Printing Functional Electronic Circuits and Components

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PRINTING FUNCTIONAL ELECTRONIC CIRCUITS AND COMPONENTS

by

Ahmed Tausif Aijazi

A dissertation submitted to the Graduate College in partial fulfillment of the requirements for the degree of Doctor of Philosophy Chemical and Paper Engineering Western Michigan University December 2014

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The purpose of this study was to investigate the challenges in printing reliable multilayer flexible circuits, devices and components. Gravure was used as the primary printing process for this work, but due to some limitations of gravure, other printing methods were also investigated. At first a systematic study was done to determine the optimum parameters for the gravure printing of sub 50 micron lines. Commercially available silver nanoparticle inks were printed on a lab scale gravure printer, Accupress®. The highest resolution line that was electrically conductive was 36µm wide. The 9µm, 18µm and 27µm lines were printed but were not repeatable, nor conductive. The failure of these lines to conduct was due to the excessive amount of blade pressure required to remove streaking. At such high pressures, ink was wiped-out from the cells reducing the volume of ink transfer. These problems were found to be associated with the design of the inking system on the Accupress which is a non-conventional design and does not represent commercial practice. The press was specifically designed for printed electronics applications.

After investigating the printing of fine lines, printing of passive components was studied. Due to the inability to attain sufficient electrical performance with gravure printing process, screen printing was used to fabricate inductive coils. Copper based ink was used to print the coils. Even though suitable curing was not achieved
mathematically calculated results show a promising future of copper based inks. To extend the study to other passive components, capacitors were printed using silver based inks. The thickness and quality of two layers of conductive material separated by a thin layer of insulating film defines the performance of the final device. After successful printing of capacitors they were electrically characterized and yields were measured. Although this work was done with a limited material set, the trends discovered can be extended to other ink sets.

Next, organic light emitting diodes were printed using multiple printing methods to enable the benefits of each process. The biggest challenge was to form a uniform, pinhole free film. Polymers were dissolved in solvents and other additives to make them printable. To compare and verify the functionality of the OLED structure all layers were also spin coated. Improved performance of the printed device was observed compared to spin coated devices due to smoother and thinner emissive polymer layers. The printed polymer layers were flat and uniform over relatively large area suggesting the use of roll-to-roll manufacturing for thin film based OLEDs is possible.
O LORD! INCREASE ME IN KNOWLEDGE
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Ahmed Tausif Aijazi
# Table of Contents

ACKNOWLEDGMENTS ........................................................................................................ ii

LIST OF FIGURES ........................................................................................................vi

1 - INTRODUCTION ..................................................................................................... 1

2 - BACKGROUND AND OVERVIEW ...................................................................... 5

  2.1 - Printing for the manufacture of electronics ............................................... 6

  2.2 - Available Printing Technologies ................................................................. 10

    2.2.1 - Non-Impact Printing ............................................................................... 10

    2.2.2 – Impact Printing ..................................................................................... 12

  2.3 - Gravure process for printed electronics ....................................................... 17

    2.3.1 - Basic Principles of Gravure Printing .................................................... 17

    2.3.2 - Gravure Cylinder Engraving ................................................................. 19

    2.3.3 - Substrates for Gravure Printing ............................................................. 22

    2.3.4 - Functional Inks for Gravure Printing ................................................... 23

    2.3.5 - Challenges in Printing of Electronics ................................................... 29

  2.4 – Current status and recent advancements in printed electronics using direct

    gravure .................................................................................................................. 32

3 - PROBLEM STATEMENT AND OBJECTIVES ................................................... 35

  3.1 – Tasks ............................................................................................................... 36

    3.1.1 – Determination of limitations to the high yield gravure printing of sub 50micron lines........................................................................................................ 36

    3.1.2 – Passive components ............................................................................... 36

    3.1.3 – Active components ................................................................................ 37
Table of Contents—continued

4 - LIMITATIONS OF HIGH YIELD SUB 50µM GRAVURE PRINTING........... 38
  4.1 – Introduction.......................................................................................... 38
  4.2 – Experimental.......................................................................................... 39
    4.2.1 – Cylinder design .......................................................................... 40
    4.2.2 – Challenges in Rasterization.......................................................... 41
    4.2.3 – Pattern engraving ......................................................................... 42
    4.2.4 - Metallic inks ................................................................................ 45
  4.3 – Results and discussion .......................................................................... 47
    4.3.1 – Inks: Nano Ag vs Ag Precursor .................................................... 47
    4.3.2 – Blade types and configurations...................................................... 48
    4.3.3 – Cell Spacing A vs. D................................................................. 51
    4.3.5 – 9 µm and 18 µm lines ................................................................. 52
    4.3.4 – K-Proofer prints ........................................................................... 53
  4.4 – Conclusion............................................................................................... 55

5 - SCREEN PRINTED INDUCTIVE COILS USING COPPER INK FOR WIRELESS POWER........................................................................... 57
  5.1 – Introduction............................................................................................ 57
    5.1.1 – Definition of “Wireless Power” ..................................................... 58
    5.1.2 – Main components ......................................................................... 58
  5.2 – Background and Overview .................................................................... 59
  5.3 – Experimental........................................................................................... 62
    5.3.1 – Coil Fabrication ............................................................................ 63
    5.3.2 – Printability Analysis........................................................................ 65
    5.3.3 – Analysis of Electrical properties.................................................. 66
  5.4 – Results..................................................................................................... 68
  5.5 - Conclusion and further work ................................................................. 70
# Table of Contents—continued

6 - GRAVURE PRINTED CAPACITORS FOR ROLL-TO-ROLL PRODUCTION APPLICATIONS .......................................................... 71
   6.1 – Introduction .......................................................................................................................................................... 71
   6.2 – Experimental ....................................................................................................................................................... 73
       6.2.1 – Printing process ............................................................................................................................................. 73
       6.2.2 – Cylinder design for Capacitors .................................................................................................................... 75
       6.2.3 – Materials ..................................................................................................................................................... 76
       6.2.4 – Electrical characterization ........................................................................................................................... 78
   6.3 – Results and discussion ...................................................................................................................................... 78
       6.3.1 – Conductive layer ........................................................................................................................................... 80
       6.3.2 – Dielectric layer ............................................................................................................................................ 80
       6.3.3 – Final Layer ............................................................................................................................................... 81
       6.3.4 – Electrical performance .............................................................................................................................. 81
   6.4 – Conclusions ....................................................................................................................................................... 84

7 - GRAVURE PRINTED ORGANIC LIGHT EMITTING DIODES ................................................................. 86
   7.1 – Introduction ....................................................................................................................................................... 86
   7.2 – Experimental ....................................................................................................................................................... 87
       7.2.1 - Materials and structure for OLEDs ............................................................................................................. 87
       7.2.2 – Equipment ................................................................................................................................................... 89
       7.2.3 - Fabrication of OLEDs .................................................................................................................................... 90
   7.3 – Results and Discussion ..................................................................................................................................... 97
   7.4 – Conclusion ......................................................................................................................................................... 106

8 – CONCLUSION AND FUTURE OUTLOOK ................................................................................................. 107

REFERENCES ......................................................................................................................................................... 112
LIST OF FIGURES

6. Comparison of the feature size and ink thickness for different printing techniques [3] ................................................................. 16
7. Design pattern engraved on the cylinder .................................................. 40
8. Defects in automatic rasterization of the pattern ..................................... 41
9. (Top) Cylinder surface Schepers engraving 9µm & 18 µm. .................... 43
10. Cylinder surface before and after acid wash before engraving ............ 44
11. (Top) Cylinder surface Schepers engraving 9µm & 18 µm. .................... 45
12. Enlarged images for Nano Silver and Silver precursor inks at 36µ and 63µ m in cross and print direction ................................................. 47
13. Images showing different blade types and configuration and their respective doctoring ............................................................... 48
14. Images showing different blade types and configurations .................... 49
15. Printed Samples for Nano Ag and Ag Precursor ink for double blading system ................................................................. 50
16. Printed width vs designed widths with double blade and single blade configuration ................................................................. 51
List of Figures—continued

17. (left) Images showing prints for cell spacing A & D printed with lamella steel blade at mark 4 (steeper angle) on the press (right) 9µm & 18µm lines in both directions ................................................................. 52

18. Graph comparing the sheet resistivity for nano particle ink on K-proofer and AccuPress .................................................................................................................................................. 54

19. Images showing 9µm, 18 µm and 36 µm prints from K-proofer with cell spacing A ............................................................................................................................. 55


21. Simplified schematic diagram of the inductive link ................................................... 59

22. Coil designs with 100% scaling specifying the trace width and the spacing between the traces (left). Coil A with 30 turns (middle) Coil B with 20 turns (right) Coil C with 10 turns .............................................................................. 63

23. Archimedes' spiral coil (red area) is part of the spiral ................................................. 65

24. Printed coils of three designs before and after curing with Xenon® Lamp at 100% scaling (left) Coil A with 30 turns (middle) Coil B with 20 turns (right) Coil C with 10 turns ............................................................................................................. 66

25. Magnified images of the uncured (top) and cured with Xenon® coils (bottom) Breaks and uncured areas can be seen in the images (left). Coil A with 30 turns (middle) Coil B with 20 turns (right) Coil C with 10 turns .............................................................................................................. 68

26. Gravure AccuPress at WMU ....................................................................................... 73

27. Image showing the pattern for the three bands on the cylinder ............................... 75

28. Images showing the three different configurations for printing capacitors ................................................................................................................................. 79

29. The capacitance values measured for different areas of capacitors........... 82

30. The frequency response of printed capacitors ...................................................... 83

31. Comparison of the capacitance values for the two dielectrics ......................... 84

32. Device Structure for Organic polymer based Light Emitting Diode ........ 88
33. Thermal evaporator used for the fabrication of OLEDs. ....................... 89

34. The conducting side of ITO coated glass can be identified by measuring the resistance, which is low for the ITO side (left). The part of the ITO that is to be kept is masked by adhesive tape (right). ................................. 90

35. The tape is attached firmly to the surface (left), and the exposed side of ITO is immersed in the acid solution (right). ......................................................... 91

36. Chart showing the relationship of viscosity and temperature for the PEDOT:PSS ink ................................................................................................. 92

37. Z numbers for the PEDOT:PSS ink .................................................... 93

38. Flow chart for the fabrication of OLEDs using printing technologies. .... 96

39. Printed PEDOT:PSS layer at 10X magnification (Left) Printed layer without UVO treatment (Right) Same ink printed after 15mins of UVO Treatment of the substrate ................................................................. 98

40. Thickness of the PEDOT:PSS layers on ITO coated glass after 15mins of UV Ozone treatment .................................................................................. 99

41. 3D surface profile of the gravure cylinder showing engraving with 120 LPI and 160 LPI ...................................................................................................... 100

42. Thickness of the Light emitting polymer on PEDOT:PSS layer at 120LPI and 160LPI .................................................................................................. 102

43. (Left) profile for ITO coated glass (Middle) Profile for PEDOT:PSS layer .................................................................................................................. 103

44. (Left) Current Density vs Voltage (Right) Luminance vs Voltage characteristics of gravure printed and spin coated OLEDs ...................... 104

45. (Left) spin coated (Right) Gravure printed OLEDs with two printed layers ........................................................................................................ 105
The term *printed electronics* refers to the processes, used in the fabrication of electronic circuits, components and devices using conventional printing methods. Printing typically uses common printing equipment, using electrically functional inks, different substrates, creating active or passive devices, such as thin film transistors (TFT), capacitors or resistors. Printed electronics promises to enable very low-cost, low-performance electronics. It is also expected to facilitate widespread use of new applications such as flexible displays, smart labels, decorative and animated posters, and active clothing that do not require high performance. [5]

Printed electronics is mostly related to organic electronics in which one or more inks are composed of carbon based compounds, but the same process can be applied to any solution based material with certain properties. Currently, the fabrication and manufacturing of organic-based electronics and devices is done by using traditional processes, such as spin coating, dip coating and thermal vacuum depositions. These techniques are mostly limited to certain substrate sizes or are very costly and time consuming. The printing of electronics, using traditional printing techniques, offers low cost and high volume electronic devices, since printing is an additive process, which results in less material wastage. Printing also enables high throughput and does not require a class 1000 clean room; however for fabricating
electronics a controlled environment is extremely necessary. Due to these advantages, printing is being explored as a new method for electronics manufacture. More and more manufacturers are seeking to adopt printing technology as a high potential manufacturing method for mainstream electronic components and circuits.

For the printing of electronics, nearly all industrial printing methods are being explored. Similar to conventional printing, printed electronics applies ink layers sequentially [6]. To fully utilize the benefits of printed electronics, manufactures need advanced functional materials that are well suited for specific electronic applications and printing systems. Development of these materials is the most essential task for advancement in this field.

Even though all printing processes can be used for printing electronics, the unique characteristics of gravure printing make it a desirable and cost effective process. The biggest advantage of this process is that it utilizes a chrome coated cylinder as the image carrier, which is resistant to most solvents and other corrosive materials. Another advantage of this process is that it can print with high resolution, consistency and throughput. The gravure process also has the ability to do roll-to-roll printing, which is desirable due to its high throughput and potential scalability to large-scale industrial processing.

The purpose of this study is to print reliable multilayer flexible circuits with minimum trace width of 50μm. This study also includes the printing of common passive components like resistors, capacitors and inductors along with the investigation of printing semiconductor material which is the building block for components like diodes and transistors. The final outcome of this study was to identify all the parameters and elements required for printing reliable and operational electronic circuits on flexible substrates using multiple printing methods.
In the experimental section of this work, the challenges of printing extreme fine lines (sub 50 µm) is discussed. Since before undertaking industrial scale gravure printing research, initial screening experiments are required to optimize the printing process parameters and materials, a systematic study was done to find the optimum parameters for the gravure process to print sub 50 micron lines. Sub 50 micron lines were selected since they are potentially suitable for high-Q inductors, thin film transistors and interconnecting wires for use in printed circuit boards, PCBs. The results of this work provide insight into the factors that affect the gravure printing of nanosilver fine lines on an AccuPress, sheetfed gravure press. These fine lines are expected to have low surface roughness, good line edge definition, and high conductivity when annealed at low temperatures.

The knowledge gained from printing the nanosilver fine lines can be utilized to print circuit boards onto a flexible substrate. In printing PCBs the depth, shape and cylinder engraving process was evaluated, as these parameters play an important role in the final spreading of the printed lines. The capacitance between the lines was measured because it is known to limit the operational frequency of the final PCB. Different options for attaching solid state electronic components to the printed PCBs are discussed.

After fabrication of working PCBs, the goal of this research was to use the knowledge gained, to print passive components. Resistors have already been researched extensively, so for this study, inductors and capacitors were targeted. Even though gravure has several advantages, there are a few drawbacks with gravure, which required the use screen printing to obtain thicker or pin-hole free layers, to obtain the desired electrical performance.

Printed inductive coils are of interest because they can be used in wireless
power applications. This relatively new method of wirelessly transmitting power can provide convenience and ease of use along with added security and safety.

Capacitors are the building blocks of an electronic circuit. In a typical electronic product, the ratio of passive to active components is about 20:1, and about 80% of a circuit board is occupied by these passive components [7], most of which are capacitors [8]. Capacitors are basically two layers of conductive material separated by a thin layer of an insulating material. The thickness and quality of these layers is critical to the performance of the final device. This research work lays the basic groundwork for the roll-to-roll printing of this multi-layer passive component.

Using the experience and data obtained from the printed capacitors studies, transistor arrays were printed. As mentioned earlier, each printing process has its own advantages and limitations. The thin film printed transistors were obtained by use of multiple printing methods. Transistors can be manufactured using different designs; in this study a bottom gate structure was utilized.
2 - Background and Overview

Electronics continue to grow as an integral part of our daily lives. Advances in integrated circuits, ICs, designs are the main driving force for this growth. With these advancements, ICs become more powerful, smaller, and less expensive with every passing generation. As our interaction with electronics becomes more pervasive and affordable with the advancements in electronic displays, the rate at which we are adapting our social and personal practices to involve the use of electronics has begun to increase dramatically. This is evidenced by the shift in trajectories in the electronics industry over the last few years from the delivery of faster and higher performance devices, to more portable and less power-consuming devices. The cellular telephone market is the best example of this, which has broken so many paradigms on the usability, practicality, portability, and power of an electronic device and brought credence to the idea of “Electronics Everywhere” [9].

This electronics revolution and increased interest in portable electronic devices has demanded the development of new and better optimized processes for the manufacture of electronics. Printed electronics hopes to advance the idea of electronics everywhere to a higher level by enabling devices that are as flexible as a piece of plastic, as inexpensive as printed paper and as large as a billboard. With conventional electronics, whether it is an amorphous silicon thin film transistor (TFT)
display or single crystal silicon integrated circuit, none of these characteristics are feasible at present. Though cost is a universal driver for any technology, enabling electronics to be made at the cost of a printed piece of paper would allow for the integration of electronics on nearly every product in existence, to provide some intelligence to it, in an effort to make our lives better. The printing of electronics is aimed at replacing or supporting the manufacture of structures and devices that have similar functionality to that of conventionally manufactured electronics with the advantage of speed of manufacture, lower cost and less production complexity [10].

2.1 - Printing for the manufacture of electronics

This will not be the first attempt at using printing for the purposes of manufacturing electronics. The earliest reports on this can be found as far back as 50 years, when screen printing was used for the manufacture of conductors, resistors and dielectrics on ceramic substrates [11, 12]. This technique has been prevalent to create the interconnections and resistive elements of complex circuitry. Adding a few active components has further helped to create hybrid circuits[13]. However, in recent years, printing technologies have experienced immense advancements, due to the numerous innovations in the areas of engineering, computer science, information technology and chemistry. With implementation of currently available print methods towards electronics manufacturing, new value can be added to the existing technology.

It might seem easy to implement printing as a process to manufacture electronics by simply substituting graphic inks with functional inks. However, the transition is not as simple as it seems. As will be shown, there are several technological challenges to enable the fabrication of printed electronics with conventional printing presses. For example, patterning issues, which include
resolution, design rules, accuracy, registration, and yield, are crucial to the manufacture of printed electronics. Conventional printing techniques have been optimized to be visible to the human eyes whereas for printed electronics, high resolution continuous lines are required. Another truly challenging task for printed electronic devices is to achieve an accuracy level of one micron in order to become relevant to microelectronics. Further, the feature sizes used in graphic arts have not been sufficiently scaled to enable high density, and good performance electronic devices. Also, very thin, homogeneous, defect free layers need to be deposited onto substrates as accurately as possible in order to create properly functioning devices.

In this work, printing of fine metallic lines and dielectrics are shown, indicating the potential for scaling to roll to roll printing. Finally, integration issues of multi-level thin film devices have not been well understood, making it difficult to know what printing techniques are best suited for them. A printing process for interconnects, passive devices and organic thin film transistors was determined by carefully studying process modules for metals, dielectrics, and insulators separately, and exploring the compatibility between each process and material to enable high performance devices.

Even though technical expertise in printing technology is readily available, there is a great gap in integrating this expertise with the manufacturing of electronics. Traditional press makers and printers address the human visual sense for graphic arts applications, but for electronics manufacturing, accuracies beyond graphic arts products must be extended. As stated before, the most challenging task is to achieve one micron accuracy, however, there are some reduced accuracy applications, with overlay of larger patterns (displays, interconnects), where current printing resources can be applied. Triggered by these low to intermediate accuracy applications,
improvements might drive printing technologies to reduce pattern sizes from 20µm to a few nanometers [14].

To manufacture multi-level thin film devices using printing requires the understanding of surface energetics and wetting. In graphic arts printing applications, adequate wetting and surface adhesion is necessary to achieve required color and print uniformity. Color is basically controlled by the thickness of the ink film. Whereas in electronics, the quality of interface between individual layers is even more crucial, as it acts as a medium of charge carriers along or across the interface [10]. Further important factors to consider for multi-layer devices are the chemical interactions between the layers. For graphic arts color printing, intermixing of ink layers is not a problem, but for electronics this might not be true. Further problems can arise when different materials, required for multi-layer fabrication, need different solvent systems and possibly different printing processes [15].

The quality of the layer interfaces (smoothness and uniformity) created during printing also impacts the electrical device performance. During printing, shear forces are applied to the substrate and inks, increasing the chance to create texture or roughness within the printed layer. Additionally, substrate and ink properties influence the quality of the printed interface. Variations in surface smoothness, surface energy and absorption properties of substrate or poorly dispersed pigment and variation in surface tension of an ink can lead to poor ink transfer and mottle (non-uniformity) problems of a printed ink film [16]. Morphology of the printed surface and contour definition strongly depend on ink properties that determine the integrity and uniformity of the printed films (such as ink film splitting, wetting and spreading, and ink adhesion). A better understanding of these issues can lead to the fabrication of more uniform and reliable printed structures.
Most of the materials used in the printing of electronics require a thermal sintering step after they are printed. This step impacts the shrinkage of the substrate, which plays a very important role in the production of smaller structures. Also, when substrates travel through the press, they face mechanical stresses causing some dimensional changes. In the case of paper as a substrate, due to its hygroscopic nature, along with dimensional changes, other problems can also occur like curling, wavering or tightening of edges.

In electronics printing, the thickness of the layer generally dictates the conductivity of a printed layer. Film thickness will depend mostly on the printing process used, substrate absorbance and ink properties. In order to increase conductivity, the printing parameters can be adjusted so that a thicker ink layer is deposited, or the number of passes increased [17]. However, this might be limited by the integrity of the printed film and number of available printing stations. In many electronics applications, a reduced film thickness is needed to improve the electrical performance as in the case of dielectrics. Furthermore, printing inks contain additives to meet process requirements (such as viscosity, wettability, and end-use properties, etc.). The presence of such additives in conductive inks may cause an undesired change in the electrical properties of the materials, which may consequently affect performance of the final device. Printing press settings and process parameters also significantly influence the final quality of a printed layer. However, there is not enough knowledge about the relationship between printing process parameters and their influence on printed layer morphology and resulting electrical behavior. One of the objectives of this study is to gain insight into these relationships.
2.2 - Available Printing Technologies

Broadly speaking, printing technologies can be divided into two main groups, impact and non-impact printing technologies[2]. The former uses an image carrier or master, which comes in contact with the substrate to transfer the information while the later does not require a fixed image carrier and is digitally controlled. The classification of printed technologies is shown in Figure 1. The basic principles and a brief description of the two groups will now be discussed.

2.2.1 - Non-Impact Printing

![Figure 1: Overview of printing technologies [2]](image-url)
Among the non-impact printing processes listed, the prevailing technologies are electrophotography and ink-jet printing. However, other methods are also used. New physical processes that could be classified as non-impact printing are constantly being developed and researched in special fields [2]

Electrophotography is based on the selective discharging of a photoconducting drum by a laser or LED. The drum is then toned by charged ink (pigment particles). Special inks are used for electrophotography. These may be powder or liquid toners, which may vary in structure according to their composition, and contain the colorant in the form of pigments. The toner charge is configured in such a way that the charged areas of the photoconductor surface accept the toner. Therefore, the latent image on the photoconductor drum becomes visible where the toner is applied and can then be transferred onto the substrate via electrostatic forces and fused using heat and contact pressure.

Ink-jet printing, on the other hand, does not require any intermediate image carrier such as a photo-conducting drum in electrophotography. There are two general categories of ink-jet printing: continuous mode and drop-on-demand mode. In the continuous ink-jet process, only part of the continuously generated flow of small ink droplets is directed onto the substrate during printing in accordance with the image, in drop on demand ink jet processes, drops of ink are generated only if the information to be printed demand them. Drop-on-demand (DOD) ink-jet processes can be further classified according to the way that the individual ink drop is generated: thermal (bubble jet), piezo ink-jet and electrostatic ink-jet. Thermal ink-jet uses the heating of the liquid ink until it vaporizes. The ink is then ejected from the nozzle as a result of the pressure exerted by the vapor bubble. In piezo ink-jet systems, the drop is generated as a result of a change of volume within the ink chamber due to
piezoelectric effects. The pressure waves are converted to fluid velocity which leads to the drop of ink being ejected from the nozzle system[18]. Electrostatic ink-jet is based on the existence of an electrical field between the ink-jet system and the surface to be printed. The ink drop is generated due to the field forces. The ejection of ink from the nozzles occurs with the application of an electrical field and a controlled pulse (e.g., electric signal or the supply of heat) which enables the release of a drop[2].

2.2.2 – Impact Printing

There are four main techniques that fall under impact printing and use a pattern master for image transfer. These include flexography, gravure, lithography and screen-printing. Screen-printing employs a simple technique in which a screen is masked on the non-image areas and has openings in the image areas. Ink is applied by pressure to the screen and the image is reproduced on the substrate. One of the biggest advantages of screen-printing is the thickness of the printed ink film. This process is widely used in the manufacture of printed circuit boards.

![Figure 2: Schematic of the screen printing process][2]

Lithography, specifically offset lithography, is one of the most widely used graphic printing techniques, as it is used to print the majority of newspapers and short-run periodicals in the world. The lithography process prints on a substrate by means of a planographic process, which transfers the image to the substrate using a
plate and blanket contact. It makes use of a printing form that is patterned with hydrophobic and hydrophilic regions. The printing form is dampened with water, which adheres only to the hydrophilic regions of the plate, and then inked with a hydrophobic ink, which adheres only to the hydrophobic regions of the plate. This pattern of water and ink is then transferred to an intermediary offset blanket, and then to the substrate. For electronics, the use of two types of fluids to print one pattern poses unwanted constraints on the design of electronic inks, issues with cross-contamination could be difficult to control, and since most substrates for printed electronics are non-absorbent, the benefits of controlling spreading through absorption are minimal. Furthermore, offset litho makes use of two pattern transfers, one from the print master to the offset blanket, and one from the offset blanket to the substrate. This extra transfer can lead to an added loss of pattern fidelity, which is undesirable for printed electronic applications.

Flexography is essentially a rubber stamp on a roll in which the printing elements are raised above the non-printed elements. It operates similarly to

![Figure 3: Schematic of the Lithographic printing process[1]](image-url)
Gutenberg’s original printing press, where the raised surface gets inked, and the ink is then transferred to the substrate. Flexography has potential as a laboratory printing technique because the rubber printing forms are relatively easy to manufacture.

However, the mechanical deformation of the printing form is of concern for printed electronics where feature sizes must be scaled, and controlled as much as possible. Further, the polymer printing form poses limitations on the type of inks that can be printed, as inks with organic solvents can easily swell or deteriorate the form. Flexography uses low viscosity inks and resilient or soft, flexible printing plates. This printing technology requires only a slight contact pressure to enable reliable ink transfer from the printing plate to the substrate. Because of the flexible printing plates, which are now made mostly from[4] photo-polymeric plastic, printing can also be done on materials with relatively rough surfaces.

*Figure 4: Schematic of the Flexo printing process [2]*
The last printing technique to be discussed is the gravure process. Gravure, also known as rotogravure, is in some sense the inverse process of flexography. Here patterns are etched into the surface of a steel-base cylinder electroplated with copper. After engraving the cylinder is chrome plated making a hard surface finish. The engraving creates ink-holding wells, which are filled when the entire cylinder gets coated in ink. Gravure printing uses more fluid inks than flexo. Also, due to the hardness of the gravure cylinder, a higher impression pressure and a smoother, more compressible substrate is required in order to sufficiently transfer ink from the cells to the printing substrate in comparison to the other printing processes. Once the imaged cylinder is inked, a doctor blade removes the excess ink from the non-patterned areas, and the ink from the wells is transferred to the substrate. Direct gravure provides the highest resolution and pattern fidelity of these techniques because it uses a metallic printing form, which does not suffer from deformation or solvent swelling. Furthermore, ink is transferred directly to the substrate, avoiding the need for a secondary transfer process. Because of the materials used in the printing of the form, the gravure printing process can be run at higher speeds. This allows for a large number of prints in a short time. The downside however, is that gravure rolls are very expensive to pattern, and the patterning process is fairly slow making gravure less

\[ Figure 5: \text{Schematic of the gravure printing process} [4] \]
ideal for day-to-day print jobs. Until recently, direct gravure was not amenable for printing on solid substrates. However, with the advent of the AccuPress® from Ohio Gravure Technologies, it is now possible to print on solid substrates using direct gravure. Generally, offset gravure is used to print on solid, rigid substrates utilizing a double-transfer method, reducing overall resolution.

The choice of print method for electronics manufacturing depends on the feature size (resolution) requirements and ink film thickness desired. As for electrical performance, the thickness of the printed layer is important. Every process has its own advantages and disadvantages. A comparison of the feature size and the ink film thickness that can be accomplished by each printing method is shown in Figure 6. Another important factor affecting the choice of print method is the identification of a suitable functional ink chemistry and viscosity. From the viscosity point of view, lithography uses mostly oil-based paste inks, whereas flexography and gravure need fluid ink to assure adequate ink flow from the engraved cells of the anilox roll or

![Figure 6: Comparison of the feature size and ink thickness for different printing techniques.][3]
gravure cylinder. With ink-jet printing, it is very important to employ low viscosity inks of controlled surface tension. In order to avoid nozzle clogging, the particle sizes of materials within the ink need to be smaller than the dimensions of the orifice.

2.3 - Gravure process for printed electronics

Gravure printing is the premier printing process that has the ability to produce very high quality prints at very high speeds. The robustness of its image carrier is also advantageous, contributing to very good print stability over time [19]. Another unique feature of the gravure printing process is that it is capable of depositing variable film thicknesses, which cannot be achieved by flexography and lithography. These advantages of gravure printing make it a very promising process for printed electronics applications. The gravure printing process has been used for printing electronics for more than two decades now. Earliest attempts can be dated back to the early 1990s when Mizuno and Okazaki at Dai Nippon Printing demonstrated the printing of a black matrix for color filters in active matrix displays using the offset gravure process [20]. After this initial attempt, a process to manufacture amorphous silicon (a-Si:H) TFTs was developed [21]. This process used the offset gravure process to print the resist. An etched glass intaglio cylinder was used to transfer patterns to the offset roller. The achieved feature sizes were as small as 10 μm.

2.3.1 - Basic Principles of Gravure Printing

The operating principle of gravure printing is mechanically much simpler when compared to the other printing processes. The process is largely associated with high print quality output with low variation throughout the print run. It has four basic components to each printing unit: an engraved cylinder, ink fountain, doctor blade, and impression roller.
The heart of a gravure press is the gravure cylinder, which carries the image design to be printed. A gravure cylinder is composed of a thick-walled steel base electroplated with copper and then polished to a predetermined diameter. Having a precise diameter gravure cylinder on every print station is very critical, since any variances in diameter, as little as two thousandths of an inch, can significantly affect print registration. The cylinders are electroplated with a thin layer of chromium after engraving to protect the copper layer against scratches and abrasion caused by the doctor blade during printing. The main function of the doctor blade is to shear and remove the excess ink off the surface of the engraved cylinder. Pressure is applied to the doctor blade to assure uniform contact along the length of the cylinder. Similarly, a mounting angle is given to the blade to wipe the surface cleanly. The pressure and angle of the blade must be carefully adjusted to prevent premature wear of the cylinder. The doctor blade oscillates back and forth to prevent the accumulation of ink particles or blade chips underneath the doctor blade, which could cause premature wear.

There are many other factors influencing gravure print quality, such as substrate properties (smoothness, compressibility, porosity and ink receptivity, wettability, etc.) and ink properties (ink chemistry, viscosity, rheological behavior, solvent evaporation rate and drying, etc.). Furthermore, process parameters, such as doctor blade angle and pressure, impression pressure and speed, have tremendous effects on the quality of the printed ink film. Preparation of the image carrier by different engraving methods is also an important factor that influences print quality since ink release from the engraved cells will depend on the width and depth of the cells.
2.3.2 - Gravure Cylinder Engraving

In gravure printing, the image is always broken up into separate cells and the ink spreading on the substrate through these cells then create solid images. The image carrier can be engraved using several different methods which include chemical etching, electromechanical engraving and laser engraving. Each of these techniques produce different type of cells. Even though the electromechanical engraving dominates the engraving industry, for printed electronics, the combination of indirect laser ablation with chemical etching or direct laser may prove more suitable.

2.3.2.1 - Chemical Etching

In the traditional chemical etching process, a thin layer of water-soluble photopolymer is coated onto the copper plated base cylinder. The photopolymer is then directly imaged. The cylinder is then exposed to a UV light that hardens the non-image areas and leaves the unexposed image areas soft enough to be washed away in water. While the non-image areas are protected by the exposed photopolymer, the copper in the image areas is etched away with ferric chloride of a very precisely controlled concentration and temperature [22]. After the photopolymer is removed from the cylinder, it is chrome plated and polished.

By combining laser technology and chemical etching developments, advancements were made in photoresist imaging in the year 1995. In this type of imaging, a photoresist is evaporated by the laser that leaves the image areas unprotected so they can be chemically etched. This process is also known as laser ablation and it provides the highest degree of precision, accuracy and cell quality [4]. For this process, a spot size is typically 10 µm.

2.3.2.2 - Electromechanical Engraving

Electromechanical engraving is based on the cutting of cells into the copper-
plated cylinder using a diamond stylus. This is the most common method in gravure cylinder imaging. The diamond stylus cuts cells of various size and depths by varying the cutting angle and amplitude of the stylus. The various depths and openings of the cells govern the amount of ink transferred. The screen angle of the cells is determined by the speed of the rotating cylinder. With this method, all lines and shapes are composed of discrete cells resulting in lines and text having ragged edges typical for gravure, due to the diamond shape of the cells. This effect is quite often reduced visually by adding partial cells in the adjacent nested rows [4]. Even then, the discrete cells have ragged edges and poor contour definition which are disadvantageous for electronic printing since uniform and straight lines are needed [10].

HELL Gravure Systems introduced Xtreme Engraving technology [23]. This technology is able to engrave at a very high resolution (up to 2000 l/cm for security applications). By retaining the advantages of electromechanical engraving and being simple, stable and inexpensive, this technology proves to be a very promising new technology for high quality reproduction of cylinders. In addition to this, Xtreme is capable of engraving the contours that run vertically and horizontally as closed and continuous lines. This would seem to be a very beneficial technology for the gravure printing of very fine lines for electronics manufacturing. However, no work considering such application has yet been reported. The packaging sector has tested the application of Xtreme technology and has predicted that it will also succeed in security printing [24].

Max Daetwyler Corporation also introduced a new engraving system called TransScribe™ that is capable of producing both fine line art and process works with a single engraving head, while Xtreme Engraving, on the other hand, requires two heads. However, both systems use a special screening technique whereby the
engraving stylus is controlled only via a computer signal. Daetwyler's TransScribe™ would be more suitable for engravers looking for a versatile solution, while Hell's Xtreme Engraving seems to evoke interest in niche applications [25].

2.3.2.3 - Laser Engraving

Laser engraving consists of focusing a laser beam onto the surface of a gravure cylinder and local vaporization of the image-carrier material. Max Daetwyler Corporation first introduced this technology in 1996 [4]. The difference between laser and other technologies is that a laser engraves into a zinc layer, since copper does not absorb laser energy efficiently. Thermal energy of the pulsating laser beam evaporates the zinc material to produce the grooves. Laser engraving facilitates the production of a wider range of cell shapes and sizes. Typically, laser engraved cells have round shapes with depths around 35 µm or less [10]. A spherical section shape of cells is believed to be better at ensuring ink release and providing higher print density. The new shapes also make it possible to use high viscosity inks as compared to traditional electromechanically engraved cylinders[26]. Another reason may also be due to the fact that laser engraved cells are shallower (maximum depth 35 microns) compared to electromechanically engraved cells with up to 60 micron depths with a wider opening. Laser engraving has also proved to be able to produce a more uniform printed layer [27].

2.3.2.4 - Microstar Engraving

Microstar engraving is a relatively new form of engraving that was introduced by Ohio Gravure Technologies. The gravure cylinder is prepared using a cylindrical steel core, which is then coated with a thick copper layer of about 2 mm, following by the engraving copper layer of about 80 micron. After copper electroplating, the cylinder is polished to avoid any vibrations during printing and to smooth the surface.
and allow for engraving. This method of patterning uses a precisely controlled diamond stylus to engrave the cylinder. It is an electro mechanical form of engraving with extreme precision. Due to the tip of the diamond stylus, the engraved cells are pyramidal in shape. This shape also determines the relationship between depth and the width of the cells. After engraving is complete, a light polishing step is generally performed to remove any asperities or burrs caused by the engraving process. The cylinder is then electroplated with a fine (5–8 μm) but hard layer of chrome. Generally, in the graphic arts industry after chrome plating, the cylinder is polished as a final step to give a smoother printing surface. However for electronics printing, this polishing step can be avoided to keep fine patterns on the cylinder.

2.3.3 - Substrates for Gravure Printing

Gravure being a very versatile process can accommodate a number of substrates for a wide variety of applications. The commonly used substrates are Polyethylene Terephthalate (PET), Polypropylene (PP), Polyvinyl Chloride (PVC) and various types of paper. Smoothness of the substrate is one of the most critical properties for gravure printing. Optimal contact between a substrate and engraved cells is better with a smoother surface, which promotes ink transfer. Ink spreading and the overall quality of the printed ink layer are also affected by the smoothness of the substrate. Printing on rougher substrates can result in print related problems, such as missing dots, which result in poor print quality. Uneven contact between the ink filled cells and the paper surface is a reason for variations in ink film thickness, causing variations in electrical performance. As per topographical studies of gravure printed substrates, missing dots in gravure printing are caused mainly due to the uneven surface of the substrate [28].

In addition to smoothness and laydown/penetration, other surface properties,
such as wettability and ink adhesion are very important, especially with plastic substrates, where the non-porous character inhibits penetration of ink into the substrate structure. The surface chemistry of the substrates must be compatible with the ink’s chemistry[2]. Solvent-based inks are of lower surface tension than water-based inks, which usually require the addition of co-solvents and surfactants to decrease their surface tension and improve wettability.

2.3.4 - Functional Inks for Gravure Printing

Gravure printing requires inks to be mobile, low in viscosity and fast drying. Depending on the speed and the pressure applied during printing the typical operating viscosity of gravure inks ranges from 15 - 20 mPas or cP [2]. Publication gravure inks are less viscous than packaging gravure inks. Among packaging inks, white inks have typically higher viscosities than colored inks.

Gravure inks can be either solvent or water based. Alcohol/ester mixes are used in a majority of solvent based packaging inks except some more specialized applications, where hydrocarbon and ketone solvents can be used more readily. Resins act as binders and help bind the ink on to the substrate. A wide range of resins can be used for manufacturing gravure inks again depending on the solvent system and application. Water-based acrylic ink chemistry is also well established and widely used mainly in product gravure printing (such as wall coverings, floor coverings, gift-wraps, etc.) [29]. UV-curable and hot melt inks for gravure printing are also used [30].

Fluid gravure inks may contain up to 65% of solvent resulting in the printing of thin ink layers. This is advantageous for printing of organic semiconductors, which require a high solvent content to assure the complete solubility of the organic semiconductor. On the other hand, it might not be ideal for inks using conductive
metal particles, where particle content can be up to 75% by mass for good particle-to-particle contact upon drying. Subsequently, these inks are of high viscosity which leads to higher ink transfer [31], but may cause integrity problems. Additionally, the low levels of solvents and binder in these inks may result in poor adhesion [32].

Conductive inks are used specifically for printing conductive layers for the manufacture of electronics. The formulations of these inks vary from graphic inks. These inks usually have metallic pigments that help conduct electrical charge and can have a conductive or non-conductive polymer vehicle dispersed in a suitable solvent. Commonly used metallic pigments are silver, gold, copper, nickel or platinum. Amongst these, silver is most commonly used. The benefits of using silver is that it forms a thin oxide layer that also has low resistance [33]. Different types of carbon black material are used as fillers for functional inks. For the purpose of printing conductors, there are several formulations under study that include conductive polymers, solvent based (xylene, toluene) polyaniline inks [32, 34] and PEDOT:PSS inks [35].

The most effective conductive ink used so far in printed electronic applications has been silver, especially in display applications. In addition, advances in the production of nano Ag particles have made Ag suitable for the printing of micro passive components. Inks manufactured using copper have also undergone much technological advancement making them commercially available. These inks reportedly transform into a true copper thin-film upon photonic curing [36]. As far as the solvents are concerned, some solvents can affect the conductivity of inks, whereas some co-solvents have the ability to enhance the conductive properties of an ink [37].

As mentioned in Chapter 2, the ability to deposit functional materials via solution has been the key enabler to printed electronics. For metals, various
approaches have been used to formulate inks that provide metallic films. They key component of these inks categorize their type, listed here: conducting polymers, metal flakes, metal nanoparticles, and metal-organic/metal-salt precursors. The most obvious approach to obtaining a conducting film from solution is to use a powder of an elemental metal. This is perhaps why metal flake inks are the most widely used and lowest cost. Ink formulation can be as simple as taking pieces of a metal and grinding them down to micrometer sized flakes using a ball mill, then dispersing the resulting flakes in a solvent/polymer mixture to provide an ink of the required viscosity. The ink provides conductive films thanks to the physical contact between metal flakes which provide a percolation network for electrons to travel through. The simplicity of the manufacturing process makes the ink cost only a fraction more than the raw materials cost. Because the ink relies almost exclusively on physical contact between large metallic flakes, the processing temperature need only be high enough to remove the inks solvent and harden any binder or polymer material to give the film mechanical stability. The size of the flakes is determined by a variety of ball milling parameters but is normally limited to creating flakes or particles which are larger than 1 um [38]. This is by far the largest drawback to using flake inks for thin film electronic devices as the roughness of the film is only good as the smallest particle. Consequently, metal flake inks have never been adopted for use at the device level. A much less likely candidate for conductive inks has been found in conducting polymers. It is generally considered that elemental metals are great conductors of electricity while organic polymers are good insulators. However organic molecules can exhibit a high degree of electron delocalization if they are synthesized with a high level of alternating single and double bonds between carbons, creating a conjugated system. Conjugated organic molecules are often semiconducting, as described in
Chapter 1. Conducting polymers can be made metallic by oxidatively doping the semiconductor, removing electrons from the system, leaving an excess of holes.

In general polymers are easy to dissolve and inks with good rheological behavior can be made with them. Conducting polymers are more difficult to formulate as an ink, because the materials are often salt-like, making it difficult to dissolve them into organic solvents. Further their conductivity is highly dependent on their oxidative state, which is susceptible to degradation by oxygen and atmospheric moisture. Finally, their synthesis can be complex compared to metals and thus fail to bring a considerable cost advantage, yet provide orders of magnitude higher resistivity. However, their electronic compatibility with organic semiconductors, their low temperature processing, and relatively smooth films have allowed conducting polymers to obtain the widest adoption in thin-film devices of any printable conductor, particularly in organic light emitting diodes.

Another candidate conductor ink family is based on metallic nanoparticles. Nanoparticle based inks provide highly conductive films at low processing temperatures. They take advantage of the fact that the melting temperature of the metals they use is significantly depressed as the materials are constrained to nanometer-scale crystals [7][8][9]. The resulting films are composed of a large percentage of elemental metals with a relatively low quantity of organic compounds. Aside from polymeric conductive inks, and flake inks, they are the most widely studied and produced.

Silver has become the most widely adopted metal for printable inks. Silver is considerably less expensive than gold, despite it being the best understood nanoparticle system, and does not exhibit a serious loss in conductivity due to oxidation as does copper and aluminum which form insulating oxides (silver oxide is
conductive). Further, a wide variety of synthetic approaches to silver nanoparticles have been developed including the reduction of silver ions with or without capping agents, photoreduction in reverse micelles, and thermal decomposition in organic solvents [12]. The diversity of synthetic pathways has facilitated the formulation of printable inks with silver nanoparticles. Silver nanoparticle inks can be made with a wide range of mass loading, varying from 10% up to 80% silver by mass, and a wide range of viscosities, ranging from < 10 cP inks for ink-jet printing to 10,000 cP pastes for screen printing and thick film applications [39]. Most of these formulations require sintering temperatures above 200° C to achieve full conversion of the inks, yet achieve conductive films at temperatures as low as 150° C with moderately higher resistivities. In general, nanoparticle inks are excellent candidates for printed electronics because of the high performance films they produce, the wide variety of available materials (and therefore work-functions), and the plastic compatible temperatures at which they can be processed. Yet issues of colloidal stability, printability, film roughness, purity of their final films, and susceptibility to electro migration have not been fully resolved, and are under investigation in order to allow the broad adoption of these materials for semiconductor device use.

A final class of conductor inks is based on metal-containing precursors. Metal-organic complexes, organometallics, and metal salts have been used as photosensitive materials for photographic film, precursors for deposition of III-V materials with metal-o-organic chemical vapor deposition (MOCVD), sol-gel processing, and as facile methods to deposit anti-static, and reflective films. Organometallic compounds are chemical compounds containing bonds between carbon and a metal and are broadly studied in the field of organometallic chemistry. Their uses as precursors to metallic traces for microelectronics begin in plating...
processes for printed circuit boards. Direct patterning of such materials has existed for some time. In 1987 a demonstration was made using ink-jet printing to pattern a silver metalorganic decomposition (MOD) ink, as well as a high-k dielectric, such as lead titanate for hybrid microelectronic circuits [13]. Matsushita Electric Industrial Co. filed patents in 1991 on the use of organometallics to deposit and intaglio print transparent conducting oxides, as well as metals of various types[14][15]. In 1993, Sceisi et al. reported using a spin-on gold metalorganic and laser direct writing to pattern interconnects on silicon dioxide [16]. By then, others had demonstrated the use of organometallics for mask repair, microelectronic interconnects, and contacts to optoelectronic devices. More recently, better formulations of organometallic and metal-salt complexes have become available that exhibit better stability, and lower processing temperature than previously reported. One such example was recently presented by Wu [40]. In this work, a solution of a silver salt such as silver acetate, an ethanolamine, and a long chain carboxylic acid were dissolved in an alcohol solvent. The silver salt in this solution is known to self-reduce to silver at high temperatures, or readily by exposure to a strong reducing agent such as NaBH₄. The addition of weak reducing agents such as ethanolamine and carboxylic acid improved ink stability, and enabled the use of low processing temperatures. The chain length of the carboxylic acid was adjusted to control the reaction rate and rate of evaporation of the acid, improving the film uniformity. With such an approach, inks were formulated with up to 20% mass loading of silver. Further, the lines they provided were thin, smooth and uniform in thickness with a conductivity of 105 S/cm. Organometallic inks tend to be lower cost than their nanoparticle counterparts. In fact, sometimes they are the same precursors used to synthesize nanoparticles. They are also easier to prepare into an ink of better stability and rheological properties than a nanoparticle or
flake-based ink, because they are true solvent/solute systems [41]. However, they provide low viscosity inks, and because of their low mass loading can lead to films of poor mechanical quality as described below. Finally, like nanoparticle inks, their final films retain residual ligands, stabilizers, and reactants in them that can leach into or react with the materials they come into contact with. The goal in printing these inks is to print low-resistance interconnects, and contacts to thin film devices using gravure.

This work focuses mainly on the use of metal nanoparticle and organometallic inks because they provide the best combination of smooth thin films and low resistance. Flake inks are not further discussed because the minimum pitch, film thickness, and roughness they provide is larger than intended for the scope of this work.

Conductive polymers are not further discussed because they are well studied for these applications, and because they provide films of relatively high resistivity, which hampers the speed of the circuits they would be used to create. However, it is worthy to note that there is still potential to use these polymers as contact layers to semiconductors, where specific band alignments may be required, and their sparse use would not dramatically increase resistance in a circuit. Before describing the printing of these materials, a discussion of roughness is in order, as it turns out that the roughness of these films is a critical component to their successful adoption in microelectronics, more specifically, in thin film devices.

2.3.5 - Challenges in Printing of Electronics

The most challenging task for printing would be to print patterns that are crucial to electronics. These patterns must include a high-resolution design, accuracy, registration and yield. In order to become relevant to microelectronics, the printing method used would need to achieve a one-micron accuracy level.
Triggered by promising applications with intermediate accuracy requirements, improvements might drive printing technologies to reduce pattern sizes from 20 µm to 100 nm and to improve overlay from 20 µm to sub-micron levels[14].

In printing, adequate wetting and surface adhesion are necessary for sufficient ink film integrity. In graphic printing, a specific color is achieved by printing one color on top of another and the density of each color is controlled by adjusting the ink film thickness. In color printing, if the layers of each ink are mixed, the color does not change and the final outcome is not impacted. Whereas in electronics printing, the quality of the interface between individual layers is crucial, since it functions as a conveyor of charge carriers across or along the interface [10]. Further difficulties can arise when each layer uses a different material set and possibly different printing process [15]. There is a need to research this area of interfaces created during printing of materials and their effect on device performance.

During printing, shear forces are applied to the substrate and inks, increasing the chance to create texture or roughness of the printed layer. Additionally, substrate and ink properties influence quality of the printed interface. Variations in surface smoothness, surface energy and absorption properties of substrate or poorly dispersed pigment and variations in the surface tension of an ink will lead to poor ink transfer and non-uniformity problems within the printed ink films.

Morphology of the printed surface and contour definition strongly depend on the ink properties that determine the integrity and uniformity of the printed films (such as ink film splitting, wetting and spreading, and ink adhesion). A better understanding of these issues can lead to the fabrication of more uniform and reliable printed structures.

Shrinkage of the substrate plays a very important role in the production of
smaller structures. Substrates, especially polymer films, face mechanical stress as they travel through the press or during the transfer of liquids on the substrate by rollers.

The thickness of the printed layer generally determines the electrical conductivity. This thickness will largely depend on the printing process, ink rheology and substrate absorbance. In order to increase conductivity, the printing can be adjusted so that thicker ink layers are deposited, or by simply increasing the number of passes [17]. However, all this will depend on the behavior and capability of the printing substrate and number of available print stations. Many applications also demand that the thickness of the ink film be lower. This can pose a problem in obtaining the desired conductivity of an ink film or the printing of a thin uniform dielectric layer.

Another important factor affecting the choice of print method is chemistry and viscosity of the ink. From the viscosity point of view, lithography and screen printing use mostly highly viscous paste inks, whereas flexography and gravure need fluid inks to assure adequate ink flow from the gravure cylinder cells. With ink-jet printing, it is very important to employ low viscosity inks. Furthermore, some ink formulations include various additives improving ink working and end use properties. This might change the electrical properties of functional inks and thus influence the overall performance of electronic structures.

Printing press settings and process parameters also significantly influence the final quality of the printed layer. However, not enough information is available about the relationship between printing process parameters and their influence on printed layer morphology and resulting electrical behavior.
2.4 – Current status and recent advancements in printed electronics using direct gravure

As mentioned above, the gravure printing process has been used for printing electronics for more than two decades but, in the recent years, it has gained enormous prominence due to the advancements in functional materials and their formulation as inks. Another reason for this importance is the commercial availability of these materials. In 2002, the gravure printing of functional materials for electronics was reported by Gamota et al., [37] where gold nanoparticle inks, polymer dielectrics, and organic semiconductors were combined to fabricate thin film transistors. But these transistors were made using the offset gravure printing process [42]. The minimum feature sizes reported were 50 μm and since the registration capabilities were poor, the devices used non-overlapping contacts yielding fairly low performance.

Soon afterwards, the ink-transfer of metallic inks on ceramic substrates was studied by Pudas, [43], using offset gravure. He continued his work in demonstrating printed antennas on ceramic substrates [44]. After the successful printing on ceramic, he worked with plastic substrates and was able to demonstrate the ability to print feature sizes as small as 20 μm [33]. As stated, all these early demonstrations used offset gravure instead of direct gravure and the cylinders used were made of brass. The patterning on the cylinder was done by laminating pre-exposed photoresist. The laminated photoresist was then developed and the cylinder was etched producing cells of 20–60 μm depth. The etched cells were uniform over the whole pattern area, allowing him to achieve reasonably small patterns. Offset gravure has also been used for fabricating passive electronic devices mostly with one layer of material, such as industrial UHF-RFID antennas, inter-digitated capacitors and spiral inductors [45].
Until 2005, there were fewer reports on the direct and multi-layer printing of functional inks, especially at higher speeds. In 2005, Tuomikoski demonstrated the fabrication of organic light emitting diodes using direct gravure [46] which required multilayer printing. Multi-layer printing requires the compatibility of surface tension and surface energy of inks and substrates to be used. He further advanced his work by printing multi-layer OLEDs for lighting applications [47] and more recently direct gravure was used for the deposition of indium tin oxide nanoparticles for transparent electrodes [48]. Another recent report for printing indium tin oxide using direct gravure compared the effect of different cell sizes on the performance of the printed layers [49].

Direct gravure in combination with other printing techniques has also been reported for the fabrication of thin film transistors. In 2007, Huebler reported the successful fabrication of printed ring oscillators [50]. In 2009, Jeongdai Jo of Korea institute of Machinery and Materials demonstrated the fabrication of fully printed organic thin film transistor using direct gravure roll printing [51].

Also, during the course of this research work, the use of direct gravure for printing electronics has been demonstrated by at least three more groups: the group of Cho in South Korea, the group at the Institute of Print and Media Technology, Chemnitz University of Technology, Germany [52] and Subramanian’s group at the University of California, Berkeley [53]. In their work, these groups demonstrated the printing of interconnect lines and thin film transistors on flexible substrates using direct gravure and a combination of other printing techniques. Though these groups demonstrated some of the earliest circuits fabricated using mass-printing techniques, their performance is somewhat hindered by large feature sizes.

This work is complementary in the fact that it identifies all the parameters for
demonstrating gravure as a feasible process for printed electronics. This work begins with a thorough discussion of the challenges in printing extremely fine lines to lay the foundation for the printing of hybrid circuit boards, and active and passive electronic devices. This work also characterizes the properties of high-quality patterned thin film functional materials that enable circuits and devices with significantly better performance than previously demonstrated. The final aim of this work was to develop a ‘Recipe’ for fully printed, functional electronic circuits for roll-to-roll production.
3 - **Problem Statement and Objectives**

To effectively utilize printing processes in the manufacturing of electronic devices and circuits, the optimization of current printing processes, materials and substrates is required. To achieve such a challenging task, the development of functional, solution processable materials is necessary, as well as a thorough evaluation of the factors affecting the quality of printed features with respect to their electrical behavior. Since the requirements for printed functional layers differ from those for visual images, the full potential of the different printing processes is not yet known.

The main purpose of this study was to investigate the challenges in printing reliable multilayer flexible circuits, devices and components of sub 50μm trace widths. Gravure was used as the primary printing process for this work, but due to some limitations of gravure, other printing methods were also investigated. This study also includes the printing of common passive components such as resistors, capacitors and inductors along with the investigation of printing a semiconductor material, which is the building block for active components such as diodes and transistors. The final desired outcome of this study was to identify parameters and elements required for printing reliable and operational electronic circuits on flexible substrates by multiple print methods.
3.1 – Tasks

In order to achieve the main objective of this work, the following tasks were performed:

3.1.1 – Determination of limitations to the high yield gravure printing of sub 50 micron lines

Task 1 consisted of a systematic study to determine the optimum parameters for the gravure printing of sub 50 micron lines, which could be potentially suitable for high-Q inductors and interconnecting wires for use in printed PCBs. Commercially available silver nanoparticle ink were used and the printability of the ink studied. Printability here means all properties that could help to increase the printed features’ conductivity and thus functionality, such as trace spreading, edge sharpness and ink film thickness uniformity.

3.1.2 – Passive components

This task entailed the printing of passive components, which included inductors and capacitors. Due to the inability to attain sufficient electrical performance by the gravure printing process in the early stages of this work, other printing methods, in particular, screen printing needed to be investigated to fabricate high performing inductors. Printed inductive coils can be used in wireless power applications.

A sub task of this step was to print capacitors, which consist basically of two layers of conductive material separated by a thin layer of insulating film. The thickness and quality of these layers is critical to the performance of the final device, so the device was fully characterized when its successful printing was done.
3.1.3 – Active components

Using the experience and data gained from the previous tasks, next, organic light emitting diodes were printed. Since each printing process has its own advantages and limitations the organic light emitting diodes were printed using multiple printing methods to enable the benefits of each process to be utilized. The objective of this work was to demonstrate the ability of printing organic light emitting diodes (OLEDs). Currently, processing and fabrication of thin films for OLEDs is carried out using traditional techniques such as spin coating and vapor deposition methods. However, these techniques have several disadvantages, e.g. material wastage and high processing times, and therefore tremendous benefits are gained by incorporating printing in the deposition of thin films for OLEDs. However, there are quite a few challenges when using printing technologies. The biggest challenge is to make the materials printable and to form a uniform, pinhole free film after printing. For this study, the materials were dissolved in solvents along with some resins. Along with printing, all functional layers were spin coated to form the OLED structure as a means to verify the functionality of the structure.
4 - LIMITATIONS OF HIGH YIELD SUB 50µM GRAVURE PRINTING

4.1 – Introduction

As the arena of flexible electronics progresses towards commercialization, conventional printing techniques with high resolution, consistency and throughput can be used to rapidly manufacture some or many necessary components of a particular device. Roll-to-roll printing is desirable because of its fast throughput and potential scalability to large-scale industrial processing. It has been successfully utilized for fabricating passive devices with only one layer of material, such as industrial UHF-RFID antennas, inter-digitated capacitors and spiral inductors [45],[33]. However, there has been less success with printing very fine lines of sub 50µm, especially at higher speeds.

Also, for the advancement of thin film transistors, there is a need to better understand the processes for fabricating smooth, narrow sub 50µm fine lines. In TFTs, extremely fine lines are important for improving the specific gate capacitance of parallel-plate capacitors because they allow the dielectric layer above the conductive layer to be as thin as possible, which allows for lower voltage operation. Researchers have printed entire transistors using high-speed printing technologies, however, only top-gate thin-film transistors (TFTs) have been achieved because the
gate lines were printed with silver flake ink which were too rough to be used in bottom-gate TFTs [50, 54]. Top-gate TFTs are non-ideal because they tend to have lower mobilities than bottom-gate TFTs [55]. In contrast to flake inks, nano-particle inks are good candidates for printed electronics because they form smooth, highly conductive printed lines after being annealed at low plastic-compatible temperatures [56], thus allowing for bottom-gate TFTs. Narrow and straight lines are also essential for scaling interconnects, fabricating high-Q inductors, and reducing the channel length and overlap capacitance for TFTs, which improves the circuit performance.

There have been a number of studies done by several groups from both the electronics industry [20, 21, 57] and the conventional printing industry [48, 58, 59] on various aspects of gravure, including fluid release from gravure cells [30, 60], as well as gravure coating quality as a function of different operating parameters [61-63]. However, these studies have used large cell sizes, and have not focused specifically on printed lines for electronics applications. This report, in contrast, uses a variety of cell sizes and focuses specifically on the limitations of scaling and optimization of conductive sub 50 µm fine lines. The findings lay the basic groundwork for further studies on roll-to-roll printed electronics. At first, the printing behavior of fine lines was examined, which are engraved on a gravure cylinder using microstar engraving technology. Next, a comparison was made between prints of two different blade types and their configurations. And finally, a comparison was made between the results of the two different inks used.

4.2 – Experimental

The gravure press used for this study was from Ohio Gravure Technologies. This machine is specially designed for R&D purposes. It is smaller than an industrial
scale press but has all the capabilities of an industrial press. It uses a cylinder of 15 inch diameter which is within the range of a narrow web industrial printer. The printable area for this machine was limited to 30 mm by 30 mm. The biggest difference between an AccuPress and an industrial scale printer is the inking system. In an industrial scale press, the ink is carried in a pan, which is under the cylinder and the cylinder is submerged in it. The doctor blade is located just after the inking pan to wipe off all the additional ink, whereas on the AccuPress, the ink is laid down from a reservoir made of a doctor blade leaning to a gravure engraved cylinder. To compare the results from the AccuPress to more traditional gravure ink doctoring, a K-Proofer with Microstar engraved plates was also used to evaluate quality of the printed fine lines.

4.2.1 – Cylinder design

The test cylinder was patterned with the design shown in Figure 7. This design contains lines in the print and cross directions and at 45°. Each line had four different cell wall thicknesses of 10%, 15%, 20% and 25% of the width of the lines coded as A, B, C and D, respectively. The design pattern also contains a checkerboard pattern with some isolated single cells and a circle test pattern. Five different widths 9µm, 18µm, 36µm, 54µm & 63µm of the same pattern were engraved on the cylinder. As discussed in Chapter 2, in Microstar engraving a very precisely controlled diamond stylus is used to engrave the cylinder. Cell depth and cell width is controlled by how

![Figure 7: Design pattern engraved on the cylinder](image)
much the stylus intrudes into the cylinder.

For typical graphic arts applications, the cell sizes must be kept to strict tolerances of a few micrometers over the entire cylinder surface, since even minute variations can cause undesirable defects visible to the naked eye. The cell uniformity requirements are even more stringent for printed electronics, because the final printed feature must meet electrical specifications. It is shown in the literature [38] that the maximum tolerable variance in cell size and spacing for small cells is less than 1µm, because even slight variations in cell size can result in large variations in printed line width and thickness. The patterning requirements required for printed electronics are therefore pushing the limits of what is currently possible with graphic art printing technology.

4.2.2 – Challenges in Rasterization

When the design was rasterized for cylinder engraving, a pixilated pattern was evident having jagged edges for the cells, as shown in the Figure 8. Another problem that was encountered was the location of individual pixels. When calculating the

![Image](image.png)

*Figure 8: Defects in automatic rasterization of the pattern*
position of each pixel, the rounding off error added up to result in varying cell wall thicknesses and other, missing or extra, pixel problems. Due to these problems, a difference in features was visible based on the degree of orientation. To resolve this problem, the whole pattern was rasterized and manual adjustments made to the final output to remove the defects before engraving.

4.2.3 – Pattern engraving

In order to make gravure a viable process for electronics, engraving resolution is critical for better performance, lower power and lower cost. The minimum size of printed features is determined by the size of the patterns on the roll, the amount of ink deposited, and the wetting properties of the ink. The cylinder for the AccuPress® was prepared using a cylindrical steel core, which was then coated with a thick copper layer of about 200µm. After coating, it was balanced to avoid any vibrations during printing. This copper coated core was then polished to smooth the surface and allow for engraving. Microstar engraving technology from Ohio Gravure Technologies was used for engraving the cylinder. As discussed in earlier chapters, this method of patterning uses a precisely controlled diamond stylus to engrave the cylinder. Because of the shape of the stylus the cells were pyramidal. This also determined the relationship between depth and the width of the cells. After engraving was complete, a light polishing step was performed to remove any asperities or burrs caused by the engraving process. The cylinder was then electroplated with a fine (5–8 µm) but hard layer of chrome. Generally, in the graphic arts industry after chrome plating, the cylinder is polished as a final step to give a smoother printing surface. However for this study the last step of final polishing was not performed. This was due to the depth of cells and feature size of the pattern that was engraved. If the surface were polished, there would be a possibility of reducing the depth of cells for our pattern as a result of
which they would hold less ink, thus impacting the performance of the printed fine lines.

Identical materials and processes were used for engraving the K-proofer plates. White light interferometry was used to evaluate the engraved plates for K-proofer (Figure 9). As can be seen the shape of the cell is pyramidal with the maximum cell depth of 2 µm for 9 µm pattern, 4µm for 18µm, linearly increasing to a maximum depth of 18 µm for 63 µm pattern. From these values, theoretical volumes of ink for each cell were calculated.

Even though the materials used for the cylinder and K-proofer plates are prevalent in the gravure industry, the cylinder surface after patterning showed defects in the form of scratches and particulate matter, which increased the RMS roughness of the surface to be around 300 nm. The surface and the shape properties of the non-
patterned area are equally important as the patterned area as residual ink becomes a hindrance to reliability for electronic devices. This roughness value is large enough to cause streaks when printing with silver nanoparticle inks. There were adequate amounts of silver deposited in the non-image area to make undesired conductive patterns, which shorted out intended features. In order to improve the surface roughness and remove the streaks from the prints, this cylinder was stripped and again prepared with an additional step for engraving the same pattern. After the copper was coated on the steel core, the additional step of an acid wash was performed. Hydrochloric acid was used to wash the copper coated steel core, giving a smoother surface for engraving as shown in Figure 10. After engraving was completed, the cylinder was electroplated with a thin layer of chrome. Again, the last polishing step was not performed to avoid any loss of cell depth. By adding the acid wash step before engraving, the RMS surface roughness improved to 88 nm.

As a basis of comparison the same design was also prepared using indirect laser engraving method by Rotadyne (Cincinnati, OH), referred to as Schepers engraving. This method is essentially a wet etching method in which the copper plated steel core is masked with a photoresist. A laser is used to pattern the photoresist after which ferric chloride solution is used to isotropically etch the copper

![Figure 10: Cylinder surface before and after acid wash before engraving.](image)
layer. The laser patterning system avoids the need to have a photo resist for each design. It also provides better registration of the pattern to the axis of the cylinder. Since the etching is isotropic, the yielded cells are hemispherical in shapes, which for a given cell width provides more ink volume than comparable cell engraved with Microstar engraving. The downside is that the designed patterns must take into account the growth of the etched cell in all three directions. Additionally, the minimum cell size is limited by the point size of the laser and sharp corners are difficult to achieve because of the shape of laser beam. Due to these limitations defects like missing dots and ablated chrome areas on the surface were observed on the surface of the cylinder (Figure 11).

4.2.4 - Metallic inks

After the cylinders were engraved, printing trials were performed on the AccuPress® and K-proofer using the two types of engravings (Microstar and Schepers) each with the same pattern discussed above. On the AccuPress®, samples were printed using a 1” steel beveled doctor blade. Print speeds were set to 100 m/s. Upon examination of the prints, other types of doctor blades and different blade angle and pressure settings were used to evaluate the best conditions for ink doctoring and

Figure 11: (Top) Cylinder surface Schepers engraving 9µm & 18 µm.
image quality. The substrate used for all experiments was Melinex® ST505, a thermally treated PET from DuPont Teijin Films. All printed samples were thermally dried at 130ºC for 15 min. using a precession heating oven. Two different inks were tested from Inktec (Korea). One being a nano silver ink (TEC-PR-020) containing particles ranging from 5-10nm in size and the other being an organometallic silver precursor ink (TEC-PR-010). Silver nanoparticle based inks have the advantage of melting at lower temperature. As typical for most solvent based inks, these solutions show considerable shear thinning. The shear thinning behavior of the ink is important because the gravure process induces very high shear rates on the ink during the doctoring and transfer processes.

Prints made with these two inks and both types of engraving were studied for line gain and ink film thickness for multiple press configurations. The effects of the inks, the cell widths, and cell depths on the width and thickness of printed lines were studied. Measurements were made using an ImageXpert system from KDY Inc. and a Wyko white light interferometer. The thickness and cross sections of each printed line was measured using phase shift interferometry. Even though such profilometers are designed to study features on only one material at a time or materials with very similar indices of refraction, it was possible to calibrate the measurements to eliminate the effects of index mismatch between the printed silver lines and PET substrate. Images and readings from both instruments (ImageXpert and Wyko) allowed for easy extraction of width, height and the overall shape of the line. This also enabled large-scale defects, such as aggregation of the nanoparticles or microscopic pinholes in printed lines, to be observed.
4.3 – Results and discussion

After initial printing with the two different inks, the ‘best’ samples were selected; based on their clarity in print and absence of visible disconnects. On each of the samples, a few streaks were observed. These streaks were attributed to the polishing marks on the cylinder. Based on the ImageXpert results from these initial prints, a more extensive study was performed varying the set-up on press to determine the influence of the process-set-up on print quality and electrical performance.

4.3.1 – Inks: Nano Ag vs Ag Precursor

When printing the two different inks, all other conditions were kept the same (blade type, configuration and pressure). The captured microscopic images of the samples printed with the two inks are shown in Figure 12. The design widths of the four images on the left are 36 µm while for the four images on the right are 63 µm. All these images are for cell wall spacing A, which is 10% of the cell size. The blade used here was a 1” lamella steel blade with a backing blade, 200 µm thick and 2 mm away from the edge of the doctor blade. As can be seen from the images in Figure 12, the nano silver ink, spread more in comparison to the organometallic silver precursor ink, however, the edges of the lines were about 2 times smoother on a RMS

![Figure 12: Enlarged images for Nano Silver and Silver precursor inks at 36µ and 63µm in cross and print direction.](image-url)
roughness scale. The quality of the lines was also compared in the print and cross print directions. For the 36 µm lines in the cross direction, not enough precursor ink was transferred onto the substrate to form a continuous line, whereas for the nano particle ink, a conducting continuous line was printed. This was due to the fact that the nano-particle ink was solvent based that spreads more on the PET substrate. This phenomenon is also visible on the 63µm printed lines. The edges of the lines printed with precursor ink followed the pattern of the engraved cells so the edges are rougher in comparison to the nano particle ink. This was visible for both engraving types (Microstar and Schepers). The 63µm designed line printed as 152 µm lines in the print direction. This is an increase of 141% in comparison to only a 17% increase for the organo-metallic precursor ink. Similar results were obtained for the cross direction and other lines shown in the Figure 12.

4.3.2 – Blade types and configurations

To determine the influence of blade angle and blade types on print quality, experiments were performed using two different types of blade setups to doctor the surface of the cylinder at two different blade angles. The blade angles on the AccuPress are denoted as ‘mark-3’ and ‘mark-4’. Mark-4 represents a steeper blade

Figure 13: Images showing different blade types and configuration and their respective doctoring
angle while mark-3 gives a shallower angle. Images for the two angle settings are shown in Figure 13. This figure also shows the two different blade types that were used, lamella and beveled. The difference being in the area of surface contact the edge of the blade has with the cylinder. Both blades were made of steel. Images on the right of Figure13 show the prints obtained from the four different blade settings. These 63µm designed lines were printed in the cross direction with the nano-particle silver ink and cell spacing A on the AccuPress®. It can be clearly seen that both the type and configurations of the blade produced streaks in printing. However, the beveled edge blade produced more streaks compared to the lamella blade, which created undesirable electrical connections between adjacent lines. The line width gains from the two blade types were similar with the exception being that the lamella blade produced more gain at shallower angles while the beveled blade produced more
gain at the steeper angle. Comparing the two blade types, the best prints were achieved with the 1” steel lamella set at ‘mark-3’ on press. The streaks on the prints were caused by the inking system on the AccuPress. In order to completely remove the streaks, a new blade configuration was examined. Two blades, one lamella steel and other polymer beveled, were placed one on top of the other with a 3mm gap between the two, as shown in Figure 14. The blade pressure on the press was then increased enough to make the steel blade touch the cylinder. This arrangement of blades is not commonly practiced by the gravure printing industry. With this configuration, when the prints were made, all the streaks were eliminated giving clean and streak free printed lines (Figure 15). However, the 9 and 18 micron fine lines failed to print. As discussed, the printing process can be separated into two parts, cell emptying, and ink spreading. As the relationship between cell size and printed dot

![Figure 15: Printed Samples for Nano Ag and Ag Precursor ink for double blading system.](image-url)
size is not linear [38], the ink must first come in contact with the substrate, then transfer to the substrate and finally spread. Clearly, if the cells do not have enough ink to transfer, a pattern will not be printed. Naturally, the ink volume is dependent on the width and depth of the cells, and blade pressure that is exerted during the wiping step. If too much pressure is exerted and the cells are not deep enough, most of the ink from the cells will be wiped-out leaving less ink to transfer. This lower volume might not be enough to form a continuous line thus creating electrical discontinuities. The amount of ink transferred will also impact the resultant ink spreading. Figure 16 compares the widths of lines at different designed widths printed with the single and double blade configurations using the silver nano particle ink.

4.3.3 – Cell Spacing A vs. D

Figure 17 compares the printed samples of cell spacing A (10% of cell width) and D (25% of the cell width) for the 54µm lines, organo-metallic silver precursor
ink, in both the print and cross directions. Cell spacing is referred to as the distance from center-to-center of the cells. A 10\% cell spacing means that the ratio of cell spacing to cell width is 1.10, similarly for cell spacing D the ratio is 1.25. As discussed above if this ratio is too big, lines become scalloped. The results presented here are only for uniform lines that do not display any scalloping. From the images of Figure 17, the measured edge raggedness of the lines for cell spacing A (10\%) was half that for cell spacing D (25\%). However, the gains were 2.5 times higher in cross print direction. For print direction, not much difference was observed in the edge raggedness and was measured to be 1.15 times more for cell spacing D as compared to cell spacing A. Spreading was also more for A than D. Similar results were achieved for other line widths. As visible in the figure that for cell spacing D, the individual ink dots are evident and printed lines appears to be strings of pearls. The string of pearls effect is more prominent in the cross direction compared to the print direction (Figure 17).

4.3.5 – 9 \( \mu \text{m} \) and 18 \( \mu \text{m} \) lines

Due to the interest of fine lines in applications of microelectronics, the minimum achievable dimension in both width and thickness is of great significance.
As mentioned above, the 9 \( \mu \)m and 18 \( \mu \)m pattern were engraved with Microstar engraving technology and were printed with nano-particle silver ink using a 1” lamella blade at steeper angle, “Mark 3” on the press. Figure 17 shows images of the 9 \( \mu \)m and 18 \( \mu \)m printed lines in both print and cross direction. From the images, it is clear that the 9 \( \mu \)m line failed to print while the 18\( \mu \)m line printed but failed to conduct. Also, the prints were not clear and unwanted streaks were printed. These streaks were due to the polishing marks on the cylinder surface. The cylinder surface needs to be smooth enough to not print streaks and rough enough to carry the ink [3]. The surface roughness (RMS) of the cylinder used was around 4 \( \mu \)m which is twice the value recommended by the ink supplier for nano particle ink. The inking system on the AccuPress also contributed in creating those streaks. As discussed in section 4.2 the design of inking system on the AccuPress is such that the ink needs to be applied on top of the blade which is pressed in contact with the cylinder. This allows some of the ink to flow through the voids in the pattern and deposit on the other side of the blade. Due to this occurrence, when the cylinder is rotated, the nano silver particles spread on the blade, which creates streaks on the cylinder that are transferred to the substrate.

4.3.4 – K-Proofer prints

Printed samples of the same pattern were obtained with a K-Proofer using a plate which was Microstar engraving. For the K-proofer, a plate is made from an engraved cylinder sleeve commonly known as Ballard shell, with cells that are engraved with diamond indentation. These generally give less volume as compared to wet etching. However, the cells can be more precisely engraved with a diamond stylus. Also a better aspect ratio of cell width to cell depth can be achieved [38] by electromechanical engraving. As shown in Figure 19, no streaking was observed in
the prints obtained from the K-Proofer, however the printed lines were not conductive as the cells were too shallow to produce conductive lines. The images in Figure 19 also shows the lines printed at different thicknesses than the AccuPress prints. Figure 18 compares the sheet resistivity of the conductive lines for the AccuPress and K-proofer prints. As can be seen from the graph the 9 µm and 18 µm lines were not conductive as the depth of the cells was not enough to get sufficient ink transferred on the substrate for continuous lines. The 36µm line was printed with sheet resistivity of 1.36 Ω/□, which was 11% higher than what was achieved from the AccuPress. The same trend was observed for 54 µm and 63 µm lines. This was due to the difference in surface roughness of the engraved image carrier and the inking system of two printers. Hypothetically the surface roughness was sufficiently uniform to not retain any ink during the wiping process and only transfer ink from the engraved cells, however, as discussed above the inking system of AccuPress® is different than what would be found on a conventional gravure press. As a result, the ink did not wipe completely clean during printing.

Figure 18: Graph comparing the sheet resistivity for nano particle ink on K-proofer and AccuPress.
4.4– Conclusion

This study focused on the gravure printing of fine silver lines, which are potentially suitable for printing TFTs, high-Q inductors, parallel-plate capacitors and interconnecting wires for printed circuit boards. A number of important process variables were identified for the gravure printing of such lines. Cell wall spacing was found to be the most significant as it influenced the amount of ink spreading which impacted the electrical conductivity of the printed lines. The best fine line print quality was achieved when the cell spacing to cell width ratios were within 10% to 25% of cell size.

The highest resolution line that was electrically conductive was 36 µm wide. The 9 µm, 18 µm and 27 µm lines were printed, but were not repeatable nor conductive. The failure of these lines to conduct was due to the excessive amount of blade pressure required to remove streaking. At such high pressures, ink was wiped-out from the cells reducing the volume of ink transfer. This resulted in missing dots and discontinuities in the printed lines. However, when the same pattern was printed
using a K-proofer, no streaking was observed. Based on these findings it was concluded that the ink system on the AccuPress was contributing to the streaking problems. Even though there were no streaks in printed samples obtained with the K-proofer, fine lines less than 36 µm were not conductive. The failure of the lines to conduct was determined to be the result of the cells engraved with the Microstar being too shallow to carry sufficient ink to print continuous and conductive lines.

Comparing the prints from the K-proofer with the AccuPress, it can be concluded that a conventional gravure press could produce fine lines without streaks, if the cells could be engraved deeper to carry a higher ink volume. Overall, the electrical conductivity and print quality of the 36 µm nano particle lines was acceptable for multiple applications. The results show promise for the possible roll-to-roll printing of TFTs, with likely applications in a range of printed electronics systems. Although this work focused on the printing of two silver inks, the results can be extended to other inks as well. This report lays the foundation for future roll-to-roll gravure print studies.
5 - SCREEN PRINTED INDUCTIVE COILS USING COPPER INK FOR WIRELESS POWER

5.1 – Introduction

In the past decade, the use of wireless technologies, like mobile phones and Internet, has drastically increased in our daily lives. Taking the model from these technologies, the demand for wireless operation of electronic devices has increased significantly. This new power transmission method can provide convenience and ease of use along with added security and safety.

The concept of transmitting power wirelessly has been around for a long time. Nicola Tesla was the first to propose theories of wireless power transmission during late 1800s and early 1900s [64]. After World War II, notable efforts were made to use the new microwave technology developed during the war. A nationally televised

Figure 20: Electric toothbrush- Image courtesy[1]
demonstration of a microwave powered helicopter at the Spencer Laboratory of the Raytheon Co., in 1964 was the result of these early efforts and broadly introduced the concept of wireless power transmission to scientific and engineering communities and to the public [65]. Subsequent development efforts have centered on improving the overall efficiency of the power transmission method. The technology base was greatly expanded due to the requirements of the applications, such as implantable electronic devices, charging of microelectronic devices, RFIDs etc. One of the simplest examples of its use today is the rechargeable toothbrush, shown in Figure 20, which works on this principle of inductive wireless power transfer. Inductive wireless power transfer, or magnetic coupling, is used where wireless power transfer between the inductively coupled transmitter and receiver system occurs within a short distance (near-field).

5.1.1 – Definition of “Wireless Power”

A wireless power transmission system is defined as one that efficiently transmits electric power from one point to another through the vacuum of space or the Earth's atmosphere, without the use of wires or any other substance. Wireless power transmission is distinguished from free-space point to point communication systems by its high efficiency, by the comparatively high levels of power being handled, and by its technology and physical components that are distinctly different from those used in communication systems.

5.1.2 – Main components

Figure 21 shows a very simplified schematic diagram of the inductive link. There will always be other circuit elements that will impact the performance of the
link. For simplicity, they are not shown here. In the Figure, L1 denotes the primary coil and L2 the secondary and they need to be aligned in order to transfer power efficiently. Coil windings have distributed parasitic resistance and capacitance associated with them, each of which contributes in the power loss and overall reduced efficiency.

5.2 – Background and Overview

Design and optimization of efficient inductive power transmission links have been well studied over the past few years [66-68]. More recently there have been a number of publications proposing new approaches to the same optimization problems [69, 70]. It is also well known from electro-magnetics that the values of L1, L2 and M in Figure 21 are dependent on the coil geometries, which in general terms can also include their relative distance, orientation, and number of turns. Hence, it can be concluded that the geometry of the coil is one of the most important factors in defining the link power efficiency.

Most of the coil designs for wireless power have been based on coils made of filament wires. Wire-wound coils, however, cannot be batch-fabricated or reduced in size without the use of sophisticated machinery. Therefore, to achieve reduced sizes and faster production methods, the shape and geometry of the coils are modified to be planar and lithographically produced on rigid or flexible substrates similar to printed
circuit boards (PCB).

Photolithography involves the use of a photo-resistive film and mask to create the desired image to be printed. UV light is shined through the mask onto the film, which becomes either harder or softer, depending on the type of film used. The non-hardened areas are then washed away and the exposed substrate chemically etched to produce the desired image. The problem with photolithography is that it’s a subtractive process, which means there is substantial waste generated during the multiple etching and washing steps. It is also much slower due to the multiple steps involved and etching on flexible substrates can have unpredictable results. However, small feature size can be easily achieved by this method.

Another technique to make these coils is to print using different printing methods. Coils of different designs have been successfully screen and inkjet printed on flexible substrates. Of the two print methods just mentioned, screen-printing has been more widely researched. Printed coils rather than wired coils offer more flexibility in optimizing their geometry and aspect ratio, deeming them attractive for fitting into small, sensitive places such as interior of the human body. They can also adjust to the surface curvature if printed on thin flexible substrates such as polyimide or they can be printed directly onto the surface itself such as in flexible packaging. Recently, the use of printed coils to power a display on a cereal box and wireless countertops were revealed at the consumer electronics show. The demonstration of using printed coils in consumer products applications is just one example of some of envisioned uses for this technology. The cost of printed coils is also much lower compared to the wired or lithographically produced due to the ability to produce them at higher speeds.
When dealing with the printing of coils the selection of printing method and the choice of printable conductive ink will greatly impact the thickness, conductivity and other parameters for the coils. As mentioned above, screen printing is a more popular printing method for printing microelectronic devices due to its simplicity and ease of use. This method also produces considerable ink film thickness, which is the functional requirement for the coils.

Screen-printing for microelectronic devices is very similar to textile screen-printing. A negative image of the desired structure is created on a mesh screen. This screen is then placed over a substrate, and functional ink to form the electronic structure is passed over mesh with a squeegee, which pushes the ink through the mesh to the substrate. The mesh spacing controls the amount of ink applied and determines the resolution of the image that can be printed. It is relatively cheap, and capable of higher speeds for mass production using rotary screens. The screens used are more durable than traditional photolithography masks and are excellent for printing on flexible substrates. Despite these advantages, it is unable to achieve the high resolution of photolithography.

For the conductive inks, silver and copper were the two choices due to their high conductivities. Both inks are comparable in conductivity (1.58 x 10^{-8} and 1.68 x 10^{-8}\text{n}\Omega.\text{m} @ 20^\circ\text{C}, respectively)[71, 72]. However, the conductivity of their oxides is greatly different. Copper oxides are non-conductive, whereas silver oxides are conductive. This difference has led the conductive ink manufacturers to look more into the use of silver than copper. Recently, NovaCentrix has developed copper inks that eliminate this concern [73]. The NovaCentrix technology uses proprietary PulseForge® technology, which uses brief, extremely high-powered pulses of light
from special custom lamps to convert copper oxide to a stable conductive copper. Though this extra processing step requires some additional time and capital investment, the cost savings for copper instead of silver warrants studies to determine its viability in applications where silver is being used.

In this study, we investigated the performance of three different coil designs having various line gaps, printed using the NovaCentrix screen-printable copper ink. Printability analysis was done after printing, to check for any print defects and their possible causes. Ink film thickness was also measured and then the analysis of electrical properties was done. The resistivity of the inks, induction of the coils and print attributes of the coils were measured.

5.3 – Experimental

As mentioned earlier, three different designs of the coils were printed, each with different number of turns, gap spacing and line width. The designs of these coils are proprietary of “Fulton Innovation” [74] and were designed to investigate maximum performance for their wireless power product “eCoupled”. Figure 22 shows the three coil designs with the trace width and the spacing between the traces. Coil A is designed to have 30 number of turns with trace width and the spacing of 0.175 mm, coil B has 20 number of turns with trace width of 0.175 and gap spacing of 0.35 mm, while coil C having the lowest number of turns equal to 10 with the same trace width of 0.175 mm and the spacing of 0.825 mm. Each of these coils has the same inner diameter of 22 mm and the outer diameter of 43 mm due to which the spacing between the traces varies.

PET film Melinex ST 505 from “DuPont Teijin films” was selected as the
substrate of the printed coils described herein because of its non-absorptivity and heat stability [75].

5.3.1 – Coil Fabrication

The coils were screen printed using a semi-automatic press MSP-485 from Affiliated Manufacturers, Inc. (AMI) using a 325 mesh size screen, with steel as the screen material. The 12 inch screen was designed to have three samples of each coil design to check for the repeatability. Therefore, in each ‘good’ print we produced nine coils, three of each design.

5.3.1.1 – Screen Printing

As the first step, squeegee was leveled on a flat surface and then the squeegee pressure was adjusted based on the substrate thickness. Selection of the squeegee in terms of hardness is also a factor that can affect the print [76]. Ink properties also

![Figure 22: Coil designs with 100% scaling specifying the trace width and the spacing between the traces (left). Coil A with 30 turns (middle) Coil B with 20 turns (right) Coil C with 10 turns.](image-url)
define the squeegee hardness [76]. For printing these coils, a relatively hard squeegee was used so that a sharp and crisp image could be obtained. Next the screen was placed on the printer and leveled using a two dimensional level. Then, the snap off distance was set to 60 µm to obtain a crisp and sharp image. Snap off distance also impacts the print quality [76]. Although contact print can produce thicker prints, which is a performance requirement, but it also tends to spread the ink, filling the gaps between the coil lines.

Since the copper ink we used is water based, the print mode was set to the print flood mode, which means the printer will first run the print sequence then the flood sequence. The flood sequence was used after printing to prevent the ink from drying in the screen openings, which can result in the clogging of the mesh. The squeegee pressure for the flood sequence was adjusted to assure that the screen stayed flooded with ink between subsequent prints. After making these adjustments, the substrate was placed on the stage of the printer and the run cycle was executed.

5.3.1.2 – Photonic Curing

After printing, the coil samples were separated for photonic curing. As discussed above the copper ink from Novacentrix contains copper oxide and a reducing agent to form metal copper after photonic curing. The reducing agent requires activation energy within a certain range to form metal copper. If excess energy is supplied the copper traces oxidizes and gets damaged, if less energy is supplied the copper oxide does not reduce to metal copper. The sheet resistance of metal copper is inversely proportional to the energy exposure of the photonic curing[77]. When the exposed energy is less than 3.98 J/cm², sintering of the CuO layer is not possible[77]. The energy is too low for solvent vaporization, the chemical
reduction of CuO as well as elimination of its organic stabilizers and the sintering process. To get absolute conversion to metal copper, proprietary PulseForge technology needs to be used. A similar system developed by Xenon® having similar properties was used for the curing of reduction of copper oxide to metal copper. The Xenon system flashes very high intensity UV-visible light for very short time intervals; about 1 ms. The lamp for the Xenon system is radial, so it flashes light on circular areas of 3 inch diameter. The samples were flashed with different light intensity levels and the distance between the sample and the lamp was also varied to determine the optimum cure condition. The number of flashes that samples were exposed to was also varied. Even after all these variations, complete curing was not achieved and damage was visible in some of the printed samples.

5.3.2 – Printability Analysis

Since curing created damage to the samples by vaporizing some of copper, line widths and gap spacings were measured prior to curing. Measurements were performed using an ImageXpert® (KDY Inc.) system and ImageXpert® analysis software. For each coil design, multiple ROIs (region of interest) were selected but all

Figure 23: Archimedes' spiral coil (red area) is part of the spiral.
measurements were made in the same region. Then the average and standard deviation values were calculated. This was important to get accurate results. The thicknesses of the ink films were measured using a Technidyne Caliper Tester. Substrate thickness was subtracted from the printed sample thickness to get the ink film thickness. Multiple readings were taken and averaged.

5.3.3 – Analysis of Electrical properties

Due to difficulties in curing the samples without damage, the resistance and inductance could not be measured. The copper ink used had CuO as the core component which is supposed to be reduced to Cu in the curing process which could only be achieved using PulseForge technology. However, using the measured

Figure 24: Printed coils of three designs before and after curing with Xenon® Lamp at 100% scaling (left) Coil A with 30 turns (middle) Coil B with 20 turns (right) Coil C with 10 turns.
dimensions of the coils, estimates of the resistance were made, to determine the achievable performance if a NovaCentrix unit could be used. In order to calculate the resistance we need the length of the trace of the spiral coil, its width and the thickness.

Since the coil is part of Archimedes’ spiral, as shown in Figure 24, to accurately calculate the length of the trace we need to consider the equation of the spiral which is given in polar coordinates by [78].

\[
r = a\theta \quad \ldots \ldots .5.1
\]

Where ‘r’ is the radius, ‘\(\theta\)’ is the angle in radians and ‘a’ is a constant, which controls the spacing between the consecutive traces and is equal to

\[
a = \frac{\text{spacing between centers of trace}}{2\pi} \quad \ldots \ldots .5.2
\]

In order to calculate the length of the trace of the coil arc length of the spiral, which is measured from \(\theta = 0\) in the positive ‘\(\theta\)’ direction, should be calculated from [78]

\[
L_\theta = \frac{1}{2}a(\theta\sqrt{1 + \theta^2} + \sinh^{-1}\theta) \quad \ldots \ldots .5.3
\]

Where, \(\theta = 2\pi \times \text{No. of turns from origin}\)

Number of turns from the origin can be calculated by dividing the radius with the spacing of the coil and since the arc length calculated from the equation above
will be from the origin, therefore the length of the coil (red part in Figure 23) will

\[ \text{be} L_{\text{coils}} = L_{\text{outer}} - L_{\text{inner}} \ldots \ldots 5.4 \]

Once we find the length, the resistance can then be calculated by the sheet resistance given in the data sheet of the ink using the equation

\[ R = \text{Sheet resistance} \times \left( \frac{L}{W} \right) \times \left( \frac{\text{Ref Thickness}}{\text{Thickness}} \right) \ldots \ldots 5.5 \]

where ‘L’ is the length of the spiral coil and ‘W’ is the average width of the line. ‘Ref Thickness’ is the thickness at which sheet resistance is defined in the datasheet of the ink and ‘Thickness’ is the actual ink film thickness.

5.4 – Results

After printing, the ‘best’ samples were selected, two from each coil design;
Figure 25 top and Figure 25 bottom show the images for printed coils before curing and after curing with the Xenon® Lamp. It can be seen clearly that the printed samples are ‘good’ before they were cured, but after curing the line breaks are visible which makes them nonconductive and unusable as coils. It was also observed that the areas that were in direct contact with the Xenon light (top of the print) were curing well, but the bottom parts of the print remained uncured. Changes in the intensity of the light and the distance of sample from the light did not improved curing. Although an increase in intensity after a certain value blasted the copper off the substrate leaving disconnection points in the sample. Measured and designed values for trace width, spacing and thickness are shown in Table 1.

Calculated values of the length and resistance of the coils are also given in the Table 1. To calculate the resistance, sheet resistance of 60 Ωm from the data sheet of the ink was used. The reference thickness given for this value was 10µm, which gives an estimated value for the resistance that can be achieved. All values were measured.

<table>
<thead>
<tr>
<th>Coil</th>
<th># Of Turns</th>
<th>Calculated perimeter of coil (mm)</th>
<th>Line Width (µm)</th>
<th>Gap Spacing (µm)</th>
<th>Ink Film Thickness (µm)</th>
<th>Calculated Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Designed</td>
<td>Measured</td>
<td>Designed</td>
<td>Measured</td>
</tr>
<tr>
<td>A</td>
<td>30</td>
<td>3804.48</td>
<td>Average</td>
<td>175</td>
<td>175</td>
<td>117.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SD</td>
<td>31.2</td>
<td>25.3</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>2352.31</td>
<td>Average</td>
<td>175</td>
<td>350</td>
<td>345.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SD</td>
<td>26.0</td>
<td>20.4</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>1103.12</td>
<td>Average</td>
<td>175</td>
<td>825</td>
<td>992.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SD</td>
<td>12.5</td>
<td>10.6</td>
<td>1</td>
</tr>
</tbody>
</table>

*Table 1: Results for all the three coil designs calculated and measured before curing.*
before curing to get an estimate of the resistance if proper curing is achieved.

**5.5 - Conclusion and further work**

It can be concluded from the results given above, that working coils with estimated resistance values could be printed using the Novacentrix Metalon® ICI-020 copper ink, if proper curing is achieved. It can also be concluded that the system developed by Xenon® for curing, is different from the PulseForge® from Novacentrix. The spectra of the light could be similar but it is not the same. Since Novacentrix copper ink contains copper oxide and reducing agent to form metal copper after PulseForge curing, therefore it requires exact curing regime to avoid oxidation and damage to copper traces. However in terms of printability, Metalon® ICI-020 is a frontrunner in copper based inks.

One of the things needed to be explored further is the curing of these coils with PulseForge® technology or measurement and comparison to these results. Another thing that needs to be tested is to add a short interval thermal stabilization step before they are cured with the Xenon® lamp. The addition of this step may excite the copper oxide molecules to allow the UV component from the lamp to reach and penetrate to the bottom of the print. The thermal stabilization step can also be replaced with a lower intensity narrow band UV light system such as the one by Fusion UV systems, Inc. Another suggestion for further work is to print these coils on an uncoated paper substrate, which would help in the absorption of the solvents in the ink to determine if any energy benefits could be realized.
6 - GRAVURE PRINTED CAPACITORS FOR ROLL-TO-ROLL PRODUCTION APPLICATIONS

6.1 – Introduction

The basic building blocks of an electronic circuit consist of active and passive components on a printed circuit board (PCB). These passive components include capacitors, resistors, and inductors. In a typical electronic product, the ratio of passive to active components is about 20:1, and about 80% of the board is occupied by these passive components [7], most of which are capacitors [8]. Recent advancements in the area of printed electronics have attracted significant attention in the manufacturer of passive components. Printed components avoid complex, expensive and time-consuming photolithography processes. This also reduces the number of manufacturing processing steps, cost and material usage [79, 80]. In addition, its low-temperature processing enables the use of plastic substrates in flexible electronics.

This relatively new area of printed electronics also promises to enable new applications such as RFID tags, displays and chemical sensors. Compared to traditional methods of manufacturing silicon integrated circuits, printing has several characteristics that may allow it to be both faster and cheaper. First, printing is a large area pattern deposition technique that allows for the roll-to-roll processing of functional materials onto a variety of substrates, including paper and plastic. Second,
printing is an all-additive process, so that limited excess material is deposited and material and waste disposal costs can be reduced. Finally, printing does not require the expensive equipment that vacuum processing, photolithography, and other processes associated with traditional semiconductor manufacturing requirements. For these reasons, printing is an attractive fabrication technique for applications that can exploit its low cost per unit area, while accepting its performance drawbacks.

Critical to the development of printed electronics is the establishment of a manufacture-able printing technique with high resolution, consistency and throughput. Roll-to-roll printing is desirable because of its fast throughput and potential scalability to large-scale industrial processing. It has been successfully utilized for fabricating passive devices with only one layer of material, such as industrial UHF-RFID antennas [81], inter-digitated capacitors and spiral inductors [33, 45]. However, there has been less success in the printing of multi-layers of functional inks, especially at higher speeds. Multi-layer printing requires the compatibility of surface energy of areas to be printed and surface tension of inks, drying requirements and substrates being used.

This work lays the basic groundwork for the roll-to-roll printing of multi-layer passive components. Capacitors are primarily two layers of conductive material separated by a thin layer of insulating film. The thickness and quality of these layers is critical to the performance of the final device. To date, there have been a number of studies on gravure coating quality as a function of different operating parameters [61-63]. However, these studies have used large cell sizes to coat large areas, and have not focused specifically on the pattern printing and compatibility of layers for electronics applications. This work, in contrast, uses different cell sizes for different
layers and focuses specifically on the compatibility of layers. Capacitors were printed on a lab scale gravure press on a flexible plastic substrate and their electrical properties were characterized. Furthermore, the performance of different dielectric inks was compared. Finally, the electrical performance of printed capacitors was compared with theoretical values calculated from basic capacitor equations.

6.2 – Experimental

6.2.1 – Printing process

Gravure is a roll-to-roll printing technique, which has high throughput, long print runs, a high uniformity of print, and is highly versatile. In the gravure printing process, an engraved cylinder is rolled over a moving substrate, typically paper or plastic. A tightly pressed blade, called the doctor blade, wipes off excess ink from the non-image areas of the cylinder surface before contacting a substrate (Figure 26). Gravure printing is an attractive process because it is mechanically simple, with fewer controlling variables than competing high-speed printing processes such as flexography or offset lithography.

Figure 26: Gravure AccuPress at WMU
For this study, printing was performed using a sheet-fed gravure AccuPress® from Ohio Gravure Technologies (see Figure 26). This press was specially designed for R&D purposes. The main advantage of this press is it has all the capabilities of an industrial gravure press. It uses a cylinder of 381mm (15”) diameter, which is within the range of a narrow web industrial press. The print size for this machine is limited to 300 mm by 300 mm. Printing on any flat substrate is aided by a plane and rigid carrier covered with an impression blanket (thickness of impression blanket 2.5 mm, Shore A hardness of 86) to support the substrate. The carrier was manually fed between the back-up roller and rotating printing cylinder.

The printing nip was created by the contact between substrate and cylinder. The rotation of the cylinder pushed the substrate through the nip transferring the ink from engraved cells onto the test substrate. The gravure printing process can be separated into the two actions of cell emptying and ink spreading. As a filled cell approaches the substrate (nip), ink is pulled out of the cell. The ink then spreads on the substrate. The final width, thickness and uniformity of the printed layer are highly dependent on the cell emptying process, which is affected by a number of variables. These include the cell width, cell aspect ratio, print speed, ink viscosity, and ink/substrate surface energies. Cells with smaller widths and larger aspect ratios tend to empty proportionally less ink than wider cells because they have a larger surface area to volume ratio, which results in greater adhesive forces that keep the ink in the cell. In contrast, substrates with high surface energy will tend to pull the ink out of the cell [3]. A printing speed of 1.2 m/s was used for all print trials. The print speed is important, because it determines the shear applied to the ink. Higher viscosity inks tend to empty less completely than lower viscosity inks [38]. The viscosity of the ink
depends on the shear applied and the shear resistance of the ink, among other factors.

After the drop leaves the cell, based on the surface tension of the ink, it will seek to minimize its interfacial surface energy with the substrate. If the drop has a low surface tension relative to the surface energy of the substrate, it will tend to spread more, since the larger interface will lower the overall surface energy. Thus, the size of a printed dot can be minimized by either increasing the ink surface tension or decreasing the surface energy of the substrate [82]. After printing, the sample was detached from the vacuum platen and dried as described in the next section.

6.2.2 – Cylinder design for Capacitors

All three layers of the capacitors were designed and engraved on a single cylinder. Seven different size capacitors were designed with overlapping electrode areas from 0.125 in\(^2\) (3.175 mm\(^2\)) to 1 in\(^2\) (25.4 mm\(^2\)). The designs used for all three layers is shown in Figure 27. The actual dimension of the surrounding box is 2.5 in\(^2\). A test pattern with meander line resistors was also included in the design. This was done to enable the DC resistance of the conductive printed layer to be measured. After the pattern was designed, it was rotated by 45\(^\circ\). This was done because previous studies showed [3] horizontally printed lines to print less favorably due to drag-out.

Figure 27: Image showing the pattern for the three bands on the cylinder. Red and blue being the top and bottom electrode layers and green being the dielectric layer.
Drag-out occurs when an ink is dragged out of the cells in the print direction by the doctor blade.

The gravure cylinder was engraved by RotaDyne Decorative Technologies (Cincinnati, OH). The dielectric layer was engraved using conventional electromagnetic engraving methods while the conductive layers were engraved using an indirect laser method. Indirect laser engraving involves laser ablation of a protective mask on a copper surface, followed by a chemical etching of the copper layer [83]. After etching, the cylinder was chromium plated and finished using traditional methods [84]. A typical shape of engraved cell resembles a squared cup. For this work, a target cell depth of 30 µm was used.

6.2.3 – Materials

Commercially available inks were used for this study, but the viscosities were adjusted. Ink viscosity plays an important role in ink transfer and spreading. A low ink viscosity can cause a print to “bleed out” and reduce image sharpness [3]. A low viscosity can also result in a thin printed film affecting the electrical performance. If the ink is too viscous, then the ink will not freely flow and spread which can result in printed areas of non-uniform thickness. The optimal ink viscosity will result in a smooth layer with maximum printed thickness. Thicker layers tend to have more uniform print heights, because they allow more time for capillary flow, thus allowing for a smoother top layer to settle [85].

A silver-based conductive ink, containing silver nanoparticles (TEC-PR-020 by Inktec®, Inc.), was used in this work, for all conductive layers. The particle size of silver conductive filler is reported on the technical data sheet to be between 20–50 nm. The steady flow properties of the conductive ink were measured with an AR
2000 Advanced Rheometer (TA Instruments). It was observed that the viscosity of the ink increased from 35 cP – 2600 cP over the measured range of shear rates. The viscosity versus shear rate is dependent on the particle size, particle shape, resin system and solids content. Unfortunately, the composition of the silver ink used is proprietary to the manufacturer, limiting the user to only control the solids content. The solids content was adjusted by adding appropriate solvents (isopropyl alcohol) [86]. Based on initial print trials, the solids content was adjusted to approximately 40% wt as higher contents were giving bad print results. After printing, the samples were cured in a hot air convection oven at 120 °C for 20 min. Two UV curable polymer based dielectric inks were used to isolate the top and bottom electrodes of the capacitors. The two dielectrics used were; PMA-1210P-004 by JNC corporation (Tokyo, Japan) with a viscosity of 17.7 cP and UV Clear Coat from Ecology Coatings (Clifton Park, NY). These inks were cured using a Fusion UV curing system equipped with a D-lamp.

The capacitors were printed on Melinex® ST505 PET film which is a heat stabilized film. It is pretreated on both sides for improved adhesion. The thickness of the PET film was 130µm. prior to printing, the substrates were cleaned in subsequent baths of de-ionized water and isopropyl alcohol, then dried. White light interferometry analysis of the PET film after cleaning showed a RMS roughness value of about 14 nm. The surface energy of the film was measured to be 49.08 mN/m (dispersive: 38.27; polar: 10.8). Measurements were performed using a First Ten Angstrom dynamic contact angle measurement device. Surface energies were calculated from the equilibrium contact angles obtained for methylene iodide and deionized water data using Owens Wendt Method[87].
6.2.4 – Electrical characterization

As a measure of electrical performance, the sheet resistivities of the top and bottom conductive layers were measured with a four point probe sensing station. In this work, a SMR Probe head from Bridge Technology was used, which was connected to a Keithley 2400 multi meter through an Ethernet cable. In this method, four equally spaced probes are brought in contact with the deposited layer. The two outer probes are employed for sourcing the current and the two inner probes are used for measuring the voltage across the layer. The sheet resistivity can be calculated from this measured voltage and applied source current.

After printing all the layers of the capacitors, the conductivity between the top and bottom electrodes was measured to check for isolation and any possible leakages. All leaky capacitors were discarded. Finally for the capacitance measurements, frequencies ranging from 100Hz – 1MHz were applied and the impedance response was measured. Based on the response, capacitance values were calculated. These measurements were performed using an LCR meter (Agilent, E4980A). The LCR meter measures the complex impedance of the capacitor at multiple frequencies, determines the magnitude of the impedance and the reactance or phase difference. It is measured as R + jX and converted to the appropriate units for recording. Based on the complex impedance observed from the measurement, it is possible to analyze the performance of the device. In this case, the dielectric is insulating the two plates so by applying voltage to the device, the LCR meter measures the capacitance for different frequencies.

6.3 – Results and discussion

To fabricate a parallel plate capacitor, the bottom conductive layer was printed
onto the PET substrate. This was followed by the printing of the dielectric layer and sequential printing of the top conductive layer. The bottom conductive layer was sintered before printing the dielectric and the dielectric was UV cured before printing the top conductive layers. This sequence of printing and drying was performed to prevent the bottom conductive layer from cracking due to the dielectric layer being absorbed into the conductive layer. After the initial printing of the two dielectric inks, the ‘best’ samples were selected. The selection process was based on the clarity of print and visible absence of pinholes.

From these prints, a detailed analysis was performed and results were compared to determine the optimum print and electrical settings. The ink film thickness and roughness of the printed layers were measured with a vertical scanning interferometry (VSI) using a WYKO RST-Plus microscope. The ink film thickness and roughness results are shown in Figure 28. Layer quality was evaluated in terms of the roughness of the printed layer. The sheet resistivity of the conductive layer was measured as an indicator of the electrical performance of that layer.

Figure 28: Images showing the three different configurations for printing capacitors
6.3.1 – Conductive layer

The first layer for fabricating the capacitors was printed using nano silver ink on an AccuPress using a 0.875” wide MDC® ultra-life doctor blade from Daetwyler. The blade material was steel with a thickness of 0.006” and lamella tip. The blade pressure and angle were setup to give streak free prints. A cylinder pressure of 100 µm was selected, which means the cylinder will press 100 µm further after just touching the substrate. This pressure influences the ink transfer volume and amount of ink spreading in the final print. After printing, the samples were sintered in a convection oven at 120ºC for 20 min. No pinholes were observed in the printed layer. A smooth, consistent layer with a roughness value of 112 nm ± 13 nm was achieved. The thickness of the sintered layer was measured to be 396 nm ± 28 nm. Sheet resistivity was measured by four probe method and it was found to be 0.46Ω/□ ±0.07. All results reported are an average of five measurements.

6.3.2 – Dielectric layer

Two different dielectrics were printed on top of the first silver layer. When printing with the two different dielectric inks, all other conditions were kept the same (blade type, configuration and impression pressure). They were printed using the same blade setup as for silver ink, except the angle was made shallower to mark ‘4’on the press (see Figure 13) The number of printed dielectric layers was also changed to control the electrical characteristics of the printed capacitors because capacitance is strongly influenced by the thickness and dielectric constant of a dielectric layer between two parallel conductive plates. Roughness and thickness values for both dielectrics for single and double layers are shown in Figure 28. For a single dielectric layer, the relative dielectric constant estimated from the equation,
\[ \varepsilon_r = \frac{Ct}{(A \varepsilon_0) }, \]

Where \( C \) is the capacitance, \( t \) is the thickness of the printed dielectric layer (1.06 \( \mu \)m), \( A \) is the capacitor area and \( \varepsilon_0 \) the permittivity in vacuum \( (8.85 \times 10^{-14} \text{ F/cm}) \) is 7.4. An important observation to note was that for capacitor with two layers of dielectric, the capacitance was not halved. This was because near voids or minimum distances from the first layer the capacitance was most significantly affected (more charge accumulated where the thickness is the thinnest). By adding a second layer, not only pin-holes are filled but potentially low areas are also filled which increases the distance between the two conducting layer hence reducing the capacitance. Another reason might be the effect of particle sedimentation over time.

### 6.3.3 – Final Layer

The final conductive layer was printed by again using the nano-silver ink and the same doctor blade setup. Due to the roughness of the dielectric layer, the final layer was not conductive enough. Sheet resistivity was around 10k\( \Omega / \square \). To decrease this value, another layer of silver was printed after which the sheet resistivity improved to 1.25 \( \Omega / \square \) \( \pm 0.79 \)

### 6.3.4 – Electrical performance

As mentioned above, after printing the capacitors the measurements were performed with a LCR meter (Agilent, E4980A). Figure 29 shows the capacitance measured for all the areas that were printed. Yield values were also calculated. Complex impedance between top and bottom electrode were measured for all printed samples using LCR meter (Agilent E4980A) in the frequency range of 100Hz – 1MHz. Table 2 shows the yield for the number of working capacitors obtained for each dielectric. Due to appearance of pinholes in the printed dielectric layer, there
was a conductive path through the dielectric for some of the printed capacitors therefore they didn’t show performance as a capacitor. It is seen from the results that the two layers of printed UV-coating showed the better performance as a dielectric in terms of number of working capacitors in comparison to the one layer UV-coating and PMA samples.

<table>
<thead>
<tr>
<th>Area/Dielectric [mm²]</th>
<th>UV 1 Layer [%]</th>
<th>UV 2 Layers [%]</th>
<th>PMA [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>100</td>
<td>100</td>
<td>17</td>
</tr>
<tr>
<td>18</td>
<td>100</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>36</td>
<td>100</td>
<td>100</td>
<td>33</td>
</tr>
<tr>
<td>72</td>
<td>100</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>144</td>
<td>0</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>625</td>
<td>0</td>
<td>100</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure 29: The capacitance values measured for different areas of capacitors.

Table 2: Table summarizing the yield values for the capacitors printed.
The capacitance measurement was performed in the same frequency range. Figure 29 shows the capacitance with change in area for the capacitors printed with PMA as a dielectric and 1 layer UV coating, respectively. As indicated, increasing the overlapping area the amount of capacitance increased and a higher capacitance was observed for the one layer UV coating condition.

All the capacitors fabricated with two layers of the UV-coating applied showed performance as a capacitor, but the amount of the capacitance decreased due to the increased thickness of the dielectric layer. The change in capacitance with frequency is shown in Figure 30 for the area of 18 mm$^2$ for all dielectrics. In the same effective area higher capacitance was observed for the printed sample using the UV-Coating as a dielectric. The relative dielectric constant was calculated using:

![Capacitance vs. Frequency (18 mm$^2$)](image_url)

**Figure 30: The frequency response of printed capacitors**
Where $C$ is measured capacitance, $d$ in the thickness of dielectric, $A$ is effective area and $\varepsilon_0$ is permittivity in vacuum, which is equal to $8.85 \times 10^{-14}$ F/cm.

The calculated dielectric constant for single layer of UV-coating is 2.34 and for Poly methyl acrylate (PMA) is 4.3.

6.4 – Conclusions

This work showed the ability to gravure print capacitors on a plastic substrate on a small-scale. Thus, the potential for scale-up to higher speed roll-to-roll production was not tested, but is possible. Two different dielectric inks were used. The differences in ink characteristics led to different layer thickness, hence different electrical performance for the two inks. Although this work was done with a limited...
material set, the trends discovered will be useful in the investigation of other ink sets as well. It was also shown that the engraving specifications and optimization of processes to produce high resolution and high registration device structures is required to fully utilize the potential of gravure printing for electronics manufacturing. Factors for improving the wetting properties and layers compatibility were also discussed.

Overall, gravure-printed capacitors are promising because of their high electrical performance, high yield values and potential scalability to industry. This work lays the foundation for future studies on roll-to-roll fully printed electronics devices, which will help to usher in a world where printed electronics become ubiquitous and a host of new applications are enabled.
7 - GraVure Printed Organic Light Emitting Diodes

7.1 – Introduction

Conjugated polymers are organic macromolecules that are characterized by a backbone chain of alternating double- and single-bonds. Their overlapping p-orbitals create a system of delocalized \( \pi \)-electrons, which can result in interesting and useful optical and electronic properties. The \( \pi \)-electrons can be easier moved from one bond to the other, what makes conjugated polymers to be one-dimensional semiconductors. Like inorganic semiconductors they can be doped, to increase their conductivity extremely. These polymers are very promising and attractive materials for use in electroluminescent displays [88], photovoltaic, transistors, sensors and polymer microsystems, because they combine the optoelectronic properties of semiconductors with the processing advantages and mechanical properties of plastics. Currently, processing and fabrication of thin films for polymeric electronics is carried out using traditional techniques such as spin coating and vapor deposition. However, this technique has several disadvantages, e.g. material wastage and time constrains, and therefore tremendous benefits are gained by incorporating printing technique in the deposition of polymer thin films for OLEDs [89]. In order to incorporate printing for fabrication of electronic devices, there are quite a few challenges. The biggest
challenge is to make the materials printable and form a uniform, pinhole free film after printing. This can be achieved by modifying the rheological properties of the ink. The printing method used and its parameters also play an important role in achieving desired results. Gravure printing technology is one of the fastest and most cost effective roll-to-roll techniques practiced with adequate patterning resolution and low process temperature [90], which can easily be incorporated for printing of electronics. In this technique, the pattern to be printed is engraved on a metal cylinder. The engraved cells are filled with ink that is transferred to the substrate when the cylinder is brought into contact with the surface of the substrate. During printing, the excess ink is removed from the cylinder by the use of a flexible doctor blade. This ensures that the cells are filled with an exact volume of ink.

The objective of this study was to demonstrate the proof of concept for fabricating Organic light Emitting Diodes (OLEDs) using printing technologies. This study was done using a lab scale inkjet and gravure printer. It is known that the electroluminescence performance of the device is highly sensitive to film morphology. The surface characteristics and their impact on the performance of the finished device are discussed. For this study, the materials were dissolved in solvents along with some other additives to achieve uniform and homogenous layers. Along with printing, the materials were also spin coated to form the OLED structure, to verify the functionality and compare the results of the structure.

7.2 – Experimental

7.2.1 - Materials and structure for OLEDs

A range of material is available for fabricating OLEDs, however their
performance depends on the number of layers and the morphology of the layers. For this study, it was decided to use the simplest of OLED structure to demonstrate a proof of concept. The OLED consisted of four layers structured as ITO/PEDOT:PSS/MEH-PPV/AL. Figure 32 shows the structure of polymer based OLED and how each of the layers was deposited. ITO coated glass was purchased from Sigma-Aldrich. The hole injection layer of poly (3,4-ethylenedioxythiophene) doped with polystyrenesulfonate (PEDOT:PSS) was obtained from Heraeus (Germany), which was supplied in the form of an inkjet ink. This layer was deposited with a Fujifilm’s Dimatix inkjet printer.

For the light emitting polymer, a conjugated organic material was used. These materials act like semiconductors and will, if applied in OLED device geometry, yield some sort of luminescence response. Some materials are, of course, much better suited than others and the choice of material was made based on various criteria such as stability, purity, ease of availability, and efficiency of the final device. One of the

*Figure 32: Device Structure for Organic polymer based Light Emitting Diode*
polymer materials easily available that fulfills many of the criteria just mentioned is Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, Mw ~ 280000 g/mol). This material was obtained in solid form from Sigma Aldrich Co., which was formulated into an ink by adding a solvent and resin. These two layers (PEDOT:PSS and MEH-PPV) were sandwiched between the indium tin oxide (ITO) anode coated glass substrate and a metallic aluminum cathode evaporated onto the sample as a final step. The sheet resistivity of the ITO coated glass was 3±1 Ω/□. After the thermal evaporation, a silver epoxy was used to form a contact between the anode and cathode.

7.2.2 – Equipment

In terms of equipment, the requirements were an inkjet printer for application of the PEDOT:PSS layer, a gravure printing press for depositing the active layer and an evaporator for application of the metallic cathode. The inkjet printer used for this study was Fujifilm’s Dimatix and the gravure press used was AccuPress from Ohio Gravure Technologies. A bell jar thermal evaporator from Varian was used for this work, as shown in Figure 33.

Figure 33: Thermal evaporator used for the fabrication of OLEDs.
The thicknesses and morphologies of the polymer films, dots and lines were determined using a white light interferometry microscope (WYKO). Current-voltage characteristics of the OLEDs were measured using a Keithley 2400 source measurement unit and the luminescence was measured with an illuminance meter (Sekonic L-308S).

7.2.3 - Fabrication of OLEDs

The fabrication of the OLED device started with the substrate, which was a glass slide with a very thin layer (4±0.85 nm) of ITO. The ITO layer was patterned for the reason that when making connections to the electrodes, in the completed device, there is a high risk of developing a short-circuit. If this happens, an electrical connection created between the front and back electrode of the device produce low voltages and to a lesser, extent a lower short-circuit current. To avoid this type of failure, the ITO was removed in the area where the back electrode connection was made.

The simplest way of achieving this was to create a mask with ordinary tape, then etch the non-masked area. The conducting side of the glass-ITO slide was found

![Image](image-url)

*Figure 34: The conducting side of ITO coated glass can be identified by measuring the resistance, which is low for the ITO side (left). The part of the ITO that is to be kept is masked by adhesive tape (right).*
by measuring the resistance with a simple multi meter, carefully rubbing the tape against the surface of the ITO side of glass to adhere it firmly (shown in Figures 34 and 35). The cavities extending to the edge of the taped/glass acted as a channel for the acid, to etching the sample. The masked glass slide was then submerged in a 20% w/v solution of HCl at a temperature of 50°C. After being submerged for 15-20 minutes, the sample was removed and rinsed with water. The surface resistance was then checked to assure that the areas etched were no longer conductive. When complete etching was observed, the tape was removed and the slide again washed with deionized water followed by acetone. It was found that it was extremely important to wash the device immediately after etching to assure the complete removal of any traces of the acid solutions. Failure to do it resulted in poor definition of the etched area.

After etching and rinsing with water, the ITO side was rubbed with an acetone dampened lens paper prior to being placed in a beaker of acetone contained in an
ultrasonic bath. The sample was sonicated in this bath for 5–15 min. to remove any tape residues and soluble organic material surface contaminants. Though there are several lithographic methods available for creating patterns by etching; the tape method was just fast and simple.

7.2.3.1 – Hole injection Layer (PEDOT:PSS)

Before printing the hole injection layer, the etched slides were again cleaned to remove any surface contaminants. This time, the slides were submerged in a beaker of isopropanol and ultra sonicated for 10 minutes.

After being cleaned by this process, the hole injection PEDOT:PSS layer was applied to the ITO coated area of the glass slide. The PEDOT:PSS layer was applied to improve the surface roughness of the substrate and stabilize the electrical contact between the transparent anode and the active layer. The PEDOT:PSS ink was inkjet printed using a Fuji Film Dimatix printer. Before printing, the properties of the ink were characterized. The surface tension of the ink was measured using pendant drop

![Figure 36: Chart showing the relationship of viscosity and temperature for the PEDOT:PSS ink](image.png)
method. The surface tension of the ink was measured to be 27.25 mN/m. The change in ink viscosity with temperature was also measured using the AR 2000 Advanced Rheometer (TA Instruments). These viscosity measurements were done at constant shear rate of 1/1000 per second. Figure 36 shows the change in viscosity with the increasing temperature. As shown, the viscosity ranges from 7cP – 9cP, which is within the range for inkjet printing.

Z-Number calculations were performed to determine if the ink was jettable from the Dimatix printer (Figure 37). The Z-Number is a unit less number that is defined as follows:

\[
Z = \frac{(d \rho \gamma)^{1/2}}{\eta}
\]

Where d is the diameter of the nozzle, \( \eta \) is the viscosity, \( \gamma \) is the surface tension and \( \rho \) is the density. For the ink to jet correctly, the Z-Number for the ink has to be greater than 2 [91]. As shown in Figure 37, the Z-number was above 2 for the

![Figure 37: Z numbers for the PEDOT:PSS ink.](image-url)
entire temperature range tested.

Once it was confirmed that the ink would jet from the printer, the cartridge was filled with ink and per Dimatix’ recommendations, the filled cartridge was left in a water bath for 16 hours to de-air before printing. After observing that the first prints were non-uniform, a UV Ozone treatment was performed for 15 min. to increase the surface energy of the film and improve ink wetting. This enabled a uniform layer of hole injection layer to be printed. Immediately after printing, the samples were transferred to an enclosed container and held under vacuum. Before the slides were used, the PEDOT:PSS layer had to be heated in an oven or on a hot plate to a temperature of 120–200°C for 50–60 min to dry the film completely. This drying step was performed immediately prior to use.

7.2.3.2 – Light emitting polymer (LEP) Layer

The active material was first spin coated to verify the functionality of the material. To prepare the solution for this process, an appropriate amount of MEH-PPV (Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) was weighed and dissolved in chloroform to form a 0.05% wt solution. The solvent (chloroform) was added with a glass pipette. The temperature of the solution was then raised by placing the beaker of the solution on a hot plate to increase the rate of dissolution of MEH-PPV in chloroform. A glass rod was used to stir the polymer to assist in dissolving. Once completely dissolved, the solution was cooled and filtered through a micro filter using a syringe. This eliminated undesirable particles that might have been formed upon cooling. The slides were then rinsed with a clean solvent (Isopropyl alcohol) while spinning to remove any dust particles. To form an even, homogenous film, dust particles need to be removed completely. The particle-free
solution was first spin coated on the dust-free glass-ITO/PEDOT:PSS substrates to obtain a sample as a control for comparison. The connection area for the ITO contact at the end of the slide that had not been etched was then cleaned with a cotton bud wetted with solvent (IPA).

Once it was confirmed by the spin coating experiments that the LEP material was functional, an ink was prepared for gravure printing by adding an acrylic resin Elvacite 2045 to the solution to increase the ink viscosity and improve the ink leveling properties. Uniform layers were achieved by adding 2.5% wt of the resin. The ink was printed on the glass-ITO/PEDOT:PSS substrate using an AccuPress printer at a speed of 1.2m/sec. A lamella steel doctor blade was used to doctor the ink at ‘mark-4’ (Figure 13), which corresponds to a steeper angle on press.

7.2.3.3 – Evaporating the Cathode Layer

The final step in the process of fabricating the device was evaporating the back aluminum electrode. The glass slide was placed in a suitable mask into a thermal evaporator. The mask defined the back electrode geometry. Poly(ethylene-terephthalate) (PET) along with aluminum foil was used to create the mask. Three slits of about 5 mm x 25 mm were cut into the aluminum foil using an X-Acto knife to form the mask. The sample was then placed on the mask and wrapped in an aluminum foil. The wrapped sample was then placed in the thermal evaporator. An aluminum wire was wrapped onto a tungsten wire for connection to the electrodes of the thermal evaporator. The chamber was then closed and the pressure of the chamber rose to $1 \times 10^{-6}$ mbar, at which time the metal cathode was evaporated. Once the evaporator cooled, in approximately 10–20 min., the completed devices were recovered and used for measurements.
7.2.3.4 – Flow chart for fabricating OLEDs

Figure 38: Flow chart for the fabrication of OLEDs using printing technologies.
7.3 – Results and Discussion

The key concerns in processing a fully printed OLED on glass substrate are meeting the needed requirement of uniform printed layers. Such layers can only be achieved by modifying the characteristics of the ink properly for the printing process and optimizing the printing parameters. In printing, the ink and substrate properties play a vital role in the formation of a polymer film. Printing parameters need to be optimized and adjusted to attain the proper wetting of the ink on the substrate. Additionally, for the printing of a polymer layer on a rigid substrate with a copper engraved, chromium plated, rigid gravure cylinder is a challenge in itself. Although the principle of gravure printing is simple and straightforward, there are many variables that affect print quality. Furthermore, an OLED has a multi-layer structure, so the properties of the layer below will impact the printing conditions used to print the layer above.

In order to print an even, homogeneous, defect-free layer for polymer electronics, the ink formulation for the specific printing method needs to be optimized. Generally, the main components of functional inks are polymers, solvents and additives. The performance of the completed device is impacted by the electronic properties of the polymers. From a printer’s perspective, polymers used for formulating an ink should ensure adequate adhesion on the substrate and sufficient ink viscosity. The final ink viscosity is dependent on the molecular weight of polymers and their concentration in solution among other things. To achieve an appropriate viscosity for a particular printing process and to improve print quality, different additives like rheology modifiers and surfactants in small quantities, normally only a few percent of the total weight, [92] are added. Surfactants improve
the wetting of the ink on the substrate while the rheology modifiers changes the rheological properties such as viscosity of the ink. However, these additives affect the electrical properties of the organic semiconductor and therefore extensive use of additives can severely impact the performance of a device. Another method to improve the wettability of the ink on a substrate is to increase the surface energy of the substrate. This can be achieved by several methods. One of the common ways is to do a UV Ozone treatment, which oxidizes any impurities from the surface of the substrate. Also, while formulating inks the whole device structure needs to be considered, as the layer below should not be dissolved in the layer above.

To enhance the injection of holes into the light-emitting layer, PEDOT:PSS was printed on top of the etched ITO coated substrate. This hole injection layer also improved the smoothness of the ITO surface. In order to achieve a functional OLED device, it was necessary to have a uniform and pinhole free PEDOT:PSS film. If it is non-uniform in thickness, the electric field will be inconsistent causing a non-uniform emission of light. After the initial inkjet printing of the PEDOT:PSS, a non-uniform layer was observed. These variations were most likely due to the high surface tension

![Printed PEDOT:PSS layer at 10X magnification](image)  
![Printed layer without UVO treatment](image)  
![Same ink printed after 15mins of UVO Treatment of the substrate](image)

*Figure 39: Printed PEDOT:PSS layer at 10X magnification (Left) Printed layer without UVO treatment (Right) Same ink printed after 15mins of UVO Treatment of the substrate*
of the ink. To accommodate for the higher surface tension, the surface energy of the substrate was increased by treating it with UV Ozone for 15 min. Figure 40 shows the images at 10x magnification of the inkjet printed PEDOT:PSS before and after treating the substrate with UV Ozone. Both films were inkjet printed using the nozzle temperature of 30°C and a firing voltage of 40V. The drop spacing was set to be 45 µm and the cartridge angle of 6.86°. The jetting frequency was set to 5 kHz. After printing, the sample was cured in the oven for 25 min at 115°C.

The thickness of inkjet printed film can be controlled by varying the drop spacing and the drop volume. The surface tension of the ink and the surface energy of the substrate also played a role in the dry film thickness. The surface energetics altered the spreading of the ink on the substrate, hence defining the thickness on the sample at a particular drop spacing. The measured dry film thickness of the hole injection layer of PEDOT:PSS on ITO coated glass substrate after 15 min of UV

![PEDOT:PSS Layer thickness vs Drop spacing](image)

*Figure 40: Thickness of the PEDOT:PSS layers on ITO coated glass after 15mins of UV Ozone treatment*
Ozone treatment at three different drop spacing are shown in Figure 41.

The thickness of the printed layer can also be controlled by varying the polymer concentration in the ink. The ink received from Heraeus was composed of approximately 2.5% solid content of PEDOT:PSS solution. Commonly, a layer thickness around 60-70 nm is used in polymer OLED structure[47]. The layer thicknesses with inkjet printed PEDOT:PSS ranged from 40 nm to 120 nm can be obtained with drop spacing of 25 μm to 45 μm. A drop spacing of 45 was chosen due to the good PEDOT:PSS layer uniformity, as presented in Figure 35, and the appropriate layer thickness achieved for OLED applications.

The light emitting polymer Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) layer was gravure printed on top of the inkjet printed PEDOT:PSS layer. The solubility of this orange emitting material was good in solvents such as xylene, chloro-benzene, and chloroform, so initial printing tests were done with these solvents. However, the printability was significantly different with each of the three solvents. Experiments were started with 0.5% wt polymer concentration dissolved in one of the above-mentioned solvents at a time. With the

\[\text{Figure 41: 3D surface profile of the gravure cylinder showing engraving with 120 LPI and 160 LPI.}\]
three solvents, films were printed at 120 lpi and 160 lpi resolution, which corresponds to 211 μm and 158 μm cell opening with cell depths of 64 μm and 49 μm as shown in Figure 42. Since the cylinder was electromechanically engraved with a pyramidal stylus with an angle of 120° and screen angle of 45°, the theoretical ink volumes were 21.33 cm³/m² (μm) and 16.34 cm³/m² (μm) for the two different LPI settings. Relatively larger and deeper opening cells were selected in order to deposit enough material to form a pin hole free layer of emitting polymer.

As mentioned above the printed layer homogeneity with the three solvents was significantly different. Streaks and patterns were observed in the films formed from the solutions based on chloro-benzene and xylene. This was due to higher-boiling point and higher viscosities of the solution. Chloroform on the other hand produced some small cell patterns on the printed film, but much less than in chloro-benzene or xylene based inks. Hence, it was chosen due to the good solubility and printability properties. Even though chloroform should not be favored as it is not the ideal choice for industrial scale gravure printing process due to its unsuitability and health hazards but for presenting the proof of concept this was selected.

An initial polymer concentration of 0.5% wt was chosen in anticipation of having appropriate layer thickness range. However, other higher polymer concentrations of 0.75% wt and 1.0% wt were tested, but no improvement to the layer thickness and uniformity was observed. The light emitting polymer, composed of 7mg/ml of MEH-PPV was dissolved in chloroform, was gravure printed on top of inkjet printed PEDOT:PSS layer. The small cell patterns were visible on the layer surface due to the quick evaporation of chloroform before it levels completely. To achieve homogeneous film quality, resin was added. Elvacite, an acrylic based resin
was used to control the evaporation and viscosity of the ink. Three different samples of ink having 0.25% wt, 0.5% wt and 0.75% wt of Elvacite solutions were prepared and tested using the same gravure cylinder of 120 lpi and 160 lpi. Best results were achieved with a concentration of 0.5% wt of MEH-PPV and 0.25% wt of acrylic based resin. After printing, the ink film thickness values were measured using white light interferometry and as predicted, the theoretical values differ from the measured values. The theoretical film thicknesses for the MEH-PPV emitting layer were 213 nm for 120 LPI and 163 nm for 160 LPI. As compared to the measured layer thicknesses 102 nm, and 76 nm with the above-mentioned cell depths, approximately 47% of the ink was transferred to the PEDOT:PSS layer.

The dependence between the thicknesses of the gravure printed light emitting layer and the cell opening (resolution) can be seen in Figure 43. The desired layer

Figure 42: Thickness of the Light emitting polymer on PEDOT:PSS layer at 120LPI and 160LPI
thickness for a light emitting layer can be obtained by choosing the appropriate cell opening at constant cell depth and polymer concentration. 2D and 3D surface profile of all the layers are shown in Figure 44, indicating good uniformity of printed PEDOT:PSS and light emitting layer at microscopic scale. However, some streaks were still visible for the light emitting layer and were visible more during light emission. Further investigation of suitable solvent mixtures and additives for the light emitting polymer ink is required. After successful printing of the light emitting polymer with required thickness value, aluminum was thermally evaporated to provide the cathode layer for the OLED. The thickness of the aluminum layer ranged from 32 nm to 56 nm.

Luminance vs. voltage and current density vs. voltage measurement results of spin coated and printed PEDOT:PSS/MEH-PPV OLED structures can be seen in Figure 39. These were processed with the same polymer solutions using the same device structure achieving similar layer thicknesses. The gravure printed and spin
coated OLEDs had a turn-on voltage of 4.7 V. Brightness levels of 100 cd/m^2 and 1000 cd/m^2 were achieved for spin coated OLEDs at 8.3 V and 14.1V. The corresponding brightness levels for gravure printed OLEDs were achieved at 6.2 V and 13.6 V, respectively indicating 1.1 times higher efficiency of gravure printed OLEDs compared to the spin coated devices.

This work was more focused on the printability of the polymer based inks and optimization of printing process flow, rather than the performance of the OLEDs produced. The current efficiency of the gravure printed OLEDs were higher than those of spin coated OLEDs. This can be seen in the LIV characteristics in Figure 45. Spin coated devices were processed with the same procedure, except for the hole injection layer (PEDOT:PSS) and light emitting layer (MEH-PPV) were spin coated at 2500 rpm and 2000 rpm respectively. With an optimized spin coating process for laying down MEH-PPV layers, a brightness level of 1000 cd/m^2 was achieved at 14V. Due to higher thickness variation in gravure printed light emission layer compared to spin coated layers, variation in LIV characteristics of the gravure printed OLEDs was observed. The gravure printed light emission layers had a variation of ±26 nm in

Figure 44: (Left) Current Density vs Voltage (Right) Luminance vs Voltage characteristics of gravure printed and spin coated OLEDs.
thickness whereas with spin coating the variation was ±9 nm. The performance characteristics of the printed devices were also varied due to the higher number of variables to be controlled in the gravure printing process. However, this OLED performance data clearly indicate that gravure printing has indeed great promise for replacing the conventional fabrication process for OLEDs. Performance variation in printed OLEDs can be controlled by further optimization of ink formulation and printing process parameters.

The brightness over the printed light emitting area was significantly inhomogeneous. However, the potential of gravure printing as an OLED deposition method was shown successfully. The inhomogeneity was due to the thickness variations, in terms of streaks and cell pattern transfer in the gravure printed films. Additionally, high resistivity of ITO leads to a brighter illumination near the edge close to the anode contacts than the area away from the contact. Additional conductive lines can be printed [93], which have not been used in these structures to resolve the ITO resistivity problem. Figure 46 shows photograph of two orange emitting OLEDs. The first one with spin coated light emission layer, while the other one with printed hole-injection and emission layer.
7.4 – Conclusion

Polymer based OLEDs were fabricated successfully using gravure and inkjet printing techniques. Ink for light emission was prepared by dissolving MEH-PPV in chloroform. Improved performance compared with spin coating resulted from smoother and thinner emissive MEH-PPV layers, due to the appropriate physical properties of the two-component solvent. The printed polymer layers achieved flat uniformity over relatively large area showing the possibility of using roll-to-roll manufacturing for thin film based polymer LEDs. There is a potential for lowering the cost by using printing as a production method for these LEDs. The use of printing for processing such OLEDs can be beneficial in packaging and general display applications in which the cost advantage of the processing method is crucial. This work suggests that further optimization of the printed emissive layers would improve OLEDs’ performances to levels comparable to those of OLEDs fabricated by conventional ways. However, currently, due to adequate advancements in printing equipment, it is a challenge in itself to upscale a lab-scale process to a large scale production.
8 – Conclusion and Future Outlook

This work demonstrated that electronic components like conductive metal lines, capacitors, and Organic LEDs could be fabricated using gravure and other printing techniques. Clearly, gravure may not be suitable for every layer in an electronic component, but it can be one of more valuable print methods used. Two major shortcomings that prevent it from being a universally applicable tool is the pressure applied by the gravure roll while transferring the ink to substrate and the inability of the doctor blade to perfectly wipe the ink from non-image areas of the patterned cylinder on AccuPress, gravure press used in this work. The pressure exerted by the cylinder can cause structural damage to soft materials like polymers, making it unsuitable for printing all the layers of polymeric devices, as shown in Chapter 7 when printing OLEDs. Normally, gravure uses electrostatic assist, which allows for decreased impression pressure, but the AccuPress was not equipped with that feature. A second limitation of the AccuPress is the lack of perfect wiping of the non-image areas of its gravure cylinder, which could possibly be caused by a combination of microstar engraving and improper roughness of the face of cylinder. This limitation resulted in residual material being deposited between the gravure patterns. This caused interferences and short circuits as shown in Chapter 4, while printing fine lines. As was demonstrated with the fabrication of OLEDs, ink-jet
printing can be leveraged to overcome these problems, as it is a non-contact method that can deposit material exclusively where desired. Another weakness of gravure microstar engraving is the layer thickness of deposited ink. Of course, this thickness is a combination of printing parameters and ink specifications, but the microstar engraved cylinder for gravure can only deposit a fraction of what can be achieved with screen printing. In cases where thickness of the dried layer is a critical factor in the electrical performance of a device, microstar engraving may not be the best suited printing set up. Due to these limitations the development and understanding of multiple printing and deposition processes is essential to achieve the best results.

To industrialize the manufacturing of electronics using any printing technique, there still remain a few challenges. The abilities of current technologies, to deposit patterned thin films with thickness and shape uniformity, and roughness comparable to their vacuum deposited counterparts, is still limited. Chapter 4 described the challenges in finding suitable inks, inking system and engraving techniques for depositing thin metal lines that could be used as contacts to thin film devices at plastic compatible temperatures. A wide range of nanoparticle inks are available, however their rheological properties still need to be improved. It was demonstrated that organometallic inks could provide a replacement for these inks. However, due to the nature of these inks, they have relatively low metal content by volume, and thus cannot be used for high performance applications. Furthermore, mass loading becomes a limiting factor for electrical performance of these inks. Comparing the prints from two different inking systems it was demonstrated that a conventional gravure press could produce fine lines without streaks, if the cells could be engraved deeper to carry a higher ink volume. The results discussed in chapter 4 show promise for the possible roll-to-roll printing of TFTs, and similar devices in a range of printed
electronics systems. Although this work focused on two techniques of cylinder engraving, the results can be extended to other engraving technologies laying down foundation for future roll-to-roll gravure print studies.

The limits of printing gravure on AccuPress on the amount of ink deposited by microgravure engraving and excess pressure needed, due to missing ESA or using shallow engraving, have been largely technological, as demonstrated in Chapter 4. Even with these limitations, gravure can be a promising printing technique for roll-to-roll production of electronics. Fabrication of certain electronic components does not require high ink film thickness and can work with cylinder pressure. As demonstrated in Chapter 6, capacitors on plastic substrates can be fabricated with gravure. It was shown that using different dielectric inks with differences in ink characteristics, lead to different layer thickness, and hence altered electrical performance. Although capacitors were fabricated from a limited material set, the trends discovered could be useful for investigating other ink sets. It was also shown that the engraving specifications and optimization of processes to produce high resolution and high registration device structures is required to fully utilize the potential of gravure printing for electronics manufacturing. Overall, gravure-printed capacitors are promising, because of their high electrical performance, high yield values and potential scalability to industry.

As mentioned earlier, gravure microengraving in combination with printing on the AccuPress have limitations in regards to ink film thickness and due to which electrical performance is impacted. Taking into account these limitations, this work was extended to screen printing technologies. For printing passive devices like inductive coils, conductivity of the pattern needs to be higher. This can be achieved by increasing the ink film thickness. In Chapter 5, it was shown that functional
inductive coils could be printed using the copper based ink, if proper curing is achieved. It was also demonstrated that the curing system currently available from different suppliers are different. The differences may lie in the spectrum of light or the light intensity, curing temperature and time of pulse flash. In terms of printability, copper based inks show a promising future for electronics printing. Curing of these inks need to be set for exact conditions of reducing CuO to Cu. If the conditions are not exactly met, reverse oxidation can occur, as shown by Novacentrix and conductivity decreases. Also a short interval thermal stabilization step can be added before curing that may excite the copper oxide molecules to allow the UV light from the lamp to reach and penetrate to the bottom of the print. The thermal stabilization step can also be replaced with a lower intensity narrow band UV light system.

After successful fabrication of passive devices, this study was extended to active devices and prototypes for organic light emitting diodes were made. Since, each printing process has its own advantages and limitations, the organic light emitting diodes were printed using multiple printing methods to enable the benefits of each process utilized. It is known that the electroluminescence performance of the device is highly sensitive to film morphology. The surface characteristics and their impact on the performance of the finished device were discussed in Chapter 7. Currently, processing and fabrication of thin films for OLEDs is carried out using traditional techniques such as spin coating and vapor deposition methods. These techniques have several disadvantages, which can be minimized by incorporating printing. However, printing technologies have their own disadvantages. The biggest challenge is to make the materials printable and to form a uniform, pinhole free film after printing. Improved performance was achieved by using gravure and inkjet printing techniques compared to spin coating due to smoother and thinner emissive
polymer layers. The printed polymer layers achieved flat uniformity over relatively large area showing the capability to use roll-to-roll manufacturing for thin film based polymer LEDs. There is a potential for lowering the cost by using printing as a production method for such LEDs. The use of printing for OLEDs can be beneficial in packaging, in which the cost of processing is crucial. This work suggests that further optimization of the printed emissive layers can improve PLED performance to levels comparable to those fabricated by conventional ways.

Currently, due to limitations in printing equipment, it is a challenge in itself to upscale a lab-scale process to a large scale production. The development of printed electronic devices requires a much larger effort in optimizing the interplay between printing processes and material interfaces. Another area that needs to be explored is printing on coated and uncoated paper substrates, which would help in the absorption of the solvents in the ink. There is definitely a large opportunity for improving device performance, stability, and reliability by optimizing these interfaces. Only until recently has the focus begun to shift away from purely optimizing the devices, to optimizing the material interfaces and contacts to improve device performance. This work has demonstrated that gravure is a good patterning method and that it deserves careful consideration in any manufacturing process for printed devices. This work lays the foundation for future studies on roll-to-roll fully printed electronics devices, which will help to usher in a world where printed electronics become ubiquitous and a host of new applications are enabled.
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