Improving quality of inkjet printed metal nano-particle conductors

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Abstract

During the last couple of years several ink manufacturers have presented metal nano-particle inks for inkjet printing. These inks provide low resistances on plastic and paper substrates, thus enabling manufacturing of high-conductivity conductors that could be used in circuit boards.

Inkjet printing of a commercial silver nano-particle ink on paper and plastic substrates has been investigated. The focus has been on making narrow lines and low resistance structures by varying substrate type, substrate temperature during printing and ink drop size.

It has been found that the metal nano-particle inkjet inks are suitable for making conductors. Also the inkjet technology itself is ready to produce fine details required in circuit board manufacturing.

Introduction

Inkjet printing is the only non-contact printing method which means that the printhead and substrate are in no contact during printing. This makes inkjet printing a substrate independent method i.e. it is possible to print on all kinds of substrates ranging from smooth to rough and even 3D surfaces. When printing electronics this is especially important since electronic devices may require components on very odd-shaped surfaces.

Printable conductive materials, especially metals, are very expensive. Material consumption in inkjet printing is relatively small compared to other printing technologies where several ink liters can go to waste even during set-up. In euros this can mean several tens of thousands and also less environmental loading. Inkjet printing also enables manufacturing of small volumes and even customized products, precise dosing of small material drops, layering of materials and easy integration of printing equipment into existing production lines.

Inkjet printing can be used for fabricating conductors, passive components and other circuit board components, transistors, display elements and RFID components from jettable solders, epoxies, conductive and semi-conductive polymers, metal particles and metal nano-particles, transparent conductors, dielectric and resistor materials as well as ferrite materials. The focus in this paper is on inkjet printing conductors with metal nano-particle inks.

Inkjet printable metal nano-particle ink

Ink development for inkjet printing is a challenging task because of strict demands on the jettable material. Besides correct viscosity and surface tension the particles present in the ink have to be below 1 µm in diameter and the ink has to be stable when in the printhead. This means that the particles are not allowed to agglomerate. Furthermore, the inks shouldn't sedimentate into the printhead walls, foam or dry into the nozzles. This makes it very difficult to develop inkjet printable conductive materials, but nano-particle technology has offered one solution.

In inkjet printable metal nano-particle inks, the particles are mono-dispersed in a solvent to form a colloid. In order to make a low-viscosity ink the solids content is typically kept around 20 wt-%. The individual metal particles are protected by a polymer shell to prevent aggregation and remain evenly dispersed, and to promote adhesion to the substrate. Conductivity is established through contact between the metal particles. The curing or the sintering process provides this contact by making the polymer shell move away, allowing the particles to touch each other. Further curing will enlarge the contact area between the particles and finally volatilize the polymer shell, thus increasing the conductivity.

Inkjet printing conductors

Conductors are materials that contain movable charges of electricity and they are usually made from metals such as copper, silver, gold or aluminum. They are used in circuit boards and RFID antennas, but are also basic building blocks for many other electric components and applications.

Conductors are inkjet printed by printing lines of different size and shape. When printing conductors it is important to have continuous, narrow lines with smooth edges. The factors affecting the final performance of inkjet printed conductors include print resolution, drop size, ink properties, interactions between ink and substrate such as spreading, penetration and absorption, as well as curing conditions.

Experimental work

The objective of this paper is to investigate factors affecting the quality i.e. electric performance and print quality of inkjet printed conductors. In print quality the main focus is on line width. When making electronic components it is important to have even several hundreds of conductors in an area of 1 cm^2. When decreasing the line width even with 10 µm a significant increase in the amount of lines in 1 cm^2 is achieved.

Factors affecting the quality of the conductors that were investigated include drop size, resolution, amount of ink layers, substrate type and temperature of the substrate during printing. Also the stability of the resistance of the printed conductors over time was studied. Heating of the substrate during printing is assumed to prevent the ink from spreading on the substrate, because the heat of the substrate starts the curing process immediately as the ink drop hits the substrate surface. Besides preventing ink spreading, heating the substrate also provides a pre-curing step needed for improving the electrical performance and surface structure of the conductor as suggested in [1].

Inkjet printing environment

The state-of-the-art inkjet research environment at VTT was used for printing the test samples. The research environment consists of industrial, piezo-electric printheads for two-colour printing and an Apollo II control unit both from Spectra, as well as an XY precision table with a positional repeatability of 1 µm from iTi. Attached to the printing environment is a high-speed CCD camera for investigating properties of the ink drops hitting the substrate surface as a function of time. With this camera-based system, the interactions between ink and substrate were studied from the moment the ink drop hit the substrate surface to one second.

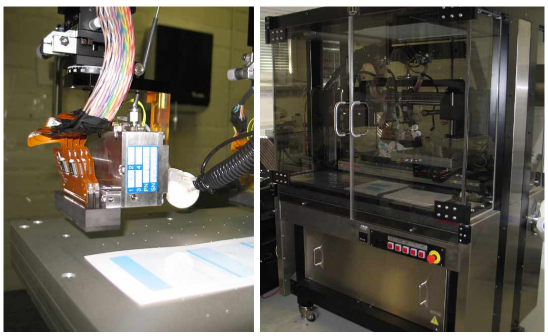

Figure 1. *Inkjet printing environment used in the printing trials based on industrial printheads from Spectra (left) and XY precision table from iTi (right). The substrate is placed on the moving grey platen under the stationary printheads.*

Two different printheads were used: SX-128 with 10 pl drop size and Nova AAA with 80 pl drop size. Nova AAA was used for investigating different amounts of ink layers (1, 2 and 3 layers) and resistance stability over time (0-18 weeks). SX-128 was used for investigating line widths on different substrates and the effect of heated substrate. The substrate was heated by heating the platen where the sample is placed to 50 ^{o}C. After printing, the paper samples were offline-cured in a heat chamber at 100 ^{o}C for 30 minutes and the plastic substrates at 120 ^{o}C for 30 minutes.

Materials

Inkjet printable silver nano-particle ink (AG-IJ-G-100-S1) from Cabot Printable Electronics and Displays was used to print conductor patterns on different substrates. The ink can be cured at low temperatures such as 100-200 ^{o}C and should produce resistances as low as 100-500 mOhm/square. The ink is designed to be printed with the printheads manufactured by Spectra.

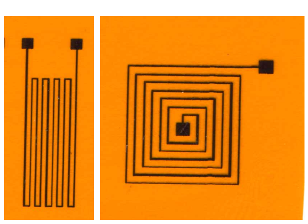

Figure 2. *Resistor patterns inkjet printed on polyimide film with silver nano-particle ink.*

The substrates used were coated photographic paper, polyimide film and PEN film. Polyimide and PEN are typical substrates for electronic applications. Photographic paper represents the best substrate option for inkjet printing.

The printed test pattern consisted of lines of different widths, resistor patterns such as in Figure 2, dots and solid areas.

Measurements

The print quality of the samples was analyzed with Scanner IAS and Personal IAS image analysis systems from QEA. Special attention was paid to line width.

The resistance of the printed patterns was measured using a universal digital oscilloscope. The square resistance (R_{square}) values were calculated from the resistance (R), line width (w) and line length (l) values using equation 1.

$$R_{square} = R \times w/l \qquad (1)$$

The square resistance value eliminates the effect of the dimensions of the measured area, thus making it possible to compare resistance values from different samples. The smaller the resistance value, the better the conductivity of the conductor.

Results

In Figure 3, the silver nano-particle ink drops hitting the different substrates are presented as a function of time. The drops are 80 pl in volume. It can be seen that on the plain paper (uncoated copy paper, 80 g/m^2) the ink dot spreads and penetrates considerably, but on other substrates remains a nice circle. Because of ink spreading the structures printed on plain paper weren't conductive, thus indicating that only little ink spreading and penetration is preferred when inkjet printing conductors.

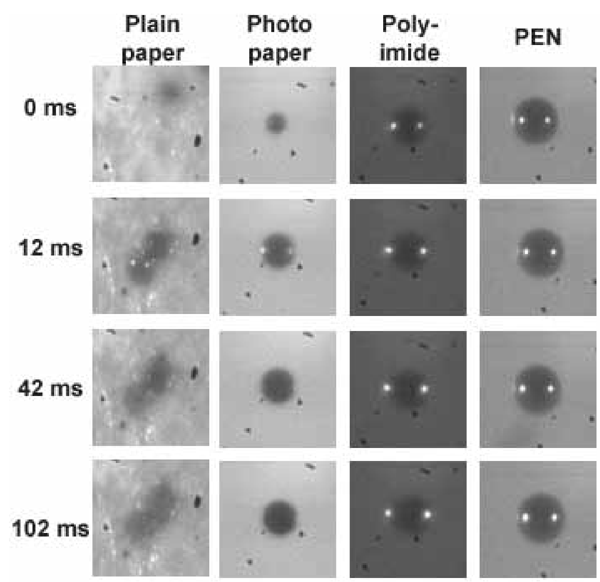

Figure 3. *80 pl inkjet printed silver nano-particle ink drops on different substrates as a function of time after the drop hits the substrate surface.*

Figure 4 presents microscopic images of the conductors printed on different substrates. The lines seem to have very smooth edges except on photo paper the lines look like dots on top of each other. The edge roughness on plastic substrates was measured to be between 1-2 µm, but on photo paper between 2-7 µm. For all substrates the hole percentage of the lines was practically 0 %.

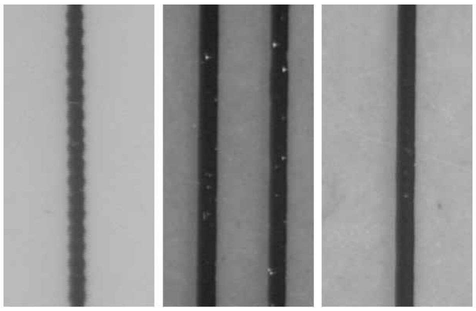

Figure 4. *Inkjet printed silver nano-particle conductors on different substrates, from left: photo paper, polyimide and PEN.*

Figure 5 presents the topographic profile of a silver nano-particle conductor inkjet printed on polyimide film. The conductor has a very smooth height profile although some coffee stain effect typical for inkjet printing can be seen i.e. there is more ink in the edges of the conductor than in the middle area.

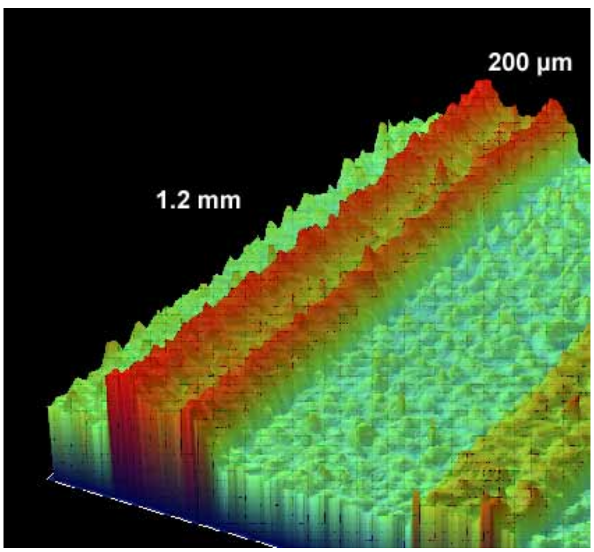

Figure 5. Surface topography profile of an inkjet printed silver nano-particle conductor on polyimide film. The average height of the conductor is 0.30-0.50 µm.

From the print quality point of view the conductors looked good. Also the resistance measurements confirmed that the conductors work. The square resistance values were between 80-2500 mOhm/square.

The effect of ink and substrate combination

Figure 6 presents the line width on different substrates as a function of the number of ink layers. With the polyimide substrate the lines with 2 and 3 ink layers spread a lot, thus resulting in compact areas rather than separate lines. The samples were printed with an 80 pl printhead.

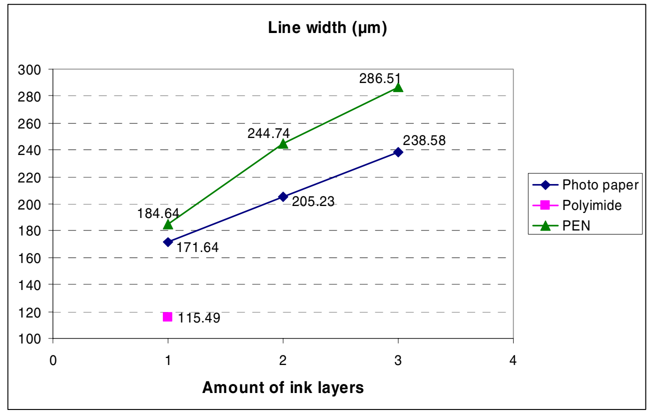

Figure 6. *The line width of silver nano-particle conductors on different substrates as a function of the number of ink layers.*

By increasing the amount of ink layers the line width increases, but at the same time square resistance decreases slightly i.e. electric performance improves. Table 1 presents the square resistance values on different substrates with a varying number of ink layers.

Table 1. The square resistance (Ohm/square) of different substrates with a varying number of ink layers.

Substrate	Ink layers	R_{square}
Photo paper	1	19.69
Photo paper	2	0.27
Photo paper	3	0.08
Polyimide	1	0.5
Polyimide	2	0.3
Polyimide	3	0.2
PEN	1	0.3
PEN	2	0.3
PEN	3	0.3

It was also tested if the square resistance values remained constant over time. When making electronic components it is important that the conductor preserves its electric performance over a long period of time. Figure 7 presents the square resistance on different substrates with one ink layer as a function of time.

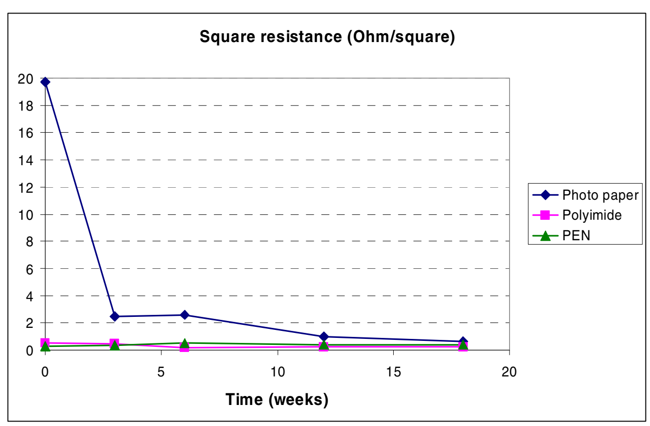

Figure 7. *The square resistance of silver nano-particle conductors on different substrates as a function of time.*

It can be seen that with plastic substrates the electric performance remains at the same level over time. With the paper substrate, the electric performance improves over time and reaches the same level as the plastic substrates only after 12 weeks. It may be that the curing process hasn't been good enough for the paper substrate and the conductors cure completely only after several weeks. However, the same effect wasn't observed with 2 and 3 ink layers that reached the same square resistance level as the plastic substrates already immediately after curing. This may be because there is more ink on these samples that compensates for the insufficient curing process.

The effect of heated substrate

Because the line width with 80 pl printhead was very big the 10 pl printhead was used for making narrower lines with 1 ink layer. Table 2 summarizes the line width results for different substrates. The substrate temperature was room temperature (around 24 °C) and 50 °C during printing. It can be seen that by heating the substrate from room temperature to 50 °C, the line width decreases approximately 10-15 µm. Also compared to printing with the 80 pl printhead the line width decreases more than 100 µm with each substrate.

Table 2. The line width of inkjet printed silver nano-particle conductors on different substrates at different substrate temperature.

Substrate (°C)	Photo paper	Polyimide	PEN
24	87.01	66.73	66.63
50	70.08	53.62	58.72

The effect of printing parameters

Figure 8 presents lines printed on polyimide with different print resolutions. With low resolution, the lines are formed from separated dots and the lines are not conductive. But increasing the resolution dots are placed closer to each other, thus producing continuous lines.

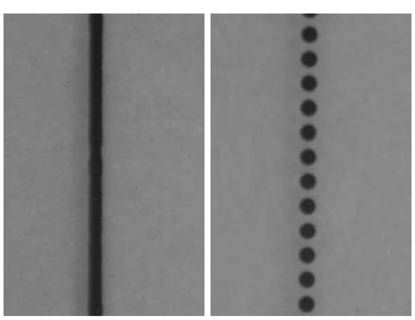

Figure 8. *Inkjet printed silver nano-particle conductors on polyimide film with different resolutions. From left: 600 dpi and 400 dpi.*

One way to have an effect on the line width is by controlling the drive voltage of the printhead. The drive voltage has a direct effect on the drop size in the scale of ± 2-5 pl depending on the printhead. The decrease in drive voltage decreases the drop size. The recommended drive voltage by the ink manufacturer is 110 V, but also different voltages of 75 V and 100 V were tested with the 10 pl printhead. Table 3 summarizes these results on polyimide and photo paper.

Table 3. The line width of inkjet printed silver nano-particle conductors on different substrates with different drive voltage.

Drive voltage (V)	Photo paper	Polyimide
75	49.57	47.64
100	60.16	61.67
110	87.01	66.73

A decrease in drive voltage decreases the line width significantly. The line width is decreased more by decreasing the drive voltage than by heating the substrate.

Conclusions

It has been shown that it is possible to inkjet print narrow metal nano-particle conductors with good print quality and electric performance. Because the printheads used in this study are designed for industrial applications, it is shown that it is possible to manufacture conductors also in an industrial scale. However, there still remain challenges in the industrial production of conductors, because a heated substrate can result in ink drying in nozzles during long processes. It is also more challenging from the jettability point of view to print reliably with small drop sizes such as 10 pl than with larger drop sizes. But with good control of the interactions between ink and substrate, printing and curing conditions as well as print settings, good results can be achieved.

References

[1] K. Eiroma, L. Hakola, The effect of curing conditions on the performance of inkjet printed nanoparticle conductors, Proc. NTNE2006, Helsinki, Finland, poster. (2006).

[2] J. Heilmann, The Application of Inkjet for the Printing of PDLC Display Cells, Proc. IS&T NIP 21, Baltimore, USA. (2005).

[3] J. Heilmann, H. Juhola, H. Linna, L. Hakola, Image quality measurements in the quality control of printed electronics, Proc. TAGA Microtech, Swansea, Wales. (2003).

Acknowledgements

The author would like to thank research assistant Seppo Kuosmanen for his valuable help in preparing and measuring samples.

Author Biography

Mrs. Liisa Hakola graduated as Master of Science from Helsinki University of Technology in 2002 and her Master's Thesis was about the effect of ink composition on print quality of inkjet printing. She has studied Graphic Arts and paper technology. Since her graduation Liisa has worked at VTT, Technical Research Centre of Finland, as a research scientist. Her research work focuses on inkjet printing, digital package printing, new coding methods as well as using inkjet printing as a manufacturing technology.