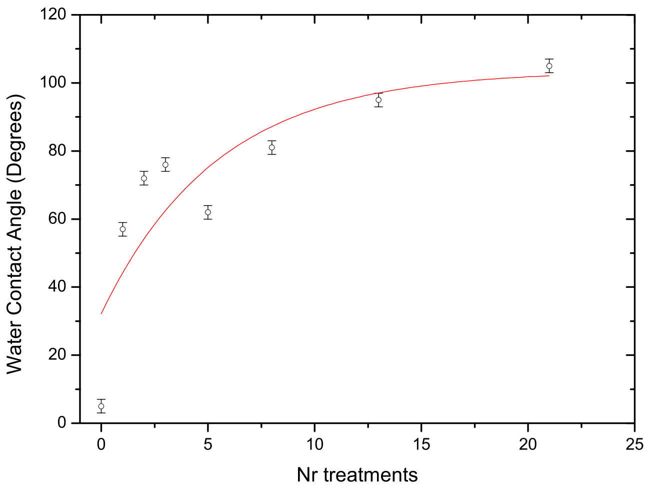

Figure 4. *Water Contact Angle versus nr of treatments of a glass substrate treated with HMDSO/ N_2 plasma (flow:200 ml/min N_2 and 20 ml/min HMDSO saturated N_2, Print Height 75 µm) (line is only shown to aid the eye of the reader)*

The water contact angle (WCA) was measured for increasing number of treatments at a constant print height of 75 µm. The WCA increases from <5 to 105 degrees after 20 treatments (figure 4). For DEGDMA the contact angle changes from 32 to 46 degrees after 2 treatments on glass. This indicates that the HMDSO-plasma treatment changes the surface of the substrate to a more hydrophobic nature. Next glass substrates were treated twice with single pixel wide plasma lines with the above mentioned HMDSO/N_2 gas mixture. The areas in-between the lines were left untreated. Change in wetted area was visualized by inkjet printing DEGDMA droplets on to the substrate and determining the droplet diameters (figure 5).As can be seen, the droplet diameter changes from 125 µm in the untreated "hydrophilic" areas to approx. 75 µm for the treated "hydrophobic" areas. At large intervals between the lines, the single lines are approx. 1 mm wide. At smaller intervals between the plasma printed lines the individual lines merge into a single hydrophobic area. These results are in agreement with the results from the air plasma experiments.

Lastly, in order to obtain smaller hydrophilic tracks, hydrophilic and hydrophobic treatments were combined. Pretreatment of the substrate with either N_2-plasma or UV/Ozone, the substrate was made hydrophilic, resulting in a contact angle for DEGDMA smaller than 10 degrees. Next the substrate was treated with HMDSO/N_2-plasma areas with decreasing gap intervals of 5 mm up to 0.3 mm. Figure 6 and figure 7 show the results of this experiment. In figure 6 the microscopic images of the hydrophilic areas surrounded by the hydrophobic areas are shown for different intervals. Clearly visible is the change in wetting behaviour between the hydrophilic areas and the hydrophobic areas at the top and bottom of the images. For the intervals smaller than 1 mm changes in wettability could only be determined using imaging software.

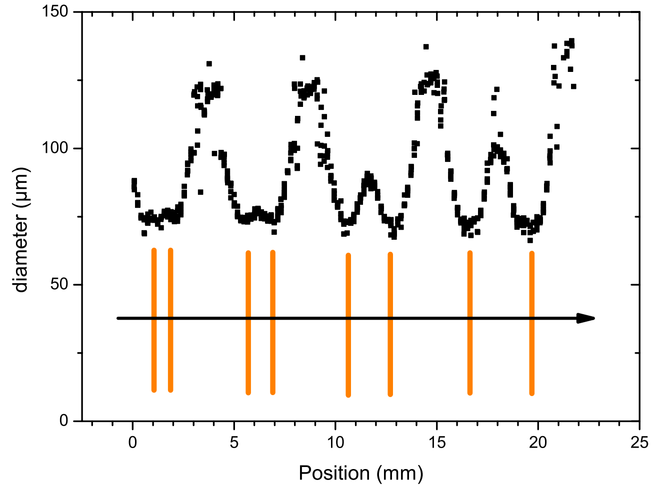

Figure 5. *Droplet diameters of inkjet printed DEGDMA for a cross scan of plasma printed (orange) lines). 200 ml/min N_2 plasma with 20 ml/min saturated HMDSO/N_2 plasma (print height 200 µm, two treatments on glass)*

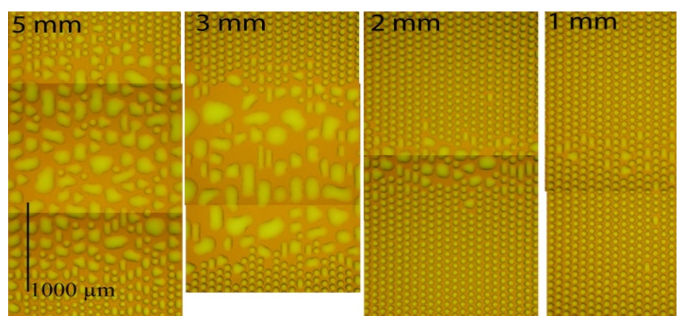

Figure 6. *Microscopic images of inkjet printed DEGDMA droplets (350 dpi) on HMDSO/ N_2-plasma treated glass slides (1 treatment at 75 µm at 90 dpi). The glass slide was pretreated with a N_2 plasma (5 treatments).The areas with increased wetting correspond with the white areas in the bitmap for the given distances.*

Figure 7 shows the experimentally determined width of the hydrophilic area vs. the gap distance in the original hydrophobic bitmap. As can be seen, the hydrophilic area is smaller than the original gap in the bitmap between the HMDSO treated areas and is decreasing linearly with decreasing gap. With a HMDSO-plasma spotsize on the substrate of approx. 400 µm at 75 µm print height this is to be expected.

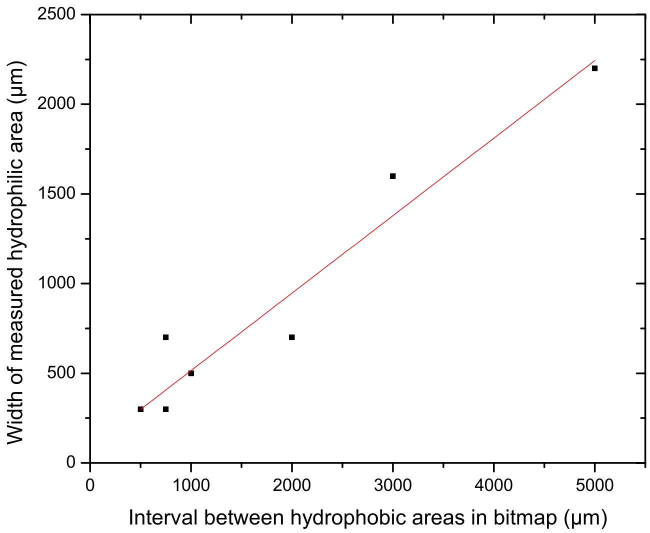

Figure 7 *Measured width of hydrophilic area versus width of intervals between hydrophobic HMDSO-treated areas.*

Conclusions

In summary, we showed it is possible to selectively change the wetting behaviour of liquids using different types of plasma. For air and nitrogen plasma increased wetting of printed materials could be achieved on both polycarbonate and glass substrates. We also showed that using HMDSO as precursor in the plasma gas increases the contact angle for water from <10 up to 105 degrees and from 32 to 46 degrees for DEGDMA, making the substrate more hydrophobic. Furthermore, minimal track widths of approx. 300 µm were found for a single pixel wide plasma printed line, independent of the plasma gas used. The option to create small hydrophilic lines by hydrophilic pretreatment of the substrate followed by hydrophobic HMDSO plasma treatment of the surrounding area showed no further gain in decreasing the minimal track width below 300 µm. With a plasma needle of 200 µm in the Innophysics POD24 print head it is believed no further decrease in track width below 300 µm can be achieved. Further improvements in plasma print resolution should be sought in decreasing the size of the plasma cloud by possibly decreasing the size of the plasma needle.

Acknowledgements

We would like to thank Alquin Stevens and Wouter Brok from Innophysics as well as Roel Aben, from Fontys University of Applied Sciences for their cooperation and feedback. Furthermore we would like to thank the “Stichting Innovatie Alliantie” for their funding of this project

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