# Printing Methods for Printed Electronics

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## Abstract

*Printing is certainly one of, if not the fastest, least expensive, and highest volume manufacturing technique. Its use for the deposition of functional materials offers enormous advantages for the preparation of devices over large areas, on virtually any substrate, and potentially inexpensively. Although printing processes have existed for thousands of years, it has only been relatively recently that the materials have become available for printing functional, particularly electronic devices.*

*A wide variety of different printing processes can be used for printed electronics. Digital Fabrication of electronic devices can incorporate either high volume printing processes – those that use a physical master (printing plate or cylinder), archaically known as "analog" printing, or techniques that don't use a physical master (also known as "digital" printing processes). Impact as well as non-impact printing processes are important. For device fabrication, the printing process flow depends on many factors, some of which are dictated by material properties, others are determined by printing related factors such as resolution, registration, and economic considerations.*

*This article will focus on the printing processes used for printed electronics, giving specific examples, as well as trends, challenges, needs, and future opportunities.*

## Introduction

Printed Electronics refers to the use of printing processes to make electronic devices. In this work, the term Printed Electronics will be used, however, there are a number of other closely related terms to describe the field, such as Printable Electronics, Organic Electronics, Plastic Electronics, Flexible Electronics, Macroelectronics, Polymer Electronics, and Wide Area Electronics. All of these terms have slightly different meanings/implications.

The term printing is bandied about rather carelessly when describing manufacturing processes. In fact, the terms flexible substrates, coating, and roll to roll processing/manufacturing are all frequently confused with printing processes. Printing can be defined either as a process that deposits materials (usually from a liquid) onto a substrate, such as ink on movable type, or more broadly, as a process that transfers an image or pattern onto a substrate. This latter definition includes processes such as embossing. In either sense, printing refers to the process of reproduction. Other non-printing deposition processes (for example vacuum deposition) can be used with flexible substrates, and (less commonly) in roll to roll processes. Coating is very similar to printing, and is certainly a roll to roll fabrication process, but with the distinction that patterning is usually not employed.

Printing processes have been described as "continuously working high speed microstructuring technologies suitable for flexible substrates"[1]. Printing can be considered to be one of the fastest, least expensive, and highest volume manufacturing techniques. Its use for the fabrication of functional materials offers enormous potential advantages for the preparation of inexpensive devices over large areas on virtually any substrate. Although printing processes have existed for thousands of years, it has only been relatively recently that the materials have become available for printing functional, particularly electrically functional devices.

There are many other reasons for the recent interest in Printed Electronics. Printing can transfer materials or patterns over very large areas, compared with conventional microelectronics fabrication. Moreover, the patterns can be transferred with extremely high thoughput. For example, coverage rates of 60 $m^2$/sec can be achieved with Gravure printing. If one considers printing to be a manufacturing process (which it is when functional inks are used), it can certainly be one of the lowest cost manufacturing processes. Another significant advantage of printing is that it can be used to deposit almost any material, and on virtually any substrate. This is particularly significant when compared with conventional microelectronics manufacturing which generally uses volatile(able) inorganic materials deposited in high vacuum on a few kinds of substrates. Printing usually deposits material at low temperatures, and in ambient environments. Printing equipment is very common, and much less expensive than conventional semiconductor manufacturing tools. A state of the art semiconductor fabrication facility costs in excess of a billion dollars! One of the most significant advantages of printing is that it can be used to deposit materials additively, i.e. materials are deposited only where desired, as opposed to subtractive processes which deposit materials everywhere, then remove them in the positions where they are not wanted. All else being equal, additive printing processes are more desireable for economic and environmental reasons. In general, fewer steps are required to pattern a layer by printing, than by semiconductor fabrication, which requires many extra steps such as preparing masks, depositing and etching photoresist, etc. Printing processes are also relatively easily integrated with each other, and hybrid printing is usually required for the fabrication of most kinds of devices. With printing, it is easy to change the pattern to be printed, and this can even be done inline to customize devices (i.e. each one could be different), etc. The economics of printing allow it to be highly scaleable. It is possible to produce relatively small numbers of devices (for example, rapid prototyping) economically, as well as very high volumes and large areas.

A wide variety of devices and products have been produced using printing. Some examples include antennas, displays, transistors, integrated circuits, three dimensional structures, sensors, actuators, batteries, and photovoltaics. We could be on the verge of a technological revolution as more and more devices are fabricated using printing. Analysts estimate that the Printed Electronics industry (which hardly even exists today) will be significant in just a few years. IDTechEx predicts that the Global

Market will be over $5M in 2011, and $300M by 2027. By 2025, the sale of organic electronics will have overtaken that for silicon chips by a large margin of close to $250 billion.[2]

## Patterning Techniques

Many different printing processes can be used in printed electronics. A detailed review of each of them is beyond the scope of this work, and has been given elsewhere[3-6].

In conventional silicon microelectronics, patterning is most often done using photolithography (not to be confused with offset lithography). In photolithography, the material to be patterned is first covered with a photoresist. By exposing through a mask, only certain regions of the photoresist are exposed to energy (usually UV light). The exposure causes a change in solubility of the photoresist. In a positive photoresist, the exposed part is made more soluble. In a negative photoresist, the exposed portion is made less soluble. Subsequently, the soluble areas of the resist are dissolved away (developed). The substrate and remaining photoresist are then exposed to an etchant, which removes the underlying material that is not protected by photoresist. The photoresist that remains on the patterned material can then be removed. This is an example of a subtractive process. The active material is deposited initially over the entire area, and selected areas of it are removed. Although very well established, this photolithographic process is very involved, uses extremely expensive equipment, requires many steps, is time consuming, and subtractive. Most importantly, this process is not generally compatible with many organic electronic materials or flexible substrates. The harsh conditions required for dissolving resists, etching the underlying layers, and removing the photoresist will destroy the activity of most organic electronic materials. Furthermore, the temperatures and solvents required are incompatible with most types of flexible substrates of interest. However, the feature sizes that can be achieved by photolithographic processes are much smaller than those that can be obtained using most printing processes.

One of the major attractions of printable electronics is the possibility to do many of the things that are not possible in conventional microelectronic fabrication processes. Printable electronics offers opportunities to avoid photolithographic patterning and many of its limitations. Organic and inorganic materials can be made to be soluble and/or solution processable. This enables a variety of deposition techniques that are not possible for conventional inorganic semiconductor materials. Solution processability enables printing or printing like process to be used. If one considers (conventional graphic) printing a manufacturing processes, it is easy to realize that it must be one of the highest volume and lowest cost manufacturing processes known. Printing presses commonly run at speeds of hundreds of m/min. with webs several meters wide, and are used to deposit (and cure) many different materials simultaneously. Printing produces large areas very quickly and inexpensively. By using printing processes (or ones like them) to deposit functional materials, one can produce functional devices in high volume very economically. Such is the appeal of printed electronics. Making this happen, however, will require much effort and development, not only of new materials, but also deposition processes for using these materials. And like most other processes, for optimal performance, the materials will need to be developed with the process and conditions in mind. The disadvantages of photolithography offer great new opportunities for patterning materials, and also new challenges.

### *Physical phenomena*

In order to print/pattern a material, one must be able to differentiate between different regions (where material is to be deposited or removed). This differentiation can be based upon several different kinds of physical or chemical process.

In addition to photolithography, functional materials can be patterned using a variety of other types of physical processes (Table 1). Many patterning techniques are based on the principle of relief. Regions of the printing plate or cylinder (stamp) which are to accept the ink are at different heights. Depending on the process, these different heights can be used to differentiate where the functional material (ink) goes. In flexographic printing (flexography), letterpress printing, and soft lithographic techniques, raised areas receive the ink and transfer it to the substrate (Figure 1a). In other processes (intaglio, gravure, and pad (offset gravure)), ink is spread over a smooth surface which contains depressed areas which receive the ink (Figure 1b). A blade scrapes off the excess ink, as well as forces ink into the depressions. The ink which is held in the depressions can then be transferred to the substrate.

One can also differentiate different regions of a printing plate or cylinder by their surface energy (wetting properties). One can produce a printing plate which has some areas which are hydrophilic (water loving) and other areas which are hydrophobic (water repelling, oil loving, oleophilic). Oil base inks will stick to the hydrophobic (oleophilic) areas and not to the hydrophilic areas (Figure 1c). Offset lithographic printing (lithography) works in this manner. This is one of the oldest printing processes known, and is based upon the familiar principle that “oil and water don’t mix”.

One of the simplest techniques for patterning a material is to use a mask which physically prevents deposition of material in areas covered by the mask. Examples of this include screen and stencil printing (Figure 1d).

The most common patterning techniques in printed electronics use direct deposition techniques. These techniques apply the functional material of interest through a nozzle directly to the substrate of interest. These techniques don’t require a physical master (printing plate or cylinder), and can be done without ever touching the substrate. Historically, these techniques have been called “Digital” printing techniques. However, this term is no longer meaningful and should not be used, since virtually all modern printing techniques rely heavily on digital imaging. Direct deposition processes are serial deposition techniques (ink is only applied to one position at a time) and are not well suited for covering large areas. Of these techniques, ink-jet printing (Figure 1e) is the most commonly used. There has also been a lot of recent interest in Aerosol Jet printing, using equipment developed by Optomec[7]. Work by this author has shown that continuous liquid dispensing (as opposed to ink-jet printing, where individual droplets are dispensed) can be used to prepare functional devices and pattern a variety of materials. These materials can have very smooth surfaces and high aspect ratios[8-11].

Although additive deposition processes are generally preferred for materials usage and economics, there are also some subtractive printing-like processes that can be used remove material from portions of a uniformly coated substrate, thereby leaving functional material only where desired. Two such processes are laser ablation and embossing. Laser ablation exposes portions of a material to a sufficiently high energy laser to ablate (essentially evaporate) the material. Embossing operates by exerting high pressures over small areas (like cutting) to rearrange material surfaces.

The final class of process that can be used for patterning functional materials is energy or force assisted transfer. Two examples of this are laser transfer, and electrophotography. Laser transfer is commonly used in thermal printing. It is similar to laser ablation, discussed above, except that the laser energy is used to transfer material from a donor sheet to the substrate. Although material is only transferred where it is exposed by the laser, this technique does require a donor that is the size of the substrate, of which, only a small part is usually transferred. In electrophotography (also known as Xerography), toners are transferred based upon electrostatic charge.

**Table 1. Printing processes and the physical phenomena they are based upon.**

| Physical Phenomena | Printing Processes |
|---|---|
| Relief | Flexography, Letterpress, Gravure, Pad, Soft lithography, Microcontact |
| Surface energy | Offset lithography, Dewetting, Patterned coating |
| Masking | Screen, Stencil |
| Dispensing | Ink-jet, MicroPen, Dip Pen Nanolithography (DPN) |
| Material removal | Laser ablation |
| Surface rearrangement | Embossing, Imprinting, Nano Imprint Lithography (NIL) |
| Energy/force assisted transfer | Laser transfer, Electrophotography |

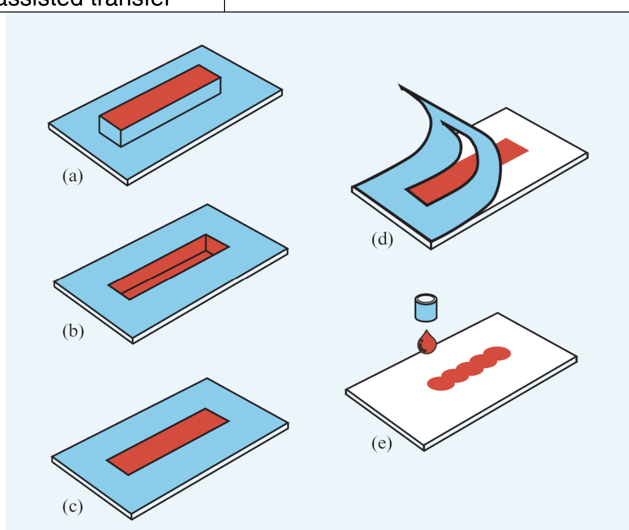


***Figure 1**. Schematic diagram of different types of printing processes. Copyright 2001, IBM.*

## ***Printing/patterning process taxonomy***

Based upon the types of physical processes discussed above, one can define a taxonomy of printing/patterning processes (Figure 2)[3-6]. The first level of differentiation is whether or not the printing process uses a physical master (printing plate or cylinder). Historically, this classification was known as “analog” for those processes requiring a physical master, and digital for those which do not. However, as mentioned above, all printing processes practiced today make extensive use of digital images and technology. Even the processes historically known as “analog” are performed digitally today. Image files are created with computers, and printing plates or cylinders (physical masters) are made with digital processes (like laser rastering, etc.). Today, when used to describe printing processes, the terms analog and digital are have little meaning, and can even be misleading. They should no longer be used to describe types of printing processes. Instead, these families of processes can be better classified by whether or not they employ a physical master (printing plate), or by whether they are serial (one location) or parallel (multiple location) deposition techniques.

Processes which use a physical master can be further differentiated by whether or not the master has relief (areas of different heights). The processes where the master has relief can then be divided further into categories based upon whether the raised or lowered areas receive the ink.

A useful comparison of printing processes based upon their specifications and other important characteristics has been described previously[3-6]. Figure 3 compares two of the most important considerations - resolution (smallest feature size) and throughput[3-6]. This data was obtained from various manufacturers specifications and other published reports, and are essentially the best values reported for each individual specification for each particular technique. Note well that these specifications can only be considered very approximate, since they are dependent on many other factors. For example, the maximum resolution that can be achieved is dependent upon the printing speed, ink type, and many other specific process parameters. Furthermore, these specifications were derived for graphic applications, not functional ones. Even though a particular specification can be achieved in a graphics application, this doesn’t mean that a functional material will still maintain its functionality when printed under these same conditions. For example, when a conductive trace is printed at the maximum resolution, it may not maintain its conductivity, or not over very long distances. So printed electronic applications require much more detailed evaluation, which needs to be specific to each set of materials and conditions.

## ***Printing process considerations***

For printing electronics, there are three major types of considerations in determining the printing process used. Techniques are chosen based upon their suitability for printing the desired materials (viscoelastic properties), as well as by their capability to print the desired feature sizes (lateral resolution, ink thickness, surface uniformity) required by the device. Economic considerations such as process throughput are also important.

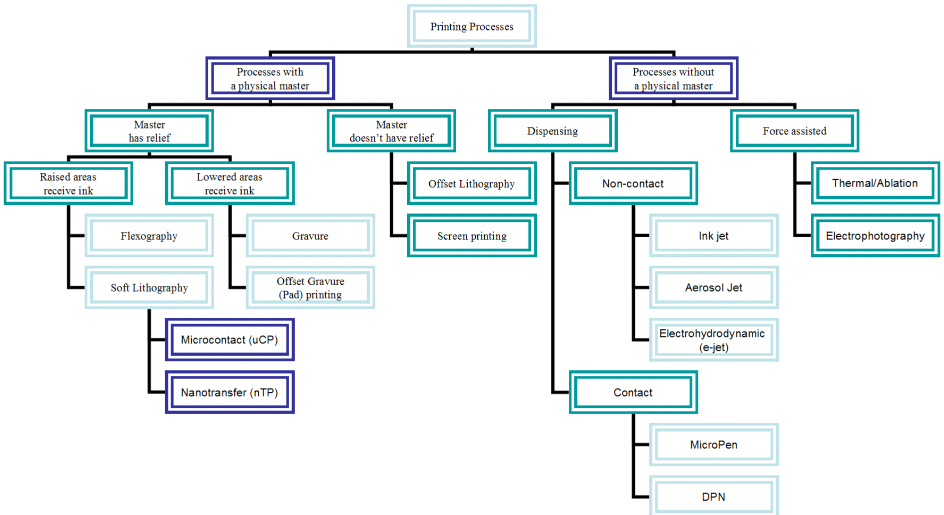


***Figure 2**. Taxonomy of printing processes. © 2008, Printed Electronics Consulting*

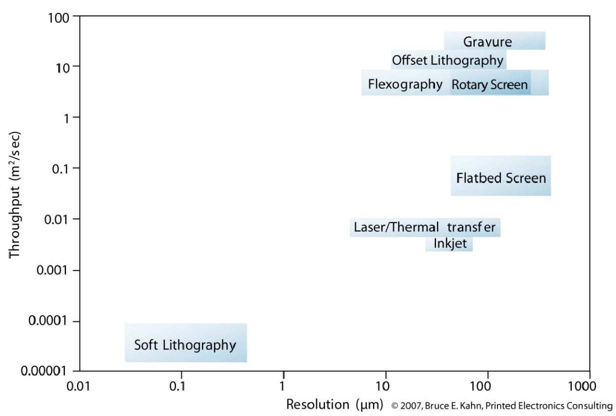


***Figure 3**. Throughput vs. Resolution of Different Kinds of Printing Processes. © 2007 Printed Electronics Consulting.*

### *Physical (size) requirements*

Lateral resolution is essentially the dimension (in a direction parallel to the substrate) of the smallest feature that can be printed. The maximum lateral resolution (minimum feature size) is fairly similar for most printing processes and is approximately 20-100 µm. Exceptions to this are thermal/ablation which can achieve resolutions < 10 µm and soft lithography which can achieve resolutions < 100 nm. Ink-jet printing is capable of resolutions on the order of a few microns when combined with surface energy patterning.

Similarly, the ink thicknesses (perpendicular to the substrate) that can be achieved are also relatively similar for most printing processes – on the order of a few microns. Offset lithography typically prints layers on the order of a micron or so. Ink-jet printing and thermal/ablation printing can print layers that are less than a micron thick. Soft lithographic processes are typically used to pattern monolayers of materials (typically self assembled monolayers), which are often less than 1 nm thick.

The desired layer thickness is highly dependent upon the particular application. Specific printing processes may be dictated based upon these requirements. Soft lithography, ink-jet, thermal/ablation, and offset lithography are best for printing thin layers. For many electronic applications (for example, RFID antennas), high conductivity is required. In general, the more material that is deposited, the higher the electrical conductivity. Other applications which depend upon the amount of material deposited (like battery electrodes) also require thick layers. Screen printing is often used for these purposes, because it has the ability to deposit the thickest ink layers. Flexographic printing is also receiving increased interest for some of these applications. Although it can't deposit as much ink as screen printing, it has a much greater throughput.

In addition to resolution and film thickness requirements, the layer to layer registration requirements for printed electronics are extremely important, and currently leave much room for improvement. Although in many cases, printing processes are able to achieve resolutions on the order of microns, the layer to layer registration errors are often orders of magnitude higher. Registrations errors on the order of 100 µm are not uncommon. In order to take advantage of high resolutions in a multilayer device, the layer to layer registration must be at least as good. To complicate matters even further, flexible substrates are not dimensionally stable. As a function of heat or chemical treatment, flexible substrates can change their shape and size. Over large areas, this change can result in serious misalignment errors between subsequent layers, and often device failure. Even though higher resolutions (in a single layer) can be achieved, devices are often limited by the much lower layer to layer registration errors. Although equipment improvements are possible, they can not, by themselves, account for the substrate dimensional changes.

Several strategies have been used to minimize the effect of these registration errors. Substrates can be optimized by heat treatment, etc. to increase their dimensional stability. With serial deposition techniques (most notably, ink-jet printing), online optical monitoring/adjustment is possible. With inline optical monitoring, fiducial marks can be used to detect the underlying structure or dimension changes, and the pattern to be printed adjusted accordingly. This is one of the most significant advantages of serial deposition techniques. Another strategy that can be used to improve registration errors is to implement "self alignment" or "self assembly" techniques. Here, the structure or chemical nature of the underlying layers is used to guide the deposition of subsequent layers. There has been relatively little done using these strategies, and much improvement is still necessary and possible.

### *Material requirements*

In contrast to the lateral resolution and ink thickness, which are relatively similar for most printing processes, there is a large range (~ 10,000 X) of viscosities used for the different printing processes. Ink-jet inks require the lowest viscosity, typically less than 20 cP. At the opposite extreme, offset lithographic inks are the most viscous, and require shear thinning behavior. Needless to say, the solubility and viscoelastic characteristics of the functional materials place critical constraints on which printing processes can be used.

Since there is such an enormous difference in the viscosity (and more generally, the viscoelastic behavior) of the inks required by the different printing processes, the printing process needs to be tailored to (or can be dictated by) the materials to be deposited. Most organic semiconductor materials, for example, are sparingly soluble, and only soluble in organic solvents which have a very low viscosity. These factors require a printing process which is particularly amenable to very low viscosity inks, e.g. ink-jet printing. On the other hand, some printing processes (most notably offset lithography) require very viscous "pasty" inks. These processes are better suited for particulate dispersions (which is what almost all inks designed for graphic printing are composed of), which can be prepared very viscous. In particular, offset lithography requires relatively complex (shear thinning) rheological behavior, which is difficult to achieve with most soluble functional materials. The particle size also places limitations on the printing process. Obviously, particles can't be larger than (and really shouldn't even be close to) the desired feature sizes. For this reason, soft lithographic processes are not suited for printing most particulate dispersions.

In order to achieve all of the necessary viscoelastic characteristics, most inks used for graphic applications are complex mixtures of a variety of different components. For functional applications, it is necessary to be able to deposit materials "cleanly" and in high purity, without additives. This is particularly critical for organic semiconductors. For this reason, printing processes which require high viscosity inks (usually achieved by adding resins), are not compatible with printing organic semiconductors. The additives necessary to achieve the proper rheological behavior would all but destroy the functional behavior of the semiconductor material.

### *Economic requirements*

There is also a large difference in throughput between the different processes. The highest volume (throughput) printing process is gravure printing, which can print 60 $m^2$/sec. Offset lithography and flexography are also high volume printing processes, nearly as high as gravure printing. The printing processes which don't employ a physical master are serial printing techniques. They deposit material one position at a time, and as such, are low throughput processes. Consequently, these printing processes are not optimal for depositing ink uniformly over large areas. Soft lithography is a manual process, which patterns materials on substrates individually, and is thus a very low throughput process.

For the printing processes that require a physical master (printing plate or cylinder), there are substantial differences in the ease and expense of making plates or cylinders. Offset lithographic, and flexographic printing plates, and screen printing screens are relatively easy and inexpensive to make. Gravure printing requires expensive engraved cylinders. Pad printing plates are also relatively expensive. Soft lithography masters are produced by microelectronic processes which are very expensive for an individual master. Once the master is made, producing the stamps are relatively easy and inexpensive. The initial step in this process requires microfabrication facilities, which are not commonly available in printing environments.

Functional electronic materials, particularly organic semiconductors are very expensive and are not typically (yet) available in large scale. Commercially, these materials can cost hundreds of dollars per gram. For this reason, additive printing, and low waste are critical concerns. Also, it is important to be able to do testing with very small amounts of material. The printing processes that work best with small amounts of materials are soft lithography, pad, screen, and ink-jet printing.

### *Other considerations*

Gravure, screen, and ink-jet printing make discrete deposits of ink. In order to produce electrically continuous features, it is necessary to deposit overlapping drops (ink-jet), or control the ink properties so that the individual deposits merge together (gravure, screen). These factors influence the achievable morphology of the line edges of these processes, and can be important considerations for device fabrication.

There are also differences in the substrate requirements for some printing processes. Although all of the processes mentioned can use flexible substrates (in fact, some require it), there are other constraints and considerations placed upon the substrates in certain processes. In order for the ink to transfer properly, very smooth surfaces are required for gravure printing. Pad printing is often used on rigid substrates which are not flat (for example, coffee mugs). Printing processes that use a flexible printing plate (like flexography and soft lithography) are able to conform to the substrate, and may be more tolerant of substrate topology or defects than other printing processes.

## Challenges, Issues, and Opportunities

Although at first glance the opportunities for printed electronics may seem endless, there are many challenges and issues that can hamper the implementation of many printed electronics concepts. These issues can be attributed to either the printing process, the materials, or both. Great opportunities may be possible by solving some of these issues.

There are many material needs in printed electronics. There is always an opportunity to improve the conductivity and mobility of printable materials. Semiconductor mobility (particularly for n channel materials) is critical since it influences the speed and frequency achievable with printed electronic circuits. The need for higher mobility is responsible for a shift in emphasis from organic to inorganic nanoparticulate semiconductor materials. There is also a need for printable materials with higher dielectric constants. Many printable materials require curing in order to make them functional. There are always opportunities for reducing the curing conditions (lower temperatures for shorter times). Many printed electronic materials are not environmentally stable, and require encapsulation. There are opportunities both to improve the material stability, and to improve barrier and encapsulation materials. The latter is particularly critical for OLED's. Dimensional stability is also a critical need, particularly for substrates for printed electronics. Although printed electronics can, at least in theory, be considered environmental or "green" by virtue of reduced waste and the use of additive instead of subtractive processes, there is still much to be learned about the environmental and toxicological properties of printed electronic materials. Furthermore, the implications of printed electronic devices on the recyclability of products to which they are attached (particularly packaging) also need addressing.

There are also many opportunities for improvements in printing processes for printed electronics. There is a continuing need for smaller feature sizes, and particularly improved registration. Many processes are limited by layer to layer registration, yet more emphasis is given to improvements in resolution. For multilayer device formation, the surface and interfacial characteristics of the printed layers are critical. There are needs for the ability to print both thinner and thicker layers. Functional devices require fewer defects and better control of dust and impurities than graphics printing. Printed electronics requires the ability to fabricate multilayer devices. There needs to be better understanding of printing over complex preexisting topology. There are also opportunities for new printing processes, specifically optimized for the unique needs of printed electronics.

Opportunities also exist that can be addressed by both materials and printing processes. Increased material loading is necessary to increase process throughput. There is a great need for improved understanding of the relationship between material functionality and printability, since the two are extremely correlated. Since layer mixing needs to be avoided, there are opportunities for optimizing the solubility properties of materials to ensure solvent "orthogonality" as well as the printing material window

There are some very encouraging results for experimental printed electronic devices prepared in small research quantities. However, frequently these architectures or materials can not be scaled up, or printed in high volume without considerable loss of device performance.

There may also be some opportunities for new ways of thinking about device construction and new device architectures possible, that could result in improved device performance.

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## Author Biography


*Dr. Kahn is a consultant specializing in the multidisciplinary fields of printed electronics, organic electronics, nanotechnology, smart packaging, and Radio Frequency Identification (RFID). In addition to helping companies and governmental organizations, he writes books, articles and reports, and conducts training sessions and workshops.*

*Prior to founding Printed Electronics consulting, Dr. Kahn was a Professor at the Rochester Institute of Technology, where he started the Printable Electronics research program. Dr. Kahn's research group pursued the investigation, assessment, and development of the use of printing techniques (particularly high volume printing processes) and materials for the fabrication of electronic devices. Their work produced (both small and production scale) and characterized antennas for Radio Frequency Identification (RFID) tags, and assessed the process capabilities of a number of different printing techniques used for patterning conductive features. Dr. Kahn has developed and applied technology for printing chemical sensors. His group printed RFID antennas directly onto corrugated cardboard substrates, and investigated the affects of environment and conditioning on the electrical conductivity. Dr. Kahn is currently investigating other techniques for patterning functional organic materials, such as liquid and aerosol dispensing, and has created working organic transistors using these technique.*

*Dr. Kahn has a Ph.D. in Chemistry from the University of Nebraska, and a S. B. in Chemistry from the University of Chicago. He is the author of over 75 publications, including the recently published books Developments in Printable Organic Transistors, (Intertech-Pira, 2005), Printed and Thin Film Photovoltaics and Batteries (IDTechEx, 2007), and Printed Electronic Displays (IDTechEx, 2008). He is a frequent lecturer and author, and regularly teaches workshops in the US and abroad*