# Materials and Process Engineering for Printed and Flexible Opto-electronic Devices

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Printed opto-electronics is a revolutionary technology to fabricate electronic devices.[1] The concept consists to enable mechanically flexible, low-cost, lightweight, and large area electronics by using electronic inks and processes borrowed by the graphic art industry. Devices such as light emitters, light harvesters, circuits, and sensors would be based on a new materials set.[2] Applications like flexible displays, plastic radio frequency identification tags (RFID), disposable diagnostic devices, rollable solar cells, and simple consumer products and games represent a future multi billion dollar market. Smart objects e.g. smart packages that integrate multiple printed devices are further examples of organic electronics. Several companies, venture capitals, research institutions, and government agencies are investing in this R&D field. Regardless whether they are material providers, equipment makers, producers, and system integrators, a close collaboration between chemists, materials scientists and engineers is necessary to ensure that organic electronics becomes a large market. The purpose of this paper is to provide an overview of the materials and process requirements and applications of this technology.

### **Technology Background**

Printed electronics has not the goal to replace the conventional inorganic-based electronic industry. Rather this technology offers opportunities for new products and/or reduces the cost of certain devices by circumventing current production limitations and costs (Table 1). Traditional thin film materials deposition is accomplished with chemical vapor deposition (CVD), physical vapor deposition (PVD), and sputtering. Note that although these processes are performed in vacuum, they are not intrinsically "low speed". For instance polymer webs over 2m in width are metallized at 18 m/s for food packaging at the cost of pennies per square metre. Similarly, but at the highest degree of sophistication, liquid crystal display production is based on processing large glass plates (> 4 m<sup>2</sup>) with tact time of few minutes. Film patterning on glass (for display) and silicon wafers is accomplished using conventional photolithography. In this subtractive process the active film is deposited over

the entire substrate area, and selected film regions are removed by first coating the film with photoresist, exposing with contact or projection optics (or electrons for e-beam lithography), developing the resist, etching the underlying layer, and stripping the resist. This process consent to achieve the resolution and reliability required for the high-tech IC industry. On the other hand, photolithography is expensive, uses extremely expensive equipments (a new FAB line costs 2-3 B\$), requires several batch-to-batch steps. Consequently, the utility of employing printable materials, most of which are organic (vide infra) is to replace conventional processes for device fabrication. If organic materials can be formulated into inks (active material + solvent+additives) then rollto-roll printing or printing-like processes may be employed. Conventional printing presses used in the graphic art industry commonly run at speeds of hundreds of m/min with webs several meters wide, and are used to deposit several different types of color inks. Furthermore printing is an additive process, which minimizes material waste. If similar processes could be used to deposit functional materials, high volume inexpensive devices can be fabricated. Printed (or organic) electronics aims this goal. The main obstacle to the realization of this technology is on the material side, particularly the semiconductor (charge transporting material), since highly processable semiconductors exhibit poor charge transport performance. Furthermore it is unlikely that the same printing presses utilized for newspapers and magazines will be used for processing functional materials. Therefore, modification and optimization on the processing side are also necessary. Finally, device design architectures and circuit engineering is necessary to cope with the poorer organic materials performance and/or to take advantage of their unique properties.

## **Devices and Applications**

*Transistors and Circuits.* The field-effect transistor (FET) is the fundamental and most important component of the electronic era[2]. This object is essential in almost all electronic devices since it is the building block of the circuits (a collection of connected FETs) necessary for logic operations and memory functions, and to drive displays and sensors. The FET based on organic semiconductor (OFETs) or other printable semiconductors have the structure of a thin-film transistor (Figure 1). This is a three terminal device composed of a source, drain, and gate electrodes, a dielectric layer, and a semiconducting layer. Essentially the transistor is an electronic valve or switch where the current flow between the source and drain electrodes (for a given source-drain bias) is controlled by the magnitude of the source-gate bias (or electric field). The charge flow in the transistor channel can be

dominated by holes (positive charges) or electrons (negative charges) which define whether the semiconductor is p-type or n-type, respectively. The two most important transistor performance parameters are the charge carrier mobility ( $\mu$ , how fast holes or electrons moves) and the current on-off ratio ( $I_{on}$ : $I_{off}$ , how efficient the current can be modulated by the source-gate bias). Furthermore in order to maximize the transistor speed, the carrier mobility should be as high as possible and the distance between the source and drain electrodes (channel length) should be as small as possible. Note that the carrier mobility of printable semiconductors are about two orders of magnitude lower than crystalline inorganic materials and typical resolution for the OFET channel length (L) in printed devices are larger by the same order of magnitude. Therefore OFET circuit speeds cannot compete with those based on silicon (Si) or gallium arsenide (GaAs) and fabricated using photolithographic processes. However, when the performance requirements are relaxed and/or there are the needs for additional device functions (eg, flexibility, easy integration) and/or to reduce costs, OFETs may become very competitive.

*Displays.* One great area of opportunity for printed electronics is in backplane circuit manufacture for flexible displays. Electrophoretic displays where the image is formed by black and white charged particles are well-suited for printed transistors because of the slow switching time and minimal current flow to drive them. Furthermore, they are bi-stable, meaning that the image is retained without power. Power is only required during refresh. In these displays the contrast is independent of viewing angle, and significantly better than newsprint. Polymer dispersed liquid crystal (PDLC) and electrochromic-based displays can also be driven by printed transistors. In addition to transistors and backplanes, organic electronic materials, some of which can be solution-processed, are also used to fabricate emissive devices, such as organic light-emitting diodes (OLEDs) and polymer light-emitting diodes (PLEDs).

*Radio-Frequency Identification Tags.* Radio frequency identification (RFID) tags use radio frequency transmissions to identify, track, sort, and detect persons and items. In these devices communication takes place between a reader (interrogator) and a transponder (a chip connected to an antenna) often called a tag. RFID tags can either be active (powered by battery) or passive (powered by the reader field), and come in various forms including smart cards, tags, labels, watches and even embedded in mobile phones. The communication frequencies used depends to a large extent on the application, and range from 125KHz to 2.45 GHz. Regulations are imposed by most countries to control emissions and prevent interference with other industrial, scientific, and

medical equipment (ISM). RFID is not expected to replace bar codes in the supply chain because tags are still too expensive even though their prices have fallen to around 20 cents in volume versus 0.2 cents for a bar code label. Adoption is therefore likely to happen first for expensive items, then as technology advances and costs reduce further, it is expect to see tags on more and more products. It is commonly thought that the only way to reduce the price sufficiently, and produce billions or trillions of tags per year is by printing both the circuitry (using solution processable materials) and the antenna, in an integrated process. The major obstacle to be surmounted for all-printed RFID applications is to achieve high circuit frequency operation and rectification.

*Sensors.* The fabrication of sensors is another important opportunity for printed electronics. A variety of stimuli can be detecting using these circuits, including temperature, pressure, radiation, and chemical identity. An integrated temperature and pressure sensor array has been utilized as an artificial skin. Organic actuators have also been fabricated. These principles have been used to produce a variety of different types of devices, including tamper detecting packaging, data logging pill dispensers, chemical sensors, electronic noses and tongues, photodiodes, and light scanners.

*Photovoltaics.* Another exciting application of printed electronics is in photovoltaics, a field again currently dominated by silicon. The vision is to fabricate inexpensive, light weight, flexible, conformal, and energy efficient production of energy from the sun. These devices are composed of a charge transporting donor+charge transporting acceptor semiconductor blend sandwitched between two electrical contacts (Fig. 1).[3] Light exposure produces free carriers that are collected at the electrodes as electrical energy. The most important figure of merit is the power conversion efficiency (PCE), which measures how efficiently the incident solar energy is converted into electrical energy. The main issue is the semiconductor, which should provide high power efficiencies, be stable, and inexpensive.

#### **Printing Technologies**

Enabling the use of roll-to-roll and high throughput device fabrication technologies is the core of printed electronics. Processing achieving throughputs >  $1 \text{ m}^2$ /s are considered as "high volume", and most of the printing methodologies fall in this category. There are several considerations to determine what process can be employed based mainly on materials viscoelastic properties and the desired feature sizes (lateral resolution, film thickness, surface morphology, surface energy) required for device assembly. Some of the most important printing processes

and relevant specifications for use in electronics are shown in Table 2. Probably the most used in printed electronics are inkjet, gravure, and screen printing and their operation principles are summarized below.

Inkiet. This printing process employs a stepper motors to control the position of the print head along a stabilizer bar. As the print head slides back and forth along this bar, ink drops are ejected from the nozzle to create the pattern on the substrate. There are two primary mechanisms for ejecting drops from an inkjet nozzle. In thermal inkjet, a small portion of the ink solvent is evaporated, forcing ink out of the nozzle. In piezoelectric inkjet, a voltage is applied to a piezoelectric material which causes it to change its shape (expand), thereby forcing ink out of the nozzle. Inkjet printing is now one of the most widespread graphic art printing methodology. Furthermore, in recent years, inkjet printing has been receiving growing interest as a method to deposit functional materials with specific electrical, optical, chemical, biological, or structural functionalities onto well-defined locations on a substrate. One of the most unique and useful capabilities of inkjet printing is its capability of vary the printing pattern without making a new printing plate. Using a camera and image analysis software, the printed image can be adjusted "on the fly" to compensate somewhat for many of the registration errors that plague other types of printing process. Inkjet printing has some limitations such as stability of the printing head to aggressive solvents, inkjet inks can be subject to high mechanical shears in piezoelectric print heads, or high temperatures in thermal inkjet heads. Fluctuations in droplet volume or trajectory can adversely affect film uniformity ("coffee-stain" effect) and materials performance. Recently, a variation on inkjet printing called "Self Aligned Printing" was used to pattern features as small as 60 nm. Organic semiconductors are also commonly inkjet patterned for transistor and OLED fabrication.

*Screen printing.* Screen printing consists of three key elements: the screen which is the image carrier; the squeegee; and the ink. The screen printing process uses a porous mesh stretched tightly over a frame made of wood or metal. The mesh is made of polyester or stainless steel. A stencil is produced on the screen either manually or photochemically. The stencil defines the image to be printed in other printing technologies this would be referred to as the image plate. This technique usually produces relatively thick films and thinner films fabricated using less viscous inks often result in poorly defined printed patterns. The resolution is poor and limited by the screen size although recent presses perform much better. In organic electronics this technique has been used to fabricate top-level interconnects and contacts where the printed film thickness is not a critical factor.

It can also be used to print thick dielectric layers and passive materials for device encapsulation. Indeed, the first report of a "printed OTFT" described screen-printed carbon paste electrodes for source, drain, and gate contacts.

*Gravure*. In gravure printing the image areas consist of honeycomb shaped cells that traditionally are etched or engraved into a copper cylinder. The cylinder rotates into a ink bath called the ink pan and as the cylinder turns, the excess ink is removed by a flexible steel doctor blade. The ink remaining in the recessed cells forms the image by direct transfer to the substrate as it passes between the plate cylinder and the impression cylinder. Gravure printing is one of the highest volume printing processes, and often used commercially to produce high quality graphic materials, for example magazines. Gravure inks are fluid inks with relatively low viscosity. Thanks to the nature of the engraved cells, different amount of material can be deposited in different substrate regions enabling tuned film thicknesses. The drawback is that the printed pattern edges may be wavy. Gravure has been recently employed to fabricate dielectric and semiconducting layers for organic transistors.

#### **Electronic Materials**

Printed electronic devices need a core materials set for charge accumulation, injection, and transport as well as specific materials to enable particular device functions.[3-6] For instance, in every type of electronic device there is the need for a certain control of the current flow as well as memory. These circuits are based on FETs. This device needs three fundamental materials, the conductor, the dielectric, and the semiconductor (Table 3). Then, depending on the specific device functions additional active materials may be needed. For instance for organic LEDs (OLEDs) an emissive material is necessary for efficient conversion of electricity to light. For organic photovoltaics (OPVs), besides the materials needed for efficient charge transport, it is necessary to have a photosensitizer and/or an efficient light absorber for photon absorption and dissociation. Displays may be based on different technologies for pixel fabrication including organic emitters, electrophoretic inks (proper dyes are necessary), liquid-crystals (LC molecules are used), and electrochromic compounds. Many other types of chemicals/materials may also be necessary for device fabrication including small molecules as interfacial layers for efficient charge injection or surface energy match, additives used as dopants or stabilizers, polymers for encapsulation. Below are summarized the properties of the three key materials.

*Semiconductors*. The semiconductor is the most important material in optoelectronic devices and its key function varies depending on the device application. When used for organic transistors, it is the material where, at the

interface with the dielectric, the charge are accumulated and transported. Other electronic devices use different type of semiconductors. The design of highly efficient and easily printable organic semiconductors for OFETs is the key challenge in roll-to-roll electronics. Optimization of charge transport (hence carrier mobility) requires the semiconductor molecules being planar so that the molecular orbitals can overlap efficiently. However, this molecular design usually leads to poorly soluble materials, which are then very difficult to print. Furthermore, the semiconductor must satisfy a number of requirements for charge injection and transport related to the device structure. Obviously, for roll-to-roll printing fabrication, the organic semiconductor must be solution processable so that it can be formulated into an ink. However, good molecular design and solution processability is only part of the requirements since the charge transport in organic semiconductor films is highly dependent upon the film deposition conditions including the printing process, the solvent used in formulating the ink, active/additive component concentrations, deposition temperature, substrate morphology and surface energy. Environmental conditions during film deposition can also affect materials performance, however, some organic semiconductors are air stable and do not require inert environment during film processing.

Several organic semiconductors for OFETs have been synthesized, including those based on small molecules and polymers. P-type organic semiconductors have been shown to have carrier mobilities of ~ 10 cm<sup>2</sup>/Vs as thin-film and up to 35 cm<sup>2</sup>/Vs for single crystals. These mobility numbers are greater than that of amorphous Si, which is commonly used for large area display backplanes. However, very few exhibit good charge transport and solution processability. To this respect, probably the most promising families are those based on thiophene-containing polymers. A traditional drawback in organic electronics is the availability of electron-transporting (n-type) semiconductors, which are needed for complementary circuits applications. Furthermore, very few air-stable n-type organic semiconductors are known. In addition to organic semiconductors, sol-gel and nanoparticulate inorganic semiconductors or hybrid organic-inorganic semiconductor materials have also been investigated. These materials promise both the superior carrier mobility of inorganic semiconductors and the processability of organic materials.

*Conductors.* All electronic devices have electrical contacts and a good conductor must satisfy a number of requirements including high conductivity, appropriate work function, chemical stability, and appropriate surface energy characteristics and morphology. Materials used as conductors are metals/metal oxides and conducting  $\pi$ -

conjugated polymers. Metallic features can be fabricated in various ways including thermal evaporation, sputtering, and printing, with the latter being essential for the scope of organic electronics. Printing metal is usually achieved by using inks that contain metal particles. These particles may different substantially for morphology, sizes, and type/amount of stabilizers. Typically gold, silver, and other noble metal are employed. Nanoparticle-based inks can also be printed and subsequently sintered at temperatures (< 150 °C) compatible with inexpensive plastic foils. Metal precursors can also be used, sometimes in combination with other materials, and similarly thermally cured. Metal oxides are another class of conductive materials often used for electrodes with tin-doped indium oxide (ITO) by far the most utilized. Even though certain  $\pi$ -conjugated polymers are highly conductive, they typically exhibit far lower conductivity than metals. The most common conducting polymers used in printing conducting lines are polyaniline, polythiophenes, and polypyrroles. Among them, PEDOT:PSS (a polythiophene-based polymer) is the most largely utilized because it is commercially available and exhibits good conductivity (< 400 S/cm).

*Dielectrics.* The dielectric film is extremely important for OFETs since consents the creation of induced charges in the semiconductor upon the application of the gate field. A good dielectric material should exhibit high dielectric strength and low leakage current, and high capacitance. High gate capacitance allows higher charge density to be induced at lower gate voltages, hence reduce power consumption. The dielectric layer capacitance can be increased by using thinner films and/or or by increasing the material dielectric constant. Unfortunately, when the dielectric layer becomes too thin, film defect density and leakage current increase. Furthermore, the dielectric film surface in contact with the semiconductor should be very smooth. Since charge transport in organic semiconductors is confined in the semiconductor within a few nanometers from the semiconductor-dielectric interface, rough interfaces generate charge scattering center, which reduce carrier mobility. Again, for printed electronic applications, the dielectric material must be solution processable. A variety of materials have been used to fabricate OFETs. Absurdly, most of the work has been done using inorganic films such as silica, alumina, and titanate which are not generally printable. A variety of organic polymers including polypropylene, polyvinyl alcohol, polyvinyl phenol, poly methyl methacrylate, and have been used as dielectrics. Most of these are polymers that are widely used for other purposes, and available in bulk quantities quite inexpensive. More recently more complex formulations have been printed to fabricate OFETs. These dielectric films are usually cured either thermally or photochemically to enhance mechanical strength and improve dielectric properties.

#### **Summary and Outlook**

Printed electronics has the potential to become a significant industry within the next decade and, contrary to common opinions, much of the forecasted applications will be new and not created by eroding current electronic markets. The challenge that this technology faces are mainly related to the material performance for circuits and proper engineering of current (printing) processing methodologies for electronic device assembly. The semiconductor remains the weakest link among the current materials generation, and there are several requirements where it falls short of ideality. The most important limitations include the realization of high carrier mobility and environmentally-stable semiconductors (particularly for n-type) and the obtainment of high performance for solution-deposited semiconducting films over large area. The temporal performance stability of these materials is also of prime concern. Despite these difficulties, initial important successes in device fabrication using organic materials and a roll-to-roll processes are encouraging and several companies strongly believe that organic electronics is already a reality.

#### References

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Figure 1. Structure of an organic field-effect transistor and a photovoltaic cell and corresponding applications.

Table 1 Conventional versus organic electronics.

	Conventional Electronics	Organic/Printed Electronics			
	High performance	Low performance			
	Small area/feature size	Large area/feature size			
	High cost/unit area	Low cost/unit area			
	High capital	Low capital			
Advantage/ Disadvantage	investment	investment			
	Long production run	Short production run			
	Durable	Disposable			
	Rigid	Flexible			
	Selected markets	Everywhere			
	Photolithography	Printing			
Matariala	Semiconductor, conductor, dielectric, passive,				
iviaterials	substrate				
Device/Applications	Transistors, circuits, memory, diodes, sensors, displays, batteries, photovoltaics, conductive				
	traces, antennas, resistors, capacitors, inductors				

Electronic **Film Thickness** Ink Viscosity Resolution Registration Throughput Feature/ Technique Materials  $(\mathbf{m}^2/\mathbf{s})$ (mPas) Issues (µm) (µm) (µm) Printed High quality. Lithography  $(10-4) \times 10^2$ 50-10 >10 0.1 Conductor 1.5-0.5 Need for additives Wide range of inks.  $(5-0.5) \times 10^2$ 100-30 100-30 Screen >25 2-3 Conductor Medium quality Wide range of Conductor Flexography 5000-50 2.5-0.8 70 <200 10 substrates. Semiconductor .Medium Dielectric quality Large run length. Dielectric Gravure 5-0.5 <10 >5 60 200-50 High Semiconductor quality Nonplanar 2-1 20 >10 0.1 Pad >50 Conductor objects Conductor Laser/Thermal N/A <1 5 ?? 0.002 N/A Semiconductor Digital Conductor Inkjet 30-1 < 0.5 <10 20-5 0.5-0.01 data. Local Semiconductor registration

Table 2 Typical ink requirements, printing features, and throughputs of conventional printing methodologies. Applications and issues for conventional printing processes.

Table 3 Properties of current-generation solution-processed materials for printable electronics

Performance/	Conductor		Semiconductor		Dielectric			
Needs	Metal/ Metal Oxides	Polymers	Small Molecules	Polymers	Inorganics	Polymers	Inorganics	
Current Performance	$\sigma > 10^4 \text{ S/cm}$	$\sigma > 1$ S/cm (~10 <sup>4</sup> S/cm)	$\begin{array}{l} \mu = 1\text{-}30\\ cm^2/Vs\\ I_{on}\text{:}I_{off} > 10^6 \end{array}$	$\begin{array}{l} \mu \ = \ 0.1\text{-}10 \\ cm^2/Vs \\ I_{on}\text{:}I_{off} > 10^6 \end{array}$	$\begin{array}{l} \mu = 1 \text{-} 100 \\ cm^2/Vs \\ I_{on} \text{:} I_{off} > 10^6 \end{array}$	$J < 10^{-8} \text{ A/cm}^2$ BF > 6 MV/cm	$J < 10^{-7} \text{ A/cm}^2$ BF > 5 MV/cm	
Current Materials	Ag, Au, Cu nanoparticles. ITO	PEDOT:PS S. PANI. Polymer+C NT, graphene	Fused thiophenes, Heteroarenes, Perylenes	Polythioph enes, Naphthalen ediimides DPPs	In2O3, ZnO, IZO, IGZO	PMMA P-UV Crosslinked PVP	Sol-gel oxides Oxides-epoxy.	
Advantage	Good processability High conductivity.	Good processabilit y. Sufficient conductivity	Easy purification. Facile scale- up.	Easy ink formulation	High Mobility.	Easily printable	Tunable permittivity.	
Limitations	Costly	Low speed applications	Difficult ink formulation for printing Ambient stability	Difficult purification Few n- channel available. Ambient stability.	High processing temp. Few p- channel available. Ambient stability.	Low permittivity. High Permeability. Thick films.	Leaky. Rough surface. Thick films.	
Next Generation Targets	Reduce cost.	Enhance conductivity	Increase µ.	Increase µ.	Reduce T, Uniformirty	Reduce film thickness.	Enhance printability.	

Note:  $\sigma$  = conductivity;  $\mu$  = charge carrier mobility; J = leakage current density; BF = breakdown field