



Thesis for the degree of Licentiate, Örnköldsvik 2012

COATED SURFACES FOR INKJET-PRINTED CONDUCTORS

Thomas Öhlund

Supervisors:
Jonas Örtegren
Hans-Erik Nilsson

Digital Printing Center
Department of Information Technology and Media
Mid Sweden University, SE-891 18 Örnköldsvik, Sweden

ISSN 1652-8948
Mid Sweden University Licentiate Thesis 84
ISBN 978-91-87103-22-3

COATED SURFACES FOR INKJET-PRINTED CONDUCTORS

Thomas Öhlund

© Thomas Öhlund, 2012

Digital Printing Center
Department of Information Technology and Media
Mid Sweden University, SE-891 18 Örnsköldsvik
Sweden

Telephone: +46 (0)660-57879

Printed by Kopieringen Mid Sweden University, Sundsvall, Sweden, 2012

ISSN 1652-8948
Mid Sweden University Licentiate Thesis 84
ISBN 978-91-87103-22-3

Akademisk avhandling som med tillstånd av Mittuniversitetet framläggs till offentlig granskning för avläggande av teknologie licentiatexamen, torsdag den 7/6 2012, klockan 14:00 i Mediacenter DPC, Mittuniversitetet, Järnvägsgatan 3 Örnsköldsvik.

Seminarier kommer att hållas på svenska.

ABSTRACT

In this thesis, a number of commercially available paper substrates of various types are characterized and their characteristics related to the performance of inkjet-printed conductors using silver nanoparticle ink. The evaluated performance variables are electrical conductivity as well as the minimum achievable conductor width and the edge raggedness. It is shown that quick absorption of the ink carrier is beneficial for achieving well defined conductor geometry and high conductivity. Surface roughness with topography variations of sufficiently large amplitude and frequency is detrimental to print definition and conductivity. Porosity is another important factor, where the characteristic pore size is much more important than the total pore volume. A nearly ideal porous coating has large total pore volume but small characteristic pore size, preferably smaller than individual nanoparticles in the ink. Apparent surface energy is important for non-absorbing substrates but of limited importance for coatings with a high absorption rate.

Additionally, a concept for improving the geometric definition of inkjet-printed conductors on nonporous films has been demonstrated. By coating the films with polymer-based coatings to provide a means of ink solvent removal, minimum conductor width were reduced a factor 2 or more.

Intimately connected to the end performance of printed conductors is a well adapted sintering methodology. A comparative evaluation of a number of selective sintering methods has been performed on paper substrates with different heat tolerance. Pulsed high-power white light was found to be a good compromise between conductivity performance, reliability and production adaptability.

The purpose of the work conducted in this thesis is to increase the knowledge base in how surface characteristics of papers and flexible films affect performance of printed nanoparticle structures. This would improve selection, adaption of, or manufacturing of such substrates to suit printed high conductivity patterns such as printed antennas for packaging.

Keywords: Inkjet, Nanoparticles, Paper, Flexible Substrates, Sintering, Printed Electronics, Functional Printing

SAMMANFATTNING

I denna avhandling har ett antal kommersiellt tillgängliga papper av olika typ karaktäriserats och deras egenskaper relaterats till prestandan på inkjet-tryckta elektriska ledare tryckta med silvernanoartikelbläck. De undersökta prestandavariablerna är elektrisk ledningsförmåga samt ledarnas minimala linjebredd och kantjämnhet. Det visas att en snabb absorption av bläckets lösningsmedel är gynnsam för både väldefinierad ledningsgeometri och elektrisk ledningsförmåga. Ytråhet med topografiska variationer med tillräckligt stor amplitud och spatiell frekvens korrelerar negativt med tryckdefinition och ledningsförmåga. Porositet är ytterligare en viktig faktor, där karaktäristisk porstorlek är avsevärt viktigare än total porvolym. Nära ideala egenskaper hos en porös bestrykning synes vara en mycket hög total porvolym men med små individuella porer, med fördel mindre än de minsta metallpartiklarna i bläcket. Ytenergi är mycket betydelsefull för icke-absorberande substrat men tappar nästan all sin betydelse för bestrykningar med snabb absorption.

Ett koncept för att förbättra den geometriska definitionen på inkjet-tryckta ledare på icke-porösa flexibla filmer har visats. Genom att bestryka filmerna med vissa polymerbaserade material och därmed införa en mekanism för separering av lösningsmedel och partiklar så reducerades ledarnas minimibredd med en faktor 2 eller mer.

Intimt förknippad med den slutliga elektriska prestandan på tryckta ledare är också en väl anpassad sintringsmethodik. En jämförande utvärdering av ett flertal selektiva sintringsmethoder har genomförts på papper med olika värmetålighet. Pulsat vitt ljus med hög effekt bedömdes som en bra kompromiss mellan elektriska prestanda, tillförlitlighet och anpassningsbarhet för produktionsmiljö.

Nyttan med arbetet som presenteras i denna avhandling är att öka kunskapsbasen för hur pappers och flexibla filmers ytegenskaper påverkar prestandan på inkjet-tryckta nanopartikelstrukturer. Detta möjliggör bättre urval, anpassning av, eller tillverkning av sådana substrat för att passa tryckta mönster med hög konduktivitet; som till exempel tryckta antenner på förpackningar.

ACKNOWLEDGEMENTS

I would like to thank my Supervisors Dr. Jonas Örtegren and Professor Hans-Erik Nilsson for their assistance during my time as a Ph.D. student. I would also like to thank Henrik Andersson, Anatoliy Manuilskiy, Tomas Unander, Britta Andres, Cecilia Lidenmark and Sven Forsberg, who all have been regular contributors in discussions regarding printed electronics. I would like to thank Håkan Olin, Magnus Hummelgård, Magnus Norgren and Håkan Edlund for teaching interesting courses that have been important for this work. I am grateful to Christina Westerlind and Boel Nilsson at SCA R&D in Sundvall, as well as the employees in the paper testing laboratory at MoRe Research in Örnsköldsvik, for instrument training and valuable contributions in measurements. Finally I would like to thank all my present and former colleagues at Digital Printing Center, Örnsköldsvik, and of course all the people that I may have forgotten to include in this list. Financial support from the Swedish Agency for Economic and Regional Growth and the Kempe foundations is gratefully acknowledged.

Örnsköldsvik, April 2012

Thomas Öhlund

TABLE OF CONTENTS

ABSTRACT	III
SAMMANFATTNING.....	IV
ACKNOWLEDGEMENTS	V
ABBREVIATIONS AND ACRONYMS.....	VIII
LIST OF PAPERS	IX
1 INTRODUCTION.....	1
1.1 PROBLEM FORMULATION	2
1.2 MAIN CONTRIBUTION OF THE THESIS.....	3
2. INKJET	4
2.1 PIEZOELECTRIC INKJET.....	4
2.2 THERMAL INKJET	5
3. CONDUCTIVE INKS FOR PRINTED ELECTRONICS	6
3.1. METAL NANOPARTICLE INKJET INKS	7
3.1.1 <i>Ink stabilization</i>	8
3.1.2 <i>Coffee staining</i>	9
3.1.3 <i>Sintering</i>	10
4. FLEXIBLE SUBSTRATES FOR PRINTED ELECTRONICS.....	11
4.1 PAPER	11
4.2 POLYMER FILMS	13
5. CONDUCTOR PERFORMANCE EVALUATION	14
5.1 GEOMETRIC DEFINITION	14
5.1.1 <i>Line Width</i>	15
5.1.2 <i>Raggedness</i>	15
5.2 ELECTRICAL CONDUCTIVITY	15
5.2.1 <i>4-point electrical resistance measurements</i>	16

6	SUMMARY OF PUBLICATIONS.....	17
7	DISCUSSION	20
8	FUTURE WORK	23
9	CONCLUSIONS.....	24
10	REFERENCES.....	25

ABBREVIATIONS AND ACRONYMS

AFM.....	Atomic Force Microscopy
CIJ.....	Continuous Inkjet
DOD.....	Drop On Demand Inkjet
LWC.....	Lightweight Coated
MEMS.....	Micro-electromechanical systems
OLED.....	Organic Light-Emitting Diode
PCA.....	Principal Component Analysis
PVP.....	Polyvinylpyrrolidone, water-soluble polymer
pH.....	Logarithmic measure on concentration of hydrogen ions
PPS.....	Parker Print Surf, measurement method for surface roughness
RFID.....	Radio Frequency Identification
SEM.....	Scanning Electron Microscopy
SEM-EDS.....	Scanning Electron Microscopy-Energy Dispersive Spectroscopy
TEM.....	Transmission Electron Microscopy

LIST OF PAPERS

This thesis is mainly based on the following five papers, herein referred to by their Roman numerals:

- I T. Öhlund, H. Andersson, J. Örtegren and H-E. Nilsson, "Sintering Methods for Metal Nanoparticle Inks on Flexible Substrates", Proc. NIP25: 25th Int. Conf. on Digital Printing Tech. (2009) 614-617
- II H. Andersson, T. Öhlund, A. Manuilskiy, J. Örtegren, S. Forsberg, H-E. Nilsson, "Evaluation of InkAid surface treatment to enhance print quality of ANP silver nano-particle ink on plastic substrates", Proc. LOPE-C (2010) 241-245
- III T. Öhlund, J. Örtegren, H. Andersson, H-E. Nilsson, "The Importance of Surface Characteristics for Structure Definition of Silver Nanoparticle Ink Patterns on Paper Surfaces", Proc. NIP26: 26th Int. Conf. on Digital Printing Tech. (2010) 309-313
- IV H. Andersson, C. Lidenmark, T. Öhlund, J. Örtegren, A. Manuilskiy, S. Forsberg, H-E. Nilsson, "Evaluation of coatings applied to flexible substrates to enhance quality of inkjet printed silver nano-particle structures", IEEE Transactions on Components, Packaging and Manufacturing Technology, 2(2), pp. 342-348, 2012
- V T. Öhlund, J. Örtegren, S. Forsberg, H-E. Nilsson, "Paper Surfaces for Metal Nanoparticle Inkjet Printing", Submitted to Applied Surface Science, 2012

1 INTRODUCTION

The invention of printing technology as we know it today is usually attributed to Johannes Gutenberg back in the 15th century [1], although it is known that printing techniques were used more than a thousand years before that in Asia [2]. Since that, graphic printing has become an important part of society with extensive applications such as packaging, books and newspapers. There are indications of a continuing reduction in importance of the latter two due to competition with increasingly popular digital media. A new important concept of utilizing printing technologies has, however, emerged over the last decades, known as functional printing. With functional printing, the scope is extended beyond simply conveying text and graphics, to also including deposition of functional materials. Printable functional materials include electrically conducting [3-6], semiconducting [7, 8] or insulating materials [9], as well as materials with magnetic [10], biological [11], chemical [12], optical [13] or mechanical [14] functions. Target applications for functional printing include radio frequency identification (RFID) [15], flexible displays [16], sensors [17], printed memories [18], printed batteries [19], micro-electromechanical systems (MEMS) [20, 21], micro-optics [22] and biological material patterning [23, 24].

In recent years, the global interest in functional printing research has expanded greatly and we are now starting to see an ever increasing number of commercial applications. Most methods known in traditional graphical printing can be used and have been used for the printing of functional fluids. The main advantage of digital printing technologies is a quick and simple workflow due to the elimination of processing steps between digital pattern information and final print. Among the digital technologies, inkjet is arguably the most flexible one, in that it is a non-contact method and can be used for a wide range of fluid compositions and substrates.

1.1 Problem formulation

The interest in printed functionality on low-cost flexible substrates is steadily increasing. Sensors, RFID and other customer communication functionality are potentially important additions to future packaging and other paper media. However, the combination of paper-based substrates and inks based on functional nanoparticle materials is challenging, since paper is inherently complex both in physical and chemical composition. Also, a fairly high temperature heating process is often called for to allow sintering, finally giving a printed inorganic functional material the required performance. This is again challenging since paper substrates typically deform at the temperatures normally needed. Therefore more knowledge is desired to understand how paper surfaces interact with inorganic nanoparticle inks and which aspects of the surface are most important. Exploring alternative sintering processes compatible with paper substrates is part of the entirety when looking into the possibilities, limitations and requirements for successful application of functional nanoparticle inks on paper substrates. The following questions can be formulated:

- Which are the most important characteristics of paper surfaces for inkjet-printed nanoparticle inks?
- Can common paper characterization methods be used to estimate performance of inkjet-printed conductors?
- Do low cost paper alternatives exist that allow high performance inkjet-printed conductive features?
- How significant are the benefits of coatings on papers and smooth plastic films?
- Which methods and process conditions for sintering are appropriate for paper substrates?

1.2 Main contribution of the thesis

This thesis highlights how properties of paper surfaces, as well as sintering methodology, affect the performance of inkjet-printed conductors using metal nanoparticle inkjet inks. The thesis discusses a number of important properties; the relative importance of them, as well as suitable methods for the characterization. Such knowledge is an important prerequisite for successful fabrication of highly conductive features, such as RFID antennas, directly on paper substrates. The gained knowledge should be useful also for inkjet dispersions based on other functional nanoparticles, such as magnetic nanoparticles for memory applications or metal-oxide nanoparticles for semiconducting layers in transistors and diodes. Furthermore, the thesis shows that certain low cost-, high volume production, coated papers can be used as relatively high performance substrates for inkjet-printed conductors.

The work that was included in this thesis can be summarized as:

- A study of several sintering methods on two paper substrates with different properties. The study provides insight in the comparative performance of the methods for each paper, and how the paper properties may change the optimal sintering operational procedure. To the thesis author's knowledge, any similar study has not been performed before.
- Two studies of conductor performance on a large set of paper substrates which were extensively experimentally characterized. To the thesis author's knowledge, similar studies have not been performed before.
- Two studies focusing on the possibility to modify an existing surface with local coating to improve conductor performance. Similar studies have been made for other types of ink (Deneulin et.al), but to the thesis author's knowledge, not for metal nanoparticle ink.

2 INKJET

The earliest inkjet technology is known as continuous inkjet (CIJ). CIJ uses a continuous ink stream that is broken into droplets by acoustic pressure waves. Droplets not to be included in the printed pattern are charged during drop formation and deflected when passing an electric field. The deflected ink is collected and re-used in the process. A later development of inkjet is drop-on-demand inkjet (DOD). In DOD, the print-head ejects droplets only when they are called for in the print pattern. Below, the two most common drop-on-demand technologies will be described: piezoelectric inkjet and thermal inkjet.



Figure 1. The piezoelectric functional materials inkjet printer used during the work of this thesis.

2.1 Piezoelectric inkjet

Piezoelectric inkjet technology uses piezoelectric material in the ink-filled chamber behind the print head nozzles. The application of a voltage over the material causes it to change shape, generating a pressure pulse in the fluid that forces a droplet out of the nozzle [25]. The waveform (the change of voltage over time) is tailored for the combination of print head characteristics and fluid properties to achieve the most well-behaved droplet ejection possible. Typically the waveform contains a positive voltage section to push ink out of the nozzle, and a negative section to pull the piezo element the other direction and refill the ink chamber.

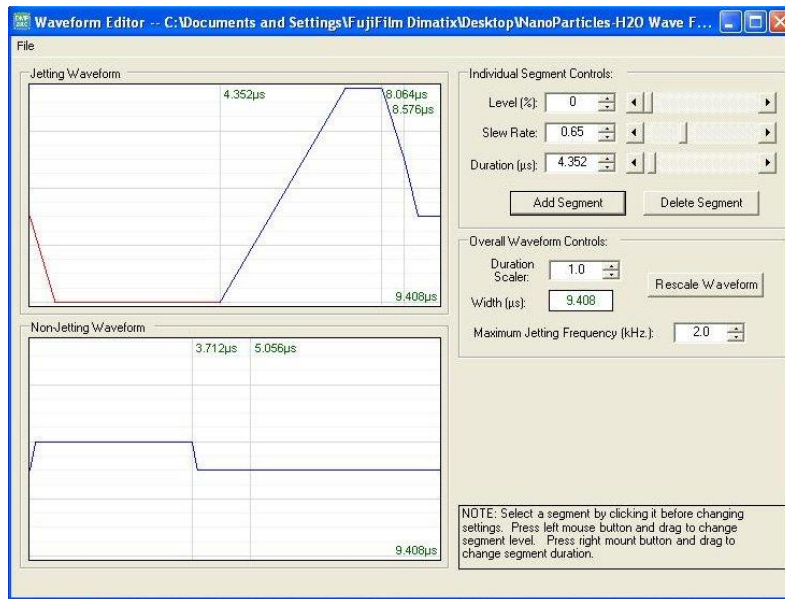


Figure 2. Waveform editor in the inkjet printer software.

In functional inkjet applications, piezoelectric print heads are traditionally used since they allow wider flexibility in the actuating waveform. Also, ink formulation is generally more flexible as there is no requirement for a volatile component.

2.2 Thermal inkjet

In thermal inkjet, each ink chamber contains a heating element. A current pulse through the heater causes rapid vaporization of the ink in the chamber to form a bubble, causing a large pressure increase. This pressure pushes a droplet of ink through the nozzle. Immediately after, condensation and contraction of the vapor bubble pulls new ink into the chamber through a channel attached to an ink reservoir [26]. As a consequence, the ink must have a volatile component for the vapor bubble to form. Advantages of the thermal inkjet technology are less complicated and lower cost construction of the print head, as well as ability to handle inks with high surface tension and low viscosity. This is a significant benefit with aqueous material dispersions for which rheology-modifying agents need to be avoided. One example is the printing of living cells. For such applications, thermal inkjet is usually exploited [23].

One could argue that the quick heating of the element in the chamber, reaching temperatures of 300-400 °C [27], would limit the usefulness of heat sensitive inks such as those with biological- or metal nanoparticle content. In practice though, the bubble builds up very quickly adjacent to the heater, so as to thermally isolate the main part of the ink from the heater. Therefore, only a small percentage of the ink is thermally affected.

3 CONDUCTIVE INKS FOR PRINTED ELECTRONICS

To be able to print an electrically conductive, or other functional material, the material typically needs to be dispersed in a carrier solution to form an ink. The rheological requirements differ depending on which printing technology that will be used. Suitable ink viscosities for different printing methods are seen in table 1.

Table 1. Comparison of viscosity ranges for different printing methods [28].

Printing method	Viscosity range (mPas)
Thermal inkjet	1-5
Piezo inkjet	5-30
Gravure	50-200
Flexography	50-500
Screen	1000-10000
Offset	40000-100000

The low viscosity and narrow viscosity range for inkjet inks are direct consequences of fluid dynamics dictating the droplet formation and ejection at the miniscule nozzles in the print head.

The viscosity for a dispersion of spherical rigid particles is given by Einstein's equation of viscosity of dispersions [29]:

$$\eta/\eta_0 = 1+2.5\phi \quad (1)$$

Where η is the viscosity of the dispersion, η_0 is the viscosity of the medium (in absence of the particles) and ϕ is the volume fraction of particles. We conclude that for nanoparticle inkjet inks, the material volume concentration needs to be sufficiently low to keep viscosity in the viable range. It follows from the limited volume concentration of solid material and the small drop volumes (in the 5-50 pL

range), that the thickness of the printed layer after drying will be low. This is a clear disadvantage if a low sheet resistivity is desired, as is usually the case when printing coils or antennas with a conductive ink. Very thin printed layers can, however, be used to advantage in other cases such as when printing parts of transistors [30] or OLED displays [31]. Among several types of conductive materials that can be formulated into inkjet inks, such as conductive polymers, carbon nanotubes and metal nanoparticles; silver nanoparticle inks have been the focus of interest throughout this thesis. Using such inks, printed layers can reach very high conductivities at high processing temperatures, and fairly high conductivities even at low processing temperatures. Because of this, they are of special interest when highly conductive features are desired on temperature sensitive substrates such as paper.

3.1. Metal nanoparticle inkjet inks

Metal nanoparticle inks of gold [32], silver [3,4] and copper [33] are all used for inkjet printing of conductive structures on various substrates. Silver is commonly used due to having the lowest resistivity of all metals, lower cost than gold and lower reactivity than copper.

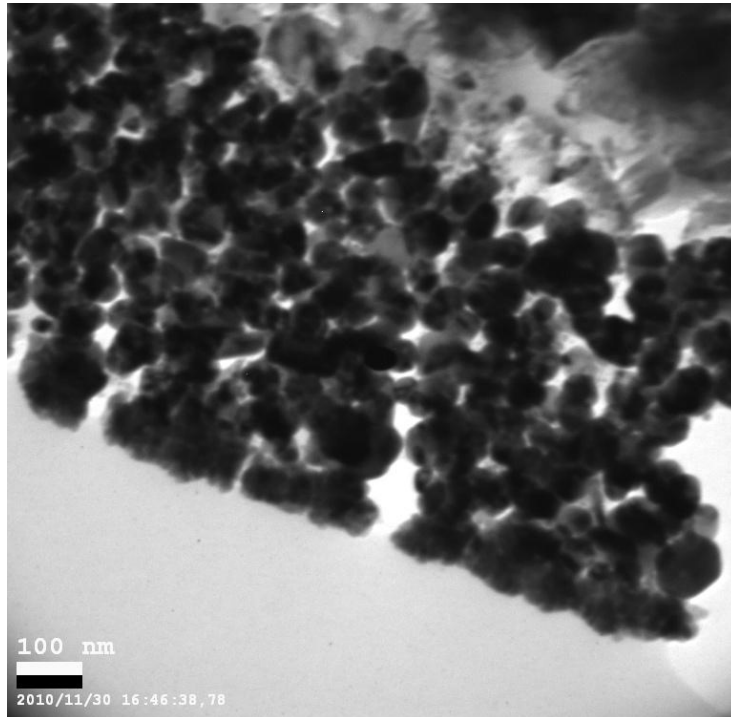


Figure 3. Dried layer of silver nanoparticles deposited on LWC paper with inkjet printing. The particles are 20-100 nm in diameter. (TEM, by Magnus Hummelgård)

3.1.1 Ink stabilization

Dispersions of solid particles in a liquid become unstable when the homogeneous distribution of particles in the medium no longer is maintained. This is most likely to happen when the heavier solid particles settle to the bottom of the ink over a period of time due to the action of gravity, making the volume concentration of particles larger at the bottom. The speed of sedimentation will be given by:

$$V_{\text{sed}} = 2(\rho_p - \rho_s)g r_p / \eta_s \quad (2)$$

Where ρ_p and ρ_s is the density of particle and solvent, respectively; g is the acceleration constant of gravity, r_p is the particle radius and η_s is the viscosity of the solvent. Particles of a metal nanoparticle inkjet ink will typically have fairly high sedimentation velocities since the particle density is high and the solvent viscosity is low. It is understood from equation (2) that the only practical means to decrease the sedimentation rate of these inks is to reduce the particle size. There are, however, practical limitations in how small metal nanoparticles can be

synthesized. The silver nanoparticle inks used within the work of this thesis have particle diameters in the 20-100 nanometer range, which is not small enough to avoid sedimentation and therefore require stabilization to maintain good stability. The key to maintaining ink stability is to prevent particles from coming so close to each other that they enter the region where attractive forces outweigh random motion forces and cause irreversible coagulation. The stabilization may be done by electrostatic stabilization, steric stabilisation, or a combination of both: electrosteric stabilization.

3.1.2 Coffee staining

One sometimes problematic effect observed with metal particle inks is known as “coffee staining”. This means that the particle concentration of deposited solution will be higher at the edges of the line/droplet. This is an effect of liquid evaporating at a higher rate at the contact line (the edge), leading to a convective flow of solution from the interior, and therefore a net transport of metal particles toward the edges of the structure [34]. It has been shown [35] that a higher concentration of particles reduces the impact of coffee staining, which is confirmed by unpublished work by the thesis author.

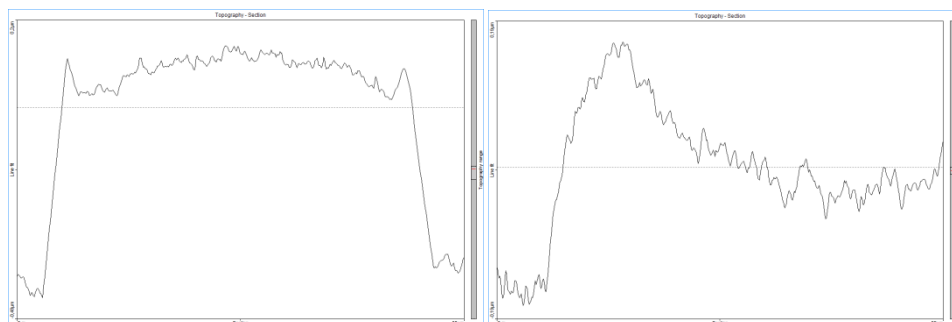


Figure 4. Coffee staining effect on mesoporous coated paper using different concentrations of dispersed silver nanoparticles. Left: 40 wt% silver, slight coffee staining visible. Right: 20 wt% silver, strong coffee staining is evident. Note that the spreading of nanoparticles is larger for the 20 wt% Ag ink, and therefore not allowing the complete conductor width to fit within the AFM scan range. (AFM scans showing cross-sections of minimum width conductors, by the thesis author)

3.1.3 Sintering

The process of sintering is sometimes described by two phases. The first phase is the curing, which starts at the temperature where particles lose their organic shell and direct particle-to-particle contact starts to form. The sintering phase starts at a higher temperature when all organic material is evaporated and a neck formation between particles is forming, that is when the individual particles are melting together into larger structures.

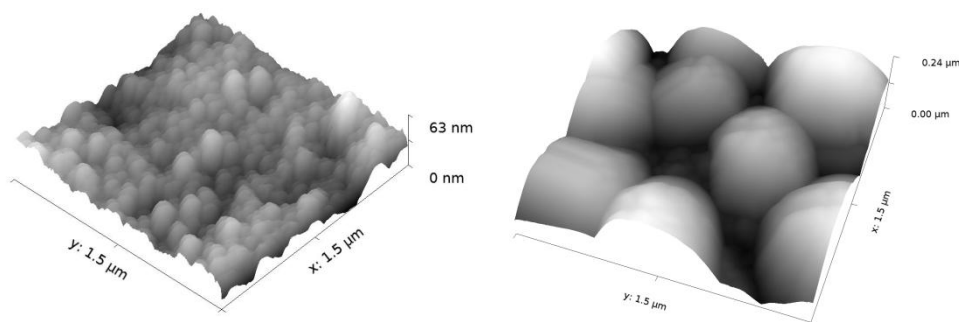


Figure 5. Particle growth during sintering of silver nanoparticle ink layer on lab-coated photo paper surface. Left: after drying at 60°C. Right: after additional heating at 180°C in 5 minutes. (AFM, by the thesis author)

Because of a very high surface/volume ratio and the large surface curvature of a nano-sized metal particle, there is a comparably large part of partially unbounded surface atoms making the melting temperature of such nanoparticles lower than the melting point of the corresponding bulk metal [36]. Generally, the smaller the particle size, the lower the temperature that is required for efficient sintering. However, the amount and composition of organic additives strongly affect critical curing temperature [37]. By using only a small amount of organic additives with weak bonding to the silver particles, like polyvinyl alcohol or dipropylene glycol (DPG), the curing temperature can be reduced.

Using an oven for heat treatment is the traditional and most common method. In some cases, a fairly low sintering temperature has to be used since the temperature needs to be kept lower than the substrate softening point to avoid substrate deformation. This might compromise conductivity performance when using heat sensitive substrates such as many papers and plastic films that cannot withstand typical sintering temperatures without deforming. In these cases, more advanced heating methods might be exploited in order to transfer a larger part of the heating energy into the printed structure as opposed to the surrounding substrate. Methods for selective sintering have been evaluated in the first paper of this thesis.

4 FLEXIBLE SUBSTRATES FOR PRINTED ELECTRONICS

4.1 Paper

The main challenge of using paper as a substrate for nanomaterials deposition is that paper is fibrous and non-uniform to its nature. High porosity and surface roughness of uncoated paper surfaces will in most cases render difficulties with reaching the intended functionality. Furthermore, paper is readily affected by environmental factors such as temperature and humidity that might change mechanical properties and cause dimensional- and roughness changes.

However, significant interest exists for using paper in printed electronics processes. The attractiveness of paper substrates for printed electronics applications derives from a number of factors:

- As a renewable resource, paper has environmental advantages compared to most other substrates.
- Industrial processes for paper production are mature and cost-efficient.
- Certain applications demands, or benefits from, flexibility. The flexibility of paper substrates can vary from very flexible to fairly stiff, depending on composition and construction.
- Due to the porous nature of paper, the weight is low, leading to reduced transport costs. The porosity also has the effect of increasing liquid absorption, which is beneficial especially for low viscosity inks, as is the case with inkjet.
- Very deep market penetration. Paper is found everywhere: in packaging, magazines, tickets and so on. Printing functional materials directly on paper surfaces is therefore of general interest.

With the inherent difficulties, actions that might be taken to increase the probability of success are:

- optimizing the printing technology and printing fluid to suit the paper substrates
- utilizing suitable coatings of the paper surface

Coatings developed mainly for inkjet photo papers, with nanosized pores designed for quickly receiving the ink carrier fluid, are of particular interest. A problem with paper substrates in general and coated papers in particular, is permanent deformation when exposed to typical sintering temperatures. Special ink formulations and/or sintering techniques may be needed. Such techniques are presented in paper I of this thesis.

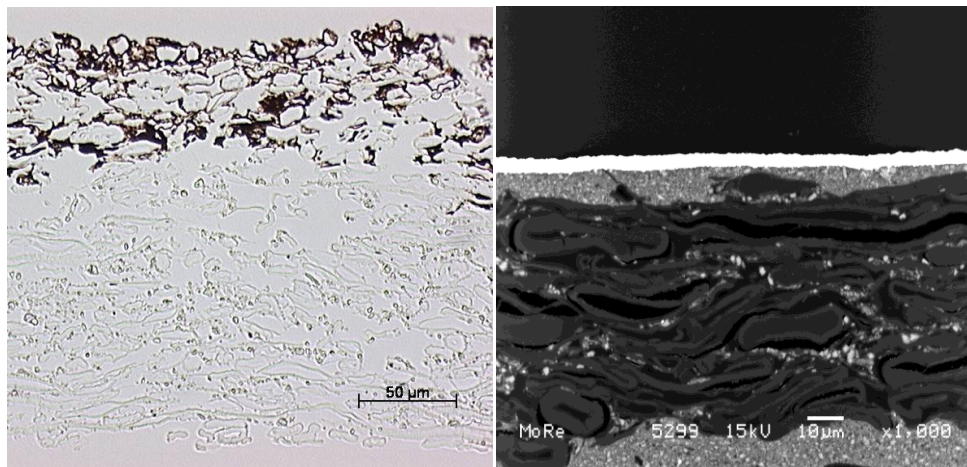


Figure 6. Cross sections of silver nanoparticle ink layer on coated papers. Left: Matte porous inkjet coating of silica aggregates. Pore sizes are too large to prevent significant penetration of particles (light microscopy). Right: LWC paper. The surface is smooth with fine pores, allowing a continuous particle film on top. (SEM)

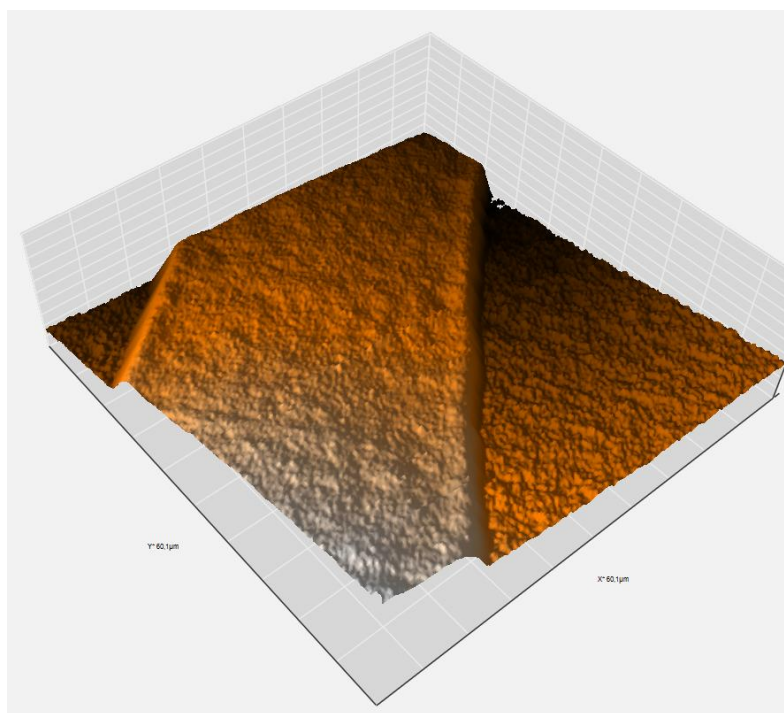


Figure 7. Inkjet-printed narrow conductor on mesoporous lab-coated photo paper. The conductor width is approximately $45\mu\text{m}$ and the height $0.5\mu\text{m}$. (AFM, by the thesis author)

4.2 Polymer films

Flexible polymer films have been used extensively for printed electronics. Compared to paper substrates, most polymer films have very smooth surfaces, homogeneous properties and no porosity. While these are benefits for some applications and printing techniques, the smooth, non-absorbing surface may be far from ideal in other instances, particularly for inkjet printing. Some of the polymer materials have high temperature stability, albeit those tend to be relatively expensive.

Polyimide (PI, Kapton) films are flexible substrates commonly used for printed electronics. A polyimide film can withstand prolonged exposure to 300°C and still keep its flexibility. The high surface energy normally causes a large ink wetting. Due to the large wetting, the smallest possible structures can generally not be achieved without modifying (lowering) surface energy. The cost of polyimide film is relatively high.

Polytetrafluorethylene (PTFE, Teflon) has excellent temperature stability and resistance to aging and chemicals. It is however expensive and its low surface energy can pose problems with “line bulging”, which can be described as unwanted, local broadening of a printed structure [38].

Polyarylate has a surface energy between PTFE and PI, which sometimes is a good compromise between line width and uniformity.

Polycarbonate (PC) and Polyethylene terephthalate (PET) are common low cost polymer materials. Their softening points are below 150°C and therefore not compatible with oven processing if high sintering temperatures are needed.

5 CONDUCTOR PERFORMANCE EVALUATION

When evaluating conductor performance, the two most important parts are assumed to be conductivity and geometric definition. High conductivity values (and small variations) are generally desired. An example where this is an important aspect is for resonance circuits in which the resistance of a printed coil should be low in relation to the inductance to give the circuit a Q-value sufficiently high for the intended function. Good geometric definition is important since it allows closer packing of printed features and smaller conductor widths, which besides less material consumption also means better reliability, less power consumption and increased capability of high frequency operation.

5.1 Geometric definition

As objective measurements of geometric definition, the corresponding parts of the ISO 13660 standard [39] for print quality evaluation are used. The 13660 standard assumes that the image to be analyzed is acquired digitally with a minimum resolution of 600 dpi. From the digital image file, the print quality measures are then extracted by pixel-level calculations defined by the standard. In this thesis, custom software is used to calculate line width and raggedness according to the description below. For the image acquirement, a flatbed scanner with an optical scanning resolution of 2400 dpi has been used. For detailed information about the calculations, the ISO standard document should be consulted. A brief description of the calculations is given below.

5.1.1 Line width

The calculation of line width is made by dividing the line into a large number of perpendicular segments, each one pixel thick; and calculating the average segment width. Each segment width is extracted using a threshold value T given by

$$T = R_{\max} - 0.6(R_{\max} - R_{\min}) \quad (3)$$

Where R_{\max} and R_{\min} are the maximal and minimal reflectance in the image, respectively.

5.1.2 Raggedness

With the same image segmentation as when calculating line width, the raggedness is calculated as the standard deviation of all distances d between the edge threshold contour and the ideal edge. The threshold value T is the same as calculated in (3).

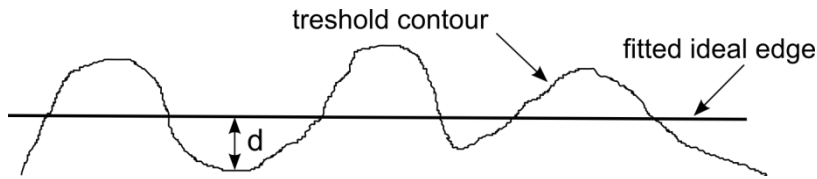


Figure 8. The raggedness calculation.

5.2 Electrical conductivity

Electrical conductivity is defined as the reciprocal of resistivity, where the resistivity ρ is defined as

$$\rho = R \cdot A / L \quad (4)$$

Where R is the electrical resistance, A the area of the cross section and L is the length of the conductor.

For thin films, a quantity known as sheet resistance R_s is commonly used where

$$R_s = \rho / t \quad (5)$$

Where t is the thickness of the film.

Within this thesis, electrical conductivity of printed conductors has been calculated by using resistance measurements together with conductor geometry measurements by AFM (film thickness) and image analysis (length and width).

5.2.1 4-point electrical resistance measurements

To improve accuracy in resistance measurements, in particular for low resistance structures, a 4-point method is commonly applied. In this method, separate probe/wire pairs are used for current-sourcing and voltage sensing functions, respectively. As illustrated in figure 9, current is sourced through the points at 1 and 4, via a pair of probes and current wires. This current generates a voltage drop across the structure to be measured according to Ohm's law $V=RI$. The current also generates a voltage drop across the current wires themselves. To avoid including that in the measurement, a pair of sense probes are placed immediately adjacent to the target resistance R_s , at points 2 and 3. Because almost no current flows in the sense wires, the voltage drop over the sense contact points and wires is extremely low and the resistance R_s is therefore effectively measured without contribution from wiring and contact-point resistances. The sense probes are normally arranged as the inside pair, and the source probes as the outside pair.

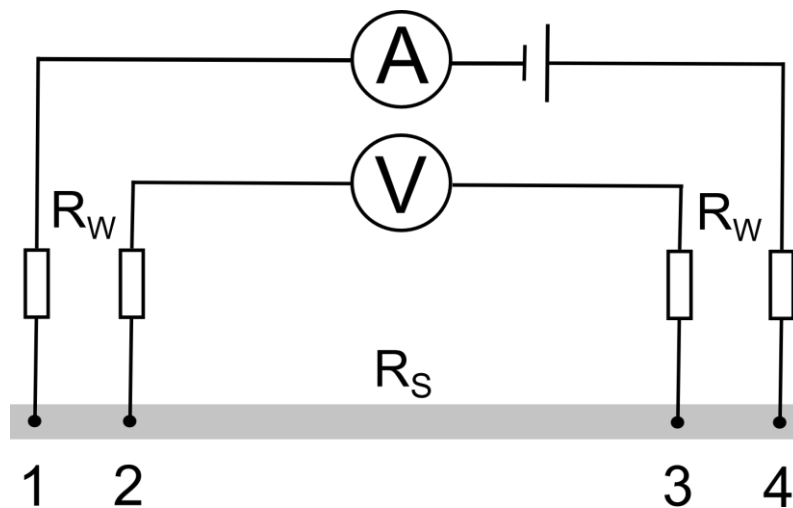


Figure 9. Schematic of 4-point resistance measurement setup. The influence of the wire resistances R_w and the contact point resistances are effectively eliminated with the setup.

6 SUMMARY OF PUBLICATIONS

The publications included in this thesis all involve inkjet printing of silver nanoparticle inks on flexible substrates.

Paper I examines different methods for selective sintering of printed conductive lines on two types of paper substrates with different heat tolerance. The selective methods are microwave sintering, electrical sintering and sintering with pulsed white light. The selective methods are compared with conventional convection sintering. For each of the methods examined, the maximum achievable conductivity for each paper is considered as well as the sintering process conditions affecting it, such as power level and sintering time. Observations of how the sintering affects the reliability of the paper/conductor combination are made, as well as observations and explanations of the overheating conditions. Some observations and conclusions are:

- It is possible to reach similar levels of conductivity for the photo paper and the laser print paper even though the surface properties of the photo paper are better adapted to inkjet printing. The reasons for this are that the laser print paper has a higher heat tolerance as well as higher adhesion to the silver nanoparticle layer, making a larger sintering energy transfer possible.
- Sintering methods that heats selectively provide faster sintering and higher conductivity, but a suitable choice of method and fine tuning of the sintering procedure is needed to maximize conductivity but still prevent damage to the ink layer or substrate.
- All selective methods resulted in better conductive performance than the conventional convection sintering, due to the limited heat tolerance of the paper substrates. The convection sintering was found more effective at shorter sintering times compared to longer times, since the shorter times allowed the temperature to be raised somewhat, resulting in higher performance overall.

- The pulsed light sintering method (photonic curing) has the attractive property of a negative feedback behavior, distributing the energy evenly over the conductive layer area and protecting it from local overexposure, since the reflectivity of the layer will increase during the sintering. The opposite, a positive feedback behavior, is inherent for the electrical and the microwave sintering methods. In particular for the microwave sintering, issues with local overheating were evident. However, the positive feedback methods resulted in the best conductivity performance at optimal conditions.

Paper I is written in cooperation with Jonas Örtégren, Henrik Andersson and Hans-Erik Nilsson. The contribution of the thesis author consists of the main part of the planning, experiments, measurements, reasoning and writing.

Paper II centers on the application of different commercial coatings on polyethylene films to improve the print definition of inkjet-printed silver nanoparticle ink. The coatings are applied in four different thicknesses using a coating applicator system. For all coating types and thicknesses, the coating improves the print definition considerably compared to the uncoated films. The electrical conductivity is found to be adversely affected for thicker coatings. The reasons for this might be attributed to a higher surface roughness and partial particle penetration into the coating.

Paper II is written in cooperation with Henrik Andersson, Anatoliy Manuilskiy, Jonas Örtégren, Sven Forsberg and Hans-Erik Nilsson. The contribution of the thesis author consists mainly of the evaluation of print quality by microscopy and image analysis, as well as parts of the reasoning and writing.

Paper III is focused on studying structure definition on various paper substrates; i.e., line width and line edge raggedness of conductive lines printed with polar and non-polar ink. The paper substrates are characterized with regards to surface material content and physiochemical properties such as apparent surface energy, absorption rate, porosity and surface roughness. A Principal Component Analysis (PCA) model is built to extract the multivariate correlations in the data. The PCA highlights that for both inks, the most important prerequisites for high print definition are high absorption rate and large total pore volume. This is consistent with the observation that all the paper substrates in the study compared favorably to a homogeneous non-absorbing polymer film. It is seen that fast absorption

dominates chemical ink-substrate interactions, such that conductor width differences between different inks is small for fast absorbing substrates but large for slow absorbing substrates. The following is observed and concluded:

- For substrates with low surface roughness and absorption rate, the print quality and conductivity rely on a well matched substrate surface energy and ink surface tension. For high surface roughness- or high absorption rate substrates, the matching is only of minor importance.
- The PCA multivariate analysis suggests that the most important factors for high geometric definition are high absorption rate and large total pore volume.
- The substrates with the highest surface roughness show significantly compromised geometric definition of the conductors due to ink feathering. On the other hand, the smoothest substrate, the non-porous polymer film, shows the worst definition of all substrates. It is argued that sufficiently low levels of surface roughness are not harmful to geometric definition but can even be beneficial, in particular if absorption is low or nonexistent.

Paper III is written in cooperation with Jonas Örtengren, Henrik Andersson and Hans-Erik Nilsson. The contribution of the thesis author consists of measurements, and the main part of the planning, experiments, reasoning and writing.

Paper IV expands the concept that was explored in paper II. In this paper, conductors of different widths are printed on polyethylene and polyimide films. It is found that the coatings improve the conductor geometric definition by 36-47% for the polyethylene film and 58-75% for the polyimide film depending on coating type and thickness. The electrical conductivity also shows the best performance for the coated polyimide substrates, where at best a conductivity corresponding to 16% of the value for bulk silver is achieved after convection sintering at 200 °C. Similarly to the observations in paper II, the thicker coatings result in lower conductivities. A possible explanation is presented where the polar solvent of the ink penetrates into- and partially dissolves the polymer coating layer below the printed pattern. The dissolved polymers are believed to diffuse into the printed layer and increase the mean particle spacing.

Paper IV is written in cooperation with Henrik Andersson, Cecilia Lidenmark, Jonas Örtégren, Anatoliy Manuilskiy, Sven Forsberg and Hans-Erik Nilsson. The contribution of the thesis author consists mainly of the evaluation of print quality by microscopy and image analysis, as well as parts of the reasoning and writing.

Paper V has the main part of the substrate selection and characterization in common with paper III. The characterization is expanded to include narrow scale investigation of surfaces and interfaces with atomic force microscopy and scanning electron microscopy. This study is focused on a thorough examination and analysis of the electrical conductivity resulting from polar silver nanoparticle ink at different sintering temperatures. Key factors and mechanisms explaining the conductivity performance for each of the paper types are suggested, and these factors are further discussed in detail. It is suggested that the importance of chemical surface-ink interactions decreases greatly as sintering temperature is raised. As a consequence, beyond a certain temperature, physical-mechanical properties of the surface dominate, among which the most crucial ones are porosity and surface roughness. It is claimed that when the characteristic pore size and short-scale surface roughness amplitudes are much smaller than the typical nanoparticle layer thickness, a continuous film will form. It is observed that a large absorption rate reduces the significance of other parameters, particularly surface energy. Furthermore, it is concluded that dimensional stability of the surface during printing and sintering is very important to avoid stress and cracks in the film, which if present, will impair the conductivity seriously.

Paper V is written in cooperation with Jonas Örtégren, Sven Forsberg and Hans-Erik Nilsson. The contribution of the thesis author consists of measurements and the main part of the planning, experiments, reasoning and writing.

7 DISCUSSION

In the case of inkjet printing on non-absorbing, flexible polymer films, it is mainly the lack of absorption that restricts the conductor performance. Since the volume ratio of particles/solvent is very low for inkjet-printable metal nanoparticle dispersions, the excessive solvent needs to be removed quickly to not compromise line definition and conductivity. The mechanisms for this can be either absorption or evaporation. To have quick evaporation on the substrate, either the ink solvent needs to be volatile or the substrate temperature needs to be high. Volatile

solvents, however, are problematic to use with inkjet since the fast evaporation will cause instability at the nozzle-air interface and clogging of the inkjet nozzles. A high substrate temperature is problematic not only because of the low temperature tolerance of most papers and polymer substrates, but also because convection will transport heat from the substrate to the nozzles above it, causing nozzle evaporation and instability. Since neither absorption nor fast evaporation is controlling the ink spreading on the non-absorbing polymer films, it follows that the combination of the surface energy of the film and the surface tension of the ink will become an important factor since it dictates the ink-surface contact angle. In paper II and paper IV, non-absorbing polymer films have been coated with polymer coatings. Although the coatings applied are not porous per se, they still provide a mechanism for solvent absorption. As a consequence, geometric definition improved significantly.

As far as the paper substrates are concerned, absorption can be thought of as a side effect of the porous nature of their construction, and in that specific sense makes paper better adapted for inkjet functional printing than most nonporous substrates such as glass sheets or polymer films. The surface porosity needs, however, to be controlled, as is also true for the related property surface roughness. Metal nanoparticle films are easily disrupted by surface perturbations or pores in the same size-of-order as the particle film thickness, which for nanoparticle inkjet dispersions may be as low as a few hundred nanometers or less. For this reason, uncoated papers are rarely usable for nanoparticle functional inks, since roughness and pores are large in comparison.

It is concluded that the paper characterization methods utilized in paper III and V are relevant for estimation of the suitability of paper substrates for inkjet-printed conductors, and therefore probably other inkjet-printed functionalities as well. For some of the methods, deviations from- and extensions to the paper industry standard measurement practices were made to better suit the coating types in question, as is described in paper V. Some paper industry standard characterization methods are not very relevant for predicting adaptability with nanoparticle conductors; this is the case with the Bentsen and PPS methods for surface roughness, as they give no information about the character of the roughness but only a single summing value. As has been concluded in paper V, the character of the roughness is important and the most important range is in the micrometer-scale region. Therefore, profilometer and AFM should be the most suitable methods for characterizing surface roughness.

Besides surface roughness, porosity is the other critical factor. Either of these two properties, if sufficiently large, will make conductive function impossible with the inks used within this thesis. With high porosity is in this case meant surface-connected pores of large size. However, if the characteristic pore size is small, a large total pore volume poses no problems; the corresponding large absorption rate will instead be beneficial for the geometric definition and conductivity. Therefore, when examining paper porosity using mercury porosimetry, the pore size distribution should be of main interest.

An interesting and important aspect is the cost/performance ratio of paper coatings for printed electronics. Although the highest performance was demonstrated on relatively expensive mesoporous coatings, it has been shown in paper III and V that low cost- high volume production coated papers of LWC type can be used as a relatively high performance substrate for inkjet-printed conductors. Since the combination of inkjet printing and nanoparticle inks generally put the highest demands on the paper with regards to absorption capability and smoothness of surface, it is expected that in most cases, the LWC paper grades will work even better for other printing methods and functional ink types.

A potential problem with printing metal nanoparticle inks on paper or low-cost polymeric films is the general need for sintering, combined with the limited heat tolerance for most of these substrates. Although sintering effects can be had at room temperature by tailoring the substrate surface chemistry to destabilize the ink dispersant polymers upon contact [40]; more efficient sintering, and therefore higher conductivity, is usually achievable only by heating the metal film to fairly high temperatures. The temperatures needed for efficient sintering will depend on the material and size of the nanoparticles, as well as the evaporation temperatures of stabilizing polymers and solvent components. Commonly the required temperature is higher than the deformation temperature of the substrate and therefore selective sintering methods should be used if the substrate heat sensitivity is not to limit the achievable conductivity. The idea of the selective methods is to exploit the difference in material properties between the metal ink and the substrate in order to transfer heat energy to the printed pattern with minimal heat transfer to the substrate. A number of sintering methods have been examined in paper I of this thesis. It was seen that the sintering process conditions, such as sintering time and applied energy, should be tuned for the entire system of method, substrate, ink and required performance.

8 FUTURE WORK

In the papers included in this thesis, much of the work has been focused on finding the important aspects of paper surfaces that improve, or restrict, the performance of inkjet-printed, electrically conducting nanoparticle layers. In this work, the focus has been to estimate the relative importance of these factors and how they interrelate to each other. In the future work it is of interest to focus in detail on the most important characteristics that were suggested by this work, isolating each characteristic in order to reach a deeper understanding of the mechanisms involved. Ongoing, soon to be published work is focused on custom-made papers with mesoporous coatings with controlled porosity and surface pH. Also, a study on printed conductors on non-porous model substrates with controlled surface roughness is among the future work planned.

As the work in this thesis suggests, inkjet-printing of conductors using metal nanoparticle ink on low-cost uncoated paper surfaces is severely challenging. To combat this, methods of coating, or in other ways improving, uncoated paper using printing technology at selected spots will be investigated.

9 CONCLUSIONS

The main objective of the thesis is to provide a basic understanding of the interaction between silver nanoparticle ink dispersions and different coated substrates.

- The end performance of printed electrically conductive features depends on considerable interplay of many factors including: printing methodology; rheological-, chemical- and material properties of the ink; chemical- and mechanical properties of the substrate; as well as the sintering method and process conditions.
- The most important surface properties for inkjet-printing of conductors are the surface roughness, the characteristic pore size and the absorption rate.
- Local coating has been evaluated as a means to enhance print quality for non-porous flexible polymer films. Thin PVP-based coatings were evaluated and found to provide significant improvements in print quality. Thin coatings provided better results for conductivity than thicker.
- Although surface roughness and porosity were found to be the most crucial parameters to control, it is suggested that sufficiently small amounts of surface roughness and porosity are nondestructive or even beneficial for conductor performance.
- Increased sintering temperatures decrease the importance of physical- and chemical surface-ink interactions to a large extent.
- Selective sintering methods should be used if highest possible electrical conductivity is a priority, and that the sintering process conditions need to be tailored to the specific combination of method, ink and substrate to reach the highest possible performance.
- It is demonstrated that it is possible to obtain high conductivity on a wide range of substrates for the same ink system by tuning the sintering method and modifying the surface properties with a suitable coating. Swellable, or other mechanically unstable coatings, are exceptions and such materials should be avoided.

10 REFERENCES

- [1] P.B. Meggs, *A history of graphic design*, John Wiley & Sons, 1998.
- [2] R. Whitfield, A. Farrer, M. British, S.J. Vainker, J. Rawson, *Caves of the thousand Buddhas: Chinese art from the silk route*, Published for the Trustees of the British Museum by British Museum Publications Ltd, 1990.
- [3] L. Hsien-Hsueh, C. Kan-Sen, H. Kuo-Cheng, Inkjet printing of nanosized silver colloids, *Nanotechnology*, 16 (2005) 2436.
- [4] D. Kim, J. Moon, Highly Conductive Ink Jet Printed Films of Nanosilver Particles for Printable Electronics, *Electrochemical and Solid-State Letters*, 8 (2005) J30-J33.
- [5] K. Kordás, T. Mustonen, G. Tóth, H. Jantunen, M. Lajunen, C. Soldano, S. Talapatra, S. Kar, R. Vajtai, P.M. Ajayan, Inkjet Printing of Electrically Conductive Patterns of Carbon Nanotubes, *Small*, 2 (2006) 1021-1025.
- [6] J. Jang, *Conducting Polymer Nanomaterials and Their Applications*
Emissive Materials Nanomaterials, in, Springer Berlin / Heidelberg, 2006, pp. 189-260.
- [7] J.Z. Wang, J. Gu, F. Zenhausern, H. Sirringhaus, Low-cost fabrication of submicron all polymer field effect transistors, *Applied Physics Letters*, 88 (2006) 133502-133503.
- [8] F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, All-Polymer Field-Effect Transistor Realized by Printing Techniques, *Science*, 265 (1994) 1684-1686.
- [9] P. Calvert, Inkjet Printing for Materials and Devices, *Chemistry of Materials*, 13 (2001) 3299-3305.
- [10] W. Voit, W. Zapka, L. Belova, K.V. Rao, Application of inkjet technology for the deposition of magnetic nanoparticles to form micron-scale structures, *Science, Measurement and Technology, IEE Proceedings -*, 150 (2003) 252-256.
- [11] J.D. Newman, A.P.F. Turner, G. Marrazza, Ink-jet printing for the fabrication of amperometric glucose biosensors, *Analytica Chimica Acta*, 262 (1992) 13-17.
- [12] M. O'Toole, R. Shepherd, G.G. Wallace, D. Diamond, Inkjet printed LED based pH chemical sensor for gas sensing, *Analytica Chimica Acta*, 652 (2009) 308-314.

- [13] J. Bharathan, Y. Yang, Polymer electroluminescent devices processed by inkjet printing: I. Polymer light-emitting logo, *Applied Physics Letters*, 72 (1998) 2660-2662.
- [14] S.F. Jahn, L. Engisch, R.R. Baumann, S. Ebert, W.A. Goedel, *Polymer Microsieves Manufactured by Inkjet Technology*, *Langmuir*, 25 (2008) 606-610.
- [15] V. Subramanian, J.M.J. Frechet, P.C. Chang, D.C. Huang, J.B. Lee, S.E. Molesa, A.R. Murphy, D.R. Redinger, S.K. Volkman, *Progress Toward Development of All-Printed RFID Tags: Materials, Processes, and Devices*, *Proceedings of the IEEE*, 93 (2005) 1330-1338.
- [16] G.H. Gelinck, H.E.A. Huitema, E. van Veenendaal, E. Cantatore, L. Schrijnemakers, J.B.P.H. van der Putten, T.C.T. Geuns, M. Beenhakkers, J.B. Giesbers, B.-H. Huisman, E.J. Meijer, E.M. Benito, F.J. Touwslager, A.W. Marsman, B.J.E. van Rens, D.M. de Leeuw, *Flexible active-matrix displays and shift registers based on solution-processed organic transistors*, *Nat Mater*, 3 (2004) 106-110.
- [17] T. Unander, H.E. Nilsson, B. Oelmann, *Printed touch sensor for interactive packaging and display*, in: *Polymers and Adhesives in Microelectronics and Photonics, 2007. Polytronic 2007. 6th International Conference on, 2007*, pp. 12-17.
- [18] T. Sekitani, K. Zaitzu, Y. Noguchi, K. Ishibe, M. Takamiya, T. Sakurai, T. Someya, *Printed Nonvolatile Memory for a Sheet-Type Communication System*, *Electron Devices, IEEE Transactions on*, 56 (2009) 1027-1035.
- [19] M. Hilder, B. Winther-Jensen, N.B. Clark, *Paper-based, printed zinc-air battery*, *Journal of Power Sources*, 194 (2009) 1135-1141.
- [20] S.B. Fuller, E.J. Wilhelm, J.M. Jacobson, *Ink-jet printed nanoparticle microelectromechanical systems*, *Microelectromechanical Systems, Journal of*, 11 (2002) 54-60.
- [21] V. Fakhfour, N. Cantale, G. Mermoud, J.Y. Kim, D. Boiko, E. Charbon, A. Martinoli, J. Brugger, *Inkjet printing of SU-8 for polymer-based MEMS a case study for microlenses*, in: *Micro Electro Mechanical Systems, 2008. MEMS 2008. IEEE 21st International Conference on, 2008*, pp. 407-410.
- [22] D.L. MacFarlane, V. Narayan, J.A. Tatum, W.R. Cox, T. Chen, D.J. Hayes, *Microjet fabrication of microlens arrays*, *Photonics Technology Letters, IEEE*, 6 (1994) 1112-1114.

- [23] T. Xu, J. Jin, C. Gregory, J.J. Hickman, T. Boland, Inkjet printing of viable mammalian cells, *Biomaterials*, 26 (2005) 93-99.
- [24] T. Xu, C.A. Gregory, P. Molnar, X. Cui, S. Jalota, S.B. Bhaduri, T. Boland, Viability and electrophysiology of neural cell structures generated by the inkjet printing method, *Biomaterials*, 27 (2006) 3580-3588.
- [25] P.-H. Chen, H.-Y. Peng, H.-Y. Liu, S.L. Chang, T.I. Wu, C.-H. Cheng, Pressure response and droplet ejection of a piezoelectric inkjet printhead, *International Journal of Mechanical Sciences*, 41 (1999) 235-248.
- [26] P.-H. Chen, W.-C. Chen, S.H. Chang, Bubble growth and ink ejection process of a thermal ink jet printhead, *International Journal of Mechanical Sciences*, 39 (1997) 683-695.
- [27] J.D.M. Ross R. Allen, and William R. Knight *Thermodynamics and Hydrodynamics of Thermal Ink Jets*, Hewlett-Packard Journal, (1985) 21-27.
- [28] H. Kipphan, *Handbook of Print Media: Technologies and Production Methods*, Springer, 2001.
- [29] K. Holmberg, B. Jönsson, *Surfactants and Polymers in Aqueous Solution*, John Wiley & Sons, 2003.
- [30] W. Ye, S. Xiao Wei, G.K.L. Goh, H.V. Demir, Y. Hong Yu, Influence of Channel Layer Thickness on the Electrical Performances of Inkjet-Printed In-Ga-Zn Oxide Thin-Film Transistors, *Electron Devices, IEEE Transactions on*, 58 (2011) 480-485.
- [31] F. Villani, P. Vacca, G. Nenna, O. Valentino, G. Burrasca, T. Fasolino, C. Minarini, D. della Sala, Inkjet Printed Polymer Layer on Flexible Substrate for OLED Applications, *The Journal of Physical Chemistry C*, 113 (2009) 13398-13402.
- [32] D. Huang, F. Liao, S. Molesa, D. Redinger, V. Subramanian, Plastic-Compatible Low Resistance Printable Gold Nanoparticle Conductors for Flexible Electronics, *Journal of The Electrochemical Society*, 150 (2003) G412-G417.
- [33] L. Youngil, C. Jun-rak, L. Kwi Jong, E.S. Nathan, K. Donghoon, Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics, *Nanotechnology*, 19 (2008) 415604.
- [34] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, T.A. Witten, Capillary flow as the cause of ring stains from dried liquid drops, *Nature*, 389 (1997) 827-829.

[35] P. Smith, D.Y. Shin, J. Stringer, B. Derby, N. Reis, Direct ink-jet printing and low temperature conversion of conductive silver patterns, *Journal of Materials Science*, 41 (2006) 4153-4158.

[36] P. Pawlow, *Z. Phys. Chem*, 65 (1909).

[37] B.J. Perelaer, A.W.M. de Laat, C.E. Hendriks, U.S. Schubert, Inkjet-printed silver tracks: low temperature curing and thermal stability investigation, *Journal of Materials Chemistry*, 18 (2008) 3209-3215.

[38] 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, *Advanced Materials*, 20 (2008) 343-345.

[39] S. International Organization for, Information technology - office equipment - measurement of image quality attributes for hardcopy output - binary monochrome text and graphic images, ISO, 1996.

[40] S. Magdassi, M. Grouchko, O. Berezin, A. Kamyshny, Triggering the Sintering of Silver Nanoparticles at Room Temperature, *ACS Nano*, 4 (2010) 1943-1948.