Mask-less Patterning Technology for the Printed Electronics Market

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Abstract

Non-impact printed electronics is an expanding market with a large variety of applications where printing technology will be used to produce devices or components on glass or polymer films such as organic LED's, (organic) solar cells, displays and RFID tags. We will describe a unique and new printing technology which enables maskless patterning of surfaces or coatings on thin (insulating) substrates. For volume production of many applications in printed electronics, very thin, patterned layers of (semi-)conducting and/or insulating polymers need to be created with high precision and extremely uniform thickness. Printing of such layers can result in significant cost reductions compared to other techniques. InnoPhysics is developing a micro plasma printing system, which can be installed on existing (inkjet) printing platforms. It can be used for substrate surface energy controlled inkjet printing but also for direct etching and deposition of thin layers. To be more specific and valuable many emerging applications demand hybrid manufacturing utilizing both slot-dye coated forms and inkjet for which etching and activation in one machine are mandatory. Deposition is under further research. We will describe the technology behind 'plasma printing', developed applications for surface energy contrast patterning and selective ink wetting and planned future developments, making use of the new technology for the creation of functional materials on flexible substrates.

Technology of plasma printing

Plasma patterning

The plasma patterning process that InnoPhysics has developed makes use of a micro dielectric barrier discharge (DBD) principle. The micro-DBD is used in a point-plate configuration where the point electrode is grounded and the plate electrode is covered by a dielectric. An AC voltage of e.g. 6kVpp(peak-peak) is applied to the plate electrode to create a plasma. The plasma that is created by the micro-DBD is used to create patterns on the dielectric. A multitude of micro-DBD reactors is switched on/off by a software defined pattern in

Discharge development

To initiate discharges in the DBD a sufficient number of initial free electrons has to be available in the gas gap. These electrons are created by background radiation. In addition a sufficiently high electric field has to be present such that these free electrons can gain energy. As a result of ionizing collisions of the free electrons with background gas molecules, positive ions are created and a plasma will develop. As a result of the plasma, charges will accumulate on the dielectric barrier, locally opposing the applied electric field and quenching the discharges. When the electric field rises again, a new discharge will initiate until the resulting deposited charge on the dielectric quenches the discharge. To sustain discharges in the DBD a varying (AC) electric field is applied.

The electric field in the DBD is created by applying a voltage across the DBD. The voltage necessary to create an electric field such that the initial free electrons are able to initiate the discharge is called the inception voltage. When the electric field is applied periodically the discharges will continue to occur.

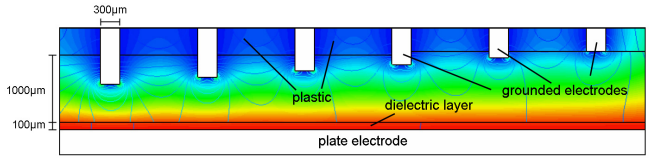

***Figure 1**. Electric field simulation of the micro-DBD*

Figure 1 shows the electric field simulation of the micro DBD for different gap distances. The point electrode is grounded and high voltage is applied to the plate electrode. The colored surfaces depicts the potential distribution (where red is the highest potential), whereas the colored lines represent the magnitude of the electric field (not E-field lines). The maximum electric field occurs at the tip of the point electrode.

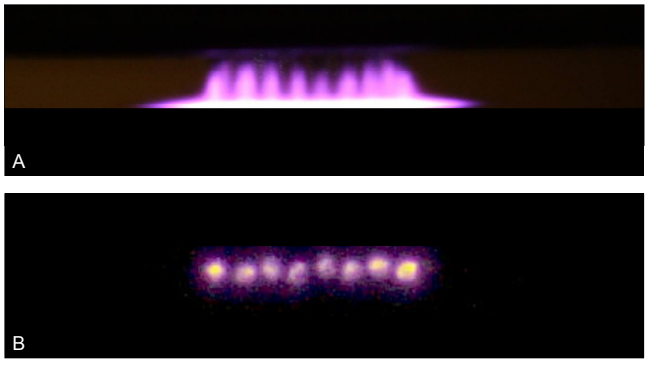

***Figure 2**. (a) Picture shows a side view of the 8 micro plasma sources. (b) Picture shows bottom view of the 8 micro plasma sources. For this picture a glass plate with a transparent conductive oxide layer (TCO) as the high-voltage electrode is used. The camera is positioned below the glass plate.*

In the discharge process reactive molecules are created which react with the substrate that is introduced in between the two

electrodes. Consequently, the physical and chemical properties of a substrate are modified. By introducing different types of gases substrates can be selectively activated (i.e., selective cleaning, wetting improvement, or grafting), thin organic and anorganic layers on substrates can be etched, or patterns of organic/anorganic layers can be deposited. So far only plasma activation and etching of organic layers has been validated.

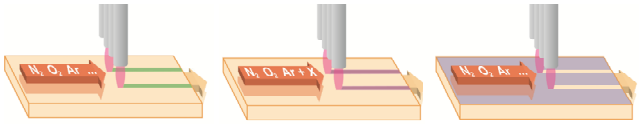

***Figure 3**. Graph shows the three basic plasma processes: plasma activation, plasma etching and plasma deposition.*

Next, two operational processes are describe in more detail; an example of thin organic layer etching to be used for surface energy contrast patterning of functional materials, and wetting improvements of a selected range of plastic substrates.

Surface energy contrast patterning

Introduction

To create surface energy contrast patterns, a three step process is used where (1) a substrate is prepared with hydrophilic layer and a hydrophobic layer as shown in Fig. 4, (2) the micro plasma system is used to etch pattern-wise the hydrophobic coating and (3) one or more functional coatings are applied on top of the patterned substrate.

***Figure 4**. The samples used in the experiments consist of a polymer substrate with a hydrophilic and a hydrophobic coating on top of it.*

The samples consist of a polymer substrate (125 µm) with a hydrophilic coating and a thin hydrophobic coating on top. The goal is to remove the hydrophobic coating at pre-defined areas, such that a large hydrophobic-hydrophilic contrast patterns is created. During the experiments several parameters are varied: process time, voltage level and gap distance (i.e. distance between the substrate and electrode). We have also studied the effects of process gas composition, flow rate and voltage frequency.

Measuring method

Quantitative results of the plasma treated areas are obtained with a droplet shape analyzer "Easydrop" of Krüss. The droplet size is 1.5 – 2 µl and droplet speed of 20 µl/s. The two testing fluids are water and diiodo-methane. Droplets of these two liquids are placed on the surface and contact angles (θc) are measured as shown in Fig. 5.

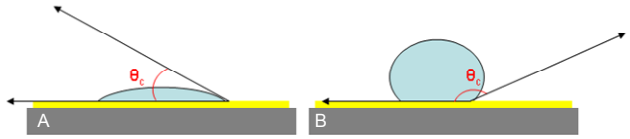

***Figure 5**. Shape and contact angle of a droplet on a A) hydrophilic surface and B) hydrophobic surface.*

Using Owens/Wendt theory [1] the surface energy is determined. Surface energy is a measure for the wettability of a surface: high surface energy (and low contact angles) are linked to a hydrophilic surface (wettable), while low surface energy (and high contact angles) means hydrophobic (non-wettable).

Print speed and effectivity

Figure 6 shows a summary of the experimental results with the micro plasma system. The goal of the experiment is to minimize the treatment time of the plasma. The surface energy is plotted as a function of the treatment time (of a 225 mm^2 area) [3].

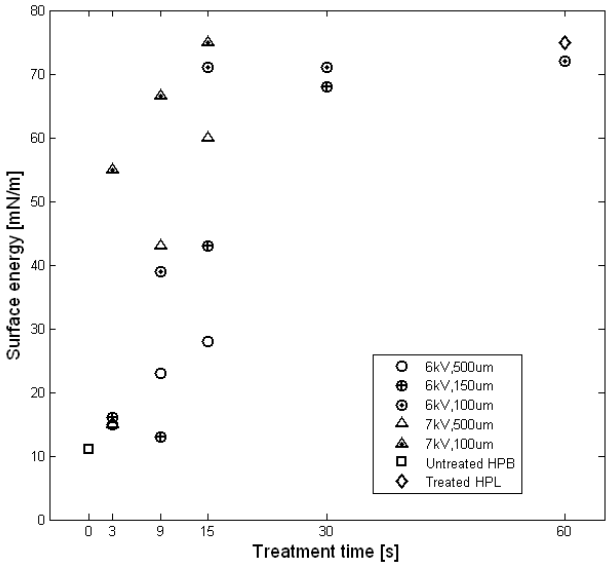

***Figure 6.** The data points denoted by the 'circular' and 'triangular' symbols are the actual etching results, while the data points denoted by the 'square' and 'diamond' are the control samples. The size of the treated area is 225 mm2.*

The measurements denoted by the 'circular' and 'triangular' symbols are the actual etching results, while the 'square' and the 'diamond' denote the data points of the control samples, which are untreated hydrophobic coating and the plasma cleaned hydrophilic coating respectively. Figure 6 shows that the etch velocity and thus the surface energy is mainly determined by the gap distance and the voltage level. When the gap distance is decreased from 500 µm

to 150 µm at an equal voltage level of 6 kVpp the surface energy increases significantly. After 15 seconds of plasma treatment with a gap of 100 µm, the surface energy is equal to the surface energy of the plasma treated hydrophilic coating, which means that the hydrophobic coating is completely removed. The surface energy after short treatment times is comparable to the untreated hydrophobic coating results (no etching). However when the voltage level is increased to 7 kVpp and the gap distance is 100 µm, even after 3 seconds of plasma clear evidence of etching can be observed. Other parameters like process gas flow rate, voltage frequency and change of the plasma composition clearly have an effect, but need to be further investigated.

Resolution

In the following test only one electrode (diameter 0.3 mm) is used. The goal of this test is to determine the minimum line width which can be created with the plasma printer. The results of the experiments are shown in Fig. 7. A ruler with a millimeter scale has been used to demonstrate the line width. In Fig. 7A show a line of approximately 1.5 mm wide is shown, which has been created with a gap distance of 100 µm and a high voltage level of 7 kVpp. Figure 7B show a line of approximately 0.3 mm wide which has been created with a gap distance of 100 µm and a high voltage level of 5 kVpp.

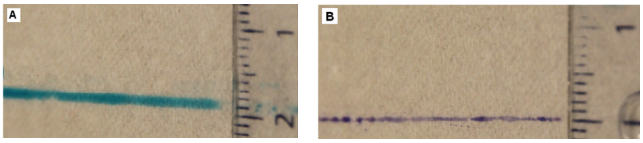

***Figure 7**. Resolution of plasma printer.*

Homogeneity

A surface area of 10 x 10 cm2 is plasma treated and divided in 100 equal areas: 50 to measure water contact angles and 50 to measure diiodomethane contact. Figure 8 shows the results of substrate which has been treated with a gap distance of 100 µm and a high voltage level of 7 kVpp.

19	40	18	41	16	41	13	42	17	42
42	16	40	13	42	14	42	18	40	15
15	39	15	40	13	41	14	41	14	40
40	15	41	14	40	12	39	11	43	11
12	43	16	42	17	43	18	41	12	41
40	14	42	14	39	13	40	12	40	13
16	43	14	43	14	42	11	42	13	41
43	14	42	15	43	12	43	12	43	13
19	43	14	42	13	43	13	41	11	39
41	15	41	15	41	15	41	16	39	14

CA Water
CA Diiodo-methane

***Figure 8**. Homogeneity of plasma treatment.*

It took 7 minutes to treat the entire surface area of 100 cm^2. The contact angles for water are 15 ° ± 4 ° and for diiodomethane 41 ° ± 2 °. This means the difference in surface energy (ΔSE) over the sample is 3 mN/m (SEmax = 75.5 mN/m and SEmin = 72.2 mN/m).

Patterning

Figure 9 shows some examples of patterns created with our plasma printer. The pictures in the upper row show how a marker pen with an 8 mm wide tip is used to expose the areas where the hydrophobic coating is removed down to the underlying hydrophilic coating. The lower picture shows the text "InnoPhysics".

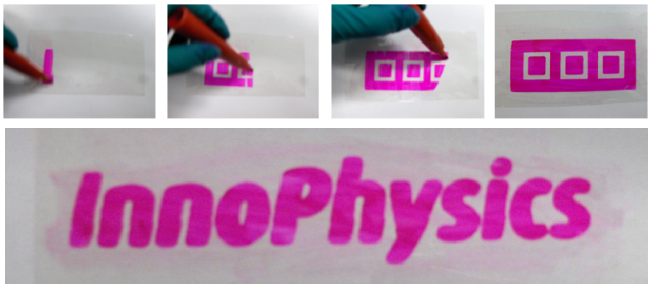

***Figure 9**. Different patterns created with the plasma printer.*

Selective ink wetting

Introduction

Because printed electronics require extremely high accuracy and reliability, the adhesion between the droplet and the substrate surface is very important. There are numerous effects that play a role e.g. disjoining pressure, local evaporation, crystallization, etc. The different substrate structures may have a smooth or a rough surface and the use of complex fluids (dispersed material, polymers) complicates the situation to a further extent. It is important to control the (de)wetting properties of the substrate, and the related spreading of the ink droplet along the substrate [2]. Producing smaller tracks of printed materials is usually done by reducing the channel diameter of the print head nozzles. However this might results in clogging of the nozzle channels.

To prevent these type of problems the plasma printer can be used to locally change the (de)wetting properties of the substrate prior to inkjet printing. This results in a better control of the substrate-fluid interaction, enabling smaller tracks, more homogenous layers and improved wetting or dewetting of the substrate. Here, a number of widely used commercial plastic substrates have been treated with the plasma printer and the effect on the surface energy change has been characterized.

Measuring method

Quantitative results of the plasma treated areas are obtained via a droplet shape analyzer. In this case we have used the "Contact angle system OCA 20"of Dataphysics. The droplet size is 4 µl and droplet speed is 20 µl/s. The two testing fluids in this case are water and ethylene-glycol.

Print speed and effectivity

Figure 10 shows the change of surface energy for different types of bare polymer substrates as function of the plasma treatment time [3]. The thickness of the substrates ranges from 100 to 250 µm. During the experiments a basic parameter set is used where the high voltage level is 6.5 kVpp, the gas flow is 1 l/min and the gap distance is 100 µm. As can be observed for all the substrates a ΔSE of around 20 mN/m can be achieved. This result is already reached after 15 seconds. Longer treatment time does not result in higher surface energy.

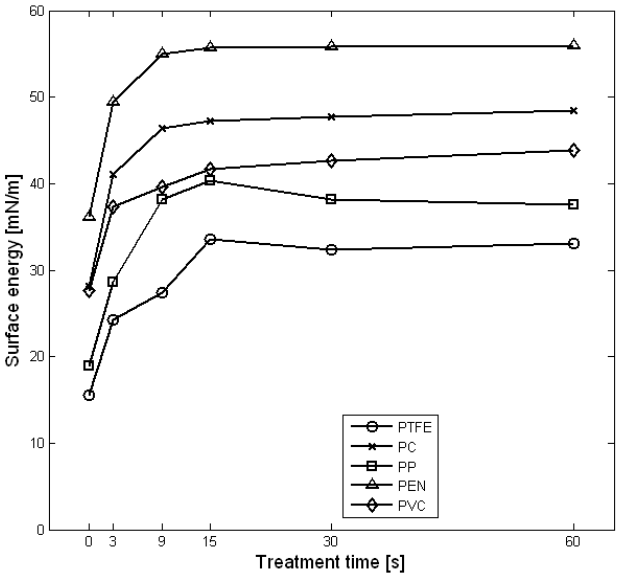

***Figure 10**. Surface energy of different polymer substrates after plasma treatment.*

Future developments

We have shown that the micro plasma system can be used for patterned plasma activation and etching of hydrophobic coatings. However for a successful market introduction the existing micro plasma system will need to be further improved w.r.t. the following industrial requirements (1) resolution: feature size < 10 µm; (2) throughput: high speed plasma processing with linear speeds of 10 m/min at 30 cm width for roll-to-roll compatibility; (3) reliability: high yield and uptime of > 95%; (4) process: wide variety of applications on different substrates. InnoPhysics executes a technology development program to improve the micro plasma system design with respect to gas flow control, plasma source design, plasma diagnostics and gap distance control. Secondly InnoPhysics is running an application development program to develop a number of new processes, including plasma deposition, to create patterns of functional materials on flexible substrates using the micro plasma system.

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References

[1] Owens, D.K. and Wendt R.C., "Estimation of the surface free energy of polymers", Journal of Applied Polymer Science, 13, 1741 (1969).
[2] Groenveld. P., "High-precision inkjet systems"
[3] It should ne noted that the treatment time is defined as the time used to treat an area of 225 mm^2 with the plasma printer including the print stage motion. The effective plasma treatment time per unit area is shorter.

Author Biographies

Dr.Ir P. Blom received a Ph.D degree in the field of high power pulsed corona discharges in 1997. In his professional career he has worked for the semi-conductor industry, rail and energy sector and the automotive industry. Since 2006 he works for InnoPhysics B.V. where he develops atmospheric plasma equipment for the printed electronics, medical and the graphics industry.

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