Miniaturized Ag/AgCl electrodes made by inkjet printing

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Goal of the project

This project aims at fabricating miniaturized Ag/AgCl electrodes inside microfluidic channels by inkjet printing. This kind of electrode is widely used to perform electrical measurements in fluids due to its interface properties. Inkjet printing has the advantage of being a low cost one-step process that doesn't a mask or complicated lithographic process.

The full device is composed of microfluidic channels which are connected by nanochannels. The main goal of this device is to characterize the conductivity of ionic solutions inside nanochannels. The standard conductivity measurement approach consists of placing wire Ag/AgCl electrodes inside four reservoirs. However, the measurements may not be stable and the conductivity of the microchannels has to be taken into account. The micro-patterned electrodes provide better stability and repeatability for measurements by eliminating the contribution of the microchannels.

Index

1)   State of the art

1.1)   Inkjet printing

The global market demand for high quality and low cost electronic components requires innovative fabrication techniques that are both faster and cheaper compared to traditional production methods. In this regard, inkjet printing with the use of inks based on metal nanoparticles (NPs), metallo-organic decomposition ink (MOD) based on metallo-organic complexes (MC) or salts of various metals is a very attractive low-cost technology for direct metallization.[1] The main advantages of inkjet printing compared to other deposition methods are one-step processing, cheap and compact equipment, and applicability to various substrates.[1]

Inkjet printing, which is widely used in office and home printers, is a non-impact dot-matrix digital printing technology, in which droplets of ink are jetted from a small orifice in a printhead, directly to a specified position on a substrate, as a result of pressure developed after an electronic signal has been sent to the printhead to create an image. Today the majority of inkjet printers are based on the drop-on-demand (DOD) methods. Most, if not all DOD printers on the market today use either thermal or piezoelectric printheads.[1]

In the last two decades, inkjet printing, which has seen commercial success since the late 1970s, has grown to be an important topic in scientific research and technology.[1]

1.2)   Ink Formulation

A major challenge in applying inkjet processes for direct writing is formulating suitable inks. [2] Both conductive and non-conductive inkjet inks are comprised of a liquid vehicle (water or an organic solvent), which determines the basic properties of the ink, and a dispersed or dissolved component providing the desired functionality. [1] In addition, they may contain various binders, dispersants, and adhesion promoters, depending on the nature of the precursor and the particular application. In the case of inks for metallization, the content of the metallic ink must be adjusted to provide the required resolution, with good adhesion and the desired electronic properties for the conducting lines. Ink composition is critical because it defines the way in which the ink can be jetted, the adhesion to the substrate, and the line resolution and profile, and it can control the mechanism of metal formation. [2]

The solvents are the primary ink vehicles that dissolve or suspend the functional material and other components of the ink. Typical solvents are organic liquids (solvent-based ink) and water (water-based ink). [3]

Water-based ink: are relatively inexpensive and environmentally friendly, but their application is limited since water-based inks require porous or specially treated substrates or even lamination to impart durability and the ink tends not to adhere to nonporous or plastic substrates. [3]

Solvent-based ink: present exceptional print quality, image durability, fast drying time and compatibility with a wide range of substrates (metal, glasses, ceramics, plastics, wood etc.). Solvent inks can be formulated with either soluble functional materials or as dispersions of submicron and nanoparticles. [3] Disadvantages of solvent-based inks include environmental and health issues (hazardous volatile organic compounds and strong odor), as well as the possibility of blocking the printhead nozzles while using fast-drying, volatile organic liquids. [3]

There are several approaches to formulate the metal precursor inks. They can be composed of dissolved organometallic compounds or polymers, colloidal suspensions of metal nanoparticles or some combination of these constituents. Using organometallic inks, the desired material is formed upon thermal decomposition of the organometallic molecule which contains the atom or atoms of interest in the final materials. Using metallic nanoparticles in an organic or polymeric vehicle or adding them to the organometallic ink is another option for enhancing the electrical behavior of the final prints. [2]

1.3) Ag/AgCl electrodes

The silver/silver-chloride electrode is by far the most common type of electrode used in research and industry due to its simple construction. The macroscopic model is comprised of silver wire coated with silver chloride, immersed in a Cl^- ion rich solution such as KCl. [4]
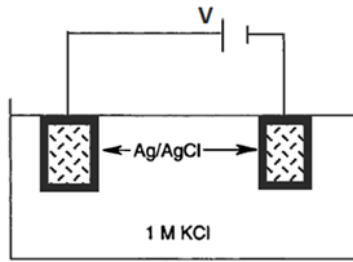
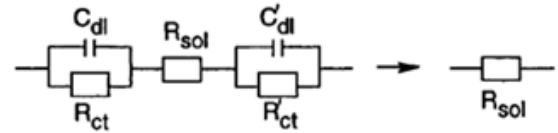Fig 1.a: Macroscopic model of Ag/AgCl electrode

Fig. 1.b: Equivalent circuit representing the electrochemical processes when a DC voltage is applied to the electrode [5]

When a dc voltage is applied between the two Ag/AgCl electrodes shown in Figure 1.a, the following process occurs at the electrode/electrolyte interface

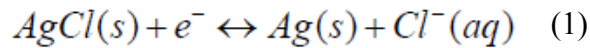$$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-(aq) \quad (1)$$

Figure 1.b shows the equivalent circuit representing this electrochemical process. Because the charge-transfer processes in eq 1 are rapid, we can neglect the impedance contributions from the double-layer capacitance (Cdl, Cdl′) and the charge-transfer resistance of the electrodes (Rct, Rct′), and the equivalent circuit can be simplified to one in which the current is governed by the solution resistance, Rsol. For these conditions, the current at the electrode is a linear function of voltage, and thus, the solution resistance can be extracted from the slope of the I-V curve. [5]

However, in such electrodes, AgCl dissolution and internal filling solution effusion pose serious threats to reference electrode stability and accuracy. According to this reaction in eq. (1), it is expected that the chlorine ion acts as the chemical species in the operation of the electrode, and its activity, which is related to its concentration, has a significant impact on the electrode potential. However, in a rich chloride filling solution, the flow of current which causes a change in chloride content, will not affect its chemical potential and is the reason for this electrode's stability. [4]

Fabricating the reference electrode is generally done in one of the following ways:

Thin film deposition: Evaporation, sputter deposition or chemical vapor deposition (CVD) of the electrode material (e.g., Ag) onto a lithographically patterned metallic lead.

Electroplating: The substrate is electrochemically treated in a bath containing cations of the required metal. Electroplating allows for higher thicknesses of the electrode material.

Screen printing: This involves pressing the electrode metal "ink" onto a surface using a blocking meshed stencil. This technique can produce the highest thickness of electrode material, but is normally done as a manual step and not integrated with automated processing techniques. [4]

After the base metal is deposited, an activation step is generally needed to create the reference material. In the case of Ag/AgCl, the silver layer must be chlorinated to produce the coating AgCl. Activation is usually done by one of the following techniques:

Direct mixture deposition: As in the case of screen printing Ag/AgCl, a compound paste is deposited directly onto the metallic surface. However, the adhesive properties of this layer to the supporting electrode might not be very good, and reliability of the electrode will depend on the homogeneity of the paste used.

Ion exchange reaction: A spontaneous chemical reaction can form the needed film. In the case of Ag/AgCl, bathing the electrode in a solution of FeCl3 is a known method to form the silver chloride layer.

Electrochemical coating: An electrochemically induced reaction allows controlled surface chemistry and a reportedly more Nernstian behavior, albeit slower than ion-exchange reactions. The AgCl coatings can be electrochemically made by anodization of silver in a HCl bath. Platinization of platinum electrodes is also done using an electrochemical coating reaction. [4]

2) Experimental setup

2.1) FUJIFILM Dimatix

The inkjet deposition system used in this project to deposit Ag patterns was the FUJIFILM Dimatix DMP-2831 available in the CMI+1. (Fig.2)

Fig2: Dimatix printer [8]

The DMP-2800 series printer allows the deposition of fluidic materials on an 8x11 inch or A4 substrate, utilizing a disposable piezo inkjet cartridge. This printer can create and define patterns over an area of about 200 x 300 mm and handle substrates up to 25 mm thick with an adjustable Z height. The temperature of the vacuum platen, which secures the substrate in place, can be adjusted up to 60°C. The DMP-2800 offers a variety of patterns using a pattern editor program. Additionally, a waveform editor and a drop-watch camera system allows manipulation of the electronic pulses to the piezo jetting device for optimization of the drop characteristics as it is ejected from the nozzle. This system enables easy printing of structures and samples for process verification and prototype creation. [6] Fig 3 shows three simultaneously printing nozzles.
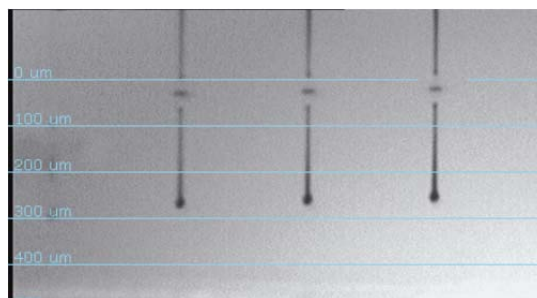

Fig 3: drop-watch camera view [6]

The most unique feature of this table printing system is the printhead itself (Fig.4). FUJIFILM Dimatix has created a MEMS-based cartridge-style printhead that allows users to fill their own fluids and print immediately with the dimatix printer in their own laboratory. To minimize waste of expensive fluids, each cartridge reservoir has a capacity of 1.5 ml. Cartridges can easily be replaced to facilitate printing of a series of fluids. Each single-use cartridge has 16 nozzles linearly spaced at 254 microns with typical drop sizes of 1 and 10 pL. [6]

The printer has nozzle three cleaning routines:

a) **blot**- refers to the cartridge coming down and making contact with the cleaning pad for the designated time.

b) **spit**- refers to jetting the nozzles for the designated time at the given frequency.

c) **purge** - refers to pushing fluid out through the jetting device with pressure (system is preset to 5psi). This process is usually used to get air out of the jetting device. [6]

Fig 4: Dimatix cartridge [6]

Dimatix is equipped with two cameras: one fiducial camera for sample observation and one for drop and nozzle observation. Some features of fiducial camera:

- Provides substrate rotation alignment using reference marks
- Allows positioning of the print origin to match substrate placement
- Provides measurement of features and locations
- Provides inspection and image capture of printed pattern or drops
- Provides cartridge alignment when using multiple cartridges
- Allows matching drop placement to previously patterned substrate [6]

System repeatability: ± 25 μm (± 0.001 in) [7]

2.2) Ag nanoparticle ink

A commercial nanoparticle-based silver ink (DGH 55LT-25C) provided by ANP (Advanced Nano Products Co., Ltd) was used to fabricate silver patterns in this project. The specifications of the product are listed in table 1.

Silver Inkjet Ink (DGH 55LT-25C)	
Solid content (%)	50 ~ 60
Viscosity (cPs)	7 ~ 16
Surface Tension	27 ~ 30
Solvent	Tetradecane
Washing Solvents	Non-polar solvents: Xylene, Hexane, Octane etc.
Curing Temp. (°C)	250
Specific resistivity ($\mu\Omega.cm$)	2.4 ~ 3
Substrate	Polymide film

Table 1: specifications of the Silver ink used in this project [9]

2.3) Ag ink printing conditions

- Optimized plate temperature: 40°C
- Optimized cartridge temperature: 28 ~ 29 °C

  Although it is possible to heat the plate until 60°C, it was observed that the use of the plate at such a temperature makes the ink cartridge heat fast to temperatures above (33 ~ 34)°. However, when the ink is heated at such a temperature, the patterns are not well printed, with the formation several satellites. Some ink leakage was observed while the print head is moving. On the other hand, a heated plate is crucial in this kind of experiment in order to evaporate the solvent of the ink so that the printed patterns do not get displaced or deformed. In order to get well printed patterns, the cartridge temperature should be around 28 ~ 29 °C.

However, if the printing continues longer time (several hours), the cartridge starts to heat to around 30 ~ 31 °C. The time to cool down the ink to the proper temperature is significantly lower when the plate is at 40°C compared to when the plate is at 60°C.

Printing with the plate at 40°C is the optimal choice for DGH 55LT-25C ink.

- <u>Optimized cleaning cycles</u>
    • Start printing:
    > Spit 500ms
    >
    > Purge 0.3s
    >
    > Blot 3s
    >
    > Blot 3s

    • During Printing:
    > No cleaning

    • After printing:
    > Blot 3s
    >
    > Blot 3s

- <u>Drop spacing</u>: 25µm
- <u>Distance between nozzle and substrate</u>: 0,6mm
    These last two parameters has not been changed during the experiments

An important remark concerns the shelf life of the ink inside the cartridge. After the usage, the cartridge is stored in a fridge. The use of the cartridge is no longer than 3 days because the nozzles get clogged. As a rule, in the second or third printing day the quality of the drops and number of working nozzles are not the same as in the first day of use. In order to solve this problem, the nozzles should be cleaned with IPA soaked clean room paper sheet each time before storing it in the fridge. This procedure increases considerably the life time of the cartridge and preserves the quality of the printing. By using this approach it was possible to print with the same cartridge after the 5 days with the same drop quality as in the first day of use.

3) Process Flow overview

The final objective is to fabricate and characterise Ag/AgCl electrodes inside micrometer-scale fluidic channels by inkjet printing. First, the microchannel system is fabricated by UV-nanoimprint using Ormostamp polymer. The stamp used in this process was prepared by UV lithography. The microchannel depth is 30 µm, length is 10-15 mm. The channels are connected by 1 mm diameter round reservoirs for liquid delivery. The schematic channel layout is shown in fig.5.
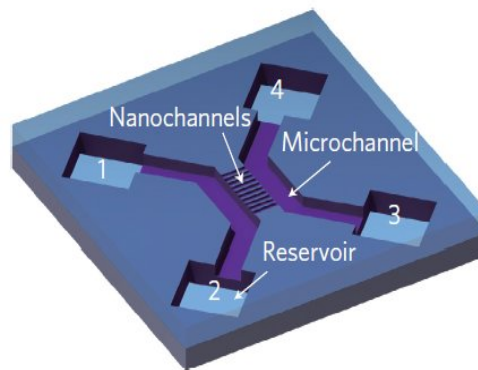

Fig5: micro and nanochannels structure [10]

Next, Ag ink lines were inkjet printed onto the topographic surface of the microchannels. A thin layer of AgCl was formed on the surface of the Ag printed patterns by chemical treatment with aqueous $FeCl_3$ in order to obtain a double layer of AgCl and Ag, characteristic of this kind of electrode.
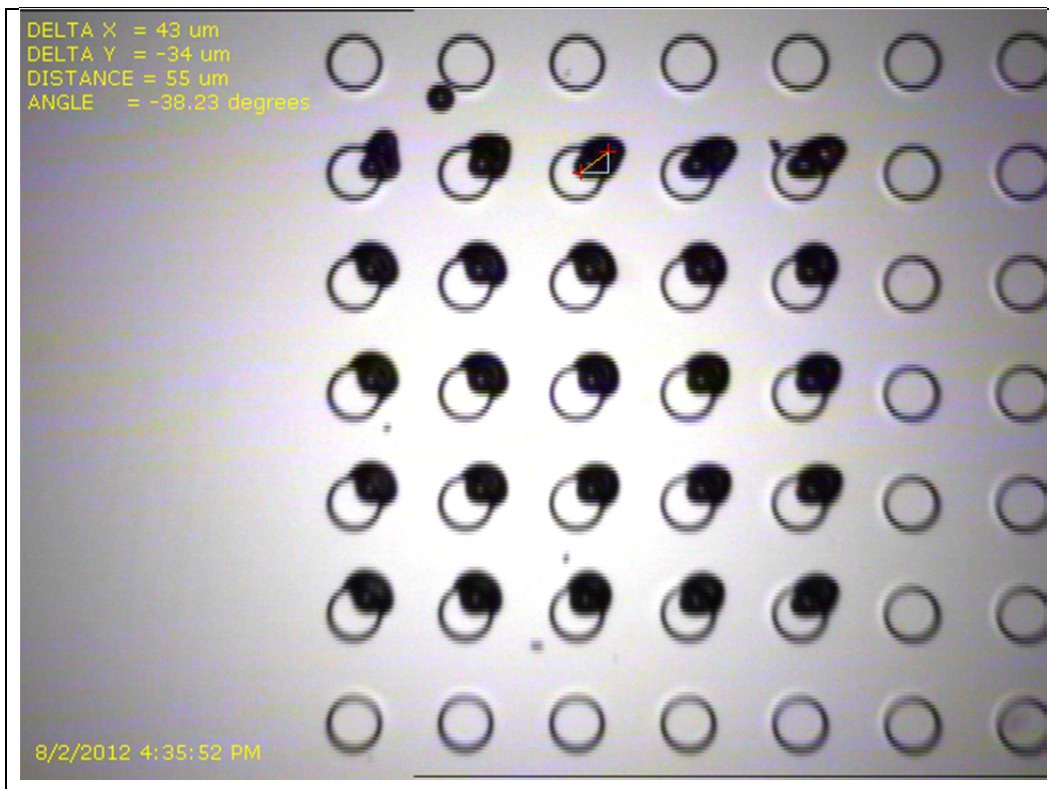
Finally, fluidic two point contact resistance measurements were performed and the results were compared with standard 1mm wire Ag/AgCl electrode in order to check the quality of the fabricated electrodes.
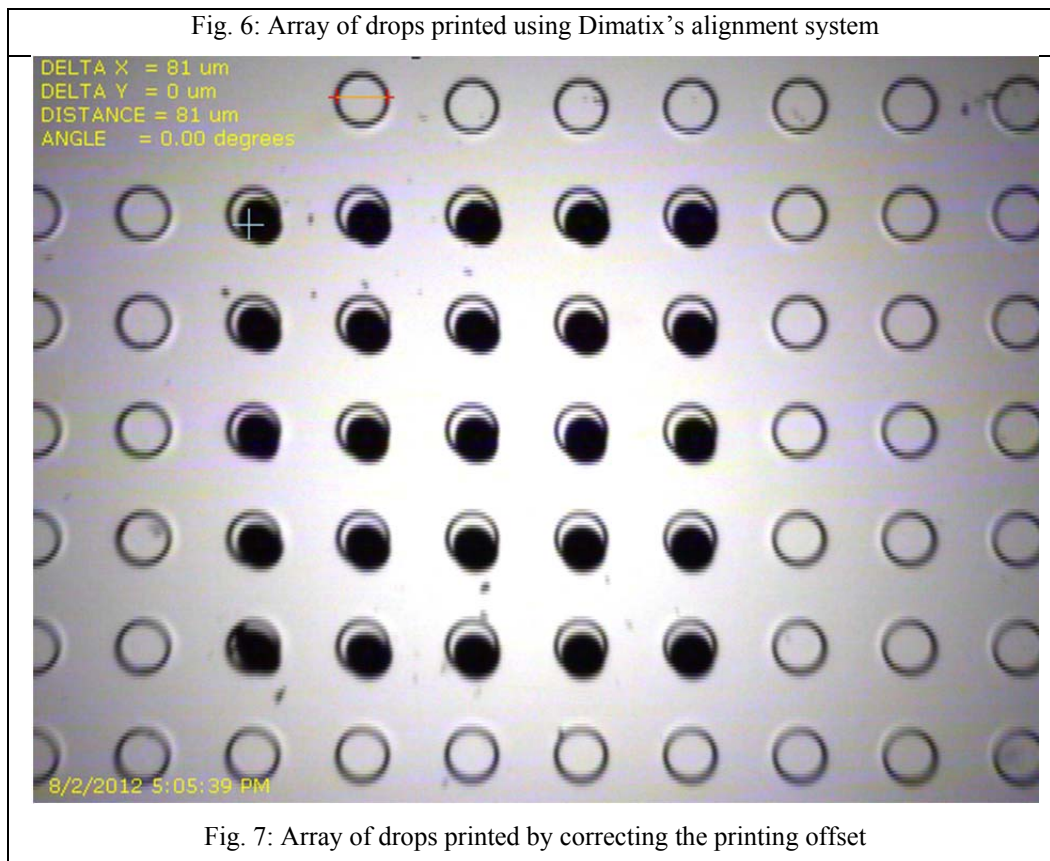
4)   Results

4.1)   Dimatix inkjet printer accuracy test

In order to test the accuracy of the inkjet printing system, a sample with regular protruding 80 µm diameter and 175 µm space circle patterns was used. Fig.6 shows an attempt of printing a 4-drop array using the standard alignment system of Dimatix software. After a number of experiments, about 55 µm shifts were observed from the expected position (fig.6).

However, we noticed that this printing offset of the alignment system is usually reproducible when samples are not changed. When printing is carried on the same samples where the reference point has previously been defined using Dimatix "set reference point" routine, it is possible to compensate this offset in order to obtain more accurate results. "Set reference point" is an additional way to position the layout on the substrate by aligning a point in the layout to a specific point on the substrate (a point is selected in the layout and a corresponding point is selected in the substrate through the Fiducial Camera window). The correction was performed and result is shown in fig.7. The measured shift from the correct position in this case is around 25 µm, the repeatability range claimed in the printer specification.

Fig. 6: Array of drops printed using Dimatix's alignment system

DELTA X = 81 um
DELTA Y = 0 um
DISTANCE = 81 um
ANGLE = 0.00 degrees

8/2/2012 5:05:39 PM

Fig. 7: Array of drops printed by correcting the printing offset

Unfortunately, the printing offset is not reproducible as it depends directly on the position and angle where and how the sample is placed, on the angle calibration performed by the software and also on the angular position of the ink cartridge, which is usually made by hand. Hence, in order to perform more accurate printing as the one shown in fig. 7, a small printing test before the actual printing is needed on the same sample were the patterns will be printed in order to check the exact position where the printing is starting and correct the offset by compensating the position of the reference point.

3.1)   Silver lines

In order to study the behaviour of printed silver in different surfaces, the Ag ink lines were printed on four different substrates: silicon, O_2 plasma treated silicon, Ormostamp and O_2 plasma treated Ormostamp. Ormostamp is a transparent hybrid polymer for micro and nanoimprinting lithography provided by micro resist technology GmbH, and is the material used to fabricated microchannels and the nanochannels. The goal to treat the samples with O_2 plasma was to explore the difference in polarity

between the treated surface (hydrophilic) and the ink (hydrophobic), in order to create better patterned structures.

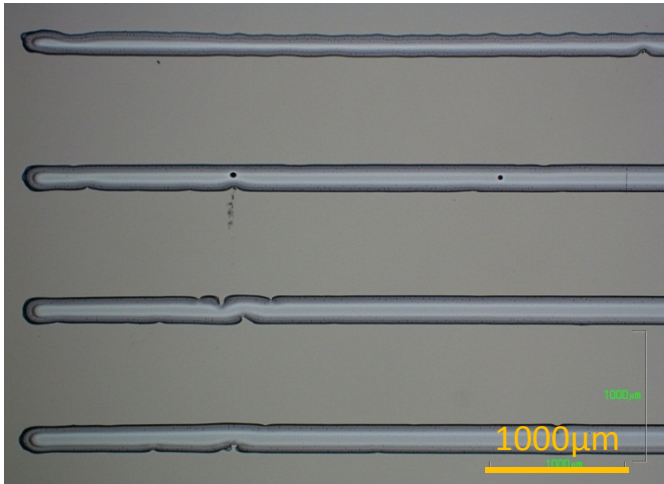Optical images of the printed lines are shown in Fig 8.1 to 8.4
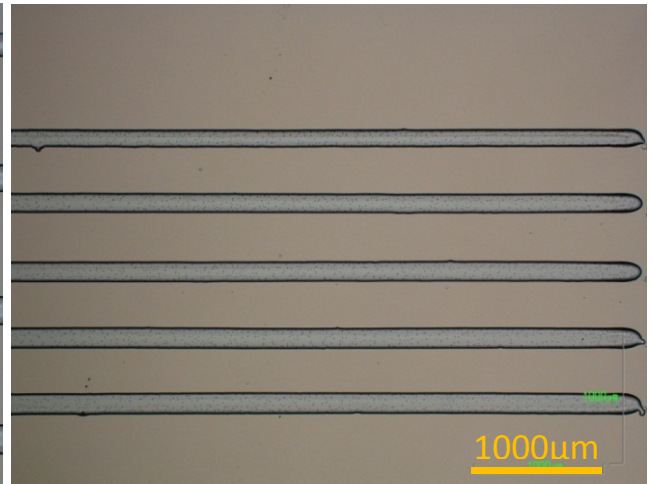

Fig 8.1: Ag ink lines printed in silicon

Fig 8.2: Ag ink lines printed in silicon O2 plasma treated

Fig 8.3: Ag ink lines printed in Ormostamp

Fig 8.4.: Ag ink lines printed in Ormostamp O2 plasma treated

The differences between the printed lines on O_2 plasma treated and non-treated surfaces were not significant since the patterns were printed using on a hot plate at 60°C, which makes the solvents of the ink evaporate fast, before the ink can spread on the surface. Although, as discussed before, printing with the plate at 60°C result in a fast heating of the ink cartridge, compromising the quality of the printed

structures. For printed lines using the plate at 40°C, the difference between treated and non-treated surface can be easily seen, as shown in fig 9 and fig. 10.
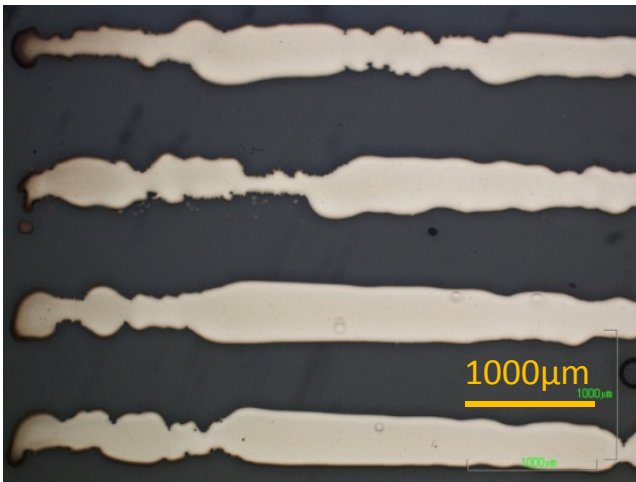

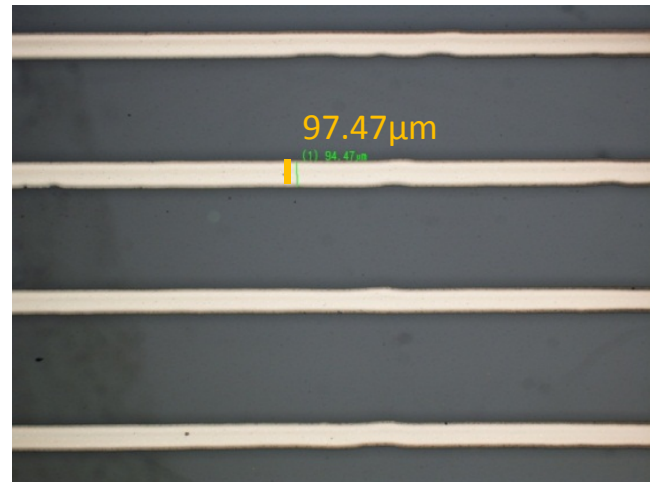Fig 9: lines printed on non-treated Ormostamp with 40°C substrate temperature

Fig.10: lines printed on O_2 treated ormostamp with 60°C substrate temperature

In order to define the patterns to print, the layout can be either draw using Dimatix's pattern editor or imported into Dimatix's pattern editor from a layout editor like L-edit or Clewin. The basic pattern, at lowest level, is a collection of rectangles that are called pattern Drop Position Arrays. Each of these rectangles may be small enough to represent a single drop, or thin enough to represent a line of drops, or large enough to represent a fully filled-in rectangular area. [8] One dimension parameter is the "Drop Spacing". The drop spacing is the center to center distance in X and Y of the drops that the DMP deposits to create the pattern. Drop spacing is adjustable between 5 and 254 μm in one micron increments. [8] The drop spacing determines the resolution or density in the X direction, and therefore is most useful for altering the fill density (amount of jetted ink per area) of lines and rectangles, or it may be used to create rows of individual drops which are spaced closer together than 254 μm. [8]

In any case, Dimatix software works with the dimensions of the patterns to be printed (not pixels). However, the dimensions and shape of real printed patterns depends strongly on the conditions of the surface such as temperature, polarity etc. Since the silver ink used in this project is based on tetradecane solvent (apolar), surface treatment with O_2 plasma allows the formation of smaller structures compared to surfaces not treated due to electrical repulsion between ink and surface.

The ideal case would be to create thick electrodes (at least 1μm thick), but less wide than 200 μm so it can fit into the microchannels. For this purpose, several lines with different dimensions were printed on Ormostamp surface treated with O_2 plasma 10 minutes before the experiment in order to study the dimension of the formed patterns and choose the proper one to fabricate the electrodes. Measurements of the dimensions were taken using a profilometer and the results are reported in table 2. The first column in the left represent the width of the lines defined in the program. The printed lines were "two-peaked", with a structure similar to the one drew in fig.11. H_1 stands for the height of the lower peak (if different height), while H_2 stands for the height of the valley. The drop spacing was kept constant and equal to 25 μm in this experiment.

Fig 11: Approximated structure of the printed patterns

Line width on dimatix software, μm	Line width, μm	Line height, μm	H2, μm
25	200	1-0	0.7
50	210	1.3	1
75	250	1.8	1.2
100	268	2-0	1.4
100	274	1.9	1.5
150	390	2.1	1.5
200	425	2.4	1.7
250	470	2.7	2

Table 2: Profile measurements for different line width defined in Dimatix software
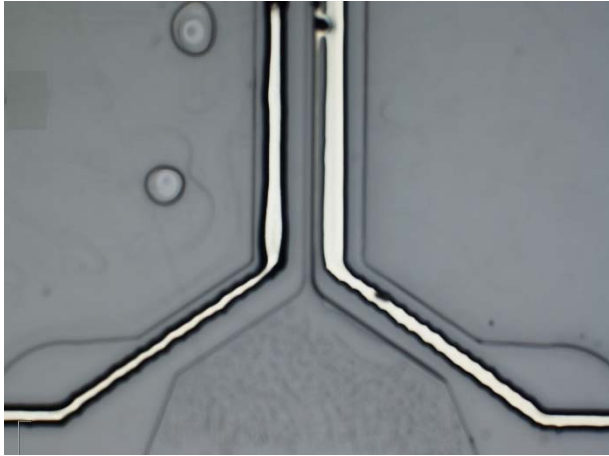
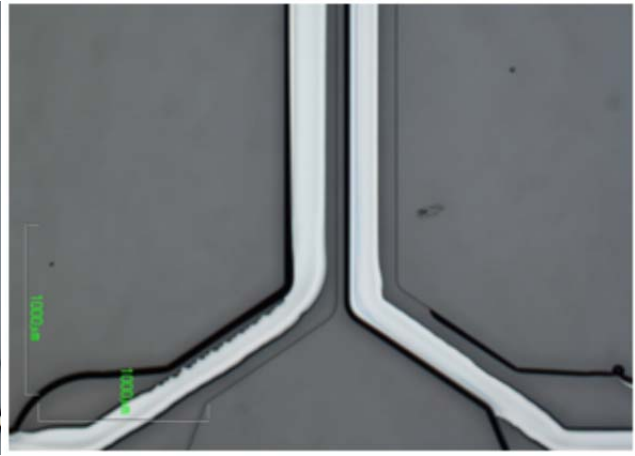Fig 12: 100 μm wide layout on just O2 plasma treated Ormostamp

Fig 13: 100 μm wide layout on Ormostamp O2 plasma treated two days before

Another important remark is about the time variable regarding O_2 plasma treated surfaces. The pictures below show the same 100 μm wide layout with the same 25 μm drop spacing printed on Ormostamp surface treated with O2 plasma 10 minutes before (fig.12) and on Ormostamp surface treated two days before (fig.13). Significant increase in line width was noticed.

3.2) Sintering Optimization

To form a conductive printed pattern, the printed ink must be sintered to create continuous connectivity and thus percolating path. Sintering is a process of welding particles together at temperatures below their melting point. [1]

The required ink sintering temperature by the recommended in the datasheet is 250°C. Heating Ormoprime/Ormostamp at this temperature changes its colour from transparent to slightly yellowish. We noticed that it is Ormoprime, the primer used to improve Ormostamp adhesion to glass, which is changing the colour. This suggests other possible changes in the polymer that may compromise the final objective of the device, for example, the shrinkage or surface roughness. The optical image in Fig. 14 shows four microchannel patterned Ormostamp samples with printed and sintered silver lines. The bottom right sample is yellow-coloured sintered at 250°C.
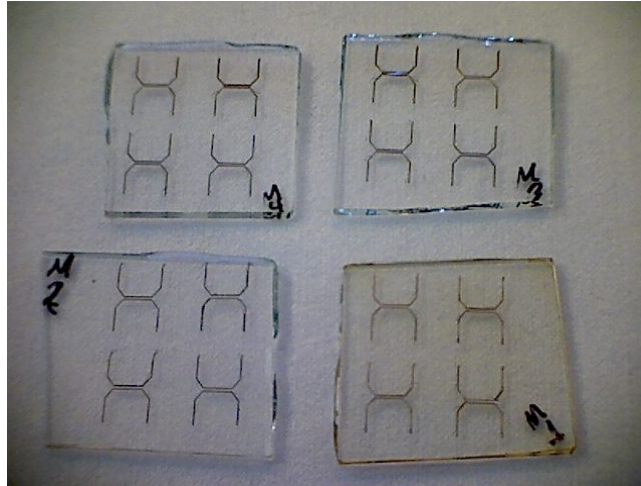
Fig 14: Ormostamp coated patterned samples with inkjet printed and sintered silver ink lines

In order to test the possibility to sinter the ink at lower temperatures the samples were sintered at 3 different temperatures: 120°C, 200°C and 250°C.

Two point- resistance measurements were performed on the printed lines. The values of resistivity achieved after sintering different samples at different temperatures are reported in tables 3.1 and 3.2. Each sample contained several lines patterned. Each column in the table represents a sample, while each line in the table represents a singular line where the measurement was taken.

	Sample 1 **120°C** **(1h)** Ω.cm	**Sample 2** **120°C + 150°C** **(1h)** Ω.cm	**Sample 3** **200°C** **(40min)** Ω.cm	**Sample 4** **200°C** **(40min)** Ω.cm
Line 1	3,99E+03	1,76E-04	8,42E-05	1,44E-04
Line 2	3,17E+03	6,64E-04	9,52E-05	1,32E-04
Line 3		1,13E-04		1,39E-04
Silver ink resistivity: 3E-6 Ω.cm ; Bulk Silver resistivity: 1,6E-6 Ω.cm				

Table3.1: Samples sintered at different temperatures. Each column represents a sample while each line a measurement

	Sample 5 200°C (40min) Ω.cm	Sample 6 200°C (40min) Ω.cm	Sample 7 250°C (35min) Ω.cm	Sample 8 200°C + 250°C (40 min) Ω.cm
Line 1	2,90E-04	Non conductive	8,39E-05	6,81E-05
Line 2	4,48E-04	Non conductive	9,59E-05	
Silver ink resistivity: 3E-6 Ω.cm ; Bulk Silver resistivity: 1,6E-6 Ω.cm				

Table3.2: Samples sintered at different temperatures. Each column represents a sample while each line a measurement

The sample sintered at 120°C had 9 orders of magnitude higher resistivity value compared with the expected resistivity value of the ink. Hence, the sample was heated again for 1h at 150°C. The resistivity after this treatment increased 7 orders of magnitude. The samples sintered at 200°C and 250°C had initially similar resistivity values ranging from (8 – 9) E-05 Ω.cm. However, after repeating the sintering experiment at 200°C, the results revealed that the resistivity is not reproducible at this temperature. Hence, even though large grains are formed in the structure at 250°C and the colour of the sample changes, it is still possible to achieve values of resistivity which are close to the expected ink resistivity values and fit the purpose of this project.

We conclude that 250°C is a minimum temperature needed to sinter silver lines printed on Ormostamp.

The surface texture of the sintered silver lines also changes depending on sintering temperature. SEM pictures of pictures sintered at different temperatures were taken and are presented in the Figures 15-17.
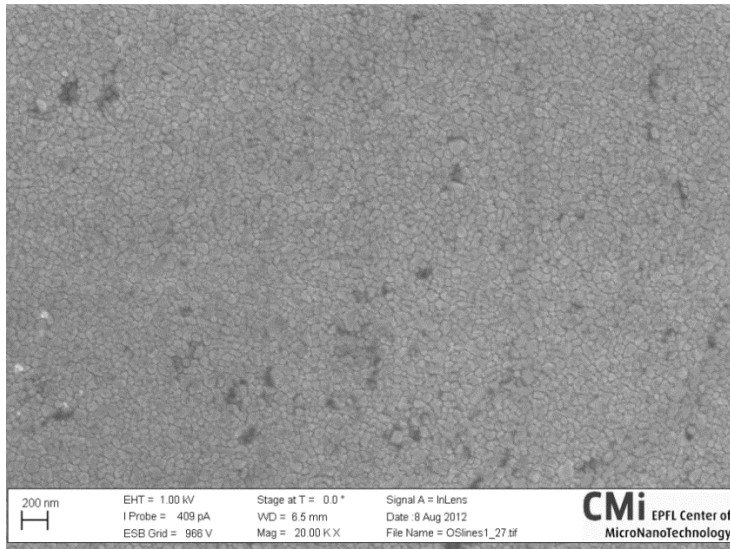
Fig 15: O2 plasma treated
Ormostamp sintered at 120°C +
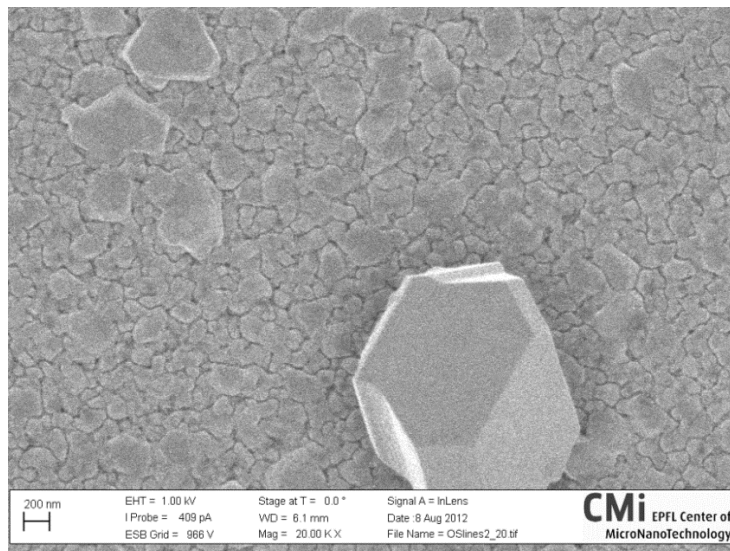150°C for 1h each

Fig 16 : O2 plasma treated
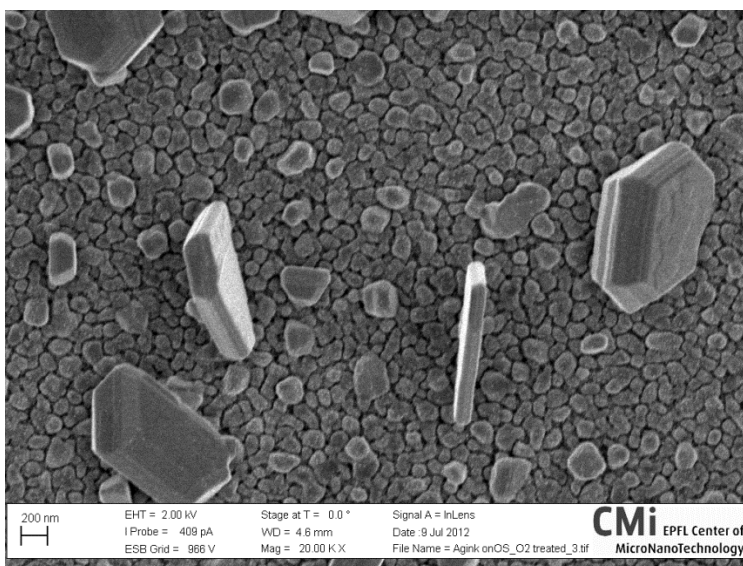Ormostamp sintered at 200°C for 40
minutes

Fig 17: O2 plasma treated
Ormostamp sintered at 250°C for 35
minutes

As it can be noticed, for the structures printed in Ormostamp there was the formation of numerous large grains when sintered at 250°C. One possible explanation for such effect could be the fact that hard baking process of Ormostamp preparation was not applied. The hard baking temperature is 130°C, therefore while sintering at a temperature higher than that two phenomena are happening at the same time: hard baking of the polymer and sintering of the nanoparticles. Surface changes in the polymer below the printed lines might affect the sintering of the ink nanoparticles. The temperature of 120°C was chosen in order to study if the formation is due to hard baking of the polymer. SEM pictures of the sample heated at 120°C for 1h and heated again at 150°C for 1h revealed dark spots, non-conductive areas. No large grains were formed, which means that the formation of large grains was not related to the hard baking of the polymer.

3.3)   AgCl formation and fluidic characterization

In order to create a AgCl layer over the sintered Ag patterns, a chemical oxidation treatment with aqueous 50mM $FeCl_3$ followed by rinsing with DI water was chosen. This process was preferred over HCl electrochemical anodization by B.J. Polk et.al [11] upon the justification that chemically oxidized electrodes tended to have more ideal Nernstian response in solutions of different chloride ion concentration. Additionally, the AgCl layer achieved by Polk et.al after 50s oxidation were around 100 nm thick, which is suitable for the dimensions required for < 1 µm thick silver lines made using inkjet printing.

This process was first tested using silver lines printed on in a silicon substrate. Silicon was chosen due to the fact that more smooth lines are formed on this substrate in order to check the formation of the AgCl layer and evaluate its thickness. Fig.18 shows cross section of Ag/AgCl lines. The thickness of AgCl achieved with 50s oxidation was around 230 nm, as shown in fig. 18.
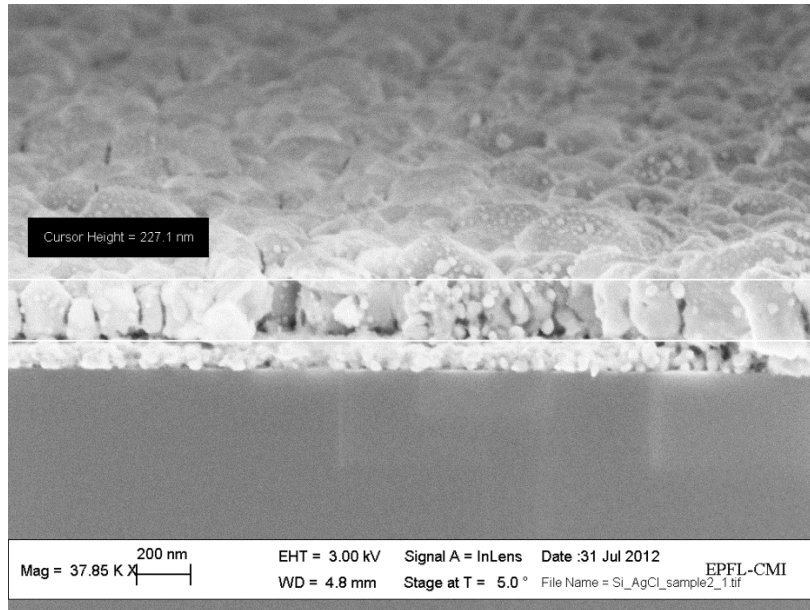
Fig 18: Ag/AgCl line cross section on silicon substrate

In order to study the fluidic resistance of the fabricated electrodes and optimizing the treatment time, arrays of 750 - 950 nm thick Ag lines printed and sintered were treated with $FeCl_3$ for time 30s, 50s and 70s. Fig. 19 shows an optical picture of the Ag (left) and Ag/AgCl (right) lines achieved after chemical oxidation with $FeCl_3$.

Fig 19: Ag/AgCl electrodes (right, dark colour) formed after chemical treatment with $FeCl_3$ over Ag lines (left)

The electrodes were tested by simply placing a well-defined (using micro-pipette) volume droplet covering two fabricated electrode lines and measuring their conductivity in different KCl solution concentrations. Attention was also made to place each drop covering the same area for all the measurements so that the measured values of conductance could be comparable. Taking into account the drop placement uncertainty the error of 25% in the conductance value was considered.

The drop placed on the lines was stable and had an evaporation rate low enough to make it possible to perform the measurements without taking into account the evaporation of the drop. Additionally, hydrophobic surface of Ormostamp allowed the drop to be fixed in place and not spread over the lines changing the electrode coverage area.

A ramping from -0.5V to 0.5V was performed in order to determine the conductance different concentration solutions of KCl. The values of conductance obtained for the three different fabricated electrodes prepared after AG reduction in $FeCl_3$ for 30s, 50s and 70s are showed in fig. 20. The results for the Mettler Toledo standard electrode were also plotted as a reference. Since the areas of the fabricated and standard electrodes are different, the change of conductance in different KCl concentrations is expected follow the same law.
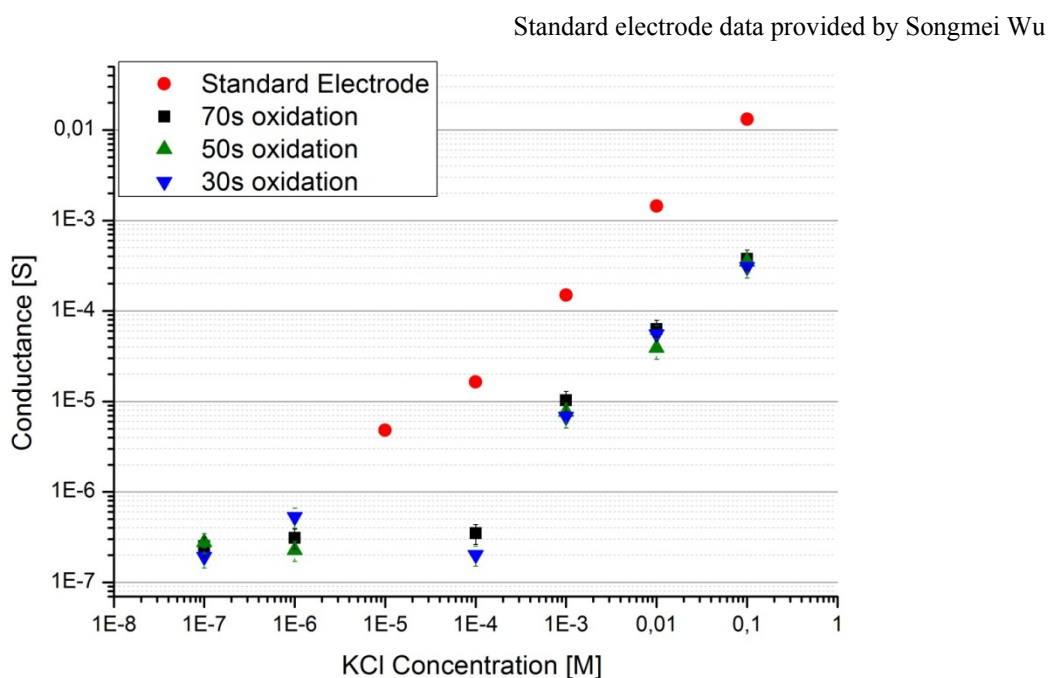

Fig 20: Fluidic measurement results for the three different fabricated electrodes compared with standard electrode performance

It can be seen from the graph that the fabricated electrodes are able to measure accurately higher concentration solutions, namely above 10^{-3}M KCl. However, the trend fails for low concentrations below 10^{-3}M KCl.

During the use of the electrode, the AgCl layer is consumed and material is transferred from one electrode to another, as shown in fig.21.

Fig 21: Ag/AgCl lines electrode after usage

Therefore, in order to have longer electrode life time, the best performing Ag/AgCl should be thick, having enough of Ag layer underneath for conductivity. However, due to the large error bar in the measurements, it is not possible to determine whether the very similar behaviour between the electrodes is due to the fact that the oxidation process already achieved its self-limiting limit at 30s oxidation or not. Therefore, one interesting experiment would be to increase significantly the oxidation time during AgCl formation (around 2 min, for instance) in order to see whether the process will achieve its self-limiting limit at a certain point, and so provide the longer life time possible for the electrode fabricated by method, or if all the Ag pattern will get corroded before it achieves it.
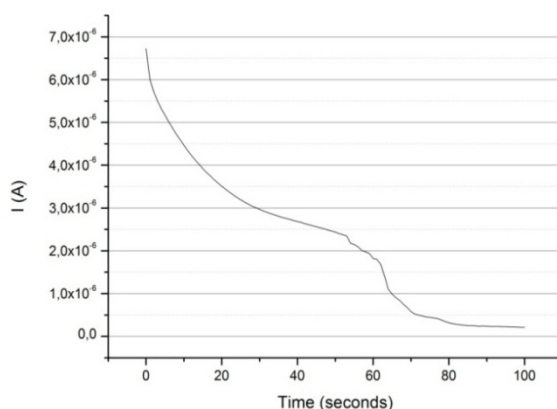

Fig 22: 0.5V continuous voltage applied to the Ag/AgCl electrode after 50s FeCl$_3$ oxidation.

3.4) Ag/AgCl lines in microchannels

Once the Ag line printing, sintering and oxidation conditions were optimized, Ag lines were inkjet patterned into the microchannels fabricated in Ormostamp. The fig.23 shows a layout of the channels and an optical picture of the Ag lines printed in 300 µm wide channels and sintered at 250°C.
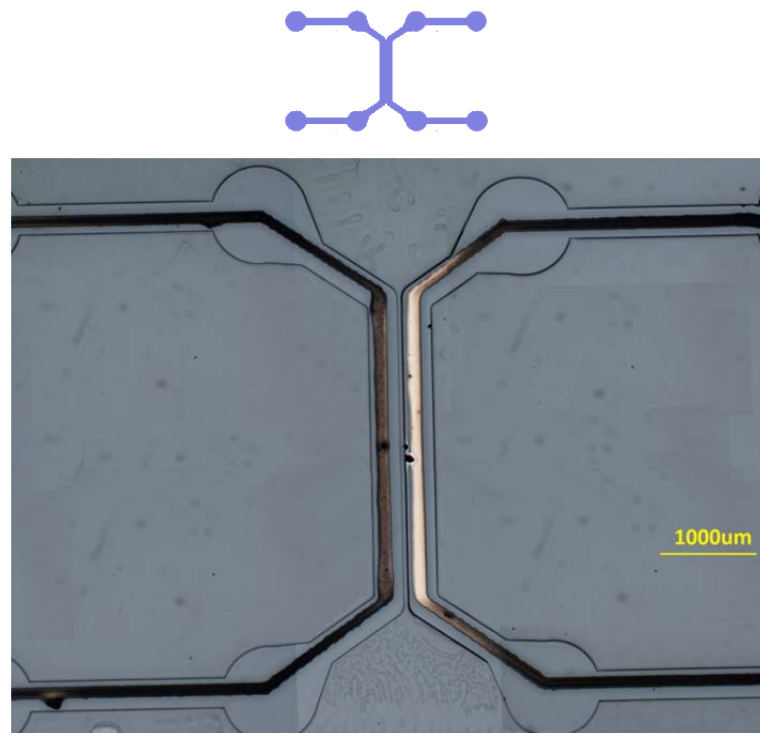

Fig 23: Ag patterns printed inside a 300µm wide channel. The thin contour marks the microchannel walls.

Resistance measurements were performed on the Ag lines. Both, left and right, wires were conductive. The resistivity and dimensions of the lines are reported in the table 3.

	Resistivity	**Width**	**Height**
Left line:	8,86E-05 Ω.cm	116 µm	1,75 µm
Right line:	6,99E-05 Ω.cm	129 µm	2,4 µm

Table3: Resistivity and profile of lines printed inside the microchannel

Further on, the same chemical treatment with aqueous 50mM FeCl$_3$ was performed in the microchannels order to form a layer of AgCl on the Ag patterns. For this purpose, a drop of 50mM FeCl$_3$ solution was placed over an area of the Ag microchannels. Hydrophobic surface of the Ormostamp make it possible to obtain a stable and well-fixed drop in a certain position of the sample, with no sliding into the channels or capillary driven flow.

Fig.24 shows the AgCl formed over a part of the Ag patterns. The picture seems brighter compared with previous because the sample needed to be illuminated so that the AgCl formation border could be visible since the Ag patterns were quite dark.
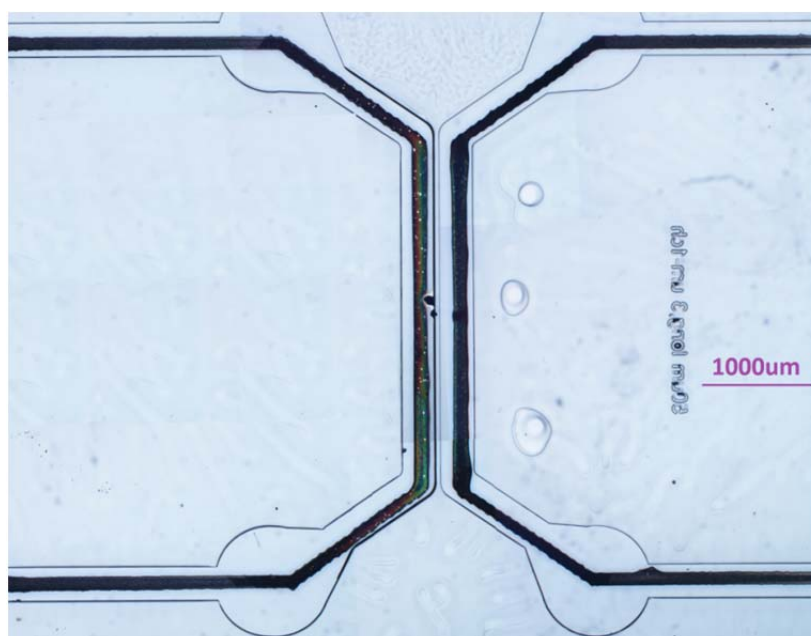

Fig 24: Ag/AgCl electrode fabricated in the microchannel

Moreover, the same fluidic measurement described in the previous section at different KCl solutions was performed using the electrode fabricated into the microchannels. The results are shown in fig. 25
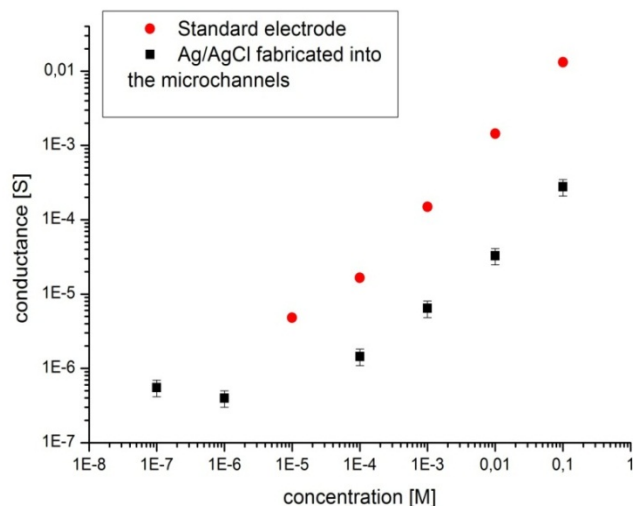
Fig 25: Fluidic measurement results for electrodes fabricated inside microchannels compared with standard electrode

The quality of the Ag/AgCl electrodes fabricated in the microchannels was better compared with the quality of the line electrodes fabricated in the previous section because in the case of microchannels the electrodes are able to measure accurately solutions above 10^{-4}M KCl, while the electrodes from previous section were able to measure accurately only solutions above 10^{-3}M KCl. One possible reason for such improvement can be the fact that the lines printed inside the microchannels were about 2 times thicker (1,75-2,3 μm) with respect to the thickness of Ag/AgCl electrode lines studied earlier, 750nm-950nm. However, it is still not sensitive to low concentration solutions, namely below 10^{-4}M KCl in the case of the microchannels.

Important remark: during the electrical measurements of the Ag patterns inside the microchannels it has been observed that, in order to achieve conductive patterns, the lines cannot touch the walls of the microchannels, even if there is a sintered flat path connecting the line in the place where the pattern touches the wall. Touching the walls compromise the conductivity.

Fig 26: Ag line touching the wall of the microchannel compromise its conductivity

5) Conclusions

80-470 µm wide silver ink lines were printed on Ormostamp polymer and silicon in order to characterize their behaviour on both substrates and optimize printing and sintering conditions. The best sintered line at 250°C printed on Ormostamp had 6,8E-05 Ω.cm resistivity. Ag patterns were printed into 300 µm wide and 30 µm deep microchannels formed in Ormostamp. Oxidation in $FeCl_3$ was used to form double layer Ag/AgCl electrodes on flat and micro-patterned surfaces. Finally, fluidic measurements were made in different KCl solutions and the miniaturized Ag/AgCl electrode proved to function properly to measure ionic conductivity of Cl^- solutions.

6) Outlook

- Conductivity measurements should be repeated in fluidic cell
- Evaluation of AgCl thickness oxidation time analysis with SEM in order to achieve maximum thickness possible
- Test and optimize the miniaturized electrode stability with time
- Printing of thicker lines by changing drop spacing in Dimatix software to increase the performance of the electrode
- Factors affecting ink stability on Ormostamp needs to be studied

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Appendix I

Ag ink lines were printed on four different substrates: silicon, O_2 plasma treated silicon, Ormostamp and O_2 plasma treated Ormostamp (as described in section 3.1). Profile measurements of the lines before and after sintering were further taken in order to study their properties after sintering. The results obtained are reported in the table 4.

Profilometer measurements revealed that before sintering the profiles printed on the four different surfaces had a two-peaked shape, like shown in fig. 11. After sintering, the lines printed on surfaces not treated with O_2 plasma kept similar two-peaked profile, while the ones treated with oxygen plasma were smoothen after the sintering. Grainy structure was typical for Ormostamp while smooth structure was typical for silicon.

It can be noticed that the width of the lines stays the same after sintering while the height shrinks up to 2.5 times.

	Before sintering		After sintering	
	Width (µm)	Height (µm)	Width (µm)	Height (µm)
Silicon	192	1,3	194	0,5
O2 plasma treated silicon	133	1,4	127	0,6
Ormostamp	135	1,2-1,4	150	1,4
O2 plasma treated Ormostamp	138	1,3-1,6	150	0,8

Table 4: profile measurements of lines printed on 4 different substrates before and after sintering