Intense pulsed light sintering and parameter optimization of various inkjet printed silver electrodes

Dana Weise[1], *Christoph Sternkiker*[1], *Reinhard R. Baumann*[1,2]

[1] *Institute for Print and Media Technology, Department of Digital Printing and Imaging Technology, Technische Universität Chemnitz, Chemnitz, Germany*
[2]*Fraunhofer Institute for Electronic Nano Systems (ENAS), Department Printed Functionalities, Chemnitz, Germany*

Abstract

Flexible and even stretchable electronic devices are showing more and more growth in interest in the field of printed electronics. Various kinds of material classes, like conducting, semi-conducting and insulating materials are used to manufacture multilayer devices, such as transistors and capacitors. One of the key components is the conductive layer, in the easiest way a resistor or contacts for diverse connections. Within the last years these metallic layers, e.g. silver copper or gold, were optimized regarding their morphological and electrical performance. On main step next to the printing process is the post-treatment, which forms in printed electronics a solid conductive structure out of the liquid printed films. New methods of selective sintering, using for example infrared (IR) radiation, microwaves or intense pulsed light (IPL) open the opportunity to form conductive metallic layers on even temperature instable substrates like polymeric foils. However, these post-treatment methodologies require detailed studies to obtain optimal results regarding the performance without damaging the base-substrates. For this purpose this research includes a detailed study on the novel method of IPL sintering technology. Various nanoparticle silver inks are inkjet printed on thin Poly(ethylene terephthalate) [PET] foil and post-treated with intense pulsed light to form conductive metal layers. It is shown, how to adjust the IPL flashing parameters depending on the silver ink to achieve highest conductivities without defects in the printed silver layers and the PET substrates.

Introduction

Printed electronic devises and its application in flexible electronics are of high interest in the resent years.[1] Here the conductive track builds on of the key component for the manufacturing of various devices like capacitors, transistors, resistors or contacts between various elements.[2] The demand for bendable and even stretchable thin substrates in combination with e.g. metallic printed films requires appropriate post-treatment methodologies, which are converting printed liquid metal films into conductive tracks without causing defects or damaging of both. The most known way to convert printed liquid patterns into solid functional films with the desired microstructure as well as electrical performance is a thermal treatment in e.g. ovens or on hotplates. Within this, solvents are evaporated, stabilizing additives and all organic parts are cast out and the metallic nano-particles (NP) merge together. In most cases high temperatures are required, which makes this process not suitable for thermal instable polymeric foils.[3] In order to achieve even on ultrathin, flexible and stretchable substrates, which cannot withstand high temperature treatments, desired electrical performances, the novel method of intense pulsed light (IPL) sintering is introduced.[4,5,6] This research includes a detailed study on the method of intense pulsed light sintering technology. The basic process, which is also known as photonic sintering, is demonstrated in figure 1.

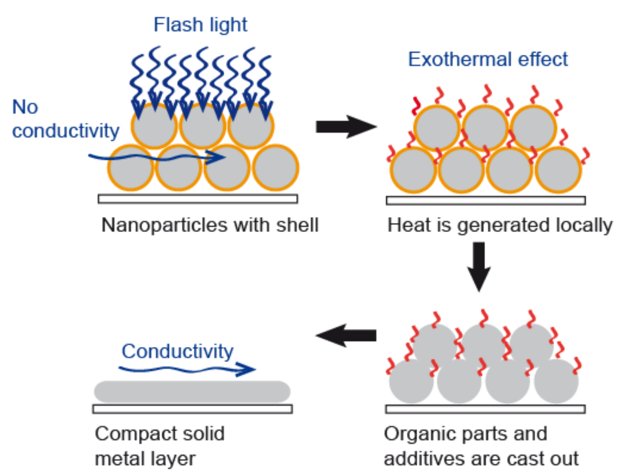

Figure 1. *Basic process of IPL sintering of an inkjet printed NP metal layer.*

By irradiating the samples with high intense light flashes only the dark NP metal ink films are selectively heated on the basis of light absorption. Polymer foils are due to their transparency not affected by the light and hence not heated. The process of photonic sintering is in the range of microseconds (µm) to milliseconds (ms). Even a drastic increase in temperature inside the printed metal layer only lasts for a few ms, which is theoretically too fast to affect the subjacent substrate. Nevertheless this heat impact has to be taken into account at the border of the heated metal layer and the polymer substrate.

In this work, various NP silver inks are inkjet printed on thin Poly(ethylene terephthalate) [PET] foils and post-treated with intense pulsed light to form conductive metal layers. The used silver inks require different sintering temperatures when it comes to a thermal treatment e.g. in an oven. Temperatures starting at 110 °C for the low sintering temperature ink up to 180 °C for the high sintering temperature ink. Based on this the goal of this research is a comparative analysis regarding the energy which is required in IPL sintering to from conductive layers. It will be demonstrated, how the IPL flashing parameters have to be adjusted depending on the used silver ink to achieve a high conductivity.

Materials and methods

Various kinds of nanoparticle silver inks were inkjet printed with the Dimatix Materials Printer 2831 (DMP) from Fujifilm Dimatix. The substrate is a Polyethylene Terephthalate (PET) foil (Melinex® 401) with 100 µm thickness from DuPont Teijin Films. The inks which are used for this research are specified in Table 1 below.

Ink name and company	Main solvents
SunTronic EMD5603 (SunJet)	Ethanediol, Ethanol
UTDAgIJ1 (UT DOTS INC)	Organic solvents (trade secret)
Sicrys I50T-11 (pvnanocell)	Tripropylene glycol mono methyl ether
Silverjet DGP-40LT-15C (Advanced Nano Products Co., Ltd	Triethylene glycol monoethyl ether

Table1: Overview to selected nanoparticle silver inks.

These silver inks are based on silver nanoparticles dispersed in various solvents and additives. Depending on the ink composition the sintering parameters of the IPL sintering will be adjusted and analyzed regarding optical and electrical performance. Therefore a set of patterns consisting of various sized squares (representing full patterns) as well as single pixel lines are printed on the PET substrate and dried at 80 °C. Flashing was carried out with the PulseForge 3200 from Novacentrix. The flashing parameters were varied according to each ink between 0.4 J/cm² (for 1 ms) and 1.4 J/cm² (for 1 ms). The optical analysis was performed with a light microscope and the electrical characteristics were determined by sheet resistance measurement, based on a 4-point probe system.

Results and discussion

Optical analysis

Microscopic images after photonic sintering for all four test inks are presented in Fig. 2. Presented are the silver electrodes with the respective minimum required flashing energy for which conductivity could be measured. As seen in Fig. 2a for the ink Silverjet DGP-40LT-15C conductivity was achieved with 0.41 J/cm² without causing visible defects. Only conspicuities are small in-homogeneities at the edges, caused from drying and solvent evaporation. Most homogeneous results could be achieved for the ink SunTronic EMD5603 with 0.41 J/cm² as well. The two other test inks Sicrys I50T-11 and UTDAgIJ1 require at least flashing energies of 0.82 J/cm² and 1.1 J/cm² respectively to obtain conductive silver electrodes. As visible in Fig. 2c and Fig. 2d these higher energies already cause minor defects at the edges, noticeable by the dark mark around the silver patterns.

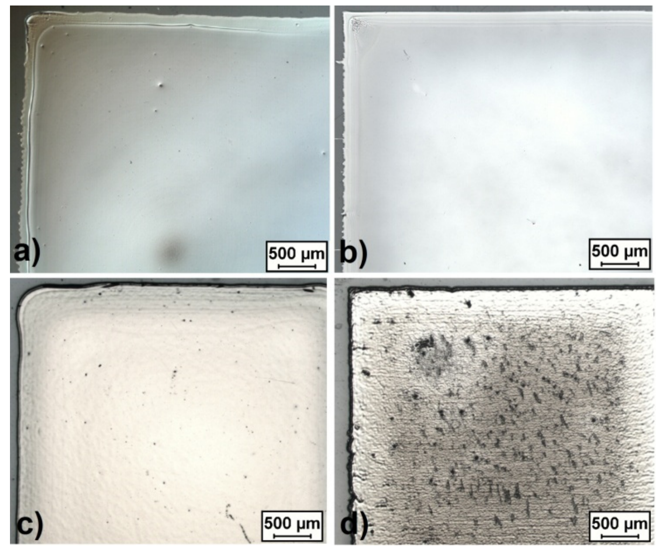

Figure 2. *Full patterns (squares, 5x5 mm²) printed with various inks and post-treated with the minimum intense pulsed light parameters required to achieve conductivity: a) Silverjet DGP-40LT-15C with 0.41 J/cm²; b) SunTronic EMD5603 with 0.41 J/cm²; c) Sicrys I50T-11 with 0.82 J/cm² and d) UTDAgIJ1 with 1.1 J/cm².*

The magnification of Fig. 2c and 2d, as presented in Fig. 3 shows the edges of the two inks Sicrys I50T-11 and UTDAgIJ1flashed with the high energies of with 0.82 J/cm² and 1.1 J/cm², respectively.

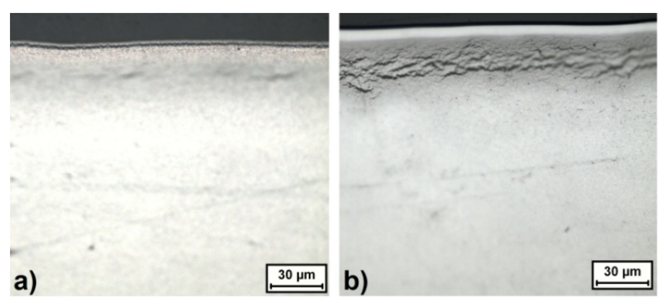

Figure 3. *Magnification of the edges from Fig. 2c and 2d: a) Sicrys I50T-11 with 0.82 J/cm² and b) UTDAgIJ1 with 1.1 J/cm².*

These high energies are required to achieve conductive patterns with these specific test inks; lower energies were not resulting in conductivity. However, such energies show a great impact on the silver layer as well as the substrate itself. Optically, these effects are seen as cracks along the edges of the silver layers (Fig. 3), mainly for the ink with the highest minimum required energy UTDAgIJ1 (Fig. 3b). Additional examinations with a surface profilometer (not presented here) have shown, that these cracks are not only in the silver layers but also in the substrate. Cracks with up to 3 µm depth into the polymer substrate could be measured and displayed. Such height differences have to be taken into account when it comes to printed electronic multilayer devices or contacting with other printed layers, e.g. for circuits.

The impact of the different flashing energies on very narrow lines is illustrated in Fig. 4. First of all it can be clearly seen, how various ink compositions with different rheological behaviors (e.g. solvent evaporation, surface tension and viscosity) define the line formation.

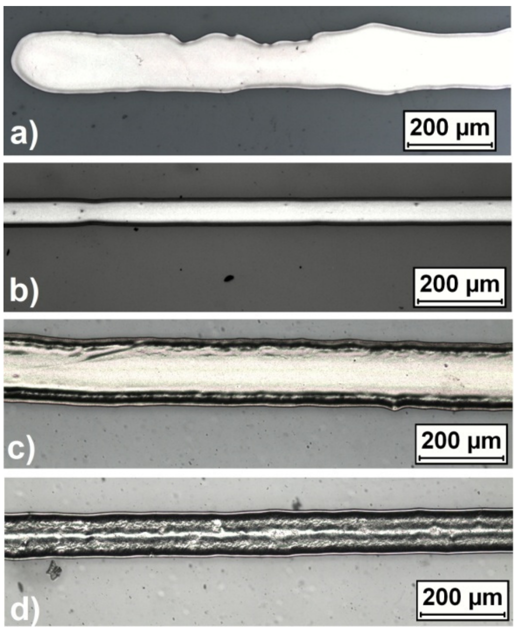

Figure 4. *Single lines (1 pixel) printed with various inks and post-treated with the minimum intense pulsed light parameters required to achieve conductivity: a) Silverjet DGP-40LT-15C with 0.41 J/cm²; b) SunTronic EMD5603 with 0.41 J/cm²; c) Sicrys I50T-11 with 0.82 J/cm² and d) UTDAgIJ1 with 1.1 J/cm².*

The inks Silverjet DGP-40LT-15C (Fig. 4a) and Sicrys I50T-11 (Fig.4c) result in widest lines compared to UTDAgIJ (Fig.4d) with slightly thinner line width and SunTronic EMD5603 (Fig. 4b) with the most narrow line width. For Silverjet DGP-40LT-15C with the lowest required flashing energies also for narrow lines no defects could be noticed. For SunTronic EMD5603 slight cracks could be detected at the edges, whereas again for Sicrys I50T-11 and UTDAgIJ (both high flashing energies) visible cracks and wrinkles are visible (especially visible at higher magnifications, not presented here).

Electrical analysis

As well as the sintering temperature in traditional oven or hotplate sintering, the applied energies in photonic sintering have a high impact on the electrical performance on the silver electrodes. As displayed in Fig. 5 each ink shows different sheet resistance at same flashing energies.

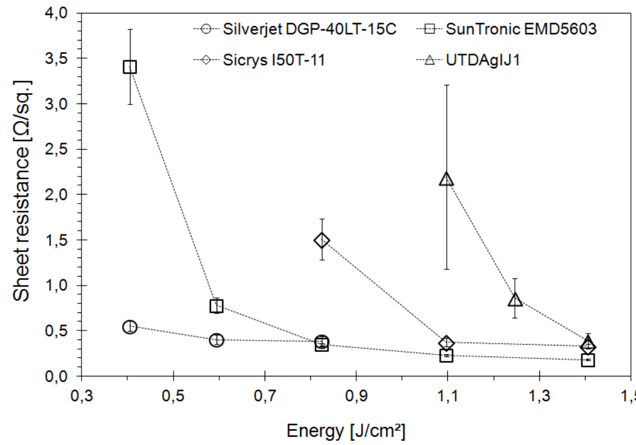

Figure 5. *Sheet resistance in dependence on flashing energies [J/cm²] for various nanoparticle silver inks.*

While the Silverjet DGP-40LT-15C reaches already a low sheet resistance of around 0.5 Ω/□ at energies of 0.41 J/cm², for other inks, like SunTronic EMD5603 the sheet resistance is still in higher range with 3.4 Ω/□. Additional the other two inks from this research were not conductive at all with this low flashing energies. The silver ink UTDAgIJ1 requires within this four test inks the highest flashing energy (1.1 J/cm²) to become conductive.

Reasons for such drastically differences in the electrical performance of these test inks are arising from the ink composition itself, amongst others this could be type, size and concentration of the nanoparticles, the addition of additives and the solvents (boiling point).

Summary

Within this research the dependency of the intense pulsed light (IPL) sintering method on printed metal films was presented. Four different nanoparticle silver inks where inkjet printed on a PET substrate and IPL sintered with various flashing energies. The dependency of the ink composition on the morphological and electrical characteristics was presented. It could be found that next to the differences in the layer formation, due to varying spreading behaviors, the fluctuation in the sheet resistance varies drastically within these four test inks. Whereas for one ink at a defined flashing energy (J/cm²) high conductive layers could be achieved, for the second ink the sheet resistance was still in a higher range and additionally for the two other test inks no conductivity could be achieved at same applied printing and sintering conditions. Each of the four inks required adjusted flashing parameters to achieve appropriate sintered and conductive silver layers. Based on the findings within this research it can be stated, that for each individual ink the optimized flashing parameters vary and need to be adjusted regarding the demands in electrical performance.

References

[1] H.W. Choi, T.L. Zhou, M. Singh, G. E. Jabbour, "Recent developments and directions in printed nanomaterials", Nanoscale vol. 7, no. 8, pp. 3338-3355, 2015.

[2] Singh, H. M. Haverinen, P. D. Dhagat, G. E. Jabbour, "Inkjet Printing—Process and Its Applications", Adv. Mater., vol. 22, pp. 673-685, 2010.

[3] J. R. Greer, R. A. Street, "Thermal cure effects on electrical performance of nanoparticle silver inks", Acta Materialia, vol. 55, no. 18, pp. 6345-6349, 2007.

[4] H. Kang, E. Sowade, R. R. Baumann, „ Direct Intense Pulsed Light Sintering of Inkjet-Printed Copper Oxide Layers within Six Milliseconds", ACS Appl. Mater. Interfaces, vol. 6, no. 3, pp. 1682-1687, 2014.

[5] J. Niittynen, R. Abbel, M. Mäntysalo, J. Perelaer, U. S. Schubert, D. Lupo,
"Alternative sintering methods compared to conventional thermal sintering for inkjet printed silver nanoparticle ink", Thin Solid Films, vol. 556, pp. 452-459, 2014.

[6] S. Wünsche, R. Abbel, J. Perelaer, U. S. Schubert, „Progress of alternative sintering approaches of inkjet-printed metal inks and their application for manufacturing of flexible electronic devices", J. Mater. Chem. C, vol. 2, no. 48, pp. 10232-10261, 2014.

Author Biography

Dana Weise obtained her masters in science (M.Sc.) at the Technische Universität Chemnitz (TUC) in Germany in 2013. She is working since 2013 as scientific researcher at the Department of Digital Printing and Imaging Technology at TUC. Her research topics include printed electrodes and resistors, inkjet printing and post-treatment methodologies, especially photonic sintering (intense pulsed light sintering). Currently she is working on her Ph.D. in the research field of photonic sintering of metal layers.