µPlasmaPrint: digital on-demand surface engineering

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Abstract: InnoPhysics has developed and commercializes the µPlasmaPrint technology, an atmospheric pressure micro-plasma system which enables area-selective functionalization by means of a dot-wise patterning of the plasma treatment/deposition with resolutions to 150 µm. Recent developments will be shown related to process feedback through surface wettability mapping and the development of new process to enable non-fouling hydrophilic coatings in biomedical devices by combining µPlasmaPrint with liquid coating dispensing.

Keywords: plasma patterning, surface functionalization, biomedical coating

1. Introduction

Plasma treatment of surfaces is a well-known technique to modify properties of surfaces, for example to decrease the hydrophobicity of plastics. It is common for surfaces to be treated integrally; however, this might be unnecessary or even undesirable: in many cases one would like to treat surfaces locally and in a patterned manner. One way of doing this would be to use a mask that shields certain parts of the surface from the plasma. InnoPhysics' way of doing this is more flexible and versatile: small individual plasmas are created only there where desired (on demand) while the plasma print head scans across the surface.

Using the digital and on demand paradigms known from inkjet printing, surfaces can be plasma treated directly from an electronic image (no mask), which allows for efficient process development and short, customized production runs with a fast turnaround time and minimal consumable usage.

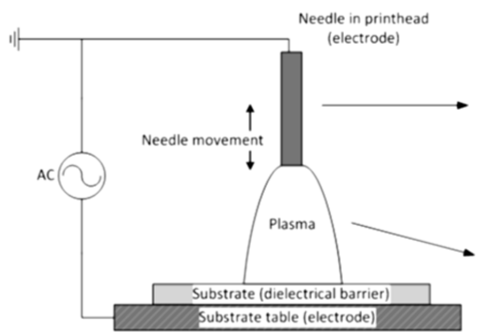
InnoPhysics has made its plasma printing technology available in the form of a Modkit, which is a kit specifically designed such that it can be integrated into different motion platforms. Once installed, the PlasmaPrint hardware can be exchanged back for the original hardware and vice versa. The control settings for the PlasmaPrint process can be integrated into an existing graphical user interface, or it can be supplied with its own user interface.

When integrated into an XYZ-motion platform, such as the Roth&Rau LP50 inkjet printer or the Roland platform, PlasmaPrint processes can be developed efficiently, allowing for effective proof-of-principle and prototype developments.

2. Experimental

The principle of µPlasma patterning [1] is shown in Figure 1. A print head consisting of two rows of twelve needles is positioned above a substrate table. The needles on the print head act as ground electrodes, whilst the substrate table is kept at high voltage to complete the electrical circuit. The substrate located on the substrate table acts as the dielectric barrier. The needles in the print head can individually, move up and down mechanically. As the needle moves closer to the substrate table at a pre-set applied voltage and chosen gas composition, the electrical breakdown is achieved and plasma ignites.

(a)



(b)

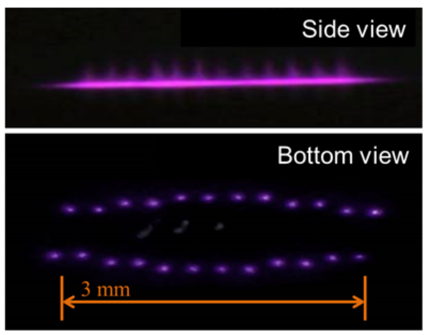


Fig. 1. Schematic drawing of µPlasma printer setup

The µPlasma setup works at ambient pressure and temperature in an open system with direct contact to the external environment. In normal operation mode, this means that the plasma will be generated in air at room temperature (22-24°C) and with a relative humidity present at that moment in time. The μPlasma setup also accommodates throughput of different gas (mixtures) like dry (compressed) air, nitrogen, argon or precursor materials to influence the reactivity of the plasma gas or to be able to deposit layers on top of the substrate. For this, gas is led through a mass flow controller, and in case of a mixture with a precursor material through a wash bottle with bubbler. Approx. 200 ml/min of gas (mixture) is needed to create a small overpressure of approx. 5 Pa in between the print head and substrate to expel (most) of the air during the μPlasma patterning.

For the construction of the Lab-on-a-chip capillaries, standard microscopic glass slides (76x26 mm2) were used. Because of the small contact angle of water on glass, i.e. less than 5 degrees, the glass slides were pre-treated with dodecyl-thiclorosilane (Sigma Aldrich), in order to make the glass hydrophobic. First, the glass was thoroughly cleaned by rinsing with deionised water, and n-propanol before being dried in air. Next, the glass slides were placed in a solution of 0.001 M dodecyl-thiclorosilane in toluene at 3°C for 30 minutes under a nitrogen atmosphere to deposit a monolayer of dodecyl-thiclorosilane (DTS) on the glass slide. After coating, the glass slides were sequentially rinsed with toluene, ethanol and deionized water and dried with nitrogen. The hydrophobic nature of the glass slides was checked by measuring the water contact angle measurement using a Dataphysics OCA-30 contact angle measurement device. Contact angles over 100° were measured for the treated glass slides. The plasma from the μPlasma printer selectively removes the DTS, exposing the original glass surface.

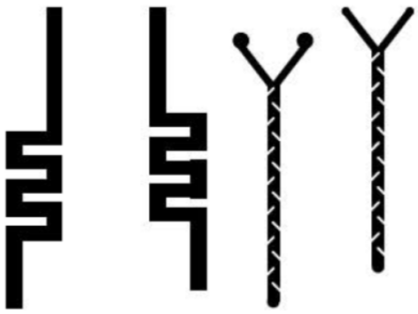


Fig. 2. Two examples of μPlasma printed structures.

Even though multiple structures were printed, in Figure 2 two examples of printed structures are shown. The structures were printed at 20 mm/s at 4.5 kV and 50 μm print height between print head and glass substrate with 90 dpi. A nitrogen flow of 200 ml/min at ambient pressure (99.999% Praxair) was used as plasma gas. To create the hydrophilic capillaries, two glass slides were μPlasma patterned upon using, among others the mirror image structures from Figure 2. After printing, the capillaries were formed by placing the glass slides on top of each other. In between the glass slides, adhesive tape (3M Scotch tape, thickness 0.10 mm) is placed to create a space between the slides. To test the functionality of the capillary design, water coloured with a dye for better visual contrast was positioned at the opening of the design. Under capillary force the water enters the reactor and fills the channel. The progress of the liquid flow through the capillary is filmed and analyzed.

3. Results

Figure 3 shows the top and bottom glass slides for the two designs presented above. For clarity the hydrophilic tracks are visualized with steam after μPlasma patterning. Water droplets form on the hydrophobic area of the glass slides, while on the plasma printed reactor design the water droplets fully wet leaving a clear surface, thus showing the printed design. On the design of Figure 3b, the hydrophobic obstructions are clearly visible. This shows that narrow tracks with high difference in wettability are obtainable through μPlasma patterning.

(a) (b)

Fig. 3. Top and bottom of the two designs from Figure 2. For clarity the hydrophilic tracks are visualized with steam.

After μPlasma patterning the glass slides with the two designs were placed on top of each other, 0.1 mm thick scotch tape was used as spacer between the slides to create a gap. Droplets of coloured water, for better visual contrast, were placed at the entrance of the designs. Under capillary pressure, the water is transported through the hydrophilic channel. The large difference in surface energy between the DTS-layer and the μPlasma treated channel prevents the water to exit the channel. In Figure 4, the coloured water flowing through the printed channels can be seen. In Figure 4b, Water with two differently coloured dyes was used to show the mixing along the length of the design from Figure 2b. Due to the hydrophobic obstructions on the top and bottom of the capillary, the flow of the water is slightly restricted and mixing along the length is enhanced.

To investigate the quality of the capillary, the filling of the line design from Figure 4 was used to analyse the

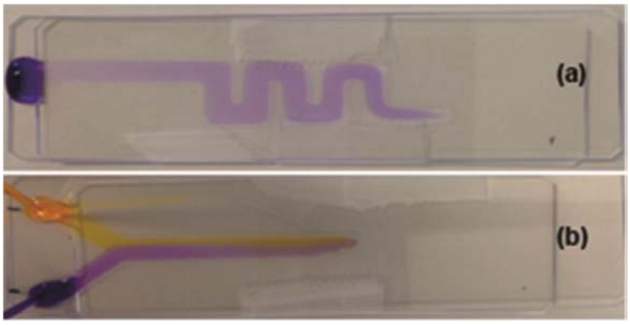


Fig. 4. Droplets of coloured water entering the two closed designs from Figure 2 (a) line structure, (b) mixer with dual inlet and hydrophobic obstructions.

velocity of the water within the capillary and compared to the Lucas -Washburn equation [2]:

$$x^2 = \frac{\gamma \cdot D_H}{4 \cdot \eta} \cdot t \qquad (1)$$

In the equation, x is the distance the water has entered the capillary (m), γ the surface tension of water (72.8 mN/m), η the viscosity of water (1 mPa·s) and t the time (s). For the hydraulic diameter DH, the dimensions of 3x0.10 mm^2 for the capillary are used, making DH=0.192 mm and the constant a γ.DH/4η = 35 cm2/s. Figure 4 shows the result of the video analysis (filmed at 25 fps). Each measurement represents a single frame. After 2.2 seconds the capillary is completely filled. Fitting the experimental results according to the esuqation results in a constant of a=38 cm2/s and an adjusted R-square of 0.9975. From the Lucas-Washburn equation, the constant was calculated at a=35 cm2/s. As the µPlasma patterning setup in reality produces wider tracks than defined by the bitmap, the hydraulic diameter in the Lucas-Washburn equation is underestimated. Taking this into account, the experiments show good agreement with the previous equation.

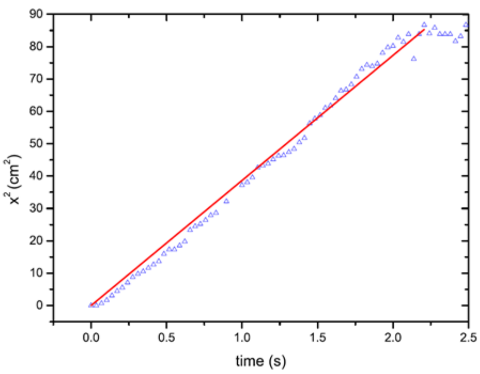


Fig. 5. Squared penetrated distance of liquid versus time for the meandering line. (Δ) experimental data, linear fit equals: x2=38·t cm2 with R2=0.9975.

4. Conclusions

Overall, this shows that µPlasma patterning can be used to create hydrophilic tracks in between two hydrophobic surfaces. To work as capillary, the plasma printed tracks do not have to be closed on all sides, as the steep gradient in wetting between the printed track and surrounding area prevents leakage out of the printed tracks.

5. References

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