Towards Paper Electronics
– Printing Transistors on Paper in a Roll-to-Roll Process

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Abstract
New value-added, intelligent products with novel functionalities, e.g., sensors and simple displays have recently received much attention in the research community. For these types of products to come into everyday use, devices with reasonable electrical performance and negligible production cost are required. One way to reduce the manufacturing cost is to fabricate the electronics on inexpensive paper substrates by using roll-to-roll techniques ("Paper Electronics"), as an alternative to conventional electronics manufactured with batch processes on glass or polymer film substrates. The current work discusses printing of electronics on paper and demonstrates, as a proof-of-concept, a hygroscopic insulator field effect transistor device (HIFET) printed on paper with a custom-built roll-to-roll hybrid printer.

Introduction
The authors have previously developed a multilayer-coated, paper-based substrate that is suitable for printed electronics and functionality [1,2]. In this multilayer structure, shown in Figure 1, a thin top-coating consisting of mineral pigments is coated on top of a dispersion-coated barrier layer. The top-coating provides well-controlled sorption properties through controlled thickness and porosity, thus enabling optimizing the printability of functional materials. The penetration of ink solvents and functional materials stops at the barrier layer, which not only improves the performance of the functional material but also eliminates potential fiber swelling and de-bonding that can occur when the solvents are allowed to penetrate into the base paper [3]. The multi-layer coated paper under consideration in the current work consists of a pre-coating and a smoothing layer on which the barrier layer is deposited. The top layer is thin and smooth (coat weight 0.5–5 g/m², layer thickness 0.3–6 µm, RMS surface roughness 55-75 nm) consisting of mineral pigments such as kaolin, precipitated calcium carbonate (PCC), silica or blends of these. All the materials in the coating structure have been chosen in order to maintain the recyclability and sustainability of the substrate. The substrate can be coated in steps, layer by layer, using conventional coating techniques such as blade, rod or reverse gravure coating. However, for industrial scale manufacturing, curtain coating appears to be a promising method since all the layers can be coated at the same time [4].

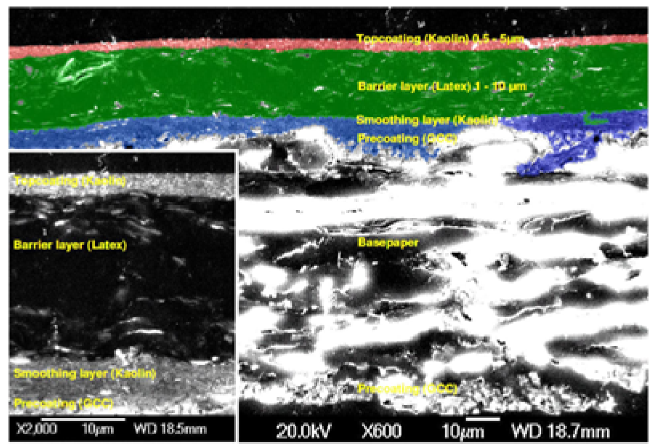

***Figure 1.** Cross-section SEM image showing the layer structure of the paper substrate: top-coating, barrier layer, smoothing layer, pre-coating and basepaper.*

Materials and Methods
The details of the multi-layer coated paper-based substrates that were used in the current work are reported elsewhere [4]. The main difference of the substrates is the thickness and the formulation of the top-coating, which controls the printability of the functional inks.

For printing of source and drain electrodes, two commercial conductive inks were used; Suntronic 5603 Ag nano particle inkjet silver ink, and Creative Materials 125-06 micron size particle flexography silver ink. Regioregular poly(3-hexylthiophene) (P3HT) dissolved in ortho-dichlorobenzene (DCB) was used as the semiconductor and poly(4-vinylphenol) (PVP) in ethylene glycol as insulator. Pedot:PSS (H.C. Starck) organic conductive polymer was used for the gate electrode.

Transistors were printed either as a batch process or with a custom-built roll-to-roll hybrid printer. In batch processing the source and drain electrodes were inkjet-printed with a drop-on-demand Dimatix Materials Printer (DMP-2800, Dimatix-Fujifilm Inc.), the semiconductor and insulator layers were spin-coated, and the gate was drop-cast. In roll-to-roll processing the printing speed was 10 m/min, the web width 100 mm and four 500 W infrared sintering units were mounted online. The source and drain electrodes were printed with flexography using an ASAHI DSH® (Shore A 69°) photopolymer printing plate with a ceramic anilox cylinder (Cheshire Engraving Cervices Ltd., cell angle 60°, line density 120 lines/cm, cell volume of 12 cm^3/m^2). A custom-built

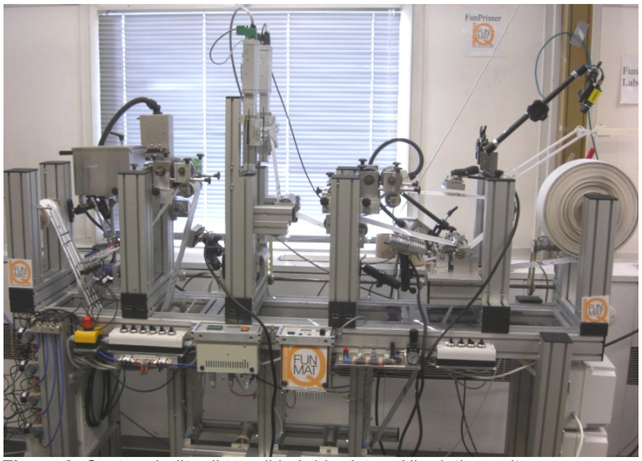

Figure 2. *Custom-built roll-to-roll hybrid printer. All printing units are exchangeable and the setup can be varied depending on the materials being printed.*

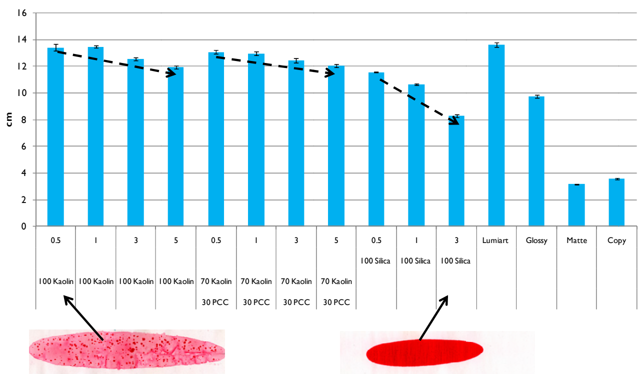

Figure 3. *The IGT print penetration test. A longer stain indicates lower pore volume in the top-coating.*

spray coating unit and inkjet printing units were used for coating or printing of the semiconductor. The inkjet printhead fed by a custom-built ink-feed setup is a 128 nozzle and 80 pl drop volume Xaar operated by Imaje 4400 controller and software. Alignment is controlled via an optical sensor detecting contrast variations underneath the printed layer. Figure 2 shows the custom-built roll-to-roll printer used.

Results

Important parameters of top-coating affecting the printability of various functional inks are thickness, porosity, pore volume, surface energy and roughness. These can be adjusted by the choice of pigment size and its distribution. A fast and quantitative method for measuring surface porosity of a substrate is the IGT print penetration test, which for the multilayer coated samples provides an indication of the pore volume of the top-coating. A test oil droplet placed on the substrate is forced through a printing nip, whereby the droplet forms an elongated stain. A long stain indicates low surface porosity. Figure 3 shows how by either changing the coat weight or the coating pigments, the total pore volume can be controlled, which is reflected in stain length. The stain length is a predictor of the obtainable line width of a functional ink.

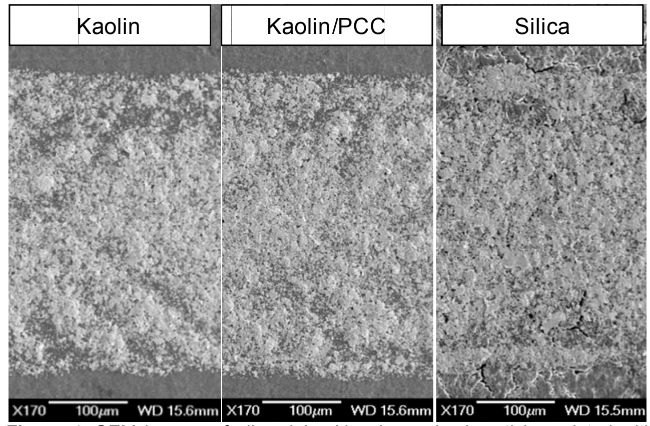

Figure 4. *SEM images of silver ink with micron-sized particles printed with flexography.*

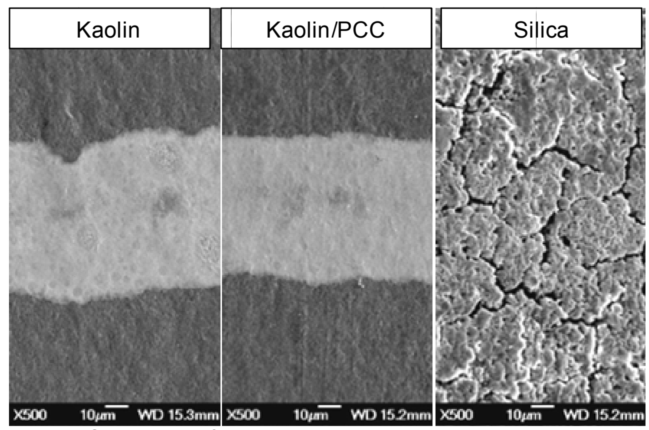

Figure 5. *SEM images of silver ink with nano-sized particles printed with inkjet.*

For printability of functional inks, surface energy and polarity are important parameters. The total surface energy increases with increasing coat weight of the top-coating. If the total surface energy is divided into its polar and dispersive components, the latter seems to remain constant regardless of the coating thickness, while the polar component increases. This can be contributed to the higher amount of dispersing agent present on the mineral pigment surfaces. Details of the surface chemical characterization can be found in [4].

Since the IGT print penetration test only provides information on pure liquid penetration, SEM images were taken to observe the possible penetration of different sized ink particles into the coating (Figures 4 and 5). The flexographic silver ink that was used consists of micron-sized flaky particles in a propylene glycol monomethyl ether acetate (PM acetate) solution. As can be seen in Figure 4, the silver particles remain on the surface on all top-coatings. The silica top-coating minimizes the characteristic squeeze effect of flexography due to the absorption of ink vehicle allowed by the porous coating.

Nano particle silver ink was printed using inkjet, which allows for narrow line widths (ca 100 µm) but requires smoother and less absorbing substrates. As can be seen in the SEM image in Figure 5, the nano particles of the silver ink penetrate into the pores of the silica coating rendering it nonconductive, but stay on the surface of both the kaolin and the kaolin/PCC blend top-

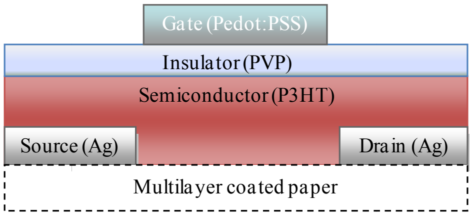

***Figure 6.** Hygroscopic Insulator Field Effect Transistor.*

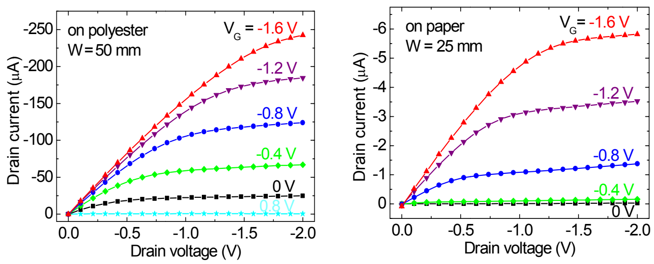

***Figure 7.** The output characteristics of organic transistors fabricated on a plastic substrate and on a recyclable multi-layer coated paper substrate. The semiconductor (PQT) on paper was applied by inkjet, while it was spin-coated on the plastic substrate. The channel length is ca. 45µm.*

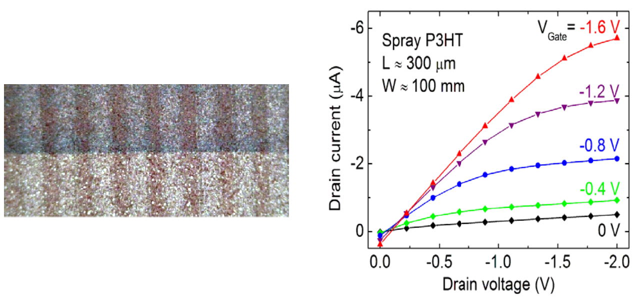

***Figure 8.** An optical image of a roll-to-roll printed transistor on paper and its output characteristics.*

coatings. When printing a semiconductor (P3HT), which is typically dissolved in solvents such as DCB or toluene, a thinner and less porous top-coating is preferable, since the low viscous solvent and along with it also the semiconductor penetrates easily into the top-coating. This means that a top-coating with a large total pore volume requires a considerable amount material to be printed in order to function.

As a proof-of-concept, transistors were printed on the paper substrate and their performance was measured. The transistor type used here is a so-called hygroscopic insulator field effect transistor (HIFET), a type of ion-modulated OFET. Figure 6 shows the top gate transistor setup [5-8]. The formation of a diffuse electric double layer, thanks to the ion motion in the polyanionic dielectric at normal room humidity, results in a high capacitance and enables low-voltage operation. The HIFET has also been shown to be rather insensitive to the thickness of the dielectric and to the surface roughness of the substrate. Therefore, the ion-modulated transistors are excellent candidates for rough substrates and large scale manufacturing for all-printed OFETs operating below 2 V.

Transistors were first printed in batch process both on the multilayer coated paper substrate and on a plastic film (Mylar A). The transistors consisted of inkjet-printed (drop spacing 25 µm) silver source and drain electrodes/contacts, P3HT as semiconductor, poly(4-vinylphenol) (PVP) as insulator and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as gate electrode. The semiconductor and insulator layers were spin-coated and the gate was drop-cast. Figure 7 shows the output characteristics of the batch process manufactured transistors.

The transistor on paper shows lower currents than on plastic, which might be due to poor semiconductor coverage on the paper substrate. Poor semiconductor ordering and impurities of the paper surface might also degrade the charge transport. Furthermore, the hysteresis was found to be larger on paper than on plastic. This could be caused by the rough insulator-semiconductor interface or electrochemical reactions in the semiconductor in contact with the paper. An advantage in the transistor characteristics on paper is that the transistor is in the off-state at 0 V, which is useful when building logic circuits.

Transistors were also printed with the roll-to-roll hybrid printer on the multilayer coated substrate. As a compromise to ensure adequate printability of both the silver electrodes and the semiconductor, a substrate with a $3 g/m^2$ kaolin top-coating was used. The source and drain silver electrodes were printed using flexography. The electrode width was ca. 350 µm, channel length ca. 300 µm and channel width 100 mm. The semiconductor (P3HT dissolved in DCB) was either spray-coated or inkjet-printed. In spray coating the thickness was controlled by adjusting the web speed while for the inkjet printing the possibility to adjust the firing frequency of the inkjet nozzle provided better control of the semiconductor thickness. The insulator (PVP) was coated using the reverse gravure technique. The gate electrode (PEDOT:PSS) was printed using either flexography or inkjet, or drop-casted. The surface tension of the water based PEDOT:PSS was lowered by addition of surfactants (Triton X-100, 0.1 volume-%) in order to ensure adequate wettability.

Figure 8 (left) shows an optical image of the gate electrode in blue, printed on top of the transparent insulator layer. Underneath is the purple semiconductor printed on top of the silver electrodes. The output characteristics are shown in the Figure 8 to the right. While the roll-to-roll printed transistor functions, there is still a clear difference to those produced with batch processing, especially when printing on plastics. One reason for this is the smaller design and narrower line widths and channel lengths enabled by the batch processing.

Concluding Remarks

In summary, we have demonstrated all-printed/coated functioning transistors on a multi-layer coated paper substrate. The devices were fabricated either as a batch process or with a custom-built roll-to-roll hybrid printer. The paper substrate can be tuned to meet criteria set by different functional inks. While the performance of the transistors produced on paper so far is modest, we see a number of potential future applications, e.g. in the field of biomedical- and chemical sensors.

Acknowledgements

XaarJet AB, Sweden is thanked for supplying the inkjet heads. The Academy of Finland is acknowledged for financial support.

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