µPlasma printing of hydrophobic and hydrophilic patterns to improve wetting behaviour for printed electronics

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Abstract

Inkjet printing is a rapidly growing technology for depositing functional materials in the production of organic electronics. Challenges lie among others in the printing of high resolution patterns with high aspect ratio of functional materials to obtain the needed functionality like e.g. conductivity. µPlasma printing is a technology which combines atmospheric plasma treatment with the versatility of digital on demand printing technology to selectively change the wetting behaviour of materials. In earlier research it was shown that with µPlasma printing it is possible to selectively improve the wetting behaviour of functional inks on polymer substrates using atmospheric air plasma. In this investigation we show it is possible to selectively change the substrate wetting behaviour using combinations of different plasmas and patterned printing. For air and nitrogen plasmas, increased wetting of printed materials could be achieved on both polycarbonate and glass substrates. A minimal track width of 320 µm for a 200 µm wide plasma needle was achieved. A combination of N_2 with HMDSO plasma increases the contact angle for water up from $<10^0$ to 105^0 and from 32^0 to 46^0 for DEGDMA making the substrate more hydrophobic. Furthermore using N_2-plasma in combination with a N_2/HMDSO plasma, hydrophobic tracks could be printed with similar minimal track width. Combining both N_2 –plasma and N_2/HMDSO plasma treatments show promising results to further decrease the track width to even smaller values

Keywords: *Plasma treatment, µPlasma printing, Inkjet printing, Surface energy, Hydrophilic, Hydrophobic*

1. Introduction

For a few decades plasmas or electrical discharges are being widely used in industrial applications. Applications include ozone generation, pollution control, lasers, lighting, flat large area displays and surface treatment. In recent years the use of dielectric-barrier discharge plasma 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. DBD plasmas are characterized by the presence of a di-electrical insulating layer between two metal electrodes in addition to discharge gap. The discharge between the two electrodes is governed by the Paschen Law [1].

The abundance of electrically charged particles like ions, electrons and radicals in plasmas can be used to modify the chemical structure of surfaces promoting wetting, adhesion, and printability of the substrate. Typically only the top atomic layers of the substrate are modified without changing the bulk properties of the material. The wetting behaviour of the material can be controlled using different gases and or combinations of gas and precursor materials. For instance using Nitrogen, Argon or Air plasma increases the surface energy of the substrate, improving the wetting behaviour. On the other hand, the use of fluoropolymers or siloxanes as precursor materials in the plasma gas can decrease the surface energy of the substrate by depositing hydrophobic groups on the surface. For instance, hexamethyl-disiloxane (HMDSO) in a nitrogen plasma grows a very smooth layer of nonpolar $Si\text{-}O_2$ network on the surface of the substrate decreasing the surface energy of glass from 68 mN/m to 20-24mN/m. This would result in a change in water contact angle from approx.. $5\text{-}10^0$ to $100\text{-}120^0$, thus changing the surface from hydrophilic to hydrophobic [2].

This control of wettability is especially interesting for polymers which are dominantly used as films and foils for packaging, and more recently as carrier for organic electronics [2g, 3]. In recent years, inkjet printing has become an rapidly growing technology for depositing functional materials like conductive inks or light emitting polymers on substrates for low cost manufacturing of organic electronics [4]. Challenges lie among others in the printing of high resolution, patterns with high aspect ratio of functional materials to obtain the needed functionality like e.g. conductivity whilst maintaining good wetting and adhesion. 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. With the recent development of the µPlasma Printing technology this however 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 [1a]. 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.

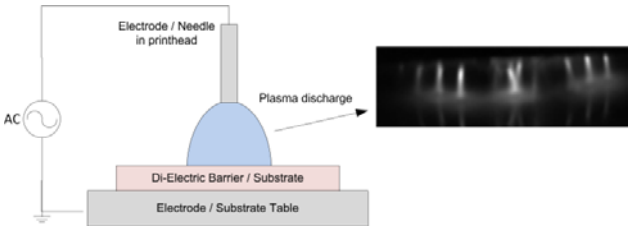

Figure 1. *DBD plasma configuration for the Innophysics POD24 µPlasma printhead. Photo on right shows multi-needle plasma discharge.*

Earlier research by the same authors showed for atmospheric air plasmas on different types of foils (PET, PEN, PE, PC and FEP) an increase of 17 mN/m on average in surface energy after 3-5 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 will continue to investigate µPlasma treatment focusing on determining the minimal µPlasma print resolution. First, we will experimentally determine the

minimal obtainable single µPlasma pixel track width using atmospheric air plasma creating hydrophobic tracks. Second, using the data from the first experiment we determine the minimal track width for a nitrogen with hexamethyl-disiloxane (HMDSO) plasma creating hydrophobic tracks. Third, we will combine the hydrophilic and hydrophobic µPlasma treatments to potentially further decrease the track width.

2. Experimental

All experiments were performed using a PiXDRO LP50 Desktop Inkjet Printer. For the µPlasma treatment an Innophysics POD24 plasma print head was used. The diameter of the needles in the print head equals 200 µm. Inkjet printing was performed using a Dimatix Spectra SE128 print head. Analysis of the samples was done using a Olympus Fluorescent microscope and image analysis software (National Instruments Vision Assistant). Contact angle measurements were performed using a Dataphysics OCA-30.

Three plasma experiments were conducted as noted earlier. The first experiment was to determine the minimal track width of a single pixel wide µPlasma treated line. A bitmap consisting of three single pixel wide 3 cm long lines, separated 0.5 cm, were plasma printed on either glass (76x22x1 mm glass slides) or polycarbonate (PC) (Goodfellow, thickness 0.125µm) substrates. Atmospheric air plasma was used as plasma gas. Experimental settings were chosen using Design of Experiments as shown in table 1.

In the second experiment, the air was replaced using a gas mixture of nitrogen and nitrogen with saturated hexamethyl-disiloxane (Sigma Aldrich) in a ratio of 160/40 ml/min. The mixture was led to the plasma print head. Squares (2x2 cm^2) were µPlasma printed with different number of treatments to determine the change in contact angle. Furthermore the same three lines as in the first experiment were printed with the nitrogen gas mixture to determine the minimal track width for a single hydrophobic treatment. In the third experiment a combination of hydrophilic (nitrogen plasma 200 ml/min) and hydrophobic (nitrogen / HMDSO plasma gas mixture) was used. In this experiment, first a glass slide was air plasma treated in a rectangle of 70x20 mm^2 (75 µm print height, 5 treatments) to create a hydrophilic area. Next the same area was treated with the above mentioned nitrogen/HMDSO gas mixture using the bitmap shown in figure 2. All plasma experiments were performed at 90 dpi.

Figure 2: *Bitmap used for experiment 3. Distance between treated (black) areas from left to right 5, 3, 2, 1, 0.5 and 0.3 mm. The black areas are respectively 5 (first and last) and 10 mm wide and 20 mm high*

After the plasma treatment, picoliter sized droplets were deposited on the treated area by inkjet printing to determine the track width by observing the change in wetting of the inkjet printed droplets. Di-ethyleneglycol-di-methacrylate (DEGDMA, Sigma Aldrich) with 0.01 wt% Coumarin 153 (Sigma Aldrich) fluorescent dye was used as ink. The contact angle of DEGDMA was found to be 32^0 on untreated glass and $<10^0$ and 46^0 on respectively air or N_2-HMDSO plasma treated glass. Droplets were inkjet printed at 200 or 315 dpi dependant on the experiment.

Table 1. *Experimental settings for Design of Experiments (plasma gas: Air)*

Parameters	Substrate	Minimum	Maximum
1: Printheight nr. of treatments	Polycarbonate	200 µm 1	880 µm 9
2: Printheight nr. of treatments	Glass	50 µm 1	280 µm 9

3. Results

To determine the minimal track width for µPlasma printing two Design of Experiments (DoE) were performed both using atmospheric air plasma. In the first DoE the effects of the print height and number of plasma treatments (table 1) was examined on a PC substrate. Results of this experiment are shown as a selection of microscope images of the printed droplets in figure 3. The track widths extracted from this figure are shown in table 2.

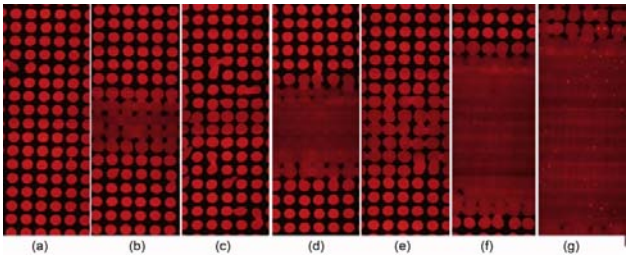

Figure 3. *Fluorescent images of air plasma treated glass, inkjet printed with DEGDMA at 115 dpi for a selection of the DoE experiment. Letters correspond with the data in Table 2. At the centre of each image a single pixel wide plasma line was printed*

As can be seen, both print height and nr. of treatments have a profound influence on the width of the wetted area created by the plasma printed horizontal line. Although the plasma always was printed as a single pixel wide line, the affected area on the substrate increases with increasing print height and number of treatments. The latter effect, the number of treatments, was reported earlier by the same authors for larger treated surfaces [5]. Figure 4 shows the complete, fitted, results for the Design in a contour plot.

The smallest width was found to be approx. 650 µm at 280 µm print height and 2 plasma treatments. The calculated model showed R^2=0.95 with print height, number of treatments, print height squared and number of treatments squared as significant terms.

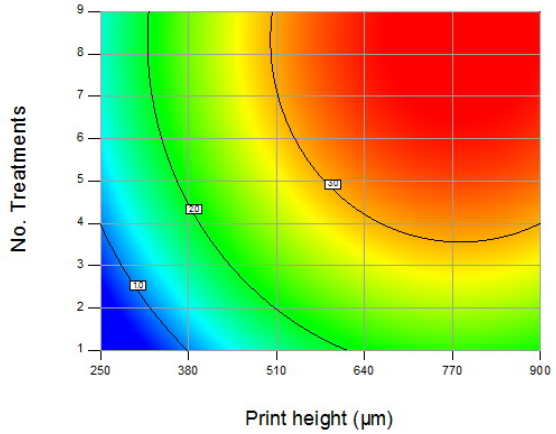

Figure 4*. Contour plot of the width (in mm) for a single pixel wide atmospheric air plasma printed line versus print height and number of plasma treatments on a polycarbonate substrate (Design of Experiments 1).*

Due to the relatively small change in wetting for DEGDMA between treated and untreated areas and the resulting small changes in droplet diameter a switch is made from PC to glass substrates. The DoE is repeated, albeit with a smaller minimal print height based on the results of the first DoE.

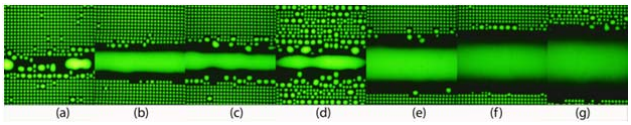

Figure 5. *Fluorescent images of air plasma treated glass, inkjet printed with DEGDMA at 300 dpi for a selection of the DoE experiment. Letters correspond with the data in Table 2. At the centre of each image a single pixel wide plasma line was printed*

A selection of microscope images with matching data of the printed droplets printed on a glass substrate are shown in figure 5 and table 2. The complete results of the DoE are shown in figure 6. Minimal track width on glass was found to be 320 µm at a print height of 50 µm and a single treatment.
The statistically derived model gave a R^2=0.93 with print height, number of treatments and number of treatments squared as significant terms.

Table 2. *Width of a single pixel line for selected air plasma treated glass experiments from figure 3 and figure 5.*

Figure	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**
Print height (µm)	200	200	280	280	540	540	800
Nr. of 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	50	50	77	163	163	163	250
Nr. of treatments	1	5	2	1	5	9	8
Width	0.32	0.52	0.47	0.36	0.93	1	1.16

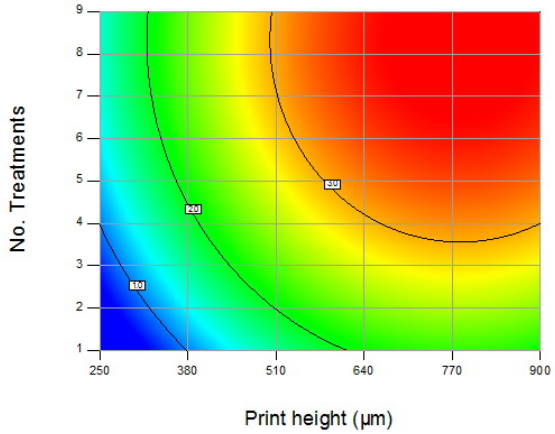

Figure 6. *Contour plot of the width (in mm) for a single pixel wide atmospheric air plasma printed line versus print height and number of plasma treatments (Design of Experiments 2).*

Although a slight difference in the two model terms exists the trend of the two experiments show great similarity. The squared dependence on print height and number of treatments can probably be ascribed to the shape and behaviour of the plasma cloud. Visual observations of the plasma cloud at higher print height with the on-board camera show a conical shape which behaves slightly irregular in time. The base of the cloud visually grows at greater print heights. The visual irregularity of the discharge would probably effect the substrate at multiple treatments enlarging the affected area. With the needle diameter of 200 µm for a single needle and a conical shape of the plasma cloud, the 320 µm track width can probably not be lowered much without the risk of potentially damaging the substrate or printhead by lowering the print head even further.
For the second set of experiments the effect of adding hexamethyl-disiloxane (HMDSO) to the plasma gas (N_2) is investigated. For this a mixture of N_2 and N_2 saturated with HMDSO was used as plasma gas. In figure 7 the water contact angle on a glass substrate treated with the above plasma gas mixture (200 ml/min N_2 plus 20 ml/min N_2 saturated with HMDSO). As can be seen the water contact angle increases from $<5^0$ for no treatment to 105^0 after 20 treatments. For DEGDMA the contact angle changes from 32^0 to 46^0 after 2 treatments on glass. This indicates that the HMDSO-plasma treatment changes the surface of the substrate to a more hydrophobic nature.

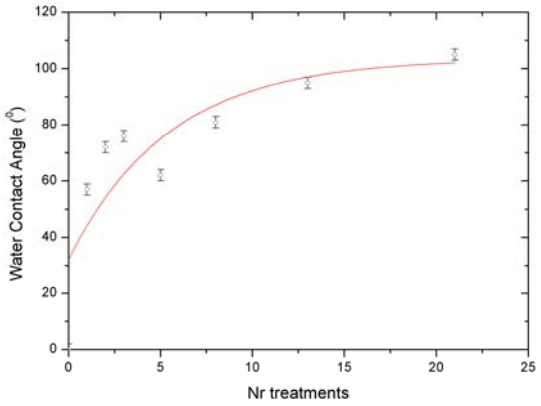

Figure 7:*Water Contact Angle versus nr of treatments of a glass substrate treated with N_2+ HMDSO plasma (flow:200 ml/min N_2 and 20 ml/min HMDSO saturated N_2) (red line is only shown to aid the eye of the reader)*

In figure 8 the droplet diameters of DEGDMA droplets, inkjet printed on a HMDSO plasma treated glass substrate are shown. The substrate was plasma treated twice with a set of one pixel lines at different distances. The area between the lines was left untreated. As can be seen the droplet diameter changes from 125 µm (untreated) to approx. 75 µm for the treated areas. Also visible is when the lines approach each other, i.e. on the left of figure 8, the treated areas overlap and no "hydrophilic" area is left in between. At larger intervals between the lines, the treated areas overlap less and the wetting of DEGDMA increases, producing larger droplets. The smallest, most hydrophobic area was found to be approx. 1 mm wide with a transition of approx. 0.5 mm wide on both sides to the hydrophilic areas.

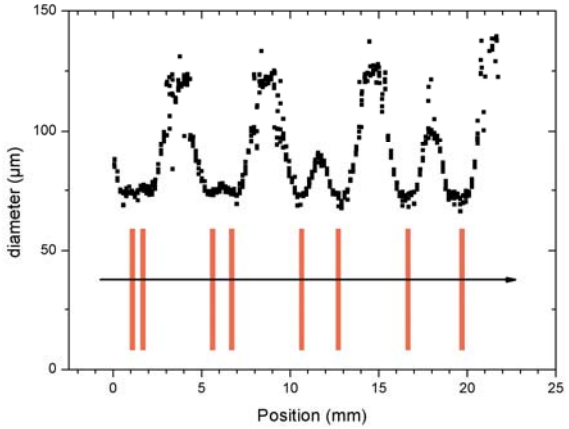

Figure 8: *Droplet diameters of inkjet printed DEGDMA for a cross scan of plasma printed (orange) lines). 200 ml/min N_2 plasma with 20 ml/min saturated HMDSO+N_2 plasma (print height 200 µm, two treatments on glass)*

In the third experiment the hydrophilic and hydrophobic plasma treatments were combined. For this a square of 70x20 mm^2 is plasma treated using only N_2 improving the wetting of the substrate. This is followed by a single treatment of N_2-HMDSO (160/40 ml/min ratio) plasma using figure 2. Figure 9 and figure 10 show the results of this experiment.

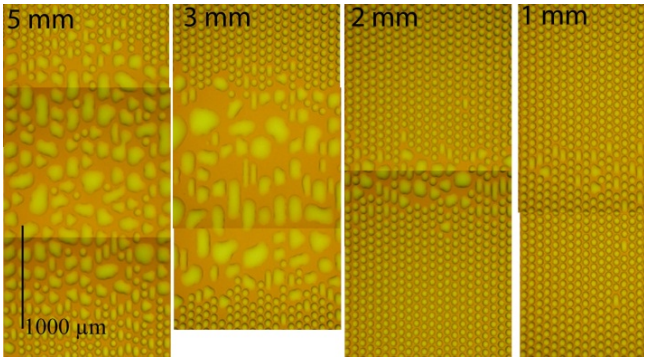

Figure 9. *Microscope images of printed bitmap (figure 2) for respectively the 5,3,2,1 mm wide white area of figure 2. Treatment is 70x20 mm rectangle N_2 plasma (5 treatments) followed by N_2+HMDSO plasma using figure 2 (one treatment) followed by inkjet printing of DEGDMA at 315 dpi.*

In figure 9 the microscopic images of the white areas of the bitmap are shown. Clearly visible is the change in wetting behaviour between the hydrophilic "white" areas and the hydrophobic areas at the top and bottom of the images. In the figure 10 the length of the hydrophilic gap is shown for the different white areas. The smallest gap that could be measured is 0.5 mm. A change in wetting behaviour for the white areas of 0.5 and 0.3 mm could not yet be determined experimentally.

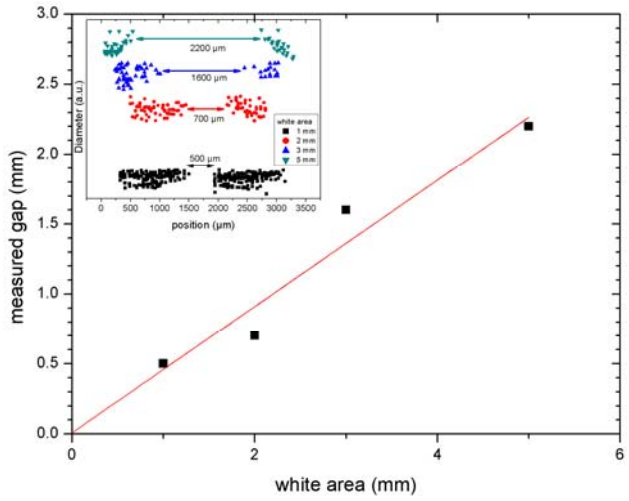

Figure 10. *Measured gap between "hydrophobic" areas versus original width of white area from bitmap determined from Figure 9. Inset shows cross scan of the droplet diameters for the "hydrophopic" area. Arrows represent the measured hydrophilic gap.*

4. Conclusions

In conclusion we showed that is possible to 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 showed that a minimal track width of 320 µm for a 200 µm wide plasma needle is possible. We also showed that using a combination of N_2 with HMDSO increases the contact angle for water up to 105^0 and 46^0 for DEGDMA making the substrate more hydrophobic. Furthermore using N_2/HMDSO gas mixture hydrophobic tracks could be printed with similar minimal track width.

Combining both N_2 and N_2/HMDSO plasma treatments show promising results to further decrease the track width to even smaller values. Further research on this point is needed.

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6. References

[1] a) W. Brok, A. Stevens, et al., Mikroniek **2011**, 32-39; b) U. Kogelschatz, B. Eliasson, et al., Pure and Applied Chemistry **1999**, *71*, 1819-1828.

[2] a) A. Lee, K. A. Mirica, et al., The Journal of Physical Chemistry B **2011**; b) E. Liston, L. Martinu, et al., Journal of adhesion science and technology **1993**, *7*, 1091-1127; c) S. C. Park and Y. B. Park, Surface and Coatings Technology **2010**, *205*, 423-429; d) V. Raballand, J. Benedikt, et al., Journal of Applied Physics **2009**, *105*, 083304-083304-083306; e) A. Sarmadi, T. Ying, et al., European polymer journal **1995**, *31*, 847-857; f) K. Schmidt-Szalowski, Z. Rżanek-Boroch, et al., Plasmas and polymers **2000**, *5*, 173-190; g) Y. Tsuchiya, K. Akutu, et al., Progress in organic coatings **1997**, *34*, 100-107; h) F. Zhi, Q. Yuchang, et al., Plasma Science and Technology **2007**, *9*, 582.

[3] a) G. Borcia, C. Anderson, et al., Applied surface science **2004**, *221*, 203-214; b) G. Borcia, C. Anderson, et al., Applied surface science **2004**, *225*, 186-197; c) E. Castro Vidaurre, C. Achete, et al., Materials Research **2002**, *5*, 37-41; d) N. De Geyter, R. Morent, et al., Surface and Coatings Technology **2007**, *201*, 7066-7075; e) H. Höcker, Pure and Applied Chemistry **2002**, *74*, 423-427.

[4] a) B. J. de Gans, P. C. Duineveld, et al., Advanced Materials **2004**, *16*, 203-213; b) E. Menard, M. A. Meitl, et al., Chem. Rev **2007**, *107*, 1117–1160; c) T. H. van Osch, J. Perelaer, et al., Advanced Materials-Deerfield Beach **2008**, *20*, 343; d) J. Perelaer, B. J. de Gans, et al., Adv. Mater **2006**, *18*, 2101-2104.

[5] M. H. A. v. Dongen, R. O. F. Verkuijlen, et al., LOPE-C (Frankfurt, Germany) **2011**, pp. 181-185.