

Printed Electronics at Western Michigan University

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Abstract

Recent research in printed electronics from our group is reviewed. Functional materials are being developed and optimized for various printing methods, such as ink-jet, gravure and flexographic printing. In particular, flexography and rotogravure printing have been employed to print RFID antennae using metallic inks. Other materials under study include conductive, semiconductive, dielectric and resistive materials for printing integrated circuits used in RFID chips on paper and paperboard substrates. Effects of printing process parameters and in depth study of paper properties are in the progress. New testing procedures and application of known testing methods are used to predict ink performance during printing, ink-paper interactions and final performance. Antenna and tag performance have been extensively characterized in our RFID testing laboratory.

Introduction

Printing is increasingly seen as a means for the fabrication of advanced functional materials, such as electronic components. These include RFID tags^{1,2}, Displays^{3,4}, solar panels⁵ and others. Printing of such devices requires conductive materials^{1,2,6,7,8,9}, semiconductive materials¹⁰ and dielectric materials¹⁰. Conducting materials (inks) may be metallic based, such as required for RFID antennae^{1,2}, or conducting polymers^{6,7,8,9,11}, as required for conducting traces and source and drain electrodes in an integrated circuit. Semiconducting materials may be based on semiconducting polymers^{10,11,12}, or small organic molecules and crystals¹³. Here, we will concentrate on inorganic metallic conducting materials, particularly silver, and conducting polymers, where our recent research has been conducted.

Lowering the cost of RFID tags is nowadays a big driving force for innovations in printable materials and associated devices. An RFID tag consists of an antenna and an integrated circuit. Currently, only 10% of RFID tag antennae are printed, typically using silver based inks^{14,15,16}. These materials may be screen-printed, flexographically printed, gravure printed, offset printed or digitally printed on a variety of substrates ranging from paper, Mylar polyester, polycarbonate, polyimide, PVC, to glass. Most silver-based materials are based on special "leafing" silver flakes¹⁷ that are designed to float to the surface during drying to promote high surface conductivity. The silver-based materials are well suited for printing RFID^{18,19} antennae and circuit interconnects, but are not appropriate for printing of contact electrodes in integrated circuit (IC) components, due to the large size of silver flakes, which however, can be overcome by employing nanosized metallic particles^{15,16}. Besides the metal filled conductive materials, solution processable conductive and semiconductive polymers are already leading to low cost sensors and cheap, disposable electronics¹¹. Our work to date has focused on two conducting polymers, polyaniline (PANI)⁶ and poly(3,4 ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)^{7,8,9}. PEDOT:PSS based inks have been used to print conductive layers⁹. This conductive polymer is commercially available as a water-soluble polyelectrolyte system with good film-forming properties, high visible light transmittance, and excellent stability²⁰. Some applications of PEDOT:PSS include antistatic coatings, conductive layers in organic light emitting diodes (OLEDs), capacitors and thin film transistors²¹. It has been reported that electrical conductivity of PEDOT:PSS can be enhanced by the addition of different organic compounds²². The conductivity improvement is strongly dependent on the chemical structure of the compound. Among the alcohols, ethylene glycol and glycerol were found to be the most efficient. Enhancement of conductivity is believed to be a result of an increased inter-chain interaction caused by conformational change of the PEDOT chains from the coil structure into expanded-coil or linear structures²³.

ICs typically consist of passive and active building blocks and require at least three main material properties for construction, such as conductivity, semiconductivity and dielectric (insulating) properties. Optimal performance of the ICs can be obtained if materials with a wide range of band gaps and conduction mechanisms (e.g. p or n) are available. Considering manufacture processes, transistors using silicon require a complicated and high precision manufacturing process that creates electronic circuits by starting with a single-crystal silicon substrate and applying a variety of processes such as oxidation, the addition of impurities (ion implantation), chemical-vapor deposition, thermal diffusion, annealing, metallization, photolithography and etching²⁴. Large scale and expensive

equipment, such as clean rooms and vacuum systems, are required. In contrast, with printed transistors, one can take advantage of the features of organic materials and, by dissolving them in a solvent, use printing technologies such as rotary press or inkjet printing to create circuits simply^{10,25}. Since these are low-temperature processes, they have excellent compatibility with plastic and paper substrates²⁶.

With the technology of flexible electronics becoming closer to device prototyping and commercial production, it is clear that the choice of substrates with desirable properties is essential in order to make this technology viable. Flexible substrates pose a number of challenges. Dimensional stability of the substrate is very important in order to ensure precise registration and resolution. Many types of substrates are also incompatible with some solvents used for organic materials⁴. Surface smoothness and cleanliness of the flexible substrate are both essential to ensure the integrity of subsequent layers and formation of a high quality interface for better device performance. Of the flexible plastic substrates, the most commonly used are polyesters^{27,28} (PET, PEN) and polyimides²⁹. Although paper is of big interest for printed electronics, there are very few reports to date^{1,2,30}.

Printed RFID Antennae

The primary focus of our project to date was to evaluate the performance of RFID antenna printed directly on packaging substrate, such as paperboard and label stock papers. RFID antennae were manufactured by two different printing processes (flexography and gravure) using silver filled conductive inks. The print pattern was designed with intention to evaluate electrical performance, as well as printability, of the two conductive inks primarily by using various features, such as conductive traces at different tone values and angles to the print direction, positive and negative line blocks and finally two different UHF RFID antennae designs (Figure 1). Three bands have been deployed to sample either different anilox roll line screens or different gravure cylinder engraving resolutions to find the most suitable image carrier parameters for desirable properties of the final prints.

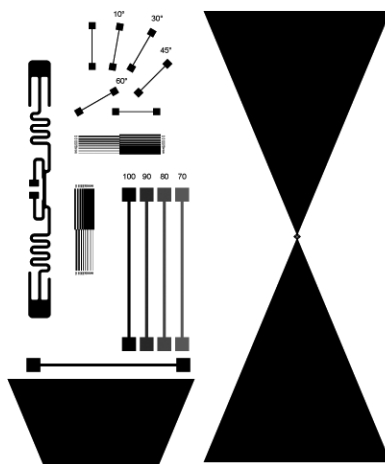


Figure 1 Illustration of the main design features included in testing print form.

Printing trials utilized 3 different silver-based inks based on difference chemistries, a solvent-based, a UV-cured and an aqueous-based. Seven different substrates were printed, consisting of 4 packaging papers and 3 packaging paperboards. In order to correlate the properties of materials used for printability and electrical performance, conductive inks and packaging substrates were fully characterized using standard methods. The summary of measured properties and methods used is given in the Table 1. Electrical characterization of printed features is given in more detail later in the article.

The definition of the printed edge is very important, in particular for RF performance. Therefore, the printed samples were analyzed for line raggedness³¹. An example of line raggedness measurement is shown in Figure 2. Raggedness is determined by the displacement of the black-white boundary line from the ideal boundary line. The ideal boundary line is determined by calculating the best-fit line through the boundary points.

Table 1 Measured properties and methods used		
Substrate characterization	Ink Characterization	Print Characterization
Roughness (PPS, Stylus Profilometry)	Rheology (Rotational Viscometry, Oscillatory Testing)	Line Width/Length (Image Analysis)
Porosity (PPS, Mercury Intrusion)	Surface Tension (Pendant Drop Analysis)	Raggedness (Image Analysis)
Pore Distribution (Mercury Intrusion, Gas Adsorption)	Particle Size Analysis (Dynamic Light Scattering)	Ink Thickness (Optical Microscopy)
Topography (Surface Scan Analysis, AFM)		Ink Film Roughness (Stylus Profilometry)
Liquid Penetration (Ultrasonic Transmission)		Electrical Resistance (AC/DC Multimeters)
Surface Energy (Contact Angle Analysis, Owens-Wendt Estimation Method)		RF Performance (RF Network Analyzer)

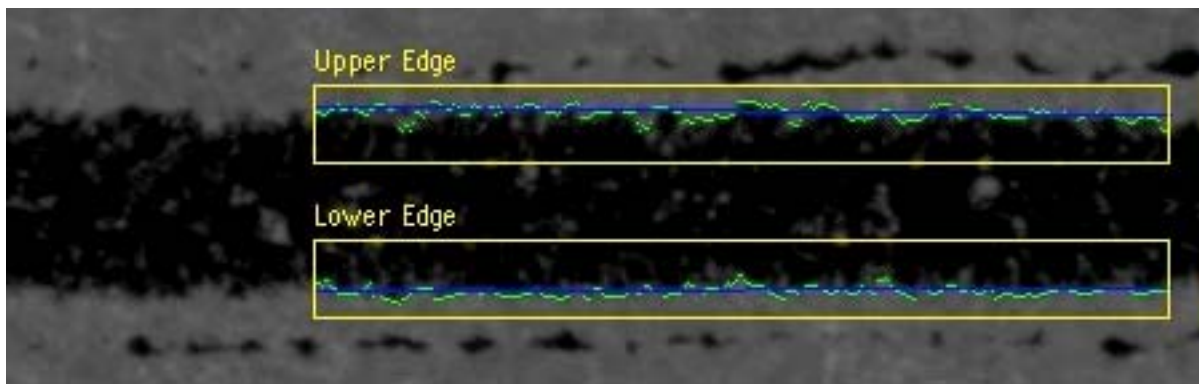


Figure 2 Example of line raggedness evaluation for a printed line.

Characterization of Electrical Performance

DC Resistivity

Determining material resistivity is accomplished by measuring the resistance of a piece of the material of known dimensions, such as a solid rod or bar or a thin line on a non-conducting substrate. As long as the material size is uniform and the cross-sectional area and length are known, the resistivity can be directly computed once the resistance is known. For this purpose, the printed line dimensions (length, width and thickness) need to be measured. The length and width of printed conductive traces was measured by image analysis and the thickness of the ink film was measured by optical microscopy. Samples for thickness measurements were embedded in a resin and then polished. Examples of an ink film cross sections are given in Figure 3.

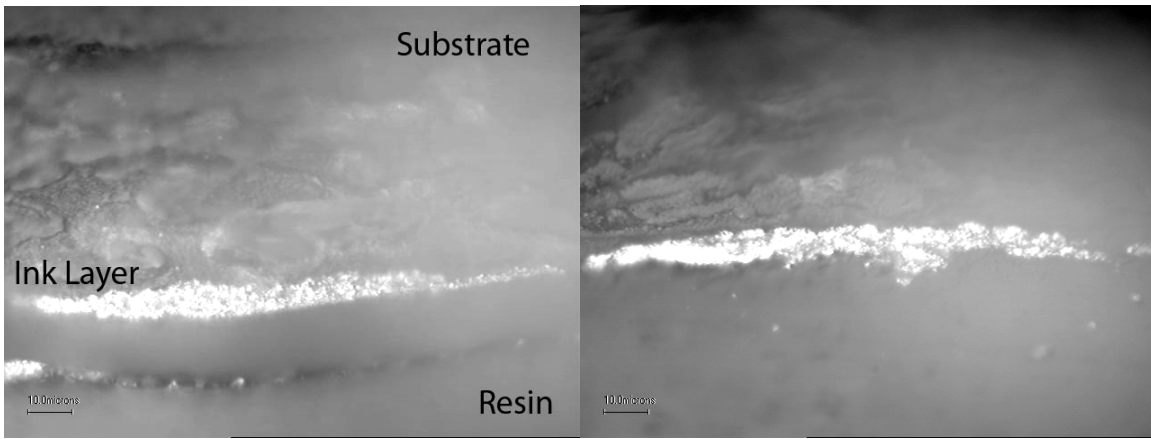


Figure 3 Illustration of ink film thickness for water-based ink 3 (left) and solvent-based ink 2 on a label paper

Figure 4 shows the results of bulk resistivity of flexographically printed samples with three ink systems on different packaging substrates. For better comparison of the different ink systems, the figure shows bulk resistivity values only up to 0.4 Ohm mil, because bulk resistivity of the ink system 3 was significantly higher than 0.4 Ohm mil. High resistivity of printed ink films resulted in poor antennae performance.

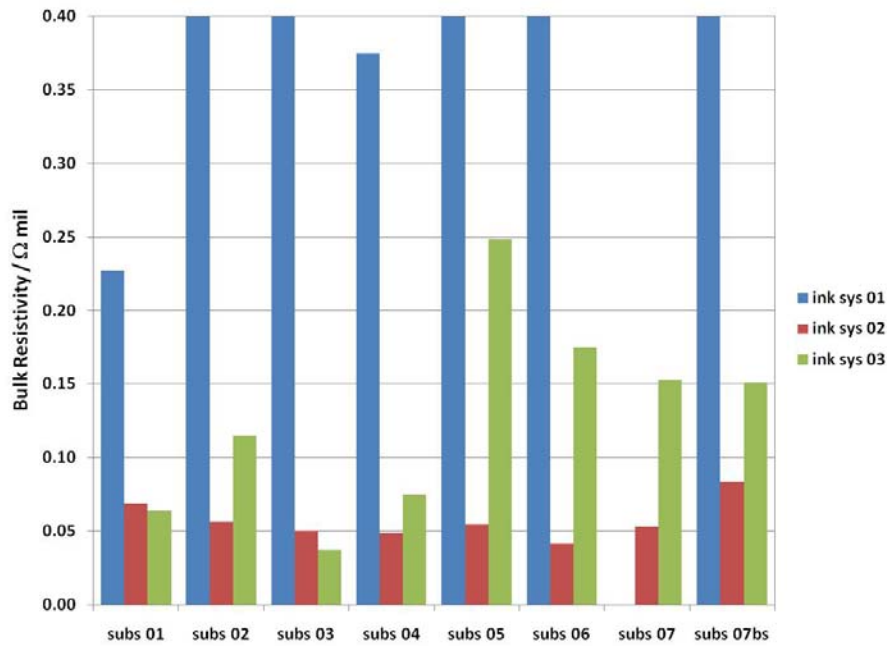


Figure 4 Bulk Resistivity

An accurate measure of resistance is obtained using a 4-point probe, where a current is caused to flow through the material using two probes at opposite ends and a voltage is measured at the desired length along the test resistor as shown in **Error! Reference source not found.5**.

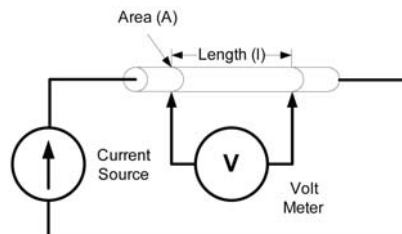


Figure 5 Four-point Resistance Measurement.

AC Impedance

A Milliohmmeter was used to perform AC impedance measurements. This instrument performs 4-point probe measurements using a 1 kHz current source reference. Using known current magnitude and phase, the device measures the magnitude and phase of the voltage waveform across the device under test (DUT) and computes the complex impedance in terms of

$$Z = R + jX \quad (1)$$

where R is the electrical resistance in Ω and X is the reactance in Ω .

The sign of X defines whether the equivalent series impedance at 1 kHz is inductive (positive) or capacitive (negative) and can be used to estimate the magnitude of the inductance or capacitance.

The electrical resistance, R , measurement should also compare directly with the DC impedance measurement, thereby, providing verification and validation of the DC measurement (Figure 6)

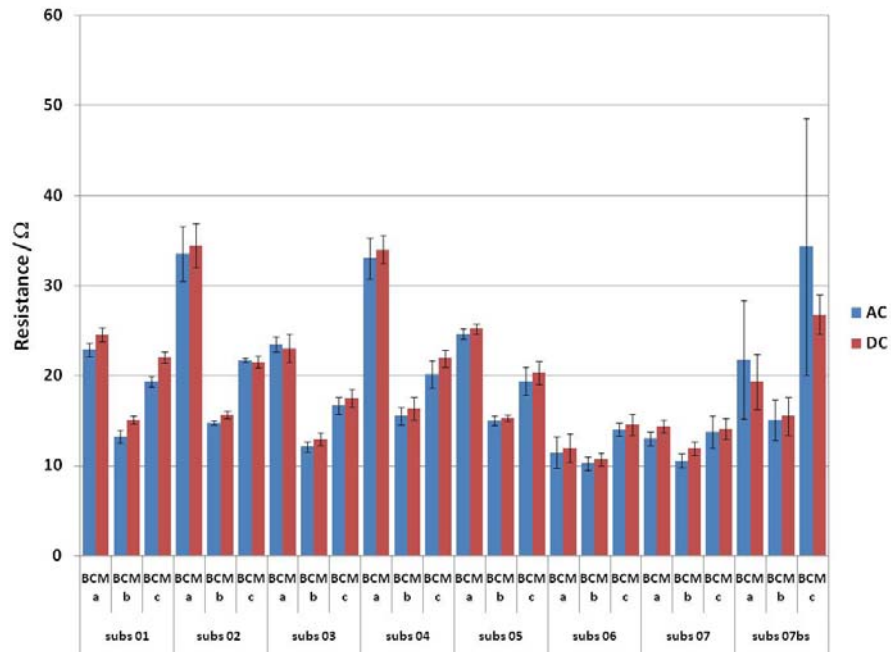


Figure 6 Comparison of AC vs. DC characteristics for measured substrates (ink system 02).

Impedance Measurement: RF

As signal frequencies increase in a conductor satisfying Ohm's Law, the electrical field and current density decays exponentially with the depth of the conductor³². The depth at which the values decay by 1/e of the surface values is defined as the RF skin depth.

$$\delta = \sqrt{\frac{2}{\omega \mu \sigma}} \quad (2)$$

where μ is the material permeability in H/m, σ is the conductivity in S/m, and ρ is the material resistivity in Ω -m. and ω is the angular frequency in Hz.

As current does not flow throughout the entire conductor, the effective RF impedance of the material will be greater than the resistance value previously defined. A new cross-sectional area term based on the skin depth must be used as

$$R_{RF} = \frac{l}{w} = \frac{l}{w} \frac{1}{w} \quad (3)$$

where w is the width of the material
 l is the length.

Based on this equation, the surface resistance of a material is defined in terms of ohms per square (based on a square of material where $l = w$).

$$R_s = \sqrt{\frac{\rho}{t}} \quad \sqrt{\frac{\rho}{t}} \quad \sqrt{\frac{\rho}{t}} \quad (4)$$

Figure 5 shows the effective RF resistance as compared to the DC resistance previously defined.

If a circular conducting rod, as shown in Figure 5, is considered of diameter, d , the comparison between the DC resistance and RF resistance can be computed. First, comparing the total resistance

$$R_{DC} = \frac{\rho l}{\pi d^2 / 4} \quad \text{versus} \quad R_{RF} = \frac{\rho l}{\pi d \delta} \quad (5)$$

where the entire circumference of the rod is assumed to be large in comparison to the skin depth for computing the RF area. Comparing these values,

$$\frac{R_{DC}}{R_{RF}} = \frac{4 d}{2 d^2} \frac{d}{\delta} \quad (6)$$

The RF resistance is then

$$R_{RF} = R_{DC} \frac{0.5d}{r} \quad (7)$$

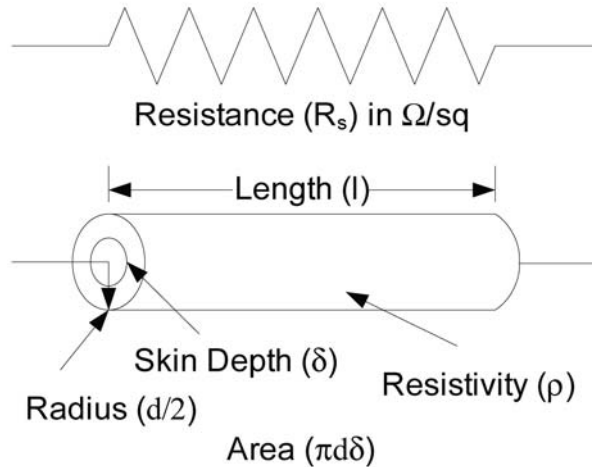


Figure 5 RF Surface Resistance

For a skin depth significantly less than the printed line height, the RF resistance is a significant multiple of the DC resistance!

To provide specific examples, the skin depth for selected metals and inks at 915 MHz, the DC resistance in $\Omega/\text{sq}/\text{mil}$ (25 μm), and the surface resistance at 915 MHz is shown in Table 1.

Table 1 RF Skin Depth for Specific Materials at 915 MHz

Material	Resistivity ρ ($\Omega\text{-nm}$)	Skin Depth δ (μm)	R_{DC} $\text{m}\Omega/\text{Sq}/\text{mil}$	R_S $\text{m}\Omega/\text{Sq}$	Reference
Silver	15.87	2.10	0.635	7.571	Resistivity ³³
Copper	16.78	2.16	0.671	7.785	Resistivity ³³
Gold	22.14	2.48	0.886	8.943	Resistivity ³³
Aluminum	26.50	2.71	1.060	9.784	Resistivity ³³
Ink 03	125.00	5.88	5.000	21.249	$\Omega/\text{Sq}/\text{mil}$ ³⁴
Ink 02	150.00	6.44	6.000	23.277	$\Omega/\text{Sq}/\text{mil}$ ³⁴
Ink-01	500.00	11.77	20.000	42.499	$\Omega/\text{Sq}/\text{mil}$ ³⁴

Note (1): in the above table $R_{DC} = \frac{\rho l}{25 m} R \frac{w}{l}$ ³⁴.

Note (2): Resistivity for metals at 293° K³³.

Antenna testing has been performed using a continuous wave RF antenna tester. The initial RF testing was performed using a laboratory antenna measurement range. This testing is intended to provide both antenna beam pattern and comparative antenna performance measures for the various printed antennae provided.

The antenna range consists of a fixed reference antenna at a defined distance to a test antenna placed on a movable pedestal (360° horizontal movement and $\pm 45^\circ$ vertical movement). A RF network analyzer is used to source a continuous wave RF signal at a known frequency and phase to the reference antenna. The antenna transmits the RF wave to the test antenna, where it is received as an input to the RF network analyzer. The network analyzer determines the incoming signals magnitude and relative phase as compared to the transmitted signal. The results are captured over an HP-IB network connection to a personal computer, where operational software controls the test and data collection. This measurement allows a three-dimensional pattern of the antenna performance to be collected for viewing and analysis. Figure 6 shows examples of antenna gain plots for water-based and solvent-based inks on one of the packaging papers.

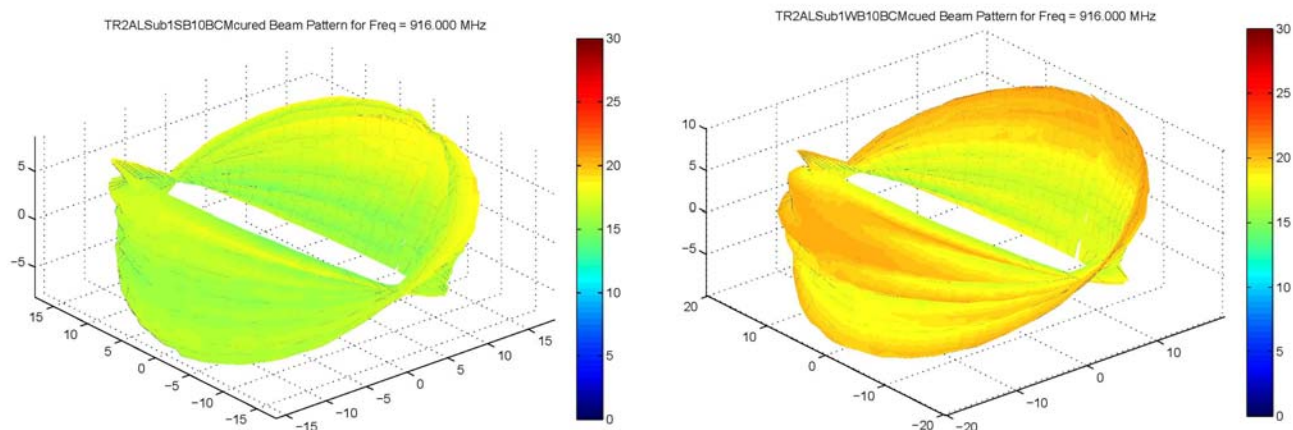


Figure 6 Antenna gain as a function of orientation for solvent based ink (left) and (water) based ink on a packaging paper.

Conclusions

Paper substrates are of great interest for printed electronics, because of extensive use in packaging. However, They pose a number of challenges for printing with functional materials. These challenges include surface irregularities and pores, nonuniform ink films and ragged lines. Suitable functional materials for printing ICs present additional challenges. We continue to progress at addressing these challenges and continue to identify and address new challenges.

Other results from printed antennae measurement are being published in various journals and have been or will be presented at appropriate conferences.

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- ¹ Wood, L., Hrehorova, E., Joyce, T., Fleming, P. D., Joyce, M. K., Pekarovicova A. and Bliznyuk, V. "Paper Substrates for Printed Electronics", *Pira Ink on Paper Symposium*, Atlanta, September 28, 2005.
- ² Cruz, M., Joyce, M. K., Fleming, P. D., Rebros, M., "Surface Topography Contribution to RFID Tag Efficiency Related To Conductivity," TAPPI Coating and Graphic Arts Conference 2007, Miami, FL, April 21 – 25, 2007
- ³ Stephen R. Forrest, "The path to ubiquitous and low-cost organic electronic appliances on plastic", *Nature* **428**, 911 (2004).
- ⁴ MacDonald, W. A., "Engineered films for display technologies," *Journal of Materials Chemistry*, 14, 1 (2004) p. 4-10.
- ⁵ D Chirvase, J Parisi, J CHummelen and V Dyakonov, "Influence of nanomorphology on the photovoltaic action of polymer–fullerene composites", *Nanotechnology* **15** (2004) 1317–1323.
- ⁶ Hrehorova, E., Wood L. K., Pekarovic, J., Pekarovicova, A., Fleming, P. D., and Bliznyuk, V., "The Properties of Conducting Polymers and Substrates for Printed Electronics", *Proceedings of IS&T Digital Fabrication 2005*, Baltimore, September 18-23, 2005, 197-202.
- ⁷ Erika Hrehorova, Alexandra Pekarovicova and Paul D. Fleming, "Gravure Printability of Conductive Polymer Inks", *Proceedings of IS&T Digital Fabrication 2006*, Denver, September 18-23, 2006.
- ⁸ Hrehorova, E., Rebros, M., Pekarovicova, A., Fleming, P. D., Bliznyuk, V. N., "Characterization of Conductive Polymer Inks based on PEDOT: PSS," Proc. of TAGA 59th Annual Technical Conference, Pittsburgh, PA, 18-21 March, 2007.
- ⁹ Erika Hrehorova, Alexandra Pekarovicova, V.N. Bliznyuk, and Paul D. Fleming, "Polymeric Materials for Printed Electronics and Their Interactions with Paper Substrates", *Proceedings of IS&T Digital Fabrication 2007*, Anchorage, September 16-21, 2007.,
- ¹⁰ A. Knobloch, A. Manuelli, A. Bernds and W. Clemens, "Fully printed integrated circuits from solution processable polymers", *J. Appl. Phys.* 96 (4) 15 August 2004.
- ¹¹ Adam Pron and Patrice Rannou, "Processible conjugated polymers: from organic semiconductors to organic metals and superconductors", *Prog. Polym. Sci.* **27**, 135-190 (2002).

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- ¹² A. R. Brown, C. P. Jarrett, D. M. de Leeuw, M. Matters, "Field-effect transistors made from solution-processed organic semiconductors" *Synthetic Metals* **88** (1997) 37-55.
- ¹³ H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin & A. Dodabalapur, "A soluble and air-stable organic semiconductor with high electronmobility", *Nature* **404**, 478-81, 30 MARCH 2000.
- ¹⁴ Blue Ramsey, David Harrison, Darren Lochun, Peter Evans and Paul Harrey, "Handbook of Conductive Lithographic Films", <http://www.brunel.ac.uk/research/cleaner/blue.html>.
- ¹⁵ Mark R. James, "Manufacturing Printed Circuit Boards Using Ink Jet Technology", Proceedings of NIP19, International Conference on Digital Printing, Society of Imaging Science and Technology, New Orleans, Sept. 28-Oct. 3, 2003, p651.
- ¹⁶ Toshihiko Oguchi, Keiki Suganami, Taizo Nanke and Toshihiko Kobayashi, "Formation of Precise Electrically Conductive Pattern Using Metal Colloid I-J Ink", Proceedings of NIP19, International Conference on Digital Printing, Society of Imaging Science and Technology, New Orleans, Sept. 28-Oct. 3, 2003, p656.
- ¹⁷ Rita Mohanty, "Silver Migration in Polymer Thick Film", *SGIA Journal*, 8, 41-45 (2004).
- ¹⁸ Woznicki, Tom, "Pads-Only Plating and Conductive Inks", *The Flex Circuit News* [On Line], Available: http://www.flexdude.com/Back_Issues/FCN1-02A.PDF, 2002.
- ¹⁹ Jennifer Rigney, "Materials and Processes for High Speed Printing for Electronic Components", Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies, Salt Lake City, 2004, pp275-278.
- ²⁰ Groenendaal, L., Jonas, F., Freitag, D., Pielartzik, H., Reynolds, J. R. "Poly (3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future," *Adv. Mater.*, 12, 7, (2000) p.481-494
- ²¹ Kirchmeyer, S., Reuter K., "Scientific importance, properties and growing applications of poly(3, 4-ethylenedioxythiophene)," *J. Mater. Chem.*, 15, (2005) p. 2077-2088
- ²² Ashizawa, S., Horikawa, R., Okuzaki, H., "Effect of Solvent on Carrier Transport in Poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate)," *Synthetic Metals*, 153, (2005) p. 5-8
- ²³ Ouyang, J., et al., "On the mechanism of conductivity enhancement in poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) film through solvent treatment," *Polymer*, 45, (2004) p. 8443-8450.
- ²⁴ Sedra, A. S., Smith, K. C., "*Microelectronic Circuits*," 5th Ed., Oxford University Press, Oxford, NY, 2004 pp. 1283.
- ²⁵ Baude, P. F., et al., "Organic Semiconductor RFID Transponders," *IEEE Int. Elect. Dev. Meeting Tech. Digest* (2003), p. 8.1.1-4.
- ²⁶ Kahn, B. E., "Developments in Printable Organic Transistors," Pira International Ltd., Surrey, UK (2005), pp. 150.
- ²⁷ Fix, W., Ullman, A., Ficker, J., Clemens, W., "Fast polymer integrated circuits," *Applied Physics Letters*, 81, 9 (2002) p. 1735-1737.
- ²⁸ Bartzsch, M., Fuegmann, U., Fischer, T., Hahn, U., Kempa, H., Preissler, K., Schmidt, G., Huebler, A., "All-printed electronics and its applications: a status report," *Proc. on IS&T's DF2006: International Conference on Digital Fabrication 2006*, Denver, CO, September 18 - 22, 2006, p. 13-16.
- ²⁹ Gelinck, G., Geuns, T., Leeuw, D., "High Performance All-Printed Integrated Circuits," *Appl. Phys. Lett.*, 77, 10 (2000) p. 1487 - 1489.
- ³⁰ Andersson, P., et al., "Active matrix displays based on all-organic electrochemical smart pixels printed on paper," *Advanced Materials*, 14, 20 (2002) p. 1460-1464.
- ³¹ Kipman, Y., "Image quality Metrics for Printers and Media", IS&T's 1998 PICS Conference, pp 183-187.
- ³² S. Ramo, J.R. Whinnery, and T. Van Duzer, "Fields and Waves in Communication Electronics," 2nd ed., John Wiley and Sons, New York, N.Y., 1984, Section 3.16 and 3.17, p. 147-154.
- ³³ "Electrical Resistivity of Pure Metals", in *CRC Handbook of Chemistry and Physics*, Internet Version 2007, (87th Edition), <<http://www.hbcnetbase.com>>, David R. Lide, ed., Taylor and Francis, Boca Raton, FL, 2007.
- ³⁴ Acheson Electronic Materials Web Site, http://www.achesonindustries.com/electronic_materials/pfdata_us.asp, Data sheets for Electrodag® PD-054, Electrodag® PD-056, and Acheson PM-500.