Inkjet Printing and Argon Plasma Sintering of an Electrode Pattern on Polymer Substrates Using Silver Nanoparticle Ink

***Oliver Pabst*,[1,2*] Jolke Perelaer,[3*] Erik Beckert,[2] Holger Becker,[4] Ulrich S. Schubert,[3] Ramona Eberhardt,[2] Andreas Tünnermann,[1,3]**
[1] Friedrich-Schiller-University Jena, Institute for Applied Physics, Jena, Germany
[2] Fraunhofer Institute for Applied Optics and Precision Engineering, Jena, Germany
[3] Friedrich-Schiller-University Jena, Laboratory of Organic and Macromolecular Chemistry, Jena, Germany
[4] Microfluidic ChipShop GmbH, Jena, Germany
E-mail: oliver.pabst@iof.fraunhofer.de **&** jolke.perelaer@uni-jena.de

Abstract

Inkjet printing and plasma sintering of a silver electrode pattern on polymer substrates for applications in microfluidic systems is presented. The pattern consists of several finger electrodes and contact pads that exhibit lateral dimensions of 30 x 80 mm². The pitch between neighboring finger electrodes is 270 µm and the smallest linewidth of the finger electrodes realized is 90 µm. Commercially available silver nanoparticle dispersion is used as ink. The electrode layout is printed onto a cyclic olefin polymer (COP) substrate. Prior to printing the substrate is activated using argon plasma in order to ensure good wetting. The as-printed features are then sintered using argon plasma. This sintering technique enables sintering of the nanoparticles in a selective manner without heating the substrate above its glass transition temperature. Sintering times are in the range of 5 to 15 minutes and the resulting resistivity of the printed features is approximately 57 times the bulk silver value.

Introduction

Drop-on-demand inkjet printing as a production technology is rapidly developing. Using this technology, different materials can be applied onto various substrates in an additive way. Therefore, no masking is required which makes inkjet printing a flexible and low cost process in contrast to standard lithography based processes.

Inkjet printing of conductive tracks has been investigated during the last years extensively. As conductive features are crucial for the function of printed electronic devices, numerous research groups are working in this field.[1] Examples of printed electronic devices include printed RFID tags and organic thin film transistors (OTFT).[2] Research on OTFTs involves all-printed devices [3] as well as hybrid devices that are fabricated using both printing and lithography processes.[4] Other popular applications that are currently under investigation are printed solar cells [5] and organic light-emitting devices.[6]

The use of silver [7] and gold nanoparticle inks [8] for the formation of conductive features is well-known and such inks are commercially available from different suppliers. The use of copper nanoparticle inks has also been reported,[9] although the sintering of copper inks is challenging due to the formation of copper oxide. Inkjet inks based on metal nanoparticles allow relatively low sintering temperatures because the melting temperature of small metal particles depends on the size of the particles.[10] This leads to melting temperatures of nanoparticles that are significantly lower than the melting temperature of the bulk metal. However, if the tracks are thermally sintered this typically involves temperatures above 200 °C, which is not suitable for temperature sensitive polymer substrates like PET and polycarbonate.

Due to this restriction, different research groups have investigated alternative sintering methods. Sintering using argon plasma with a 13.56 MHz RF generator has been successfully reported for single conductive lines.[11] Other sintering methods include microwave sintering,[7] selective laser sintering,[8] electrical sintering,[12] and sintering using a pulsed broadband lamp.[13] In the work presented here, the use of argon plasma sintering is extended to a larger electrode pattern using commercial silver nanoparticle ink.

The electrode pattern that was printed is intended for use in microfluidic devices that employ chip-based electrophoresis. At present conductive patterns in such devices are typically created using standard lithography based PVD processes or thick film processes like screen printing.[14] Both of these approaches require masking of the substrate. We therefore investigate inkjet printing as a flexible and less const intensive alternative.

Experimental Details

For printing the conductive features a commercially available silver nanoparticle dispersion in a mixture of ethanol and ethylene glycol from Cabot Corp. (Cabot CCI-300) is used as ink. Diameter of the silver nanoparticles ranges from 30 nm to 50 nm and the ink contains 20 wt% of silver. Printing is done using piezoelectric printheads from Dimatix Inc. (Galaxy 256/30, nominal droplet volume 30 pl) controlled with a Dimatix Apollo II printhead support kit. Positioning of the printhead is realized using a six-axis robot (Kuka Roboter GmbH, KR 5 sixx R650). This robot exhibits a travel range of 650 mm with a positioning accuracy of 20 µm and allows for 3D printing of structures, while for the described layout only 2D printing is necessary. Furthermore, the large travel range allows for use of custom sample mounts and other equipment like a standard hotplate for printing on heated substrates. Communication between the robot and the printhead support kit is established with custom LabVIEW based software. The robot is mounted on a granite table equipped with air suspension to ensure mechanical isolation from external vibrations. Fig. 1 shows the printing setup.

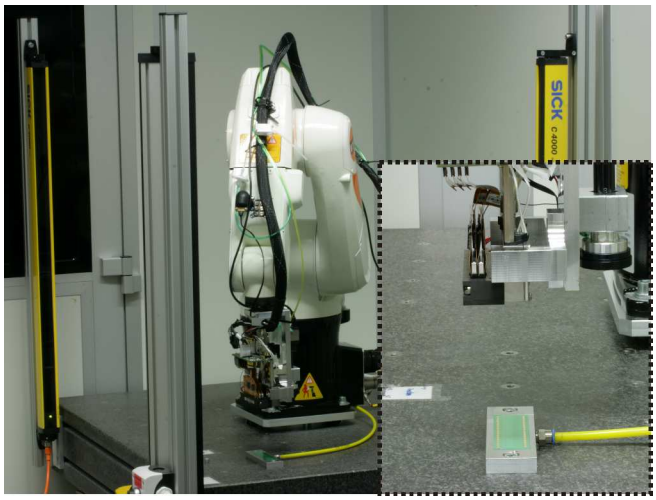

***Figure 1**. Dimatix printhead mounted on 6-axis robot, detailed view of printhead positioned over substrate holder (right).*

We have used cyclo olefin polymer (COP) foils as substrate material (Zeonor, thickness 200 µm). The glass transition temperature of these foils is 136 °C. In order to make sure that no residuals of the protective foil remain on the substrates we have cleaned them with isopropanol. Without any further pretreatment, the surface energy of the substrates is too low to ensure good wetting of the ink. Therefore, we have applied argon plasma activation prior to printing. The plasma chamber used for the activation (Plasma Finish Gmbh, Schwedt, Germany) is equipped with a 13.56 MHz RF generator. For the activation, relatively low RF power and short times were sufficient to enhance wetting. Typical parameters for the activation were RF powers in the range of 30 to 50 W, argon flow of 80 to 120 ml min^{-1} and activation times of 5 to 60 s. These parameters lead to a chamber pressure of approximately 30 Pa during activation. Contact angle of the activated substrates has been determined using de-ionized water as test fluid.

A sketch of the electrode pattern that we have printed is shown in Fig. 2. Such a pattern can be used for microfluidic chips that employ chip based electrophoresis. The layout consists of several contact pads and finger electrodes. The desired application puts the following requests on printed geometries: a finger linewidth of 70 µm is required; pitch between neighboring electrodes is 270 µm. A structure height of < 1 µm is favorable for further processing steps.

The printheads used are equipped with 256 nozzles and therefore allow for short processing times when multiple nozzles are used. For reasons of repeatability and amount of ink needed to purge the printheads we have printed the features with one single active nozzle. The electrode pattern is thus printed in several lines, process direction is indicated in Fig. 2. The image file is input into the software as a 1-bit tiff file. Each black pixel in the file corresponds to one droplet printed. In order to ensure reproducible printing conditions the ink reservoir is heated moderately to approximately 35 °C. Firing voltage of the printheads was set between 60 and 80 V with pulse durations of 10 µs. The drop spacing in process direction was varied in the range of 50 to 70 µm. With the velocity of the robot arm set between 5 and 10 cm s^{-1}, this corresponds to printing frequencies in the range of 0.7 to 2 kHz. The line pitch was varied between 50 and 100 µm.

After printing, the height of the unsintered features is measured using a white light interferometer from Zygo Inc. (New View 600). Selective argon plasma sintering is then applied with a 40 kHz plasma generator (Diener Electronic, Nagold, Germany). Plasma power was set to 150 W, typical sintering times were 5 to 15 minutes.

For the determination of resistivity, geometry and resistance of sintered structures are measured. The cross sectional area of the printed features is measured using white light interferometry. Length of the printed structures is determined using a microscope equipped with an encoded xy stage. Resistance of the printed lines is measured using a standard multimeter.

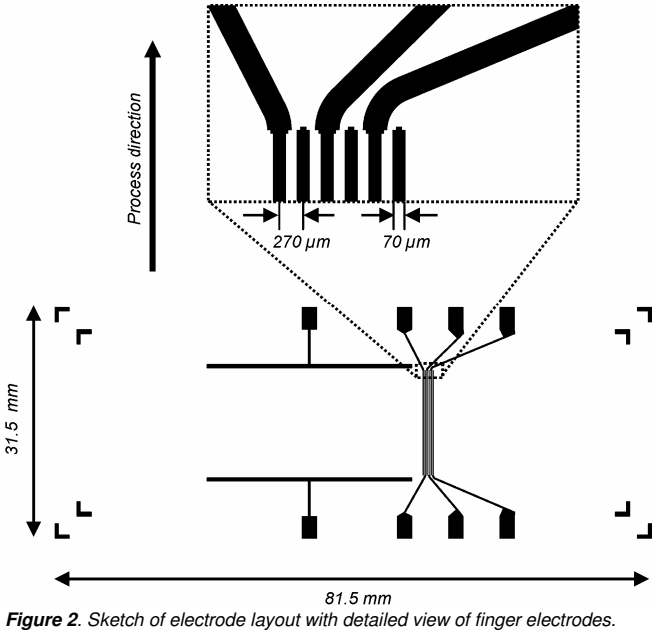

***Figure 2**. Sketch of electrode layout with detailed view of finger electrodes.*

Results and discussion

Fig. 3 shows the first version of the printed electrode pattern that we have realized. For this version, a 60 s plasma pretreatment of the substrate has been utilized, leading to a contact angle of approximately 40°. A printhead with nominal droplet diameter of 39 µm has been used. With this setup, a droplet spacing of 67 µm in process direction and a line pitch of 100 µm generated continuous lines without line bulging. Table 1 lists the detailed process parameters used for plasma activation, printing and sintering. Using these parameters the electrode pattern was successfully printed and plasma sintered as can be seen from Fig. 3. The different contact pads, alignment marks and capacitor structures were printed in the desired way and neighboring finger electrodes are not touching each other. The substrate material is not bent, the plasma treatment has thus not led to a heating of the substrate above its glass transition temperature. The height of the printed layers before sintering is 1.8 µm and approximately 200 nm after sintering. A profile plot of the finger electrodes is given in Fig 3. The finger electrodes have a width of

300 µm, which is clearly above the required value of 70 µm and not acceptable for the application in a microfluidic chip. Therefore, we have modified some of the process parameters.

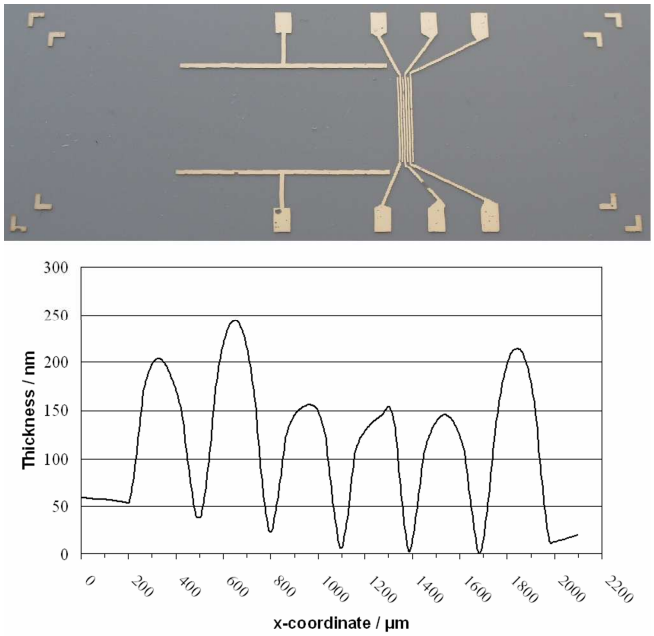

***Figure 3**. First version of inkjet printed and plasma sintered electrode pattern. Linewidth of finger electrodes is approximately 300 µm.*

As the spreading of the ink droplets on the substrate is determined by the surface tension of the ink and the surface energy of the substrate, we have modified the plasma pretreatment. Instead of 60 s of plasma treatment we have decreased the activation time to 5 s, which leads to a contact angle of 73° instead of 40°.

In order to further reduce the linewidth we have heated the COP substrate during printing to a temperature of 70 °C, which stimulates solvent evaporation during flight. This leads to smaller droplet volume and thus thinner lines. Fig. 4 shows profiles of single printed lines on a heated COP substrate.

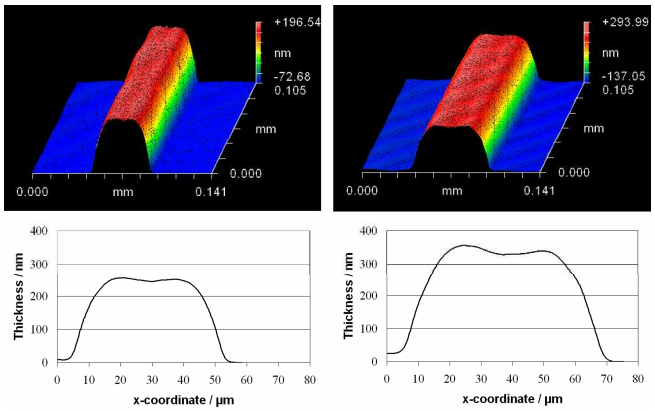

***Figure 4**. Profiles of lines printed on COP substrates heated to 70 °C. Firing voltage of the printhead was set to 60 V (left) and 80 V (right). Droplet spacing was 50 µm for both lines.*

In the left part of Fig. 4, the firing voltage of the printhead was set to 60 V, leading to a linewidth of approximately 50 µm, which is already too narrow for the desired application. We have therefore fine-tuned the linewidth by varying the firing voltage to 80 V. This leads to 70 µm wide lines as can be seen in the right part of Fig. 4. Alternatively, the droplet spacing can be altered to affect the line width.[15]

Using these optimized parameters we have printed and plasma sintered the complete electrode pattern. The result can be seen in Fig. 5. The different patterns were produced correctly. The linewidth of the finger electrodes is 90 µm, which is an increase compared to the single lines discussed above. A possible reason for this increase is a non-uniform temperature distribution on the surface of the hotplate, leading to lower temperatures at certain spots and thus to larger spreading of the droplets. Therefore, further optimization of the process parameters will be carried out in the future.

Table 1: Process parameters used for printing and sintering of the electrode pattern.

Parameter	Version 1	Version 2
RF power (activation)	30 W	30 W
Activation time	60 s	5 s
Contact angle	40°	73°
Droplet spacing	67 µm	50 µm
Line pitch	100 µm	50 µm
Substrate temperature	22 °C	70 °C
Firing voltage	60 V	80 V
Pulse width	10 µs	10 µs
RF power (sintering)	150 W	150 W
Sintering time	15 min	15 min

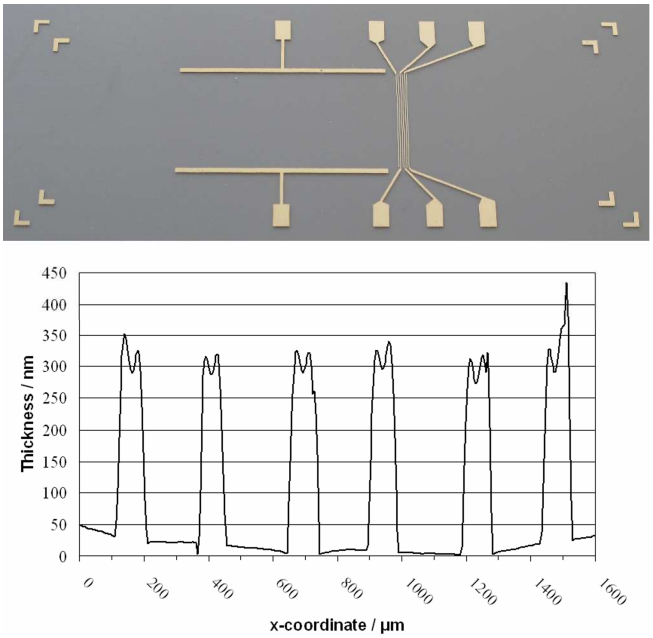

***Figure 5**. Improved version of inkjet printed and plasma sintered electrode pattern. Linewidth of finger electrodes is approximately 90 µm.*

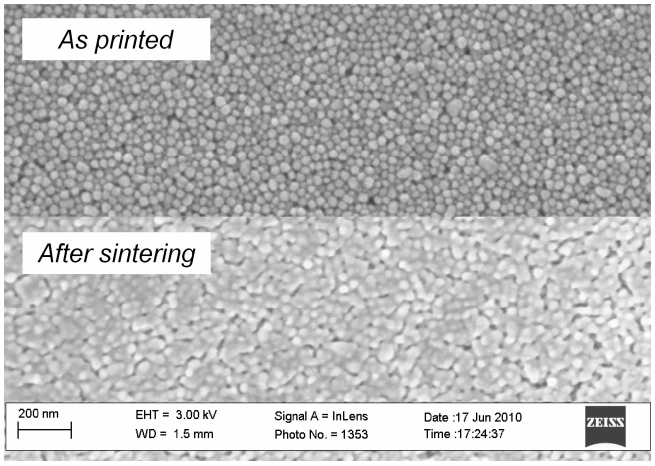

***Figure 6**. SEM images of unsintered Ag ink (upper part) and ink after 15 minutes plasma sintering (lower part).*

Fig. 6 shows SEM images of unsintered and plasma sintered ink patterns on COP. Before sintering, the individual nanoparticles with diameters of approximately 30 to 50 nm can be clearly distinguished. After 15 minutes of plasma sintering at 150 W RF power the nanoparticles have formed a coarse Ag structure. Grain and neck formation of sintered nanoparticles is visible, as well as some cavities. This sintering renders the printed structures electrically conductive. We have measured a resistivity of approximately 90 μΩ cm on the sintered pattern, which is 57 times the bulk silver resistivity. This was found to be sufficient for the desired application.

A simple tape-and-peel test has been performed to determine the adhesion of the sintered layers on the COP substrate. When applying standard office scotch tape on the sintered structures and after peeling off the tape, the sintered layers remain on the substrate without observable damage.

Conclusion

We have successfully printed and plasma sintered a larger electrode pattern on a polymer substrate. We have used commercially available silver nanoparticle suspension as ink. The linewidth of printed features was optimized between 70 and 90 μm by varying the firing voltage of the printhead and by heating the substrate. With these modifications we have printed the electrode pattern. We have shown that with the equipment used the desired resolution is possible, but still further optimization of the process parameters is necessary. Selective sintering was achieved by argon plasma exposure. This resulted in conductive features with a resistivity of approximately 57 times the bulk silver value in only 5 to 15 minutes. We have tested the adhesion of the printed features with a simple tape-and-peel test. A more detailed study on the adhesion is planned. In the future we also plan to test printing of the electrode pattern with a gold nanoparticle ink. This would be beneficial for specific applications where silver is not favorable due to its antibacterial behavior.

Acknowledgments

The work presented in this paper was part of the research and development project "Neuartige Analyse- und Überwachungstechnologie mit Querschnittcharakter" that is funded by the German Federal Ministry of Education and Research (BMBF), fund number 01RI0643, and managed by the Project Management Agency DLR (PT-DLR).

References

[1] M. Singh, H. M. Haverinen, P. Dhagat, G. E. Jabbour, "Inkjet Printing - Process and Its Applications", Adv. Mater., 22, 673 (2010).
[2] A. Dodabalapur, "Organic and Polymer Transistors for Electronics", Materials Today, 9, 4 (2006).
[3] C. W. Sele, T. Werne, R. H. Friend, H. Sirringhaus, "Lithography-Free, Self-Aligned Inkjet Printing with Sub-Hundred-Nanometer Resolution", Adv. Mater., 17, 997 (2005).
[4] J. Z. Wang, J. Gu, F. Zenhausern, H. Sirringhaus, "Low-cost Fabrication of Submicron all Polymer Field Effect Transistors", Appl. Phys. Lett., 88, 133502 (2006).
[5] C. N. Hoth, S. A. Choulis, P. Schilinsky, C. J. Brabec, "High Photovoltaic Performance of Inkjet Printed Polymer:Fullerene Blends", Adv. Mater., 19, 3973 (2007).
[6] M. Singh, H. S. Chae, J. D. Froehlich, T. Kondou, S. Li, A. Mochizuki, G. E. Jabbour, "Electroluminescence from Printed Stellate Polyhedral Oligomeric Silsesquioxanes", Soft Matter, 5, 3002 (2009).
[7] J. Perelaer, B.-J. de Gans, U. S. Schubert, "Inkjet Printing and Microwave Sintering of Conductive Silver Tracks", Adv. Mater., 18, 2101 (2006).
[8] S. H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Luscombe, J. M. J. Fréchet, D. Poulikakos, "All-Inkjet-Printed Flexible Electronics Fabrication on a Polymer Substrate by Low-Temperature High-Resolution Selective Laser Sintering of Metal Nanoparticles", Nanotechnology, 18, 345202 (2007).
[9] Y. Lee, J. Choi, K. J. Lee, N. E. Stott, D. Kim, "Large-scale Synthesis of Copper Nanoparticles by Chemically Controlled Reduction for Applications of Inkjet-printed Electronics", Nanotechnology, 19, 415604 (2008).
[10] Ph. Buffat, J.-P. Borel, "Size Effect on the Melting Temperature of Gold Particles", Phys. Rev. A, 13, 6 (1975).
[11] I. Reinhold, C. E. Hendriks, R. Eckardt, J. M. Kranenburg, J. Perelaer, R. R. Baumann, U. S. Schubert, "Argon Plasma Sintering of Inkjet Printed Silver Tracks on Polymer Substrates", J. Mater. Chem., 19, 3384 (2009).
[12] A. T. Alastalo, T. Mattila, M. L. Allen, M. J. Aronniemi, J. H. Leppäniemi, K. A. Ojanperä, M. P. Suhonen, H. Seppä, "Rapid Electrical Sintering of Nanoparticle Stuctures", Mater. Res. Soc. Symp. Proc., 1113 (2009).
[13] S. Farnsworth, I. Rawson, K. Martin, K. A. Schroder, D. Pope, "Evaluation of Tool for Processing Metallic Conductive Inks on Low Temperature Substrates", Proc. IMAPS, 001012 (2009)
[14] H. Becker, C. Gaertner, "Polymer Microfabrication Technologies for Microfluidic Systems", Anal. Bioanal. Chem., 390, 89 (2008).
[15] T. H. J. van Osch, J. Perelaer, A. W. M. de Laat, U. S. Schubert, "Inkjet Printing of Narrow Conductive Tracks on Untreated Polymeric Substrates", Adv. Mater., 20, 343 (2008).

Author Biography

Oliver Pabst is research assistant at the Friedrich-Schiller-University Jena and works at the Fraunhofer Institute for Applied Optics and Precision Engineering, Jena in the department of precision engineering. He studied Electrical Engineering at the Technical University of Berlin (TUB) and at the University of Massachusetts (Amherst, USA). He graduated from TUB with a focus on microsystems technology in 2008. His current PhD-research interests include inkjet printing of functional materials and piezoceramic actuators for applications in microoptical systems.