Ink Jet Printing of Conductive Silver Tracks from Nanoparticle Inks on Mesoporous Substrates

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Abstract

Conductive tracks are produced by ink jet printing of a commercial silver nanoparticle ink on different substrates. We observed that applying mesoporous coatings on the substrates resulted in metallic conductivity immediately after printing. The influence of the average pore size and some chemical parameters of the coatings were studied, as well as the thermal treatment after printing. We found that using substrates with slightly acidic cationic coating and small pore sizes of about 15 nm resulted in the highest conductivity for the given ink even without any thermal treatment applied. Another crucial parameter found was the smoothness of the surface, which was estimated by the surface gloss. After drying / "sintering" of the printed tracks for 9 min at 100 °C in an oven a specific resistance of 13 µΩ·cm (about eightfold that of bulk silver) could be achieved using a commercially available substrate. This is a significant higher value than recently reported conductivities obtained after heating to much higher temperatures. Additionally, some chemical post treatment of the prints by aqueous solutions can be applied for a further increase in conductivity. Furthermore, samples produced were exposed to "photonic sintering" equipment to assess the potential of this technique for inline post-processing of metallic structures on porous substrates.

Introduction

A major challenge in printed electronic applications is the production of conductive tracks for connecting / "wiring" of individual printed components. Low resistivity of the connections is essential in most cases to avoid energy losses and to operate devices at low voltages. Presently, there are no other efficient materials but metals available for wiring.

Commercially available ink jet printable stable inks of metals are commonly based on silver, as silver is not oxidized in air and silver inks are therefore processable in normal atmosphere. The silver in jetable inks is present in the form of nanoparticles. After printing, the prints have to be heated to temperatures of 150°C or higher for several minutes or even hours to achieve metallic conductivity of the printed area, which is believed to cause sintering of the individual nanoparticles to a solid silver layer. The need for heating limits the choice of usable flexible substrates.

Some recent studies [1, 2] indicated that much shorter sintering time and lower temperatures are needed when silver nanoparticle inks are printed on special porous substrates instead of foils or a special chemical treatment [3] is applied to the printed structures after drying. To explore the main factors and mechanisms for low temperature "sintering" this study was started.

Experimental

Ink jet printing of silver structures was done using a Fujifilm Dimatix Materials Printer (DMP) 2800 with 10 pL nozzle cartridges and Silverjet DGP 40LT-15C ink from ANP. The test lines were 0.5 mm in width and 20 mm in length, with larger and thicker contact pads on both sides. A dot spacing of 20 µm (1270 dpi) was used. The printed pattern is shown in figure 1.

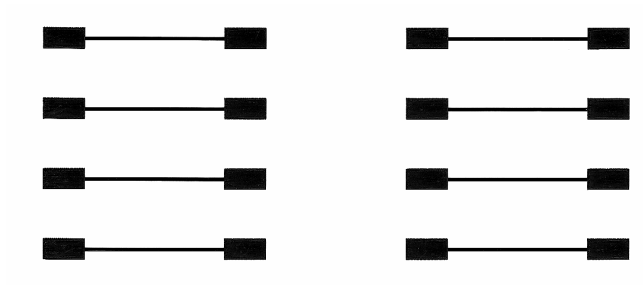

***Figure 1**. Ink jet printed test pattern used for resistivity measurements*

From the droplet size the thickness of the silver lines was calculated (assuming compact silver) to 1.1 µm (laydown 11.6 g Silver/m²). However, a gravimetric calibration showed that at the chosen ink drop speed of 7 m/s the real drop volume was significantly lower than 10 pL, resulting in a real silver laydown of 8.3 ± 0.1 g/m², and a compact silver thickness of 0.79 µm.

Resistivity measurements were performed by the four-probe (Kelvin probe) method to overcome any contact problems. The resistance was, unless otherwise mentioned, measured after 3, 6, 9 and 12 minutes of drying at 70 °C.

The substrates investigated were all based on resin (polyethylene) coated paper with an additional layer of mesoporous material. A commercially available material from Felix Schoeller ("p_e:smart" Type 3) was taken as a reference. This material also contains a mesoporous coating on resin coated paper. For the experimental substrates, different coating formulations based on various boehmite type alumina as well as fumed silica pigments and polyvinyl alcohol as a binder were applied to the resin coated paper by manual wire rod coating and dried in an oven.

Additional samples for photonic sintering were produced using Xaar126 50 pL printheads using the commercial material ("p_e:smart" Type 3) at resolution of 360 dpi. Samples were prepared without heating the substrate at a feedrate of 0.2 m/s.

Results

Porous Versus Non-porous Substrates

In figure 2 a (left), a print on the resin coated paper base itself (with a primer layer on top) as a substrate is shown, whereas figure 2 b (right) shows the same printing on the “p_e:smart” Type 3 reference substrate. The pictures clearly show the advantage of an absorptive coating regarding lateral resolution of the print. Furthermore, the absorptive coating lead to much lower resistivity of the printed line directly after printing and after temperature treatment at 70 °C, as shown in figure 3.

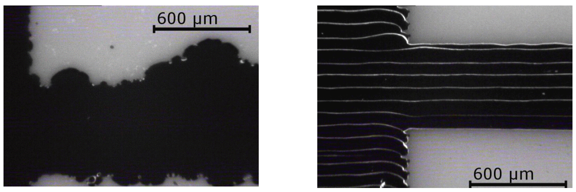

***Figure 2**. Optical micrographs of printed silver patterns, a (left): Non-absorptive substrate, b (right): Absorptive mesoporous reference substrate.*

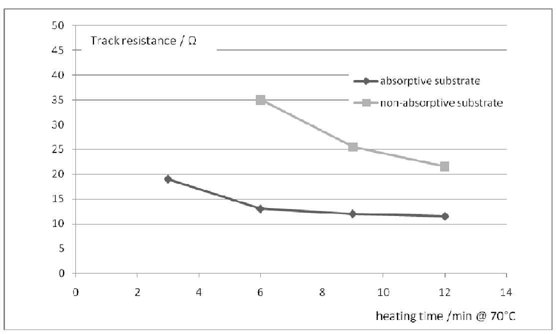

***Figure 3**. Resistance of silver lines printed on absorptive and non-absorptive substrate*

Effect of Pore Size

Coatings with a series of boehmite type alumina pigments with five different primary particle sizes were applied on the resin coated paper base. The resulting pore diameters were determined using mercury intrusion porosimetry (Porotec PASCAL 140/440). Depending on the pigment used, we observed average pore diameters between 8.2 and 32.2 nm.

On this substrate sample series, silver tracks were printed as described above, and the resistance of the tracks was determined after 6 and 12 minutes drying time at 70 °C. The measured resistance as a function of the measured average pore size in the substrate coating is shown in figure 4.

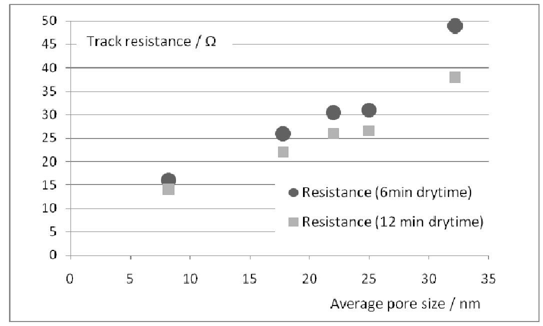

***Figure 4.** Resistance of silver lines as of function of the average pore size of the coating*

From figure 4 can be seen that there is a continuous decrease in track resistance with pore diameters below 25 nm, and the effect of increased dry time is low. However, when the pore size exceeds 25 nm, the resistance increases steeply, and the effect of dry time is more pronounced. Although the particle size of the silver nanoparticles is not disclosed by the ink manufacturer, it is believed to be in the order of some 10 nm, so this observation can be explained by the mechanism given in [1].

Effect of Substrate Smoothness / Gloss

In several lab coatings, defects in the coating could be observed. Typical defects are shown in figure 5. It is very likely that such defects can increase the resistance of the printed silver tracks, which are below 1 µm in thickness.

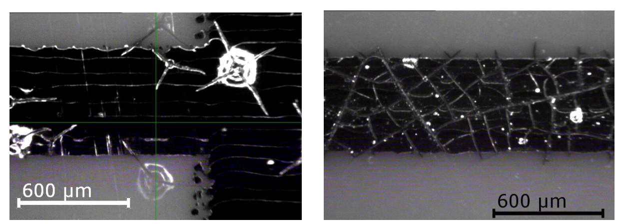

***Figure 5.**Typcal defects (“cracking”) observed in lab scale coatings.*

Beside these defects, we suspected that our lab scale coatings may have a less smother surface than industrial coatings. An easy way to characterize the smoothness of the substrates at spatial frequencies in the order of the wavelength of light is the 60° gloss value, which we took as an indicator for surface quality. In figure 6, the resistance of two lab scale and one industrial coating, all with the same coating formulation, is given as the function of 60° gloss.

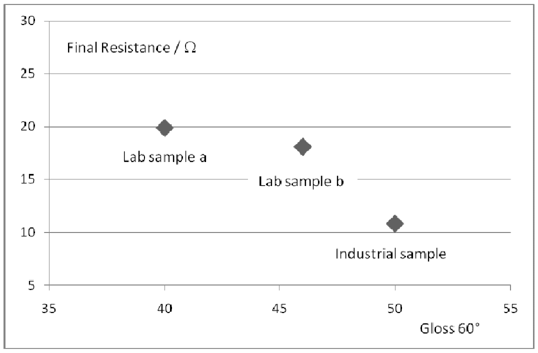

Figure 6. *Effect of surface smoothness, expressed as gloss value at 60°, on the final resistance of silver tracks.*

From figure 6 can be concluded that surface smoothness is a major factor to achieve low resistance of inkjet printed silver. Therefore, only sample substrates showing the same surface quality should be compared. Generally the surface quality of industrial coatings was found to be much better than that of lab samples, mainly due to better control of the process and the drying conditions.

Increased Drying / Sintering Temperature

In order to speed up the observed reduction of the track resistance during drying at 70 °C, the drying temperature was increased to 100 °C, which is still well below to boiling point of the ink solvent (triethylene glycol monomethyl ether, 256 °C). For the reference substrate (industrial coating, p_e:smart type 3) we found that the decrease in resistance is faster and completed after 5 minutes, and a final resistance of 7.3 ± 0.1 Ω is reached, compared to 10.8 ± 0.5 Ω which is reached after 12 min at 70°C.

Chemical Post-Treatment

There are hints from literature [3] that treating inkjet printed silver lines with salt solution may further help to decrease the resistance without heating at temperatures above 100 °C.

We treated the printed silver tracks with 1 mol/l aqueous solutions of sodium chloride, potassium chloride, ammonium chloride, ammonium sulfate and sodium nitrate. After dipping the prints for 10 s into the solution, the samples were washed for 20 s in deionized water and dried. No significant change of resistance of the silver tracks was found after this treatment, which may be due to the fact that we used already partially "cured" samples. However, an approximately 30% decrease in resistance was observed after a very short (1 second) treatment in sodium or ammonium thiocyanate solutions, which are known to form soluble complexes with silver. It seems that the merging of the individual silver nanoparticles to a compact layer can be promoted by such a treatment, but this is very difficult to handle, as the silver tracks completely were detached by the thiocyanate solutions within several seconds.

Photonic Sintering

Sintering experiments were conducted using a Xenon Corp. Sinteron 500 System equipped with a Cerasil lamp, which reliefs the UV dose. An oval reflector was used in order to be able to alter the energy density by changing the focus onto the printed substrates.

Figure 7 clearly illustrates the influence of the focal length of the used reflector. Optimum cure with singles flashes was found to lie within 1.5 inch to 2 inch from the casing of the lamp, which did not coincide with the specified focal length provided by the supplier. Optimum resistivity values were 5.5 Ω/cm for a single pixel and 3 Ω/cm for double pixel lines. The behavior of the resistivity curve can be understood by the morphological changes of the silver deposits as a result of the applied energy. At large distances, e.g. the substrate with the functional material being strongly out of focus, not enough energy is applied to the sample to reach maximum compaction and grain growth. With better matching to the focus of the illuminator, more energy is supplied to the deposit, which in turn is converted into thermal energy. This high temperature with a very short rise time, enables significant grain growth [5] and, therefore, reduction of resistive losses in the neck between two particles. In focus the thermal energy peaked the thermal stability of the material and substrate deformation was observed.

Sheet resistances were recorded for three different doses and exhibited a rapid decrease from 400 mΩ/□ at 2.5 inch to 200 mΩ/□ at 1.5 inch distance, however, with beginning deformation of the substrate around the metallic deposits.

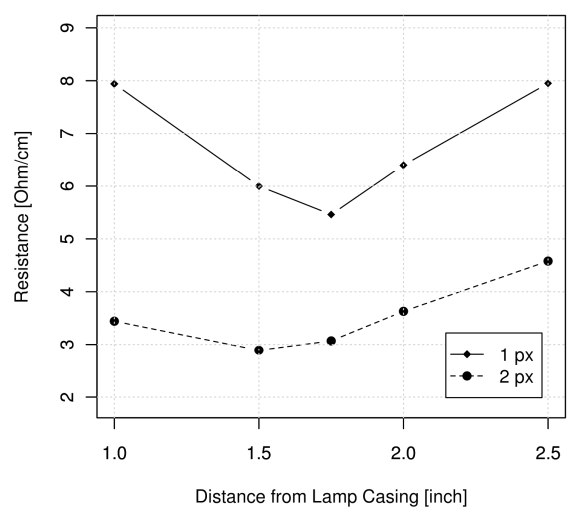

Figure 7. *Effect of focus on the electrical performance of the silver structure [SunJet UA5603, single layer, 360 x 360 DPI]*

While multilayer samples were prepared for this investigation, non of these could be sintered successfully, as adhesive failure between deposit and substrate promoted delamination. This effect is yet not fully understood, but is most probably attributed to the remaining solvent components in the deposit once the capillaries are saturated with solvent or an impermeable layer was formed by a preceding deposit. This suggests that thorough pre-drying of multilayer deposits is essential for the process to be successful.

Discussion and Conclusions

The transition of dispersed silver nanoparticles in the inkjet ink to a conductive silver track seems to involve several steps and processes.

First, the metallic particles have to be separated from the solvent or dispersion liquid, and thereby immobilized. When a mesoporous substrate is used with pore size less than the silver particle size, this can be achieved by a “filtration” process. If this filtration process is fast, a print with high accuracy is obtained, and no “coffee ring effect” is observed. Evaporation of the dispersion liquid is another possible way to immobilize the silver nanoparticles, but this process may be slower or demand elevated temperatures.

Second, the surface of the printed silver nanoparticles has to be cleaned from any insulating material to electrically contact each other. Such organic insulating materials are generally needed to stabilize the inkjet ink against sedimentation or coagulation of the silver nanoparticles before printing. We assume that a slightly acidic or cationic substrate coating can facilitate the detachment of the stabilizing molecules adsorbed to the silver surface. Experiments with anionic or slightly alkaline coatings showed much higher resistance of printed silver lines, as well as the need for increased curing temperature and time.

Third, the contact between the silver nanoparticles has to increase from point-like contacts to a porous network of fused particles, in the ideal case to a compact silver layer. In a recent paper [4] is clearly shown that this merging process occurs even at room temperature. We found for samples stored over a longer period at room temperature without a thermal drying treatment directly after printing that the resistivity decreases slightly with time even after several days.

It was furthermore shown, that alternative sintering techniques, such as photonic sintering can create results similar to those of convective oven sintering in a fraction of the interaction time. Resistivities were found to be approx. 5.5 Ω/cm for single pixel and 3 Ω/cm for two pixel wide lines, respectively. Sheet resistances for single silver layers on “p_e:smart” Type 3 were found to be 200 mΩ/□ at the onset of substrate deformation.

We conclude from our experiments that the most critical step toward inkjet printed silver tracks is the removal of molecules from the silver nanoparticle surface after printing. This step can be significantly supported by printing on mesoporous substrates due to the efficient removal of the ink dispersion liquid and much of the ink additives by a filtration process. Furthermore, a suitable chemical composition of the substrate surface promotes desorption of stabilizers adsorbed to the silver surface. A suitable thermal post-process may then be applied to convert this more optimal base into a percolation network with increased grain sizes for low resistance conductors.

References

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Author Biography

Anna Schuppert received her Master degree in material science from University Osnabrueck in 2010. This paper is largely based on her master thesis, which was sponsored by Felix Schoeller jr. She is presently working on her PhD thesis at the Max-Planck-Institute for iron research, Duesseldorf, Germany.

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Ingo Reinhold graduated in micromechanics-mechatronics with emphasis on print- and media technology from Chemnitz University of Technology in 2008. After joining Xaar’s Advanced Application Technology group in Järfälla, Sweden, he focused on advanced acoustic driving of piezo-type inkjet printheads alongside with pre- and post-processing of functional materials in digital fabrication. He is currently enrolled as a PhD student within the iPack VINN Excellence Center at the Royal Institute of Technology (KTH) in Stockholm, Sweden.

Wolfgang A. Schmidt, born 1954, holds a Ph.D. in inorganic and solid state chemistry from the University of Siegen, Germany. Presently, he is patents/IP manager at speciality paper manufacturer Felix Schoeller, Osnabrueck, Germany, also responsible for basic R&D and for R&D projects with external partners. His main focus is on imaging and printing media as well as on substrates for technical applications, e.g. printed electronics. His technological background is in the fields of paper coating, print quality, nano- and surface technology.