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Studies of Inkjet Printing Technology with Focus on Electronic Materials

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Thesis for the degree of Doctor of Technology to be presented with due permission for public examination and criticism in Tietotalo Building, Auditorium TB104, at Tampere University of Technology, on the 8th of January 2010, at 12 noon.
Abstract

Printed electronics (PE) is based on printing thin- and thick-film structures on cost-sensitive flexible substrates, such as paper-like, plastic, and on rigid substrates using a novel approach to manufacturing electronics which also enables two- or three-dimensional printing. Unlike conventional electronic manufacturing, i.e., subtractive photolithography techniques, PE is an additive processing method, whereby the functional material is deposited in a controlled manner to print the desired pattern without wasting the material. Electronics can be printed using several methods, e.g., screen printing, flexography, gravure printing, offset lithography, nano-imprint, and inkjet printing. There are several advantages to using the above methods. For example, freedom of substrate use facilitates the development of novel products. The low amount of material waste, low investment in production facilities, the versatility of the printing system, and many other benefits make PE ideal for low-cost electronics production. In addition, the data-driven nature of digital printing manufacturing methods allows fast manufacturing runs and a short time cycle from design to manufacturing, which all translate into shorter delivery times in manufacturing.

Inkjet printing technology is currently in a phase of proving its technological viability in the low-cost and high-volume manufacture of electronics. However, in technology development such change is only possible by demonstrating the reliability, durability, and applicability of the existing or novel electronic applications. In this work, inkjet printing technology was studied from the viewpoint of materials science and its potential to integrate electronic applications. The basic research concentrated on defining ink and substrate materials, their interactions, and on processing the materials with R&D/pilot line inkjet printers which all are commercially available in the technology. The applied research focused on electronic component manufacture, on selectively applying existing conventional or novel functional materials, and on defining viable material alternatives. The technology development consisted of evaluating printed structures and their materials in terms of environmental and mechanical reliability.
Preface

This work was carried out at the Department of Electronics, Faculty of Computing and Electrical Engineering, Tampere University of Technology, Tampere, Finland, during 2007-2009.

This thesis was supported by the Department of Electronics, Vicinics Industrial Consortium, and the Tuula and Yrjö Neuvo Foundation.

During the work with my research I have received support, help, and guidance from a lot of people to whom I am very grateful. I wish to express my gratitude to my former supervisor Pauliina Mansikkamäki, Ph.D., for her advice, support, and feedback during the whole research journey and for providing me the opportunity to work in her group with sufficient freedom to complete my work. I would also like to express my gratitude to Matti Mäntysalo, Ph.D., for being ever-helpful and supportive, and for sharing his knowledge and experience in microelectronics and engineering. I would also like to express my gratitude to Docent Pekka Heino. Thank you for your advice, support, and comments to finalize my dissertation. Special thanks are due to Kimmo Kaija, Ph.D., and Ville Pekkanen, M.Sc., for their fruitful collaboration and assistance. I also wish to thank to my present and former colleagues in Printable Electronics Group for a pleasant working environment and their valuable contribution to my daily work.

Most of all, I wish to express my deepest gratitude to Anna-Leena Hirvonen, Tahsin Caglar, Gulten Caglar, for their loving encouragement and my friends and relatives for their understanding and support during this long journey.

Tampere, November, 2009

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This thesis consists of an introduction and the following publications (used as references in the introduction):


Author’s Contribution

Publication 1, “Investigation of Spin-On Dielectric Materials for Inkjet Printing Technology Applications,” is the author’s contribution together with the co-authors. The author participated in developing the inkjet-printed dielectric layer, in testing each spin-on dielectrics, and in optimization the printing process. The author wrote the manuscript with the help of the co-author.

Publication 2, “An Investigation of Mechanical Performance of Silver Inkjet-Printed Structures,” is the author’s contribution. The author ran the related tests, selected the materials, design, and tests, analyzed the results, and wrote the manuscript together with the co-authors.

Publication 3, “Evaluation of Adhesion Pull-Off Performance of Nanoparticle-Based Inkjet-Printed Silver Structure on Various Substrates,” is the author’s contribution with the help of the co-authors. The author selected the test materials, designed the test setup and related tests, analyzed the results, and wrote the manuscript with the co-authors.

Publication 4, “Temperature-Dependent Reliability of Inkjet-Printed Silver Structure in Constant Humidity Environment,” is the author’s contribution with the help of co-authors. The author selected the materials, optimized the printing process, selected and ran the environmental tests, analyzed the results, and wrote the manuscript with the help of the co-author.

Publication 5, “Implementation Model of New Functional Materials to Electronics Manufacturing: Inkjet Printing Technology as a Case Study,” is the author’s and co-authors’ contribution. The author contributed to the implementation model of functional materials, studied the selected ink and substrate, described the processing properties of the ink, and wrote the manuscript with the help of the co-authors.

Publication 6, “Environmental Testing of Fine Interconnections Inkjet-Printed on Flexible Organic Substrates,” is the result of collaboration. The author selected the materials and their environmental tests, optimized the printing process, and analyzed the results. The author contributed to the simulation of the time-to-failure and the technological life of interconnections and wrote the manuscript with the help of the co-authors.
List of Abbreviations

3D Three-Dimensional
ACA Anisotropically Conductive Adhesive
AIST Advanced Industrial Science and Technology
AM Active Matrix
BST Barium Strontium Titanate
CAD Computer-Aided Design
CMOS Complementary Metal-Oxide Semiconductor
CNT Carbon Nanotube
COB Chip-On-Board
CIJ Continuous Inkjet
CTE Coefficient of Thermal Expansion
DC Direct Current
DOD Drop-On-Demand
DPI Dots-Per-Inch
ECA Electrically Conductive Adhesive
ESH Environmental, Safety, and Health
FR-4 Flame Retardant-4
IC Integrated Circuit
ICA Isotropically Conductive Adhesive
IPR Intellectual Property Right
ITO Indium Tin Oxide
LCD Liquid Crystal Display
LCP Liquid Crystal Polymer
LED Light-Emitting Diode
NCA Non-Conductive Adhesive
MEMS Microelectromechanical System
NPS Nanoparticle-Based Silver
OE Organic Electronics
OFET Organic Field-Effect Transistor
OLED Organic Light-Emitting Diode
OTR Oxygen Transmission Rate
P3HT Poly(3-Hexylthiophene)
PANI Polyaniline
PC Polycarbonate
PCB Printed Circuit Board
PE Printed Electronics
PEDOT: PSS Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)
PEN Polyethylene Naphthalate
PET Polyethylene Terephthalate
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<th>Abbr.</th>
<th>Term</th>
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<tr>
<td>PI</td>
<td>Polyimide</td>
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<tr>
<td>PM</td>
<td>Passive Matrix</td>
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<td>PP</td>
<td>Polypropylene</td>
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<tr>
<td>PQT-12</td>
<td>Poly(3,3’-dialkylquaterthiophene)</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>PV</td>
<td>Photovoltaics</td>
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<td>PVP</td>
<td>Poly(4-vinylphenol)</td>
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<tr>
<td>PWB</td>
<td>Printed Wiring Board</td>
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<tr>
<td>R2R</td>
<td>Roll-To-Roll</td>
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<td>RF</td>
<td>Radio Frequency</td>
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<td>RFID</td>
<td>Radio Frequency Identification</td>
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<tr>
<td>RGB</td>
<td>Red, Green, and Blue</td>
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<tr>
<td>RH</td>
<td>Relative Humidity</td>
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<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
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<tr>
<td>SIP</td>
<td>System-In-Package</td>
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<tr>
<td>SIJ</td>
<td>Super-Fine Inkjet</td>
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<tr>
<td>SMD</td>
<td>Surface Mounted Device</td>
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<tr>
<td>TFT</td>
<td>Thin-Film Transistor</td>
</tr>
<tr>
<td>TQM</td>
<td>Total Quality Management</td>
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<tr>
<td>UHF</td>
<td>Ultra High Frequency</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>WVTR</td>
<td>Water Vapor Transmission Rate</td>
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1. Introduction

The growing demands from consumers of electronic products for functionality, high performance, adequate product reliability, and rapid product delivery are pushing the electronic industry to find alternative manufacturing methods to respond to the demands. Future electronic products require a technology cluster to provide ambient intelligence services to connect “everything with everyone” in an attractive physical form especially in the high-tech electronics market [Erm07]. On the other hand, low-end electronic products are becoming even more cost-sensitive along with the emerging issue of manufacturing systems and materials that would significantly lower overall product costs.

Printing technologies, e.g. flexography, offset lithography, gravure, screen, and inkjet, are taking advantage of cost-sensitive, reliable approaches by using a broad range of materials. In certain applications, each printing technology offers interesting advantages. At present, electronic manufacturing can satisfy the low-cost, high performance demands by combining several printing methods on larger but cheaper substrates [Par05]. Inkjet printing technology has become an interesting alternative to satisfy the current manufacturing needs in electronics. The technology boasts a versatile additive printing method of depositing picoliter quantities of functional ink on a substrate at high precision and very low cost. In addition, inkjet printing is a contact-free process requiring no physical contact between mask template and substrate. Hence, it will open new doors to producing flexible and low-cost products. However, inkjet printing-based electronic manufacturing should deliver a complete product that would satisfy all service and support needs and convince the customer of the product’s potential value and thereby dispel any doubts of adopting the technology. Reliable and referred products will impress adopters to transfer the technology to a wider clientele.

This thesis examines comprehensively the durability, mechanical and environmental reliability, and implementation of inkjet printing technology, functional and nanomaterials, and low-cost and high performance plastic substrates for selected electronic applications [P1][P2][P3] and suggests functional electronic material alternatives for low-end and high-end electronics. In this work, low-end electronics are understood in terms of an electronic system with simplified component architecture, low electrical performance, and few material interactions, realized in an electronic product in a cost-effective way. On the other hand, high-end and system-in-foil-type electronics involve high electrical performances, a full electronic system integrated into an end product, and functional concordance and compatibility between several electronic components.

In addition, this thesis discusses the challenges of the inkjet printing process, its limitations and potential to meet the needs of the electronic industry [P4][P5][P6]. Technology development of inkjet printing was carried out in a multi-disciplinary way with scientific technology development initially constituting the essential groundwork. Some scientific findings were used for selected applications, predominantly in the electronics industry. During the knowledge transfer from applied university research to electronic industry different industrial test standards were evaluated and used to test the reliability of inkjet-printed structures.
1.1. Objectives and Scope of the Thesis

Low-cost manufacturing of electronic products to rival well-selling competitors is an important issue in reducing the overall cost of these products and in helping them reach the mass customer at an early stage. For example, at an early adoption stage, applications such as radio frequency identification (RFID) tags or organic light emitting diode (OLED) displays, which compete with barcode or liquid crystal display (LCD), might be easier to adopt if their cost or functionalities were appealing to the end user. Inkjet printing technology offers benefits such as low-cost and fewer process steps that might make the product attractive to end users. This thesis is a case study of inkjet printing technology to provide extensive information on functional materials and to solve technological problems arising during the technology implementation to the electronic industry. A second objective was to demonstrate the reliability in terms of environmental and mechanical tests of some selected inks and substrate combinations for low-end and high-end applications. This thesis introduces also several novel functional material solutions for hybrid electronic manufacturing, consisting of conventional and inkjet printing manufacturing techniques. In this work, functional materials were classified as nanoparticle-based inks (nano-ink), flexible organic substrates, and electrically conductive adhesives (ECAs). Some functional materials, including novel nanoparticles, were adopted from the conventional electronic process technology and successfully applied to inkjet printing.

1.2. Structure of the Thesis

This thesis consists of six publications, which contain the main results, and an introduction. The introduction is divided into six chapters, which provide a relevant background to the publications. Chapter 1 discusses the needs of the electronic industry and inkjet printing as an alternative method. Chapter 2 discusses contact printing technologies in general and their material requirements in printed electronics. Chapter 3 examines non-contact inkjet printing methods in detail and their material requirements in comparison with contact printing techniques. Chapter 4 details the application potential of nanoparticles and flexible organic substrates in the manufacture of electronics by inkjet printing. The chapter also extensively discusses the future trends in nanoparticles, and in addition, process, assembly, packaging and environmental requirements of inkjet printing technology to manufacture electronics. Chapter 5 discusses state of the art of inkjet printing technology in the manufacture of electronic applications such as low-end, high-end, and system-in-foil systems. The chapter also elaborates on the mechanical and environmental reliability results in connection with the selected electronic application during its implementation to electronic industry. The last chapter summarizes the potential of inkjet printing technology for the manufacture of electronics, citing its benefits and drawbacks. The publications are appended to the end of the thesis.

Publication 1 introduces a novel, alternative processing method to implement spin-on dielectric materials in inkjet printing to compensate for the lack of dielectric ink. A wide range of dielectric materials with varying characteristics were tested, and a process was developed to jet-print the dielectrics. A thin, smooth, and pin-hole-free dielectric layer was inkjetted, and the potential of spin-on dielectrics was discussed.
Publication 2 delves into the mechanical performance of silver nano-ink structures. An adhesion pull-off test setup was developed to measure the breaking force and strength between inkjet-printed layer and substrate. The paper describes the applicability of the results to mechanical modeling and the need for quantitative measurements to improve mechanical reliability. The publication further discusses the effect of sintering temperature and electronic coating and describes the other substrate material alternatives.

Publication 3 studies the potential of mechanically reliable ink-substrate combinations for the manufacture of low-cost circuits in low-end and interconnections in high-end electronics. The effect of sintering temperature on a low-metal-content nano-ink was studied to demonstrate mechanical pull-off performance. The fracture mechanism was examined, and the results were used to predict the maximum breaking strength of the inkjet-printed nano-ink on various low-cost, high-performance substrates.

Publication 4 studies the temperature-dependent reliability of an inkjet-printed low-metal-content nano-ink. Environmental tests such as temperature cycling and humidity were performed to define the performance of printed traces in low-cost circuits in low-end applications. Test results showed that the nano-ink was a reliable alternative in such applications.

Publication 5 studies the implementation model of functional materials and their current challenges in the inkjet manufacture of electronics. Challenges and solutions of the printing process were detailed for use of functional nano-ink. Moreover, the paper discusses the testing of functional inks before implementation to mass manufacture and the environmental, safety, and health (ESH) risk of nano-inks.

Publication 6 discusses the environmental reliability of inkjet-manufactured interconnections. Optimization of the printing process and modification of the substrate surface are important steps in achieving fine traces on the substrate. The paper describes the results of environmental testing of fine interconnections in low-end electronic applications in terms of their time-to-failure prediction and determining their technological life.
### 2. Printed Electronics and Contact Printing Techniques

Printable electronics (PE) is considered a versatile technology offering several benefits based on printing thin- or thick-film structures on cost-sensitive flexible or rigid substrates. Electrically functional devices can be printed using additive methods, e.g., screen printing, flexography, gravure printing, offset lithography, nano-imprint, and inkjet printing. Especially, piezo printhead-type inkjet printing technology offers substantial manufacturing advantages for tomorrow’s products, namely, component flexibility, fast manufacturing runs because of data-driven nature, less waste in manufacturing, environmentally friendly production, and low-cost products [Kar06][Rön07]. PE capabilities have been demonstrated in several applications such as fundamental active and passive electronic components, RFID tags, light emitting diode (LEDs) and OLEDs for displays, e-paper, sensors, photovoltaics (PV), active matrix (AM) or passive matrix (PM) display backplanes, membrane switches, flexible printed wiring boards (PWB), and thin batteries [San04][San05][Tuo06][Wal06][Eva01][Sko07][Gam04]. A major challenge is to produce those devices in large quantities at a reasonable profit. Roll-to-roll (R2R) or reel-to-reel processes, such as gravure printing, flexography, and offset lithography, provide many advantages in manufacturing electronic components in high volume and compatibility with large-area substrate printing. Even with several drawbacks to overcome, the additive nature of the PE process enables low-cost manufacture of components: the use of conventional plastic substrates, e.g., polypropylene (PP) and polyethylene terephthalate (PET), is limited to low temperatures (below 180ºC), whereas plastic substrates such as liquid crystal polymer (LCP) and polyimide (PI), which can resist high temperatures (180-300ºC), are again more expensive.

For a better understanding of the benefits of PE, comparison against current silicon processes demonstrates well the advantages and disadvantages of both technologies (Figure 1). Silicon processes, having been used for 30 years, are now considered a mature technology. From hereon called “conventional processes,” they have certain unquestionable advantages in performance, materials verification, e.g., characterization, reliability considerations, and material performance development, high resolution of line width/line spacing, and a long life cycle. PE should not be considered a “substitute” for the conventional processes but rather their “complement.” Yet the low production cost profile, environmental advantages in material waste, and the flexibility of either end product or production facility are inherent qualities of PE. Another advantage of PE over conventional processes is lower processing temperature in atmospheric conditions in electronics manufacture (depending on the process and materials used), whereas conventional processes usually require high temperature and a controlled, inert atmosphere. A low process temperature with PE enables implementation of temperature-sensitive substrates such as paper or plastics in electronics manufacture, especially since many organic materials cannot withstand the
high temperature requirements of conventional processes [Per07]. However, PE has its drawbacks such as feature size requirements of simple electronic circuits, defined by manufacturers for performance reasons as submicron features, whereas the narrowest printed line width is typically around 10 µm [Der07]. This line width is the starting point of Intel in 1970s where currently reached to 32 nm in their lately announced Westmere chips for early 2010. Furthermore, in some printing techniques, e.g., inkjet technology, the materials are immature, and developing functional materials constitutes a bottleneck to creating more sophisticated electronic structures. This chapter concentrates on contact printing methods, i.e., flexography, offset lithography, gravure printing, and screen printing, where printing plate or mesh (stencil screen) has direct contact with the substrate.

Figure 1. Comparison of conventional processes and PE in electronics manufacture.

2.1. Contact Printing Techniques

Offset lithography, screen, gravure, and inkjet printing are the dominant printing techniques, although almost all the previously mentioned printing techniques have been used to satisfy performance, resolution, ultra low-cost efficiency, and high volume requirements of electronics. Because the R2R described below and additive printing processes have their individual operational conditions, the rheology and drying time of ink and the conditions of curing may vary. Understandably, these parameters affect also
the formulation of the ink. For example, in organic ink formulation, the parameters may affect the chosen solution, suspensions, the simple blending process of conducting polymers and thickeners, fillers, cross-linkers, and solvents, which must be selected based on the printing process. An important property, expectedly, is then the wetting capability of the substrate, which is closely linked with the adhesion strength on the substrate. Printed and cured structures should be electrically functional and mechanically flexible for optimum final structural flexibility. On the other hand, electronic properties can vary based on the conditions selected for curing and printing [Sko07].

2.1.1. Flexography

Flexographic printing is a reliable technique, similar to the traditional rubber-stamp techniques, which have been in use for hundreds of years. These techniques differ in that the flexible stamp (also called cliché) is wrapped around rotary cylinders to enable a continuous rotary process of the system. The image plate cylinder is usually made of rubber but can also be designed from photopolymers, which can increase the resolution and lifetime or from plastic material to produce an image on different substrates, e.g., paper, plastic substrates, or metal foil [Bla05][Kar06]. To increase the processing life of the image plate cylinder, the printing plate should not be too soft nor too hard. Too soft a printing plate can wear out easily and too hard a plate can damage the substrate [Sko07]. In principle, flexography is based on a relief image pattern on the plate, which prints in a rotary fashion. The anilox roll with little cells or wells on its surface transfers the ink to the printing plate. The amount of ink to be transferred can be controlled with the size of the cells in anilox and wipes off any excess by the doctor blade before printing. Ink volume is thus precisely controllable to leave a thin film on the substrate after printing. The pressure of the impression cylinder helps transfer the ink from the printing plate and the image on to the printing substrate. The quality of the image is related to the applied pressure between plate cylinder and substrate materials and to the geometry of the anilox roll cells, depth, and volume. The thickness of the printed film can be controlled with the rotating speed, the type of the anilox roller and plate cylinder, and the pressure applied to the printing substrate [Gam04][Kar06][Sko07]. Figure 2 shows a schematic of flexography printing [Kar06].
The flexography method has several advantages and disadvantages in electronics manufacturing. The thickness of the ink film can be controlled especially over large areas. The printing ink may be either water-based or solvent-based, contributing thus to rapid drying, which makes flexography ideal for printing on materials such as plastic and foils [Sko07]. The softness of the printing plate enables printing on compressible surfaces such as cardboard. The spreading of ink outside the image area due to compressive pressure (halo effect) between the plate and the impression cylinder can be controlled by using a hard polymer cover or cushioned plates. In addition, the halo effect creates several problems with registration and size monitoring. Thus, high-quality printing is limited because of the variety of components and the pressure-sensitivity of the operation [Gam04][Kar06]. Flexography printing has been commonly used to print food packages, bags, and envelopes and recently antennas of RFID tags [San04][Mäk08].

2.1.2. Offset Lithography

Unlike the raised bumps in flexography printing, the offset lithography plate has hydrophobic and hydrophilic areas (a schematic of offset printing shown in Figure 3) [Kar06][Sko07]. In the process, hydrophobic ink is transferred to the hydrophobic areas of the printing plate. The printing image consists of image and non-image areas of varying dot sizes on metal plates. Thin metal plates holding the actual printing image are placed on the surface of the anilox roller. Because hydrophobic ink and water displace each other, the ink prints on the hydrophobic printing pattern to create an image. The offset plate simply transfers the image on to the substrate with the help of the impression cylinder.

However, wetting the printing plate is very complex. Successful printing of an image on the substrate requires precise calibration of the anilox roller and the surface energy of the offset plate. The advantages of small length scales, surface tension, and interfacial energy help separate the hydrophobic ink and water. In addition, the contrast between the contact angle of the hydrophobic/hydrophilic areas and the ink/water
contribute to the separation of ink and water to produce a printed image [Alm99] [Sko07]. Substrate rolls between the impression cylinder and the offset plate create continuous image transfer in this reproduction type known as offset lithography.

In the graphics industry, offset lithography is one of the most popular printing techniques, but it also used in the manufacture of electronics. This printing technique boasts excellent control, fast high-volume production, and high-resolution in printing electronic circuits. In addition, the manufacture of displays, sensors, passive components, and circuit boards has been demonstrated [Eva01]. Offset lithography provides thin, 1-2 µm, dry ink layer, which may require several printings to become sufficiently thick for conductivity in ink films [Bla05]. The downside, of offset lithography involves high start-up costs and start-up waste volumes on very short runs [Kar06].

![Figure 3. Schematic of offset lithographic printing. Oil-based hydrophobic ink prints on the hydrophobic areas of the substrate. Water is used to increase the resolution in the process and complex cylinder architecture to guide hydrophobic ink and water to the plate in the right configuration.](image)

### 2.1.3. Gravure Printing

Gravure printing (Figure 4) is the reverse of flexographic printing in terms of wetting the ink on the printing plate (called the rotogravure plate). In principle, ink is received from the ink reservoir directly or with an additional roller (sometimes the anilox roller is used to transfer ink from the ink reservoir) to the rotogravure plate, on which the pattern has been etched by laser or photolithography to hold the ink in the grooves. Any excess ink is removed by the doctor blade to control ink deposition before ink is transferred on to the substrate. Different amounts of material can be deposited in different locations according to the depth of the grooves. For successful printing, the surface of the substrate must be smooth enough for proper contact with the engraved grooves. Otherwise, inadequate contact occurs with the substrate, leading to reduced mechanical and electrical performance on the printed structure [Gam04][Mäk08][Sko07].
Figure 4. Schematic of gravure printing. Ink is received from the ink reservoir into the engraved grooves of the rotogravure plate, and any excess material is wiped by the doctor blade before the ink is transferred to the substrate.

Gravure printing is a high-speed process using low-viscosity materials. The system is costly, because of the expensive printing rolls compared to rubber-made rolls in flexography. On the other hand, it is very durable, and the printing rolls can well withstand various solvents [Mäk08]. For a low-viscosity ink for high printing speeds, solvents such as toluene, xylene, and alcohols are often used purely or together with water. Adequate viscosity can be achieved by thinning polymers into the above solvents in opposition to the thick ink requirements of screen and flexography printing. However, fast evaporation of the solvent and cross-linking of polymers pose a challenge in high speed printing [Sko07].

Conventional gravure printing creates a dot type image, which cannot be used to print conductive wires. However, it is possible to engrave a line structure on the rotogravure plate to manage wire printing [Mäk08]. Because different materials can be used in gravure printing, the technique is suitable for manufacturing electronics. The quality of gravure printing depends on the properties of the substrate, such as smoothness, compressibility, porosity, ink receptivity, and wettability and on the properties of the ink, e.g., its rheological behavior, solvent evaporation rate, viscosity, chemistry, and drying [Hre08]. Gravure printing has been used to manufacture ultra-high-frequency (UHF) RFID antenna [Reb08] and shown to be practical in manufacturing OLEDs [Tuo06].

2.1.4. Screen Printing

Screen printing is rather inexpensive and highly flexible for manufacturing electronics. It consumes small amounts of material with little waste and produces dry thick print layers (20-100 µm in general). Screen printing uses paste-like (high-viscosity) ink, and because it ensures adequate conductivity properties, the technology has been used to produce electronic components and PWB. Screen printing has also been used in PE for mass and small-scale production. However, it has limited resolution, limited throughput compared to R2R methods, such as gravure printing,
offset lithography, or flexography, and line roughness constitute the drawbacks of screen printing [Gam04][Par90].

Figure 5 shows the available screen printing methods, sometimes referred to “off-contact” printing. In contrast to screen printing, stencil printing is an “on-contact” (or “in-contact”) process. The stencil is a metal mask, which lies directly in contact with the surface of the board [Tar09]. In principle, the patterned, sharp-edged image on the mesh (also called stencil screen) is placed over the substrate and paste ink is squeegeed on to the substrate. The squeegee (roller in R2R) creates pressure contact against the substrate. In electronics manufacture, the screen printing mesh can contain an ultraviolet (UV) light-sensitive negative or positive image to achieve accurate printing. The mesh is usually made of polyester or stainless steel and coated with water-soluble photopolymeric material. On exposure to UV light, the image is created based on liquid photo-emulsion material, which hardens because it is insoluble. The process is finalized by washing (developing) the water-soluble image part under high water pressure. In an R2R system, the screen comes in the shape of a cylinder, and paste ink is deposited inside the cylinder. The pressure of the spatula forces the paste through the screen [Bla05][Gam04].

Figure 5. Schematic of (a) screen printing, (b) continuous R2R otary screen printing.

2.1.5. Material Requirements

For printing ink, flexography uses relatively viscous, 0.05 to 0.5 Pas, materials. Inks may be water-based, solvent-based, or UV-curable. The flexography process requires relatively high viscosity of conjugated polymers, which are usually partially soluble without additives. The right viscosity range can be achieved with several fillers.
and thickening agents. However, after formulation, the conductivity of the ink usually drops. On the other hand, wetting of the ink on the substrate is crucial, and the formulation of the ink usually calls for solvents and surfactants. Additives and surfactants are likely to decrease the electroactivity of the printed film during the formulation of printable ink material. Some functional materials have limited processability and solubility. Conductive and semiconductive polymers use aromatic and aliphatic hydrocarbons for solutions, solvents that are not compatible with photopolymer plates. In addition, flexographic plates usually swell and deform so that more resistant and reliable plate materials must be developed. Rather than aggressive solvents such as acetone and chloroform, flexography uses ethyl acetate, alcohols, and water, which are suitable for long-term use with soft rubber-like flexible stamps. Substrates suitable for flexographic printing comprise, e.g., paper, board, corrugated cardboard, flexible and rigid polymer, metal foil, and glass [Bla05][Hre08][Sko07].

In offset lithography, very viscous materials of 5 to 100 Pas have been used as printing ink to decrease the high shear forces in high-speed printing. The surface tension of the ink is about 35 mN/m and its polarity is low. Because the lithographic process requires strict control of ink rheology, commercial inks are formulated with conductive materials such as silver, copper particles or flakes, or carbon black materials. It is very difficult to formulate an organic ink to fulfill those requirements [Kar06][Nan07][Sko07]. On the other hand, water in the process may compromise the conductivity of the printed ink film, a problem that is overcome with the waterless/UV ink and waterless offset printing described in [Bla05].

Gravure printing usually uses water-based, solvent-based, or UV-curable inks with ink viscosities varying from 0.01 to 0.2 Pas and other the ink requirements depending strongly on the curing process. The high printing pressure requirements limit its applications to flexible substrates. On the other hand, the intermediate, compressible cylinder is used to print on rigid substrates. Because of nature of the cylinder, it is probably the most resistant to strong solvents. In addition, the materials must meet other requirements such as good lubricity, low abrasion, and low corrosivity to increase the life of the doctor blade and cylinder in high-volume production [Bla05][Hre08][Sko07]. Indium tin oxide (ITO) nanoparticle inks can be used in gravure printing in applications such as displays, sensors, and solar cells [Pue08]. Furthermore, other functional inks, e.g., conductive polymers, light-emitting polymers, and dielectrics, are formulated to meet the requirements of gravure printing [Hre08].

In screen printing, thick (paste-like) materials with a viscosity of about 0.1 to 50 Pas have been used as printing inks. Thanks to adjustable ink formulation, either thick or thin films can be printed with the thickness of the dry film varying from 20 nm to 100 µm [Bla05][Jab01][Tu92]. The ink must be compatible and wetted suitably for various substrates to decrease the contact angle, because it is important to achieve high adhesion between ink and substrate after curing. The electrostatic integration between ink, mesh, and substrate may affect ink transfer to the substrate and the final quality of the printed film, and problems may arise because the substrate or the ink has chemical dipoles or because the ink contains ions [Sko07]. Table 1 on page 20 summarizes several important parameters of each of the contact printing techniques and compares
those parameters with non-contact inkjet printing techniques in the following chapter [Bla05][Gam04][Hal09][Per07][Sko07][Rob99][Org08].
3. Inkjet Printing Technology

Inkjet printing technology is a non-contact method, which uses several inks jetted repeatedly from the printhead to form small droplets that can be directed accurately on to the substrate [Cag10][Buc05][Le98]. Inkjet printing methods can mainly be classified based on printhead types into continuous-mode (CIJ) and drop-on-demand (DoD) [Le98][Kip04]. The main difference between those techniques is that in the CIJ process, only part of the continuously generated flow of ink drops is directed onto substrate in accordance with the image. However, in DoD inkjet processes drops of ink are only generated if the image data to be printed requires them [Kip04]. CIJ method can be subdivided into binary deflection, multi-deflection, Hertz, and microdot. In addition, DoD inkjet techniques are subdivided into thermal, piezoelectric, electrostatic, and acoustic (Figure 6) [Le98]. On the other hand, an interesting inkjet manufacturing method, super-fine inkjet (SIJ) technique, has been developed in Japan by the National Institute of Advanced Industrial Science and Technology (AIST). SIJ that has similar printing of digital image data, such as DoD techniques, is used for super-fine line patterning in electronic miniaturization and enables precise patterning of three-dimensional (3D) materials on desired surfaces.

![Figure 6. Map of available inkjet printing techniques [Le98]. This thesis focused on shear mode heads.](image)

[Image 102x161 to 492x433]
3.1. Continuous Mode Inkjet (CIJ) Technology

In the CIJ system, the ink is broken into uniform droplets shortly after it is jetted from the nozzle. Variable droplet size is realized with jet velocity and an electrostatic field, which creates periodic excitation at the nozzle. In the traditional CIJ, a piezoelectric transducer is coupled with the printhead to provide periodic excitation; therefore, oscillations are mechanical [Uji06]. The route of droplets can be controlled with the electrical field after they leave the nozzle. Charged droplets are then directed to their intended location on the substrate. The droplets can be deflected in either a binary or multiple ways. In binary deflection, droplets are directed to a single pixel location on the substrate or to the gutter, where the ink is recirculated. In multiple deflection, drops are charged varyingly and deflected to the substrate at different levels, creating thus several pixels [May05]. In addition to these two methods, Hertz and microdot CIJ techniques are developed by the Lund Institute of Technology (Sweden) and Hitachi, respectively, in 1980s [Stu89][Le98]. Hertz’s CIJ method can be classified separately, because of the unique way of obtaining the gray scale through a burst of small drops. On the other hand, microdot CIJ technique uses small size satellite drops to print high resolution image on the substrate and recirculates the normal size drops through the gutter [Stu89].

Figure 7 shows the continuous type inkjet printing system [Piq02][Uji06]. CIJ printing is usually used in high-volume industrial production of barcodes and labels, e.g., product labels of foods or medicines, and the droplet size can be as small as 20 µm with 150 µm being the standard [Piq02]. However, in electronics manufacturing, CIJ printing produces large droplets of inadequate resolution because of the long flying distance between printhead and substrate [Bla05][Gam04].

Figure 7. Schematic of the continuous inkjet printing system. The system uses either multiple or binary deflection [Piq02][Uji06][Mei05].
3.2. Drop-on-Demand Inkjet (DoD) Technology

DoD inkjet technology uses computer-aided design (CAD) image file and provides high speed and scalability, allowing the use of high-frequency multiple nozzles. On the other hand, different types of inks can be printed in one printing process which is similar to the well-known color inkjet printer [Piq02]. DoD inkjet processes can be classified according to the way that the individual drop is generated [Kip04]. The thermal inkjet printer has an electric heater inside the nozzle that quickly raises the temperature of the ink to facilitate flow. The heated ink creates a vapor bubble, which, expanding, ejects a droplet of ink through the nozzle orifice. Water-based inks are usually preferable, because they produce more explosive bubbles than other solvents [Piq02]. However, thermal inkjet printing methods are not compatible with heat-sensitive inks and has impact on ink in general which obstruct their implementation to manufacturing of electronics [Le98][Cag10][Bla05][Gam04].

The piezoelectric inkjet system (Figure 8 [Piq02]) jets the ink using an applied voltage pulse to the electrodes of the piezoelectric element to create mechanical movement inside the ink reservoir. The volume of the ink reservoir is reduced by mechanical pressure to squirt ink out of the nozzle. Piezoelectric offers substantial benefits on use of inks and facilities electronic manufacturing. Piezoelectric printheads vary according to the geometry of the drop ejector and/or the operation of the piezoelectric element, i.e., squeeze tube, bend, push, and shear [Uji06]. Squeeze tube printhead was introduced in late 1970s and encountered difficulty in achieving jet-to-jet uniformity in its second-generation. In theory, both bend- and push-mode printheads have design where piezodrivers has direct contact to ink. However, the undesirable interaction in between piezodrivers and ink is difficult to prevent in practical implementation. In a shear-mode, the piezodriver becomes an active wall in the ink chamber and the shear action deforms the piezoplates against ink to jet a droplet which has no impact on ink [Kip04][Le98][Cag10]. Electrostatic inkjet printer uses electrical field exists between the inkjet system and the surface to be printed. It means that the electrical force is image-dependent in the inkjet nozzle system, either the forces can be balanced or the surface tension ratios between ink and outlet nozzle can be changed. Thus a drop of ink is released as a result of the field forces. In acoustic (piezo-acoustic) inkjet system, an electric voltage is applied and the channel cross-section will be deformed by the inverse piezo-electric effect to fire a droplet. This results in acoustic pressure waves inside the channel [Wij07]. At the moment, electrostatic and acoustic techniques are in the development stage that their applicability to electronic manufacturing requires further research.

The manufacture of electronic component by inkjet printing requires a wide range of functional materials, such as inorganic/organic conductors, dielectrics/insulators, semiconductors, and ECAs, which set limits on current inkjet printing methods. However, several research groups and laboratories are currently working on the formulation of these materials. In addition, it embraces high position accuracy and thickness control, precise droplet volume, and excellent layer-to-layer registration which enable the manufacture of precise and complex electronic
components in electronic miniaturization [Cag10][Kai08a]. However, there are issues to over come in DoD systems. Throughput of DoD inkjet printing systems is low and the printing speed relatively slow at the moment, 0.1 m²/sec and 15-100 m/min, respectively, compared to the R2R processes [Piq02][Gam04][Kai08a].

![Figure 8](image.png)

**Figure 8.** Schematic of the DoD inkjet printing system. The piezo electric crystal (piezo ceramic element) actuates a voltage pulse to create pressure on the diaphragm, which jets an ink droplet. Each droplet ejected from the printhead nozzles is based on a dot-matrix CAD digital image, which cuts the amount of waste and requires no recycling of ink, obviating an ink recirculation system (gutter) in CIJ printing [Cag10][Piq02][Mei05].

**Super-Fine Inkjet (SIJ) Technology**

SIJ technology was invented by Kazuhiro Murata, head of the Collaborative Research Team of Super Inkjet Technology, a section of the National Institute of AIST of Japan. SIJ is one of the most interesting techniques to form super-fine submicron wiring patterns and three-dimensional structures. The technology makes it possible to eject super-fine droplets smaller in size (at least 1/10) and volume (1/1000) than those ejected by the conventional DoD inkjet printer [Mur04][Mur07].

The SIJ printing system (Figure 9) is principally similar to other DoD systems. The droplet volume, size, and placement accuracy on the substrate can be controlled more accurately than in the currently available inkjet printing systems. The SIJ system uses an electrostatic force to add kinetic energy to the droplets to minimize the number of undesired droplets landing on the substrate. The small droplet diameter of less than a micron of nano-ink is possible to achieve which helps the solvent vaporize rapidly. Furthermore, the viscosity of the ink increases markedly in SIJ printing, accelerating the drying of each droplet [Mur07]. In addition, the substrate surface does not require any
surface treatment, e.g., hydrophobic/hydrophilic patterning, or bank patterning, to control the spreading of droplets in fine-line interconnections [Mur03].

![Diagram of the SIJ printing system](image)

**Figure 9.** Schematic of the SIJ printing system. The SIJ printer, considered part of DoD inkjet technology, is supported by the pressure regulator and a high-voltage amplifier to eject droplets at high pressure, increasing their velocity in flight [Mur08].

Several inks with an interesting material content have been used in SIJ printing such as carbon nanotubes, silver and gold nanoparticles, functional ceramics, electro-conductive polymer, and fluorescent dyes [Mur03][Mur05][Mur07]. The SIJ is appealing particularly because of its capability for super-fine interconnection patterning and fine patterning of circuit boards, miniaturization of microelectronic packages, or fabrication of 3D metal bump arrays and micro cylinders. However, the SIJ printing system is not yet commercially available, and research by industry and academia is necessary on conducting joints to improve the technology [Mur05]. In addition, boosting the throughput of the system for large-area patterning may turn out to be challenging.

### 3.3. Material Requirements

Originally, ink was formulated for inkjet printers in the graphic arts industry to achieve better visual quality and reliable prints. The inks used in the graphic arts industry are usually solvent-, oil-, or water-based, and dyes or pigments are used as colorants. The inks that are used in inkjet printing of electronics have similar physicochemical properties compared to the inks that are used in the graphic arts industry. Thus the theoretical background from graphic industry can be used to understand the ink behavior without omitting the effect of nanoparticles in nano-inks. In addition, some characteristic and ink (paste) requirements of non-contact and contact printing techniques in PE should be compared in order to evaluate the capability of nano-inks in manufacturing of electronics.
3.3.1. Theoretical Background

Functional inks that are used in inkjet printing technology have physicochemical requirements such as viscosity and surface tension which are the most important parameters. The theoretical requirements of ink viscosity and surface tension are in the range of 2-30 mPas and 25-35 dynes/cm, respectively. Even so, the viscosity range of nano-ink recommended for today’s printheads should preferably be 5-15 mPas. In addition, the density of the ink affects drop formation, which is usually described by the Reynolds (Re) and Weber (We) numbers in equations 1 and 2:

\[
Re = \frac{\rho V L}{\eta} \\
We = \frac{\rho V^2 L}{\sigma}
\]

(1)  
(2)

where \(\rho\), \(V\), \(L\), \(\eta\) are density, fluid velocity, length, and viscosity, and \(\sigma\) is surface tension. Reynolds number is a non dimensional parameter defined by the ratio of inertial forces to viscous forces and Weber number is the ratio between inertial force and the surface tension force. On the other hand, the Navier-Stokes equation describes droplet formation based on the Reynolds and Weber numbers, usually called the Ohnesorge number (Z) [Ohn36] and written as in equation 3:

\[
Z = \frac{We^{1/2}}{Re} = \frac{\eta}{(\rho d_a \sigma)^{1/2}}
\]

(3)

where \(d_a\) is the jet size measurable from the drop diameter. If Z is bigger than 2, drops can, according to Fromm [Fro84], form in the DoD system. However, according to Reis et al., Z is in the range of 1 and 10, where the lower limit is limited by viscosity and the upper limit represents unwanted satellite formation [Rei05]. In this work, these equations were used to understand the theoretical background of functional ink in inkjet printing technology. Because this thesis focused on using the materials in PE, calculations were omitted.

On the other hand, formulated nano-ink must show Newtonian behavior so that under variable temperature and pressure the shear stress of the ink remains reliable, a parameter that also to a degree defines the viscosity function of the ink. The printhead temperature may vary during printing because of the adjustment of the printing XY table temperature, and because the short distance, usually <1 mm, between printhead and substrate may increase and have an effect during long printing runs. Using nanoparticles in formulating the ink in inkjet printing has been attracting wide attention in PE. The particle distribution and the particle size of the ink define the ink’s suitability for industrial printheads in continuous printing. The particle size of the selected ink material should be less than 100 nm, and the nanoparticles should be uniform in size and homogeneously distributed in the solvent. The dispersion of nanoparticles in the ink is important to avoid aggregations, which may increase the viscosity of the ink during printing and cause undesired clogging at printhead nozzles [Cag10][Cal01]. On the other hand, a major challenge encountered during long printing runs is the drying of the printhead nozzle, which can be controlled with low-volatile ink. Fast evaporation can
promote nozzle drying if the printhead temperature keeps varying during printing. In addition, before and during printing, parameters such as droplet firing voltage, jetting waveform, printhead nozzle size, piezo printhead pulse shape, and jetting repeatability should be defined. Furthermore, droplets should be small in volume to produce narrow lines, which also increase solvent evaporation in producing complex electronic components demanding smaller physical size in microelectronics. Thus, it is important to define how droplets spread after they have reached the substrate. Drop spreading affects the thickness of the inkjet-printed film and the lateral resolution of the materials produced [Lew02]. Drop spreading can be estimated using the following equation:

$$\frac{r_{\text{max}}}{r} = \left( \frac{W e^2 + 12}{3(1 - \cos \theta) + 4 W e^2 / R e^{1/2}} \right)^{1/2}$$

where $r_{\text{max}}$ is the maximum drop radius after impact, $r$ is the initial drop radius, and $\theta$ is the contact angle between ink and substrate. In this work, the equation for drop radius was considered a supplementary tool to understand how ink behaves in printing, and further calculations were omitted, as they would have been beyond the focus of this work.

### 3.3.2. Contact versus Non-Contact Printing Techniques

In non-contact printing methods, e.g., inkjet printing, printing on non-planar surfaces is possible which enables to use irregular surfaces. Non-contact printing allows using wider variety of substrates compared to the contact printing which usually relies on paper, board, and thin-film polymers. In addition, the use of high resolution to achieve narrow printed line width is offer benefits to reduce the size of electronic system which is the purpose of microelectronics applications.

A non-contact printing method uses digital image which allows rapid changes in the electrical design and on the production line to manufacture individual products which is one of the most important advantages of the technique [Kai08a][Rön07]. However, the throughput of non-contact printing is lower than contact printing methods which currently limit the speed in mass production. Throughput of printing method is depending on many factors, such as printing speed, the area of printing for each printing cycle, operational speed of supplying a new printing substrate, the method of ink supply (continuous or intermittent), amount of printed character per each print cycle, and equipment maintenance [Kip04][Gam04][Bla05]. Table 1 summarizes several important parameters of each of the contact printing techniques and compares those parameters with non-contact inkjet printing techniques. In addition, Table 2 describes the important parameters of each of the above inkjet printing technique in detail [Bla05][Gam04][Hal09][Hon08a][Kai08a][Per07][Sko07][Rob99][Org08].
Table 1. Some characteristic and ink (paste) requirements of selected printing processes in printed electronics [Bla05][Gam04][Hal09][Kai08a][Per07][Sko07][Rob99][Org08].

<table>
<thead>
<tr>
<th>Printing form</th>
<th>Flexography</th>
<th>Offset lithography</th>
<th>Gravure printing</th>
<th>Screen printing</th>
<th>Inkjet Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relief (polymer plate)</td>
<td>Flat (Al plate)</td>
<td>Engraved cylinder</td>
<td>Stencil and mesh</td>
<td>Digital</td>
</tr>
<tr>
<td>Typical resolution</td>
<td>60</td>
<td>100-200</td>
<td>100</td>
<td>50</td>
<td>60-250</td>
</tr>
<tr>
<td>(lines/cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ink viscosity (Pas)</td>
<td>0.05-0.5</td>
<td>30-100</td>
<td>0.01-0.2</td>
<td>0.1-50</td>
<td>0.002-0.1</td>
</tr>
<tr>
<td>Substrates</td>
<td>Paper, boards, polymers</td>
<td>Paper, boards, polymers</td>
<td>Coated paper and boards, polymers</td>
<td>All</td>
<td>All, 3D possible</td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>0.5-2</td>
<td>0.5-2</td>
<td>0.5-2</td>
<td>5-25</td>
<td>0.1-3</td>
</tr>
<tr>
<td>Line width (µm)</td>
<td>20-50</td>
<td>10-15</td>
<td>10-50</td>
<td>50-150</td>
<td>1-20</td>
</tr>
<tr>
<td>Registration (µm)</td>
<td>&lt;200</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>&gt;25</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Throughput (m²/sec)</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>&lt;10</td>
<td>0.01-0.1</td>
</tr>
<tr>
<td>Printing speed (m/min)</td>
<td>100-500</td>
<td>200-800</td>
<td>100-1000</td>
<td>10-15</td>
<td>15-500</td>
</tr>
</tbody>
</table>

Table 2. Some characteristic and ink requirements of the described inkjet printing techniques [Bla05][Gam04][Hal09][Hon08a][Sko07][Org08].

<table>
<thead>
<tr>
<th>Printing form</th>
<th>CIJ</th>
<th>DoD</th>
<th>SIJ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>non-contact (digital)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolution (lines/cm)</td>
<td>60</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Ink viscosity (Pas)</td>
<td>0.002-0.025</td>
<td>0.002-0.1</td>
<td>0.008-0.03</td>
</tr>
<tr>
<td>Substrates</td>
<td>all</td>
<td>all, 3D possible</td>
<td>all, 3D possible</td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>0.1-3</td>
<td>0.2-2</td>
<td>1-3</td>
</tr>
<tr>
<td>Line width (µm)</td>
<td>20</td>
<td>&lt;10</td>
<td>1</td>
</tr>
<tr>
<td>Registration (µm)</td>
<td>-</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>Throughput (m²/sec)</td>
<td>0.1</td>
<td>0.01-0.1</td>
<td>-</td>
</tr>
<tr>
<td>Printing speed (m/min)</td>
<td>120-500</td>
<td>15-100</td>
<td>-</td>
</tr>
</tbody>
</table>
4. Applicability of Functional Materials to Manufacturing of Electronics

The growing interest in manufacturing electronic circuits by inkjet printing techniques and the latest development in organic conductive materials have enabled production of electronics and definition of the objectives of ink suppliers active in PE. According to estimates of company activities over the next five years from 2008 (Figure 10), suppliers formulating novel ink materials in PE and setting up high-volume ink manufacturing facilities will have an important role in the development and commercialization of PE. Whether functional ink (or paste) is manufactured in-house or outsourced, its applicability to PE manufacture requires an understanding of the manufacturing steps and each process step should be defined.

Figure 10. Areas of company activities in PE; figures stand for the number of active companies in each field [Idt08].

Figure 11 defines each process step in inkjet manufacture and shows the impact of ink on those steps [P5]. The functional ink in the chart (e.g., organic/inorganic conductors, semiconductors, dielectrics) is purchased mainly from ink suppliers. Ink was first evaluated in initial printing tests, in which a research-based material testing printer [Fuj09a] and a drop watcher [Ima09a] were used to define the jetting parameters of the functional ink. The results were used as a baseline for an industrial printer [Ima09b] to optimize jetting parameters for industrial printheads [Xaa09][Fuj09b]. These parameters comprised drop diameter, drop formation, flight time, drop velocity, drop angle on the XY platen, tail merge, and frequency sweep [P5]. In this chapter, some selected functional materials, i.e., nanoparticles on flexible organic substrates, are explored in detail. Furthermore, some inkjet printing, assembly, and packaging
requirements are discussed to provide technical background for the applicability of functional materials.

![Figure 11. Implementation of new functional materials in electronics manufacture [P5].](image)

## 4.1. Nanoparticles

Printable electronics is now increasingly benefiting from recent developments in nanoparticle research and exploiting the advantages of low sintering temperature requirements, which enable the use of low-cost substrates. Hence, nanoparticles offer new opportunities for manufacturing flexible electronic components and systems. The nanometer scale of particles increases the ratio of surface area to volume [Cag10][Buf76]. Because of the advantage of particle size, the sintering temperature of conductive particles such as silver (Ag) and gold (Au) can be reduced below that of their bulk form and their sintering time shortened [Cag08a][Buf76]. In addition, nanoparticles have good mechanical properties such as fatigue resistance, large surface energy, and spatial confinement, compared to their micron particle size [Won03][Ko07a], enabling printing on low-cost and temperature-sensitive flexible organic substrates. Yet nanoparticles have several disadvantages, e.g., long-term sedimentation, which sometimes causes them to agglomerate in the printhead even at low temperatures, and maintenance of the stability of the formulated ink at room temperature. Some nano-inks are preserved by either a dispersant or a polymer shell around the particles and the liquid vehicle to improve their stability at room temperature and to guarantee a longer shelf life [Cag10][P3][Cag08a][Har08].

Accordingly, some general rules can be established for nanoparticles: (1) nanoparticles should be highly dispersible in their solvent medium, (2) they should be thermally and mechanically stable without particle aggregation, and (3) they should preferably come in a narrow range of particle size for inkjet printing applications [P1] [P2][P3][P5]. In this thesis, the applicability of Ag nano-inks was studied in applications such as electronic circuits in low-end and high-end electronics.
4.1.1. Metallic Nanoparticles

Ag, Au, and copper (Cu) nanoparticles are perhaps the most investigated metallic elements for formulating inkjet printing ink and understanding their printed film properties [Bie03][Che05][Ful02][Hua03][Kim05][Par06][Per06][Sug07][Yi08][Zha07]. Ag nanoparticles are spherically very fine and highly dispersible when used in inkjet printing ink to produce flat mirror-like surfaces. Ag nanoparticles can be prepared in several ways, e.g., by electrolysis, by chemically reducing water-soluble silver salts in an aqueous medium, by gas evaporation, and by atomization [Cag10][Mag03a][Tse08]. On the other hand, Au nanoparticles have a particle diameter of less than 5 nm and low sintering temperature compared to their bulk form and are highly conductive [Buf76]. These Au nanoparticles were diluted in either alpha-terpineol or toluene as vehicle (solvent), whereas most commercially available inks consist of hydrocarbons and tetradecane [Ko07b][Ko08][Hua03][Chu04]. Au nanoparticles have a resonance light absorption property and absorb laser light, whereas the solvent is translucent and enables laser sintering of the particles [Hos98][Bie03]. The tested Au nanoparticles in [Ko07b][Ko08][Hua03][Ful02] were used to produce high-resolution source and drain electrodes for transistors; the ink was compatible with some applications in flexible electronics.

Also other nanoparticles such as platinum (Pt), palladium (Pd), and nickel (Ni) have been extensively studied for their potential to be used in compatible solvents as inkjet ink [Tse06a][Tse09]. Spherical Pt nanoparticles were formed in a polymer dispersion in a particle size of about 3-10 nm for inkjet printing technology [Ge07]. Pd nanoparticles were studied to reduce their suitable oligomers, and the formulated ink was demonstrated to pattern a Pd catalyst for electroless deposition of Ni [Tse09]. Ni nanoparticles were used in screen printing applications in their paste form in [Tse06a], but the viscosity can be decreased to suite inkjet printing media as well.

In addition, alloying metallic nanoparticles offers better mechanical and electrical properties for inkjet-printed film and cuts down the number of voids by retarding the growth of silver grains [Cag10][Oka06]. Ag-Cu nano-ink was inkjet-printed to form electrodes in organic field-effect transistor (OFET) applications on a glass substrate [Gam07]. Though alloying provides good electrical properties, oxidation of Cu and its relation to thermal treatment in air constitute the technical problems to overcome [Yi08]. Ag-Pd nanoparticles-based paste was prepared to form a fine-pitch pattern with a line and space of 30 μm/30 μm, and their potential as ink in inkjet printing media was investigated [Nak07][Par09a].

4.1.2. Ceramic Nanoparticles

Because of their tunable dielectric properties, ceramic nanoparticles are important in high frequency applications. At micro- and millimeter-wave frequencies, the particles have low loss and excellent RF power capabilities. In tunable dielectric materials, dielectric properties are tunable under the action of an applied electric or magnetic field. They are voltage-dependent and their dielectric constants value may
vary depending on the applied voltage [Jai08][Liu06]. The possibilities and requirements for inkjet printing of some ceramic particles such as zirconium (Zr) and titanium dioxide (TiO$_2$) were studied in the 1990s. Studies showed that to prevent premature gelation ceramic particles should, on average, be no larger than 10 nm [Bla96][Xia97][Atk97]. In some previous studies, zirconia (ZrO$_2$) ceramic powders were formulated to produce an ink for inkjet printing media. The ink consisted of 14.2% ZrO$_2$ with 2.8 mPas viscosity and was inkjet-printed on a paper substrate [Zha03]. Furthermore, tunable dielectric barium titanate (BaTiO$_3$) grades have been formulated for inkjet printing [Kay03][Kay07]. For instance, barium strontium titanate (BST) inkjet-printed on aluminium oxide (Al$_2$O$_3$) and magnesium oxide (MgO) substrates has been demonstrated with line widths of 100 µm and 200 µm, respectively. BaTiO$_3$ ceramic nanoparticles of particle size 100-200 nm have been inkjet-printed and a ceramic film of thickness 1.5 µm has been fabricated by multilayer deposition [Din04]. BaTiO$_3$-Ni nanoparticles with an average particle size of 60 nm have been formulated, and the ink has been inkjet-printed on flexible porous substrates [Tse06b].

Ceramic nanoparticles must be further investigated for ink formulation for inkjet printing technology. Ink design, modeling of ink dynamics during inkjet printing, robotics, and controls are only some of the current challenges in direct-write fabrication. The ceramic nanoparticles being used are still coarse, and defining the rheological properties of ceramic ink for piezo printheads is an ongoing effort. Particles of less than 100 nm are emerging in formulated nano-inks, but challenges may arise because of the overlooked volume effects and increasing drying stress of the inks [Lew02].

4.1.3. Organic and Other Nanoparticles

Organic materials may prove to be an important phase in the development of PE. They have several advantages such as low unit cost, flexibility, robustness, wide applicability, and electrical performance alternatives in several applications such as RFID tags, display backplanes, LEDs, and disposable consumer electronics [San05][Wal06]. The branch of electronics where organic materials, e.g. conductive polymers, plastics, or small molecules, are used is called organic electronics (OE), plastic electronics, or polymer electronics. OE technology can be divided into three main groups, organic dielectrics, organic semiconductors, and organic metals (consisting of colloidal nanocrystals of metals and metal nanoparticles) [San05]. Conjugated oligomers and polymers such as poly (3, 4-ethylenedioxythiophene)-poly (styrene sulfonate) (PEDOT: PSS), pentacene, and polyaniline (PANI) are some of the conductive polymers that have been thoroughly investigated in recent decades for inkjet printing applications [San05][Nog06].

However, apart from organic pigments smaller than 100 nm [Bis97], the use of organic nanoparticles to formulate ink and printing with these inks have not been widely reported. In some previous studies, functional organic nanoparticles were shown to have an average particle size of 55 nm and were inkjet-printed in oil-in-water microemulsions; the method’s potential for using many organic water insoluble molecules was described for inkjet printing [Mag03b]. Water-dispersible PANI–PSS nanoparticles of size 30 nm were inkjet-printed in sensor applications [Jan07]. Though
the synthesizing of smaller than 20-nm organic nanoparticles has been reported, preparation of nanoparticles faces many challenges in terms of synthesis and isolation [Jag06]. Other nanoparticles recently studied for inkjet printing are nanoparticle-based color pigments for conventional inkjet printing [Men99a][Men99b], diamond nanogrits on p-silicon and copper substrates [Fox00], nanosize magnetic ferrofluid grains [Sen99][Voi03], and last but not least, ultrafine ITO nanoparticles [Hon08b].

4.1.4. Future Trends of Nano-Inks in Inkjet Printing

The inks commonly used in inkjet printing technology are commercially available Ag and Au nano-inks. Their electrical properties are high and air stable compared to the performance expected of organic conductors. However, the sintering temperature of Ag and Au nano-inks is high for many low-cost organic substrates. Especially with a high metal content in the solution, the ink rarely shows the good electrical performance of its bulk form at low sintering temperatures. With these nanoparticles, laser sintering is an alternative, but the option is still being researched [Pek07a][Pek07b]. Another alternative is to lower the sintering temperature of the nano-ink by reducing its metal content and to formulate the ink with organic precursors, hence the name metallo-organic ink [Dea05]. Metallo-organic ink enables UV curing of the organic shell around nanoparticles and requires low-temperature sintering at the final sintering stage. This method has the advantage that it allows use of temperature-sensitive low-cost substrates [Wan08]. Yet another alternative is to sinter Ag nano-ink at room temperature, which opens up the choice of a wide variety of substrate materials and makes it possible to reduce thermal stress and damage problems [Sug07].

However, Ag nano-ink does have some drawbacks such as electromigration, metal corrosion, and high price. Nevertheless, its electrical and chemical problems can be controlled or minimized by alloying the ink with nanoparticles of other precious metals such as Au, Pd, and Pt. Nanoparticles such as Ni, Al, and Cu can be used to improve the electrical and mechanical properties of inkjet-printed and alloyed Ag film structures [Oka06][Nak07][Par09a]. Cu is known to oxidize and form insulating oxides on its surface and thereby compromise the conductivity of printed interconnections. Yet solutions exist to safely implement high-copper precursor ink in inkjet printing. Cu nanoparticles show relatively less electromigration than other novel metals and are less expensive than Ag or Au nanoparticles [Par07][Roz02]. Several companies such as Cabot, Applied Nanotech, Harima, and Novacentrix are actively developing and commercializing inkjet printable Cu ink. Furthermore, Ag nanoparticles were used to coat Cu flakes to create a hybrid metal-organic/metal nanoparticle ink and to produce smooth, dense, and highly conductive inkjet-printed lines [Cur01].

Emerging in inkjet printing now are low-k or high-k dielectric materials for passive component implementation in electronics. Low-k dielectric inks have the potential to be used as dielectric interlayers in multilayer structures, whereas high-k (>3.9 which is the reference dielectric value of silicon dioxide) dielectrics such as SU8 can as thin films work as good insulators and be used as transistor gate material to reduce the operating voltage. For instance, PI, poly(4-vinylphenol)(PVP), and siloxane
polymer type dielectrics have been studied, and several material suppliers such as Honeywell, Chisso, Sun Chemicals, and Polyera have commercialized such dielectric inks. However, because of their manufacturing costs and the suppliers’ intellectual property right (IPR) policies, these materials are expensive to acquire. On the other hand, dielectric materials are commonly spin-coated in microelectronics applications, and owing to their low viscosity and adequate dielectric properties, some of them can be adapted to inkjet printing [P1][Kim09a][Zha02].

Semiconductors such as poly(3,3”-dialkylquarterthiophene) (PQT-12), poly(3-hexylthiophene) (P3HT), and pentacene constitute another important material group for printing OFET and thin-film transistor (TFT). Semiconductors are expected to be environmentally, electrically, and thermally stable with a high on/off ratio and a low off-current and low processing costs. P-type semiconductors are currently the most available inks, but n-type semiconductors are emerging in the market and will enable to produce complementary metal–oxide–semiconductor (CMOS)-circuits. Even though numerous research publications on the inkjet-printing of transistors were done by research labs of universities and companies, there is a lack of commercially available semiconductor-ink. However, several companies such as Merck, Sigma-Aldrich, H.C. Starck, Polyera, and Plextronics are actively commercializing inkjettable semiconductors. Carbon nanotubes (CNTs), i.e., allotropes of carbon, are other interesting semiconductors to be used in inkjet print technology, and the business of formulating ink from them is expected to grow [Ago03][Kor06]. CNTs show very high mobility, i.e. intrinsic mobility estimates (>100,000 cm²/Vs) at room temperature [Dür04], excellent mechanical strength, and high electrical and thermal conductivity [Cao08][Lew06]. A major minus with CNTs is their current price, €1,000 per kilogram, though some companies are already producing them on an industrial scale at as low a price as €50 per kilogram [Bay05].

Attaching electronic components and integrated circuits (ICs) to a board is an important phase in the manufacture of electronics. Usually, electronic parts are either soldered in bump form or attached by electronic adhesives such as anisotropic conductive adhesives (ACA), isotropic conductive adhesives (ICA), non-conductive adhesives (NCA), and polymeric adhesives to the circuit board. However, ECAs have drawbacks such as large particle size and high viscosity, which are not suitable for jetting. Some research groups in PE and especially in inkjet printing technology have focused on this problem and inkjet-printed non-filled glue dots and ICA with resin fill. The physicochemical properties of ICA have been reported as 30 mPas and 8 µm for viscosity and particles size, respectively [Kol07][Wal06]. In addition, solder columns, bumps, and tin-lead solder balls of Sn63/Pb37 were inkjet-printed in high-density microelectronic and optoelectronic package applications at rates of over 400 bumps/sec [Hay98][Hay99][Lee08].
4.2. Flexible Organic Substrates

Organic substrates are ideal for electronics applications that require flexibility. They can easily be bent (except traditional rigid thick flame retardant 4 (FR-4) printed circuit board (PCB) without loss of function, they permit R2R processing in large-area printing, and are inexpensive and cost-effective. Some of the most common substrates used in inkjet printing technology and in our tests are PET, polyethylene naphthalate (PEN), LCP, PI, polyethylene, and PP. Organic substrates used in PE and OE should meet several requirements: surface roughness, thermal and thermomechanical properties, chemical properties, mechanical properties, optical properties, and electrical and magnetic properties [Won09]. Though most of the above flexible organic substrates are commercially available, they should be further developed to gain better barrier properties against moisture and oxygen absorption, which are their technological drawbacks. Organic substrate material suppliers active in PE comprise DuPont, DuPont Teijin (an independent firm), and 3M and substrate business developers, barrier technology providers, and applications enablers such as Coveme and Vitex Systems.

In addition, the engineering properties of flexible organic substrates must be carefully defined and selected before substrates are applied to inkjet printing [Won09][Ste06][Tay07]. The substrates should have (1) low coefficient of thermal expansion (CTE), preferably below 20 ppm/°C for silicon-based device materials, (2) low and uniform shrinkage, (3) resistance to high temperatures to process metal-enriched nano-inks, (4) smooth surface for adequate quality in a multilayer structure, which affects overall device manufacture and performance, (5) moisture resistance and barrier properties, (6) optical properties such as clarity and light transmittance for display applications, (7) rigidity to sustain flexural stress and stiffness to undergo handling (PEN Teonex® and PET Melinex® are three times stiffer than PI Kapton HN [Ste06]), and (8) commercial availability and low-price.

PI (DuPont Teijin Films Kapton® HN in our studies) is a common flexible organic substrate in electronics supplied by several manufacturers under trade names such as Kapton®, Apical®, and Upilex®. Kapton® PI offers benefits on electrical properties, chemical resistance, tear resistance, and tensile strength than any other flexible organic substrate. However, on the downside are its high moisture absorption (up to 3% depending on formulation) and its relatively high price compared to polyethylene [P2][Cag08a][Fje06]. PI is chemically etchable, which makes for traditional lithography to manufacture both complex and ordinary electronic structures. Because PI absorbs yellow in the visible, it is unsuitable for transmissive displays or bottom-emission OLED displays. PI is an amorphous, solvent cast type material, and in general amorphous films are not fully densified at near room temperature. Thus gas permeation through thin films is typically defect-limited [Cha96].

Polyester, under such trade names as Mylar®, Melinex®, and Celanar, is commonly used in flexible electronic applications and in the food packaging industry, and known—thanks to its thermoplastic characteristic which makes it heat-formed and highly recyclable—as one of the most inexpensive flexible organic substrates now on the market. Polyethylene has good flexibility, good electrical properties, and good
chemical resistance; however, it has limited suitability for soldering and is unsuited for extremely cold conditions because of its brittleness [Fje06].

PET (DuPont Teijin Films Melinex® in our studies) and PEN (DuPont Teijin Films Teonex® in our studies) are semi-crystalline film, which can be melt-cast followed by biaxial stretching and heat setting to crystallize them for wide use in flexible electronics. However, PET has traditionally been used mostly for containers of carbonated soft drinks and water bottles, and PEN for labels, laminates, and electronic circuits [Mas03]. PEN is an attractive intermediate flexible substrate in terms of cost and performance between polyester and PI. As a moisture barrier, PEN is better than PET by a factor of 5, but additional barrier technology is needed for it to meet OLED requirements. Both substrates are optically clear (transmittance of >85% in the visible) and have relatively low moisture absorption [Won09][P2][Lew06].

LCP is a high-performance multilayer substrate with excellent electrical and physical properties, good mechanical integration compatibility, and potential for low-cost flexible electronic and RF applications. Because of its hygroscopic property, LCP has very low moisture absorption, which obviates baking in the manufacture of PI. Because low moisture absorption is important in low signal-loss structures, LCP can be used in high-speed applications [Fje06]. LCP characteristics have been widely investigated in the production of low-cost RFID tags by inkjet printing, and LCP’s potential at UHF has been well documented [Geo06][Bas06a][Bas06b][Dej05][Vya07].

Organic substrates provide flexibility but not sufficient protection against water and oxygen permeation. However, moisture and oxygen absorption can be minimized or precluded using several barrier technologies now on the market. The barrier layer also resists process chemicals, strengthens the adhesion of the device film, and reduces surface roughness, all critical aspects in inkjet printing [Won09]. The main requirements of barrier layers are (1) compatible deposition in application, (2) similar permeation rate to that in Table 3, (3) mechanical robustness, (4) lifetime stability of application, and (5) resistance to other additional processes such as lithography carried out during manufacturing [Lew04][Fje06][Won09].
Table 3. Water vapor (WVTR) and oxygen transmission rate (OTR) of various barrier materials and application requirements [Imr05][Zer08][Fra07][Lew04].

<table>
<thead>
<tr>
<th>Material and application requirements</th>
<th>WVTR g/m²/day (37.8-40°C)</th>
<th>OTR cm²(STP)/ m²/day (20-23°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene terephthalate) (PET)</td>
<td>3.9-17</td>
<td>1.7-7.7</td>
</tr>
<tr>
<td>Polyethylene naphthalate (PEN)</td>
<td>7.3</td>
<td>3.0</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>1.2-5.9</td>
<td>70-550</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>1.5-5.9</td>
<td>93-300</td>
</tr>
<tr>
<td>Poly(ethylene succinate) (PES)</td>
<td>14</td>
<td>0.04</td>
</tr>
<tr>
<td>Polyimide (PI)</td>
<td>0.4-21</td>
<td>0.04-17</td>
</tr>
<tr>
<td>Liquid crystal polymer (LCP)</td>
<td>0.006-0.016</td>
<td>0.03-0.09</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>7.9-40</td>
<td>200-540</td>
</tr>
<tr>
<td>15 nm Aluminum (Al)/PET</td>
<td>0.18</td>
<td>0.2-3</td>
</tr>
<tr>
<td>SiOₓ/PET</td>
<td>-</td>
<td>0.007-0.03</td>
</tr>
<tr>
<td>ORMOCER®/PET (trademark of Fraunhofer ISC)</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>MOCON measurement limit (common permeability measurement device)</td>
<td>0.0005</td>
<td>0.005</td>
</tr>
<tr>
<td>OE and Microelectronics/ Semiconductor packaging</td>
<td>10⁻¹⁰</td>
<td>-</td>
</tr>
<tr>
<td>Solar cells</td>
<td>10⁻⁴</td>
<td>-</td>
</tr>
<tr>
<td>RFID tags</td>
<td>10⁻²</td>
<td>-</td>
</tr>
<tr>
<td>LCD</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>OLED</td>
<td>10⁻⁶</td>
<td>10⁻⁵ to 10⁻³</td>
</tr>
<tr>
<td>Food packaging</td>
<td>0.1</td>
<td>1</td>
</tr>
</tbody>
</table>

Vitex Systems uses the Barix™ barrier method to meet the requirements of OLED displays. The method employs multiple-coated inorganic (i.e., ceramic) thin film barrier layers in between monomer liquid layers on a flexible organic substrate or on an OLED display. After the substrate is coated, the full Barix™ coating will be a few microns thick [Vit04][Gra05]. Barix™ barrier method is used also as encapsulation to minimize the moisture effect in OLED displays (Figure 12). Barix™ barrier method is considered to be a complementary method to inkjet printing process to increase the moisture resistance against humidity. Barrier methods are important to use, because humidity usually affects the mechanical properties and long-term reliability of the inkjet-printed structures [P2][P3][P4][P6]. In addition, a perfect layer of a few nm of SiOₓ or SiNx, commonly used in food packaging, protects adequately against water and oxygen permeation [Lew04].
4.3. Process Requirements

Implementing functional ink in printing starts by fulfilling the rheological requirements of the inkjet printing ink for today’s commercial inkjet printheads (described in section 3.3). However, this does not mean that every ink that is rheologically formulated will fit the process window of electronics manufacture. Thus it is important to fully understand the inkjet printing process.

The process requirements involve mainly properties such as the behavior of ink droplets, the types, process temperature, and duration of sintering and curing, and the control of each printed layer to ensure the quality of the multilayer structure. The main requirements for ink are related to properties such as viscosity, surface tension, evaporation rate, particle size, solid content, and type of vehicle (solvent). In addition, it is important to evaluate the engineering properties of the substrate such as application temperature, barrier properties against moisture, and the performance expectations of electrical, optical, mechanical, and chemical properties. It is also important to analyze the compatibility of the ink with the substrate or with previously printed layers where a different ink has been used. For example, applications such as the RFID tag or smart card, which tend to use low-cost substrates such as PET, polyethylene, or paper, require a conductive ink that can be sintered at lower temperatures (preferably below 120ºC) but no narrow lines as in printing interconnections on the die in microelectronic applications.

Droplet size may also vary based on the ink-substrate interaction. On the substrate, droplet size defines the line width that can be achieved, e.g., with nanoparticle-based silver (NPS) ink and guides the electrical designer to set the system requirements accordingly. Thus the design step in electronics manufacture must be defined according to the materials (ink and substrate) and their interaction tested in advance; i.e., ink properties must be determined in advance to understand their effects during and after inkjet printing. These effects define also how ink droplets behave on
the substrate. Ink properties bearing on inkjet printing are described in Table 4 [Cag10][P1] [P2][P3][P4][P5][P6][Kai08a][Gam04].

Figure 13 (a) shows the difference in droplet size results on substrates such as PEN, PET, LCP, and PI, obtained from printing the same nano-ink with a 10-pl printhead. The smaller droplet size was achieved using a low viscosity electronic coating solvent (fluorosilane polymer in hydrofluoroether) [3m03]. Figure 13 (b) shows droplet size results after surface treatment with an electronic coating solvent diluted with 80% methoxy-nonfluorobutane (C₄F₉OCH₃) [3m05]. As a result, a 30-50% droplet diameter modification was achieved on the same substrates [Cag08b]. Finally, after the initial test, several parameters can be defined such as line width, line thickness, the electrical performance of the inkjet-printed structure, and the electronic circuit line accuracy desired for the electrical design.

Printing of fine and narrow interconnections strongly depends on controlling the droplet size on the substrate and on using a suitable printhead. Today’s commercially available printheads come with as small a drop volume as 1pl, which allows printing of as narrow as 20 µm interconnection lines, when the surface is properly treated with chemicals to modify the surface energy of the substrate and to decrease wetting. The authors in [Män07a][Män08] stress the potential of their results that inkjet-printed interconnections could be used to connect current ICs. Furthermore, silver alloy nanoparticles were used in a new method combining inkjet printing and photolithographic etching to demonstrate a line width of less than 10 µm [Oka06].

Figure 13. (a) NPS inkjet-printed with a 10-pl printhead on PEN, PET, LCP, and PI, (b) 30-50% smaller droplet size achieved with electronic surface coating [Cag08b].
Sintering and curing of conductive and dielectric materials are also essential process steps in electronics manufacture, because they define functional products in terms of their electrical, chemical, and physical performance and long-term reliability. In curing, the required heating of organic conductors, dielectrics, and semiconductors can be cured with, e.g., UV exposure, thermal treatment in the conventional oven, hot plate, infrared radiation, and laser radiation. Because these curing procedures have their advantages and disadvantages in the crosslinking of polymer chains, it is important to select the right curing process to ensure the desired electrical or insulator performance of the material. However, besides UV exposure, thermal heating, or laser radiation, conductor nano-ink can be sintered in other ways as well. For example, electrical sintering of silver nanoparticles has been reported and described as an alternative method [All08]. It is a fast method and minimizes heating of the substrate and applies

<table>
<thead>
<tr>
<th>Ink property</th>
<th>Related parameters and possible effect on inkjet printing process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>Defines the form and volume of each droplet. Increased viscosity increases the length of the primary droplet; low viscosity (&lt; 2-4 mPas) may generate satellite droplets. High viscosity (≥ 30 mPas) makes it difficult to fire droplets from nozzles, and even if they can be expelled, their volume, tail size, shape, and satellite drops are difficult to control.</td>
</tr>
<tr>
<td>Surface tension</td>
<td>Defines the velocity of the droplet tail, the breaking of the droplet, and the possible formation of satellite droplets. High surface tension requires a strong acoustic pulse. However, too low or too high surface tension may clog the nozzles.</td>
</tr>
<tr>
<td>Density</td>
<td>High ink density requires a long pulse.</td>
</tr>
<tr>
<td>Evaporation rate</td>
<td>Causes clogging of nozzles together with chemical composition and temperature of the ink. High evaporation rate limits the repeatability of shooting droplets in long printing runs.</td>
</tr>
<tr>
<td>Particle size</td>
<td>Increases the agglomeration risk and possibility of clogging the nozzles. A broad particle size distribution lowers print quality in broad-volume distribution.</td>
</tr>
<tr>
<td>Solid content</td>
<td>May increase the risk of clogging, but also defines the conductivity or dielectric property of the inkjet-printed layer and its thickness.</td>
</tr>
<tr>
<td>Vehicle (solvent)</td>
<td>Depending on the chemical properties of the vehicle, ink can be injected from nozzles for a long run. The vehicle thus prevents clogging and enables ink spreading on the substrate. Aqueous (water), tetradecane-, and ethylene glycol-based solvents are commonly used to formulate ink.</td>
</tr>
<tr>
<td>Shelf life</td>
<td>Storage procedure and conditions must be followed carefully. Expired ink changes its properties and lowers the electrical conductivity and mechanical performance of the inkjet-printed layer.</td>
</tr>
<tr>
<td>Volatility</td>
<td>Low volatile material may compensate for the risk of clogging.</td>
</tr>
<tr>
<td>Flash point</td>
<td>Flash point is the lowest temperature at which there is enough fuel vapor to ignite. It also defines the nozzle temperature setting to prevent deflagration of the solvent.</td>
</tr>
</tbody>
</table>
also to other conductive materials such as transparent ITO and semiconductors. The method simply applies direct current (DC) voltage to inkjet-printed structures and thereby provides the required heating. Heating allows nanoparticles to contact physically and enables electrical conductivity. Furthermore, it is important to single out those process steps that can curtail energy use and increase efficiency. Laser sintering of ink has a positive impact on process efficiency and on controlling the energy needed to sinter a structure [Cag10][Kes08][Kun09][Pek07b].

Usually, the manufacture of a functional electronic product requires repeated printings and thus multilayer printing. In multilayer structures, materials interact differently from droplet control on the substrate. For example, to create a capacitor structure, conductive ink is printed before and after the dielectric layer. However, the interaction of conductive and dielectric layers is challenging and may require surface treatment to control the droplets. Figure 14 shows how NPS conductive ink spreads and is controlled on a previously inkjet-printed dielectric layer [P5].

\[
\theta = 15.4 \text{ deg} \quad \theta = 46.8 \text{ deg}
\]

Figure 14. Surface energy of the substrate and surface tension of the liquid affect the resulting contact angle between an NPS ink droplet and a previously inkjet-printed dielectric layer. The contact angle measured 15.4° before and 46.8° after surface treatment [P5].

Inkjet printing with dielectric ink differs from printing with conductive nano-ink. It has various obstacles to overcome and requires drop control during printing. To print a dielectric layer, some reflow of individual drops should be allowed to eliminate pinholes and thereby to prevent electrical shorts when the layer is used as an interlayer gate dielectric in transistors. The evaporation rate and the solid content of the dielectric ink are important parameters as are viscosity, surface tension, and particle size. Printing with dielectric ink can be optimized with adequate XY platen heating and the right printing resolution [P1][Wu06][Mol03][Mol06][Hol02].

When inkjet printing has been completed, the printed product is ready for additional process steps. Assembly and packaging then follow after multilayer structures show desired electrical properties. However, on the manufacturing line a quality check, according to available product quality improvement tools (e.g., Six Sigma, total quality management (TQM), and continuous improvement), can be more efficiently made on new materials and the effects of the ink more precisely determined on functional products. For example, Six Sigma method helps to find the optimum inkjet printing parameters and their effect on the formation of droplets during long
printing runs. This technique is possible to apply (1) during the inkjetting process of conductive and dielectric inks and (2) in order to define the required amount of cleaning and surface treatment solvents to control the spreading mechanism of a droplet. Thus quality and repeatability of inkjet-printed structures in long printing runs is possible to measure. Printing parameters such as printhead temperature, applied pulse width, pulse rise/fall, applied meniscus vacuum, and drop velocity affect the inkjet printing process and naturally the inkjet-printed structure [Män09c]. According to the Six Sigma results, a better understating in terms of ink-substrate interaction and the effect on final inkjet-printed structure is achieved before implementing those ink and substrate to the production line.

Therefore, after the first test runs, one of the above quality approaches should be taken with a production-scale industrial printer to ensure optimum quality and to maximize the reliability of printing and the yield of the process steps [P5]. A quality approach helps transfer the knowledge gained from extensive test runs to industrial printers capable of high-volume manufacture of electronic parts.

4.4. Assembly, Packaging, and Environmental Requirements

The inkjet printing process should match the materials selection criteria in conventional assembly and packaging in terms of the needs of the functional electronic end product. To complete the manufacture of electronics, electronic assembly uses conventional electronic adhesive materials such as NCA, ICA, and ACA. On the other hand, passive components can be attached to a PCB using either a conductive adhesive or lead-free solder paste. In addition, the pick-and-place device is used to mount passive components. Thus the speed of inkjet printing should be considered to achieve hybrid production with conventional assembly and packaging devices and materials. Electronic adhesive materials must be flexible enough if a flexible substrate is used as board material, and the materials should maintain their functionality during the bending, mechanical power loading, and thermal changes of the board. Electronic adhesives can be applied to electronic circuits by stencil printing, screen printing, and dispensing techniques [Lic05].

However, with a flexible substrate used as board material, a conductive adhesive may be a better choice than lead-free solder paste. Figure 15 (a) shows a mechanical adhesion problem with solder paste applied by stencil printing to inkjet-printed electronic circuits. Three passive components (in the red square) got loose when the flexible board was bent. Figure 15 (b) shows the better adhesion strength of a conductive adhesive applied by stencil printing to inkjet-printed electronic circuits. Though the same mechanical bending was applied in both tests, the conductive adhesive performed well on the flexible board. The electronic circuits were here inkjet-printed with highly conductive NPS (almost 99% after sintering) on a 50-µm PI film. This new type of conductive adhesive has flexible, silver-filled epoxy, solvent-free, and thermosetting material characteristics, which enable attachment of passive components on flexible PCBs. In contrast, solder paste consists of flux and silver, which require higher temperatures (above 200ºC) to cure. Thus use of cheap substrate material is limited, because most low-cost substrates have a low glass transition (T_g) value.
Another important issue to be considered in the implementation of any material in inkjet printing-based manufacture is the materials’ environmental impact. A major advantage inkjet printing has over the current interconnection technologies exploiting photolithography and other subtractive methods is the amount of material used and wasted in electronics manufacture. Inkjet printing is an additive method, which simply adds the amount of material needed on the designed structure. This approach, which minimizes the consumption of materials such chemicals and energy to dissolve the unpolymerized resist used in the development of photolithography, thus cuts down the output of waste. In addition, the inkjet process allows use of a wide range of substrates, even easily recyclable ones that consume less manufacturing energy and contribute to fewer emissions during substrate production [Cag10][P5]. Environmental impacts can also be reduced by selecting environmentally-friendly materials that provide relatively long reliability in their life cycle. Reliability of printed structures is thus a key issue and must be evaluated together with the yield of the whole process and the functional product [Cag10][Kes08]. On the other hand, the use and handling NPS ink should be carefully monitored, because nanoparticles may enter the human body in various ways, e.g., via the skin, ingestion, and breathing [Kes08]. The health issue of nanoparticles is still a hot topic with little knowledge available and with their impact on the human body requiring further research. However, the possible health effect of the ink vehicle (solvent) is well known, and most of the chemicals used as vehicles have been extensively discussed in [Kes08].

Figure 15. (a) Passive components attached on a flexible PI substrate with (a) lead-free solder paste and (b) flexible conductive adhesive (courtesy of Juha Niittynen).
5. Application and Reliability of Inkjet-Printed Structures

Reliability is a term to use for the continuous function of operating a product or a system under stated conditions for a specified period of time [Ohr98][Sep03]. In general, statistical reliability analysis is used to understand the lifetime of the product as well as to define the viability and quality of the product before mass production. In this thesis, reliability tests are focused on mechanical and environmental testing of inkjet-printed structures and are used to understand the performance of selected ink-substrate combinations as a complementary tool before creating a functional product in several applications. Application fields of the inkjet-printed product are divided into low-end and high-end electronics. The main differences in those markets are price of used ink and substrate which defines the end product price, the electrical performance of inkjet-printed structure, compatibility in between ink and substrate, and the use of wide range of materials [P3][P4][P6].

In PE, the reliability of inkjet-printed structures has not been exhaustively explored and industrial standards are required for several extensively researched applications such as RFID tags, passive components, transistors, interconnections, and display back panel wiring [P2][P4][P6]. However, the Institute of Electrical and Electronics Engineers, Inc. (IEEE) has suggested several standards [Iee04][Iee06] for electrical requirements of organic transistors, standards that could be viewed as the organization’s interest in this particular issue [P6].

5.1. Applications of Inkjet-Printed Electronics

Printing smart cards, toys and game cards, disposable RFID tags, flexible display backplanes, diagnostic system sensors, non-volatile memory, smart textiles, PVs, and other applications requiring low-cost circuit fabrication by either inkjet printing or R2R printing techniques is a hot topic in PE and OE. In the manufacture of electronics, inkjet printing began to be used towards the end of the 20th century and is now catching the attention of several early adopters such as display and lighting manufacturers, innovative energy technology companies, novel electronic material or functional nanomaterial suppliers, high-tech electronic sensor producers, conventional graphic industry and printing device manufacturers, and enthusiastic novel technology followers from industries different from electronics. At the moment red, green, and blue (RGB) phosphors, backplane conductive layers, transparent display electrodes, ITO layers, parts of TFT structures (i.e., source, drain, and gate), emissive layers, anodes and cathodes can all be manufactured by inkjet printing technology [Cra05][Wan06] [Woo09][Cle03].
Inkjet printing technology enables cost-sensitive production combined with novel material solutions such as nano- and organic conductor inks and cheap flexible substrates, low investments in the manufacturing system, and integration with the existing manufacturing system. Inkjet printing can be used in different types of applications. Application fields of inkjet-printed electronics are possible to divide into *low-end* and *high-end* applications [P3][P4][P6]. The main differences in those markets are:

- type of ink and substrate material,
- price of used ink and substrate material which defines the price of end product,
- the electrical performance of inkjet-printed structure,
- compatibility in between ink and substrate in terms of printing resolution and droplet control on substrate in order to achieve precise and complex electrical design,
- the need of wide range of materials in the electronics application.

### 5.1.1. Low-End Applications

In *low-end applications*, the demand on reducing the total cost of product is high priority and a challenging issue. Thus the price of ink and substrate need to be considered and should be low. For example, the manufacturing cost of a RFID is currently targeted less than US 5¢ per tag [Pri05]. Low-end applications usually require a simplified component architecture and have few material interactions. Latest developments in materials and PE provide cost-sensitive alternatives to produce these applications. On the other hand, printing resolution and the need of high electric performance material are not that crucial in low-end compared to high-end applications.

We have studied inkjet printing of conductive traces with NPS ink for electronic circuits on carrier substrates and the advantages of the technology were illustrated by producing a 2.45-GHz microwave RFID antenna, a capacitive sensor, and IC interconnections [P4][P6][Cag08b][Kai08b][Män09a]. Inkjet printing of such structures calls for precise droplet control on the substrate, pinhole-free dielectric layer printing, and low temperature sintering and curing while using temperature-sensitive substrates such as PET and polyethylene (maximum operating temperature range of PET and polyethylene are respectively 115-170°C and 93°C [Car08]). Figure 16 shows the main steps of the inkjet printing of low-end electronics products (i.e. disposable RFID tag) as an example. In addition to the process steps in printing, conformal coating (for moisture, dust, chemicals, and temperature extremes) and the deposition of an adhesion promoter layer on the substrate (to increase the mechanical strength of the inkjet-printed base layer) are crucial in meeting the current technology requirements of low-end electronics [Cag08b].
Figure 16. Main steps of inkjet printing of low-end electronics products [Edw05].

In the Department of Electronics at Tampere University of Technology, the research is focused on both low-end and high-end printed electronics manufacturing by inkjet printing. Figure 17 (a) describes the keypad with five LEDs (shown as light green color) to demonstrate an example of low-end application with simple electronic architecture. Electronic system consists of NPS ink (<1000$/100ml) for connection lines, flexible organic substrate, silver epoxy-based ECA in order to attach power wires, polycarbonate (PC) keypad with carbon-based resistor ink, and five surface mounted device (SMD) LEDs. Inkjet-printed silver connection lines were printed in 600 dots-per-inch (dpi) resolution with several times printing to achieve the desired electrical performance to transmit power from adjustable power source to LEDs. Adjustable power source is possible to select as thin, flexible, and disposable battery [Enf09]. On the other hand, the same electronic architecture is developed to produce capacitive keypad which additionally consists of several conventional capacitors and resistors in order to enable low-pass current filter in this application and an IC controller to control the electric current to five LEDs (LED shown as light red color) in Figure 17 (b) [Kai08b].

Figure 17. Examples of low-end electronic application. (a) Keypad with SMD LEDs and (b) capacitive keypad with an IC controller [Kai08b] (courtesy of Juha Niittynen).

5.1.2. High-End Applications

In high-end applications, e.g., micro-electro-mechanical systems (MEMS), military and medical applications, memories, and system-in-foil, materials require high electrical performance and their interactions considered to be sophisticated. Systems-in-foil are considered a new class of electronics, in which a full electronic system is
integrated into a carrier by using a cost-sensitive approach. Systems-in-foil may contain several different technologies, e.g., conductors, discrete components, batteries, opto-electronics, sensors, memories, organic flexible displays, wireless interfaces, on a flexible substrate. Inkjet printing is a key processing technology for systems-in-foil applications because of advantages such as possibility to select a variety of materials, precise material deposition and droplet accuracy, high printing resolution, non-contact printing, and creation of unique products on laboratory scale [Bra08][Wie08][Rön07].

Selecting substrate and ink for high-end and systems-in-foil electronic applications differs from that for low-end electronics applications. In high-end applications, high-speed serial signals (>2.5 Gb/s) [Ini04] requires high conductivity. High conductivity is possible to achieve with a high-metal-content (e.g., 99%) of nano-ink after sintering. Nano-ink with high metal content usually requires high sintering temperatures, e.g., of above 200ºC. Therefore the substrate material should withstand those sintering temperatures. Some low-cost organic substrates such as PET, PEN, and polyester are thus unsuitable as long as the sintering temperature requirement of the high-metal-content nano-ink is below the $T_g$ value of the substrate. On the other hand, to print a dielectric interlayer in multilayer structures for high-end electronic packages, a thin low-k and pinhole-free dielectric layer is needed to provide effective insulation and to form high-performance crossovers in electronic packages [P1][Kai08b][Män07a][Mie08][Mie09a].

Inkjet printing technology has been studied in electronic integration technologies such as the system-in-package (SiP) [Mie08][Sai06][Tor06], in chip-on-board (CoB) [Blu07][Ein05], in high frequency electronic applications [Blu07][Gan04], in the production of 3D MEMS [Azu08][Ful02][Wal06], advanced high resolution interconnects [Sut05][Man99], polymer transistors [Boc05][Der07][Zha02], in production of channels in TFTs [Sek08], in the fabrication of passive elements [Sha02][San08], and in inkjet-printed single-crystal silicon CMOS circuits in low-end RFID applications [Joh07]. On the other hand, the production of electronic systems on low-cost flexible substrates (i.e., systems-in-foil) with several of the above components has only recently come under study, and their electrical functions and long-term durability need further research in inkjet printing technology [Bra08][Kun09][Wie08]. Nevertheless, silicon and its processing technologies seem difficult to beat in terms of electrical performance and high-volume manufacturing of miniaturized systems. However, one possibility is to use the benefits of inkjet printing and merge with conventional silicon devices (e.g. IC) to manufacture a complex electronic system.

During ink-jet printing of high-end applications, some problems may arise such as printing of the edges of discrete components, continuous droplet accuracy during high-volume manufacture, printing of conventional solder bumps, microvias that require 3D printing of droplets, and fine and narrow interconnections for high-density microelectronic system packaging. Current inkjet printing technology is incapable of printing 90º angles on the edges of discrete components or ICs. However, vertical leveling of the IC by dielectric layer printing to print interconnections on components’ active side and inkjet-printing in a wedge-type ramp to connect components are some examples of solving the current processing problem of interconnecting electronic
components by inkjet printing technology (Figure 18) [Cag10][Män08][Män09b] [Pek08].

![Figure 18](image)

**Figure 18.** (a) Vertical leveling of the IC by means of dielectric layer printing and (b) inkjet-printing in a wedge-type ramp to interconnect a component, and (c) is the inkjet-printed interconnects and daisy-chain pattern to connect bare IC and SMD components [Cag10][Män09b].

In the Department of Electronics at Tampere University of Technology, radio frequency (RF) SIP and baseband engine applications for cellular phone have been studied to demonstrate the capability of inkjet printing technology in high-end electronic application. Figure 19 describes manufactured baseband engine and RF SIP technology demonstrator with silicon ICs, conventional electronic components, and inkjet-printed interconnects [Kai08b][Kai08c][Mie08][Mie09a][Mie09b][Män07b][Män09b][Pek07c]. In these applications, a high metal content (almost 99% silver after sintering) NPS ink (>1500$/100ml) was used and ink sintered at 220-230°C. The substrate material was selected as epoxy molding compound or PI according to the temperature requirements of the NPS ink. In addition, inkjet printable epoxy-based dielectric was used to separate each crossing conductive traces [Mie08] and electronic coating solvent was applied to modify the surface of the substrate in order to produce IC interconnections [Kai08b][Män07a]. IC interconnections require high resolution to achieve precise material deposition. Thus 1270 dpi high resolution CAD image was used [Kai08b][Kai08c][Män07a][Män08].
5.2. Mechanical Testing of Inkjet-Printed Structures

Mass production of PE or OE, inkjet-printed structures should be evaluated for reliability in mechanical and environmental terms after they have been electrically characterized [P3][P4][P6]. Mechanical tests should help solve technological and engineering problems and provide reliable qualitative and quantitative results. In the electronic industry, there are several mechanical tests that are designed to measure mechanical properties of an electronic component of system. For example, drop test in general is used to measure mechanical impact of the solder interconnections on PWB during high impact drop loading. Mechanical impact is possible to study by utilizing PWB drop test device and according to the JEDEC JESD22-B111 test standard [Jes03]. On the other hand, bending tests (three- or four-point) are used to create a test condition for on-wafer measurements when test IC is under mechanical stress or to perform bending cycles until the conductors are broken [Kar07]. The reliability of solder joints is tested usually by four-point test because of the equal loading of the indenters to all solder joints. In addition, tensile test is also commonly used in electronics industry. Tensile test can be used to measure the effect of mechanical loading on the electrode resistance. In PE, drop, tensile, and bending tests can be used to test the mechanical failure of the attached surface mounted components and to understand the electrical performance of inkjet-printed electrodes in tensile test [Mer09][Kim09b]. Furthermore, adhesion test method is commonly used in industry for quality analysis to define the mechanical performance of structures. It is relatively easy to perform and provide widely reproducible results [P2][P3][Joo07][Joo08][Kay07][Kun08][Sri07][Sri09]. Some of the adhesion tests (e.g., cross hatch test) provide no direct measurements.
However, it can be assessed with a grade degree of damage in relation to reference images analysis. On the other hand, the mechanical performance of inkjet-printed structures is also affected by environmental variants. Hence mechanical tests can be combined with various environmental conditions such as (1) mechanical pull-off adhesion evaluation of inkjet-printed structures on a substrate after moisture absorption in harsh conditions or (2) varying dynamic mechanical analysis, e.g., tension, at an elevated temperature as a function of time and frequency [P2][Cag08a][Kim09b].

In this work, because easy to apply, cross hatch tests were used to determine the quality of the inkjet-printed structure. However, electrical design and modeling require further quantitative results to simulate the interfacial stress to define failure criteria [P2]. Thus pull-off adhesion testing method is commonly used in the electronics as well as its common use in paint and coating related industries. In PE, numerical values can be determined for the bond strength of inkjet-printed structures by the minimum tensile stress exerted to separate an inkjet-printed silver layer from a substrate or an inkjet-printed dielectric layer [Go103]. Results of pull-off tests provide information to evaluate, e.g., the location of peak stresses, the interfacial location of the adhesion and its fracture mechanism, the character of the fracture surface, and the mean value of the breaking strength. In this thesis, mechanical tests were focused on the adhesion strength of the inkjet-printed silver structure on varying flexible organic substrates [P2][P3]. In addition, dynamic mechanical analyses were performed to define the effect of the CTE differences in between inkjet-printed structure and substrate at elevating temperature from -60ºC to 100ºC [P2][Cag08a]. As a result, it is possible to define mechanically proper ink-substrate combination in order to produce reliable electronic application. In addition, mechanical tests can be applied to measure adhesion of inkjet-printed structure with different sintering conditions and when electronic coating applied to substrates [P2][P3][Cag08a]. In general, high sintering temperatures increase the residual mechanical stress and stress gradients of inkjet-printed structures in high-end applications [Azu08]. These combinations lower the cost of reliability tests and resemble the product’s eventual use conditions.

Figure 20 describes the test setup of the adhesion pull-off test and the material interfaces which were considered to evaluate the type of the adhesion (i.e., interfacial, cohesive, and adhesive). The material interfaces in pull-off test were lettered according to the used industrial standards to describe the failure [Iso02][Ast95]. ASTM D3359 and DIN EN ISO 2409 were used in cross hatch tests and ASTM D4541-95 and DIN EN ISO 4624 in pull-off tests to test the mechanical performance of inkjet-printed structures. Because of the nature of the adhesion pull-off test, the flexible substrate needs to be attached to inflexible smooth substrate which this technique is also used in mechanical evaluation of thin films [Tu92]. In this work, a rigid 1.5 mm-thick one-sided copper FR-4 board was selected as attachment board and copper side of the FR-4 board was considered smooth enough to attach the flexible substrate. Attachment of the aluminium pull stud to inkjet-printed NPS structures as well as attachment of the flexible substrate to rigid FR-4 board was accomplished by epoxy-based non-conductive adhesive. One of the most important criteria for selecting the adhesive material was its curing temperature which needs to be low enough to prevent undesired chemical reaction in the inkjet-printed silver structure. The adhesive’s datasheet gave a curing temperature and duration of 90ºC and 30 min, respectively [Cag08a].
Figure 20. Test setup of the adhesion pull-off test and the material interfaces [P3].

According to the results, the low-metal-content Ag nano-ink by Cabot, Corp. on a low-cost Melinex® PET substrate showed high adhesion strength (4.3-4.7 MPa) at lower sintering temperatures (150°C), making the material combination suitable for producing low-cost circuits for low-end electronic applications (described in Table 5). However, the results do not depreciate the other ink-substrate combinations but rather illustrate for electronic industry the mechanical performance of the selected materials in which ink and substrate are commonly combined to manufacture inkjet-printed low-end applications [P2][P3]. On the other hand, mechanical, electrical, and environmental reliability evaluation of ink-substrate combinations should target reliability in long life cycles in high-end applications and under demanding performance to make best use of inkjet-printed structures with other microelectronic parts such as ICs and discreet components. Most of the limited reliability studies in inkjet printing technology have focused on interconnections in electronic packaging applications [P3][Joo07][Joo08] [Sri07][Sri09]. In this thesis, a high-metal-content NPS nano-ink (57-62% before sintering, 99% after sintering) by Harima Chemicals was studied for its mechanical adhesion pull-off performance on high performance flexible substrates, i.e., Kapton® PI HN by DuPont (results shown in Table 5).

Table 5. Tested material combinations, test results, specific resistance value, and potential applications of inkjet-printed structures [P2][P3][P4].

<table>
<thead>
<tr>
<th>Material combination</th>
<th>Results (measured-predicted)</th>
<th>Specific resistance (after sintering)</th>
<th>Potential application</th>
</tr>
</thead>
</table>
| Cabot NPS-PET, sintered at 150°C for 60 minutes | Cross hatch: 5B*  
Pull-off: 4.3-4.7 MPa | 5-20 µΩ.cm | Fabrication of low-cost circuits and low-end electronics |
| Cabot NPS-PEN, sintered at 150°C for 60 minutes | Cross hatch:5B  
Pull-off:2.1-2.5 MPa | 3 µΩ.cm | High-end and systems-in-foil electronics |
| Harima NPS-PI, sintered at 150°C for 60 minutes | Cross hatch:5B  
Pull-off: 1.1-4.5 MPa | | |

*5B describes that 0% of the inkjet-printed structure was peeled off from the substrate [Iso94].
Test results in [P3] showed relatively high adhesion strength for the Harima nano-ink, i.e., a predicted 4-4.5 MPa breaking strength when the NPS thin layer fully detached from the PI substrate. Compared to other independent studies, test results in the reference Cu cladding on a standard FR-4, PCB board, had more than two times better adhesion strength [Sri07][Sri09][Nii08]. In addition, Cu traces on PI substrate, are commonly used in flexible electronic applications, showed higher adhesion result than the results in this work [Par09b][San05][Ste06][Won09]. In this point, it is possible to argue that Cu traces should not be substituted in PCB applications for inkjet-printed Ag nano-ink on either PI or FR-4 board if they are produced by photolithography and mechanical strength is crucial. However, the same nano-ink inkjet-printed on PI showed higher mechanical strength than when inkjet-printed on FR-4 [P3][Sri07][Sri09]. Other alternatives may help increase the mechanical strength, e.g., direct application of adhesion promoters, fluorocarbon (CF₄) plasma treatment of the substrate surface, and a pre-coated substrate with a thin layer of adhesion promoter [P3][Par09b].

5.3. Environmental Testing of Inkjet-Printed Structures

In everyday use, electronic devices are subjected to various environmental conditions: they are exposed to sunlight, ventilation, low or high temperature variants with humidity, and vibration, which may cause partial or total failure of a subsystem [P6]. Accelerated life tests in harsh conditions such as high humidity and high temperature usually accelerate the failure mechanism, which facilitates detection of possible failures much sooner than in the product’s regular service [P2][Sep03]. Environmental testing is a way to understand the field performance of inkjet-printed structures under repeated temperature cycling and various humidity conditions. Moisture penetrating the ink and/or substrate and temperature cycles of electronic systems may cause electronic devices to malfunction. In temperature cycling, a sudden overloading of materials may cause cracking and mechanical failure [P6][Kin96]. Especially a difference in the CTE value between inkjet-printed structure and substrate during temperature cycling might provoke failure. Furthermore, moisture causes oxidation and corrosion and thereby possible local cracks in interconnections.

In environmental testing, an industrial test standard helps understand the test condition, the testing of samples and the information gained, enabling thus comparison with other independently run tests and facilitating the transfer of research from universities to industry [P4]. However, understanding the product’s use condition also helps define test conditions, for minimum and maximum use conditions determine the range of the test variants. For instance, the environmental operational condition of RFID tags is reported as being in the temperature range of -40º to 65º at 5% - 95% non-condensing humidity or of mobile terminal hardware in the temperature range of -40º to 40º at 10% - 100% relative humidity, as defined by industrial organizations such as EPC global, ISO/IEC, and JEDEC [Epc08][Iso09][Can07]. In PE, environmental testing was used to understand the field performance of inkjet-printed structures under repeated temperature cycling and various humidity conditions [P6][Cag08b]. Environmental reliability testing of inkjet-printed structures is important to verify and to confirm the quality of printed structures before the product is marketed. In addition, such testing can
help define the necessary requirements for quality assurance. Furthermore, by combining mechanical and environmental tests, it is possible to analyze and understand the failure mechanism rapidly. In this thesis, the adhesion tests of inkjet-printed structures were also performed after humidity tests and some of the parameters related to printing process, e.g., sintering profile, electronic surface coating, were tested [P2][P3].

However, a major concern before testing environmental variants is to select the appropriate test structure. Selecting the right test structure should minimize the dimensional effect of inkjet-printed structures during electrical resistance measurements. In environmental tests, the structure has four pads, which are symmetrically and equally connected to eliminate faults that can occur during electrical measurement and thus provides reliable results. In the semiconductor industry, dimensional information on the test structure (the so-called Greek cross) is not necessary for measuring sheet resistance and minimizing the effect of joule heating (for more on joule heating and the advantage of using the Greek cross structure, see [P4][End04][Pek07a]). A Greek cross circuit (Figure 21) has four pads connected to each other at equal lengths and line width. The test structure was multiplied, and resistivity was measured of pad D to pad F (Figure 21 (b)). The distance between the two pads allowed us to measure the increase of the resistance in a long line of about 10.5 mm and secure reliable results in case changes occurred under varying conditions [P4].

![Figure 21.](image)

(a) Greek cross test structure adopted from semiconductor industry. (b) Test structure of 4.5mm x 14.5 mm inkjet-printed on selected substrates; designed line width ~190 μm [P4].

In this work, an environmental test was run for temperature cycling at -40 to 125°C for 1,000 cycles according to JEDEC JESD22-A104C as a part of widely known electronic industry standards to understand the effect of CTE mismatch on the device [Naw01]. Electrical resistance value measured real-time during the temperature cycling test and recorded to the data logger system at every 5 seconds. In this test, one minute temperature change rate was set. Soak time (dwell time) set as 15 minutes. In general, temperature cycling is also used to understand the effect of CTE mismatch on the device. However, in this work, the test was adapted to understand CTE differences between inkjet-printed nano-ink and flexible organic substrates at temperature extremes expected to cover the use conditions of many low-end and high-end electronic applications [P4][P6][Jes05][Whi05]. Nevertheless, the test standard seems to be unsuitable here because of unused solid state components that were not part of the test setup. Yet in a reference test setup, solid component attachments, e.g., passive components by ICA, were prepared to investigate the effect of the CTE mismatch by using the same test standard and the same ink-substrate combination [Kun08]. Both test
results showed that the inkjet-printed low-metal-content Ag nano-ink by Cabot, Corp. on a Teonex® PEN substrate showed promising results for use in printed conductors in low-end electronic applications. The results were also used to predict the technological life time of inkjet-printed interconnections in non-hermetic packages and as such generally applicable to consumer products [P6]. In consumer products, the average design life is 2 to 5 years, and an accelerated thermal cycling of -40ºC to 125ºC for 200 to 800 cycles is stipulated for product performance [Can07].

Resistance to high temperature/humidity was tested at 85ºC and 85% relative humidity (RH) for 1,000 hours according to EIA/JEDEC A101-B industrial test standard with the same nano-ink whose test condition was determined as harsh for electronic applications [Cae03][Suh02]. In the test, electrical resistance value measured during the humidity test and recorded to the data logger system. There was one measurement channel per structure. The electrical resistance of the inkjet-printed conductor registered no more than a 6% change, and the scanning electron and optical microscope pictures of the samples showed hardly any degradation or premature corrosion (environmental test results shown in Table 6). In addition, energy dispersive x-ray spectrometry did not detect oxygen element from the inkjet-printed Ag layer. It can be explained that either there was no oxidation in the structure or amount of oxidation layer was so small that it was difficult to detect. It is well known fact that Ag oxidation is difficult to detect compared to oxidation of Cu or aluminium [P4][P6]. Consequently, because the low-metal-content nano-ink showed no changes in its electrical function, nano-ink can be considered a reliable choice in those test conditions to fabricate for low-end applications. Hence nano-ink printing with inkjet printers boasts an alternative conductor fabrication method to screen-printed conductors in this application [Whi05].

In environmental terms, Ag has a well-known electromigration problem because of the movement of metal atoms due to a high current flow, which may cause interconnection failure in high-end electronic applications. Moisture and temperature cycling have an effect on electromigration. A continuous moist film and high relative humidity promote electromigration and may trigger it at elevated temperatures, resulting in complete malfunctioning of the electronic system [Tar07][Gui98]. Furthermore, both oxygen and water can make the situation more severe. Thus, the barrier technologies to protect sintered silver from oxygen and moisture are important because of the initial oxygen layers in the silver electrodes play an important role in the electromigration of silver [Bai05][Gui98][Tar07]. In this thesis, environmental tests showed promising results for the high-metal-content Ag nano-ink for high-end and system-in-foil electronic applications (results shown in Table 6). However, micro cracks were observed on inkjet-printed NPS after the temperature cycling test, owing possibly to the shrinkage of Kapton® PI or the wide change in the CTE value of the film in general during temperature cycling (i.e., 20-40 ppmºC) [Won09][Mas03], which produced micro cracks on the surface of the Ag nano-ink [P4]. Nevertheless, the Ag nano-ink should be further tested in subsequent research papers for electromigration on the same substrate, perhaps in combination of electrical and environmental tests.
In the manufacture of conductor routings in inkjet-printed PCBs, Cu nano-ink as the potential competitor of Ag nano-ink is the chemically slightly more reactive in elements comparison and thus the more resistant against electromigration erosion-void formation [Zeh02]. This property raises the question whether NPS ink might be a suitable alternative for conductor routings in inkjet-printed PCBs. However, Au nano-ink is an even better candidate, because it resists corrosion better than Ag and Cu nano-inks in high-end electronic applications and meets the high reliability requirements [Kri96]. In addition, Au nano-ink enables fast sintering steps by laser and cuts down the sintering time because of the advantage of its resonance light absorption. Yet another alternative is to alloy Ag nano-ink with other precious elements, e.g., Pd, Pt, and Au, to increase the ink’s overall reliability, as discussed in section 4.1 [Chu04][Ko07a][Ko07b].

**Table 6.** Tested material combinations, test results, and potential applications of inkjet-printed structures.

<table>
<thead>
<tr>
<th>Material combination</th>
<th>Change in resistance compared to initially measured value</th>
<th>Potential application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cabot NPS-PEN</td>
<td>Temp. cycling: &lt;5% Humidity: &lt;6%</td>
<td>Fabrication of low-cost circuits and low-end electronics</td>
</tr>
<tr>
<td>Cabot NPS-LCP</td>
<td>Temp. cycling: &lt;4.5% Humidity: &lt;4%</td>
<td></td>
</tr>
<tr>
<td>Harima NPS-PI</td>
<td>Temp. cycling: &lt;3% Humidity: &lt;4%</td>
<td>High-end and systems-in-foil electronics</td>
</tr>
</tbody>
</table>
6. Conclusions and Final Remarks

The electronics industry is undergoing a change in which new manufacturing technologies and their process materials are more important than ever before (disregarding the need of new materials after first generation semiconductor transistor in 1920s). It is important to reduce the cost of the entire electronics system and to use environmentally friendly production methods to manufacture electronics. Printing technologies offer substantial benefits in manufacturing low-cost electronics parts at high throughput, an emerging trend in the high-volume manufacturing of electronics. In addition, some printing technologies produce a lighter environmental load in manufacture, because of less material waste and streamlined management. At the moment, there are several printing methods available and it is possible to divide them as contact and non-contact printing. However, each printing method discussed here has its pros and cons, and a single manufacturing method is hardly sufficient or practicable to satisfy the current needs for printed and OE applications. Inkjet printing technology is an interesting method for manufacturing future electronic devices with a wide range of substrates. However, the inkjet printing has the drawbacks of low throughput and limited resolution in below micro scale in high-end electronic applications—though in the near future we are likely to see considerable improvements in terms of printing resolution.

Materials in inkjet printing technology are still in their development phase and need to be further developed. Manufacture by hybrid printing techniques helps overcome many current obstacles in materials, electrical performance, production speed, and reliability and offers significant cost reductions in high-volume production. On the other hand, other conventional manufacturing technologies and silicon devices should be used together, so called hybrid manufacturing, with inkjet printing to manufacture electronics. In this thesis, several technology demonstrators were described for low-end and high-end applications. In those applications, inkjet printing was used together with conventional silicon device (i.e. IC) and discrete components to enable hybrid electronic manufacturing. The advantages of inkjet printing technology include elimination of photolithography steps, vacuum processing, and material waste during processing, overall reduction of process and product costs, and adequate throughput.

In this research, nano-inks, flexible organic substrates, and ECAs were explored, and the requirements of their use in inkjet printing-based processes were discussed. Functional materials can be implemented in inkjet printing technology if their limitations are thoroughly understood in the inkjet printing process. In this thesis, the application-specific electrical and mechanical requirements, the properties of functional inks, the structure of the designed electronic parts, and the process variants were defined which likely to affect inkjet printing in general. During this research, several NPS ink
and substrate combinations were introduced and tested for their environmental and mechanical reliability. Mechanical (i.e., adhesion and dynamic mechanical analysis) and environmental (i.e., humidity and temperature cycling) tests methods were performed and related test setups were created to evaluate the reliability. The mechanical and environmental tests results were promising according to the used material combinations. In addition, life cycle of interconnections was evaluated for low-end applications which described to be long enough (i.e. ~1.7 years) to use in low-end and possibly in disposable electronic applications. However, commercially available barrier technologies should be used to protect the interconnections. That usually increases the life cycle of the product. Furthermore, high-end electronics and complete electronic systems-on-foil were examined in this thesis, but improving their performance requires further R&D effort in terms of inkjet printhead design and applicable materials.

Inkjet-printed NPS droplets, providing high performance in circuits, should be smaller and more accurate, and the printer should have better alignment, and motion precision. According to the research results, more precise inkjet printheads and surface modification of a substrate are needed to produce narrow and sharp-edged interconnections in microelectronic applications. This thesis offers some suggestions for producing such interconnection circuits in terms of substrate preparation and inkjet printing of nano-ink. According to the tests results, a nano-ink with a high Ag content showed promising results on a high-performance substrate for its mechanical and environmental reliability. In the literature, Ag has been described as having limited use and susceptibility to electromigration in high-current applications. However, high electrical performance in high-end applications can be achieved if the required encapsulation, system packaging, or deposition of protective layers has been performed to protect the inkjet-printed interconnections.

Nevertheless, further research and extensive evaluation are needed before integrating inkjet-printed circuit elements with functional devices and fabricating multilayer circuit devices. As future reference, research should seek to fabricate passive circuit elements, e.g., inductors, capacitors, and resistors on a large area and mechanically flexible substrates. Future work on this topic should consider also the role of the application enablers in the technology management cycle and their potential for transferring knowledge to the electronic industry. They are considered the main adopters of inkjet printing technology and promoters of commercialization, because they provide the actual functional end product. Technologically, inkjet printing devices should also meet the requirements of conventional electronic manufacturing equipment, if they are to be used as complementary tools in electronics production. However, because the speed of current pick-and-place devices now far exceeds that of current inkjet printers, it is questionable whether inkjet printing can be used as part of high-volume microelectronics manufacture.
7. References


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<th>Title</th>
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<th>Journal/Conference</th>
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PUBLICATIONS