B. Trnovec, M. Stanel, U. Hahn, A.C. Hübler, H. Kempa, R. Sangl, M. Forster*

Coated Paper for Printed Electronics

Summary
In order to prepare a suitable substrate for printed electronics, the paper surface was modified by means of coating. PET foil, which has so far been used for this purpose, is not as broadly applicable as paper substrates. The advantages of paper lie in its broad application areas, price, processability, register accuracy and environmental friendliness.
It was possible to modify paper by means of coating in a way that applied functional polymers, like PEDOT:PSS, retain their electrical functionality. The sheet resistance of printed layers is now approaching sheet resistance values of PET foil (factor 2).
An organic field effect transistor (OFET) with printed SD structures has been successfully prepared on the coated paper substrate

For quite some time now, the use of conducting polymer materials for the production of electronic devices has been on the rise. The first "plastic transistors" and ring oscillators have already been presented to the public [1,16], and at the moment scientists are working on their optimisation and efficiency. In this context, it was already possible to present ring oscillators that have been produced completely by means of mass-printing [2,16].

The technology targets the so-called low-end sector of the market, for example to produce simple circuits, disposable sensors, LED or solar cells. The success of the technology in the above mentioned application areas mainly depends on the following factors: production speed, price/performance ratio, durability, register accuracy, reproducibility etc.

Mass-printing methods have the important advantage of high production speeds. Thus, they allow for the production of higher quantities, bring down prices and enable the production of low-cost electronics.

Due to the high costs of printing material for polymer electronics, mass-printing experiments at the Institute for Print and Media Technology at Chemnitz University of Technology (pmTUC) are carried out with special laboratory printing presses. These presses have a web width of 35 mm and 140 mm. Thus, basic research can even be done with very small amounts of printing substance *(Fig. 1)*.

In order to use present findings to develop first applications and get ready for the market, researchers are busy searching for suitable substrates. So far, PET foil proved to be a suitable substrate for polymer electronics, because of its high smoothness and good electrical and barrier properties [1,2,5,15,16]. In the printing and packaging industry, however, paper and cardboard, both being all-round materials, are the predominant materials. Yet substrate requirements for printed polymer electronics (PPE) are much higher than for image printing, because homogenous, pinhole-free layers are necessary to ensure the functionality of the polymeric layers *(Fig. 2)*.

*B. Trnovec, M. Stanel, U. Hahn, A.C. Hübler, H. Kempa, Chemnitz University of Technology, Institute for Print and Media Technology, Reichenhainer Str. 70, D-09126 Chemnitz, Germany, bystrik.trnovec@mb.tu-chemnitz.de
R. Sangl, PTS, Papiertechnische Stiftung, Hess-Strasse 134, D-80797 Munich, Germany
M. Forster, University of Wuppertal, Dept. of Mathematics and Science, Macromolecular Chemistry, Gaussstr. 20, D-42097 Wuppertal, Germany

Fig. 1: Printing of SD structures; web width 35 mm

Requirements	Image printing	Printed electronics
Functional material	Pigment, colorant	Functional polymer
Resolution of structures	> 20 µm	<< 20 µm
Register of multiple layers	± 5 µm	< 5 µm
Layer thickness	≈ 1 µm	30 ... 300 nm
Layer homogeneity	Not important	Very important
Adherence of layers	Important	Important
Solvent	Optimised for price	Optimised for function
Chemical cleanness	Not important	Very important
Visual properties	Very important	Not important
Electronic properties	Not important	Very important

Fig. 2: Comparison of requirements for image and electronics printing

Functionality and performance parameters of polymer electronic devices are still inferior to that of silicon-based electronics. Nevertheless, the use of mass-printing methods offers economic advantages for the production of mass products, especially when low-cost substrates are employed.

Paper vs. foil

To improve adhesion and ink splitting, PET foil for printing has to be pre-treated with plasma [1,2]. Paper, on the other hand, is well-suited as printing substrate, but it is possible that paper and applied functional layers chemically interact.

Physical properties, such as roughness, absorptive capacity, temperature resistance and flexibility are also vitally important.

The used PET foil meets most of these requirements [5, 6, 15] However, its temperature resistance is not sufficient, the price is comparatively high and its use is ecologically questionable, because it contains oil-based raw materials.

By contrast, paper is made of natural and renewable raw materials and is recyclable. It has better temperature stability, which is very important for register-true printing of different layers for printed electronics.

In addition, the costs for common, high-quality coated paper are approximately one sixth of the costs of foil. This allows for a wide scope for optimisation of paper substrates to reach the positive characteristics of PET foil without reaching its price [2].
However, besides cellulose, paper contains other materials that can influence polymer electronic printing in many ways [12,14].

Paper finishing

The paper surface can be modified in a thermal mechanical way, i.e. calendered or coated. The research was focused on modifying papers for the specific requirements of printed electronics. The paper needs to be suitable for mass-production to keep the price advantage over PET foil [3,4].
Usual coatings consist of pigments and binders in an aqueous dispersion [13].

Experimental

The aim was to prepare a paper substrate by finishing processes suitable for mass-printing an organic field effect transistors (OFETs) *(Fig. 3)*, which can be used as basic element for further applications.
To achieve this goal, it was necessary to find suitable material combinations and surface finishing methods. At the beginning, commercially available paper kinds were analysed.

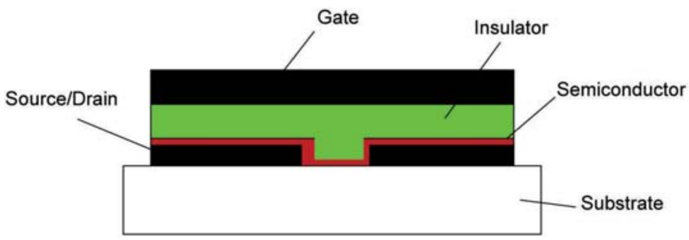

Fig. 3: OFET – Organic field effect transistor
Layers of field effect transistor with so-called "top-gate-design" [1, 2]: There is a semiconductor on top of the (printed) source/drain layer. The next layer is an insulator, whereas low k and high k materials are applied. On top, there is the gate electrode. The voltage that is applied at the gate electrode causes a field effect. Thus, the boundary layer of the semiconductor and the insulator is charged and the semiconductor is doped with free charge carriers and the current between source electrode and drain electrode can be controlled [10, 11]

Afterwards the Papiertechnische Stiftung (PTS) Munich coated raw paper with special coatings, which have been developed according to the detected requirements, at the pilot coating machine Vestra. Smoothness was adjusted by glazing before and/or after coating.
In the first part of the experimental series at the pmTUC a PEDOT:PSS dissolution was gravure printed (3.5 % polymer content) and offset printed (5.5 % polymer content) full-surface on paper.
Afterwards, the conductivity of the applied PEDOT:PSS layers was determined by calculating the sheet resistance *(Fig. 4)*.

$$R_\square = R \cdot \frac{b}{l}$$

Fig. 4: Sheet resistance:
R – measured resistance, b – width of the measured layer, l – length of the measured layer
For thin conducting layers the sheet resistance $R_\square$ is calculated by multiplying the measured ohmic resistance R with layer's width /length (b(l) ratio. The unit of sheet resistance is $\Omega_\square$ [8]

The applied quantities varied between 2 to 8 g/m², which corresponds to the quantities used in the printing of polymer electronic circuits.
Afterwards, "top-gate" transistors with PEDOT:PSS source/drain structures were mass-printed on suitable papers.
PET foil [1,2,15] and commercially available "NopaCoat Stratos" paper were taken as standard and comparative substrates, because they are already used in electronics printing.
For the first test, conventional gravure printing paper was blade-coated with a precoat of different portions of $CaCO_3$ and a final coating with varying kaolin portions. Coating composition, stretching load and temperature during calendering were varied.
In the second test, plastic pigments, including a hollow sphere pigment, kaolin and $CaCO_3$, were used in different concentrations in the final coating. The applied layer weight was 10 g/m².
In the third test, only coatings that contained kaolin as pigment were used. The binder was varied. Polyurethane (PU), starch, polyvinyl alcohol (PVOH) and a SB latex were tested.
In the fourth test, the pre-coat consisted of a barrier dispersion with included pigment. The final coating consisted of pigment-free binder dispersions.
For the production of the pre-coat the following materials were used in different concentrations (cf. sample labelling in *Fig. 6*):
B – barrier dispersion (this already includes talcum as pigment)
S – starch, L – latex, P – polyvinyl alcohol and U – polyurethane.
The top coating of approx. 5 g/m² consisted of latex, polyvinyl alcohol and polyurethane.
In the fifth test, the four best coatings (Fig. 6) were applied on a Vestra pilot coating machine with a bent blade (BB). For this purpose it was necessary to dilute the coatings.

Results

Wetting behaviour during offset and gravure printing with the first coating test was very good. The sheet resistance of the printed PEDOT:PSS with a layer thickness** of 4 g/m² was approximately 50 to 1000 times higher (70–1900 $k\Omega_\square$) than on PET foil (1.4 $kk\Omega_\square$). The average roughness Ra of base paper was approx. 1.5 µm. The roughness of coated paper was between 0.8 and 1.4 µm (PET foil: R_a = 0.01 µm).
Second test: The paper possesses good printability. At 4 g/m², sheet resistances decrease to 70 $k\Omega_\square$. The average roughness Ra of the paper sample with the highest smoothness was 0.4 µm, which is better than in the first test but still considerably higher than the roughness of PET foil.
The results suggest that there might have been partial chemical interaction causing the loss of doping in the PEDOT:PSS formulation.
It was demonstrated with bromophenol blue indicator that the pH-value of the PEDOT:PSS layers is above 4.5 while it is below 3 on PET foil. The conductivity of PEDOT:PSS is closely related to the pH-value. The best conductivities can be achieved below pH = 2 (data sheet HC Starck).
Having the same layer thickness, the pH-value of PEDOT:PSS layers on "NopaCoat Stratos" is 2 values higher than that of PEDOT:PSS layers on PET foil. The sheet resistance decreases logarithmically with decreasing pH-value (*Fig. 5)*.
Third test: On kaolin-coated papers the best sheet resistance at 4 g/m² was 11.7 $k\Omega_\square$ (binder: starch). However, this value is still too high compared to PET foil. The roughness of these paper samples was between 0.3 and 0.7 µm.

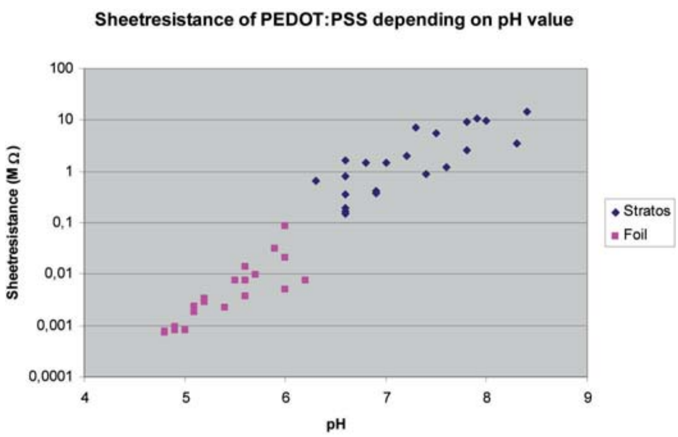

Fig. 5: Sheet resistance of printed PEDOT:PSS on paper (Stratos) and on PET foil in relation to the pH-value of the PEDOT:PSS layers

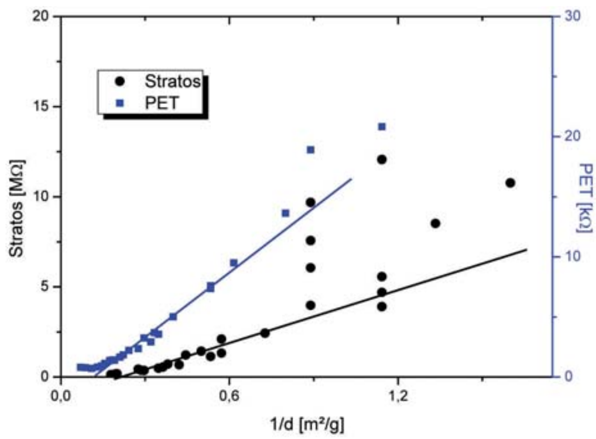

Fig. 7: Sheet resistances on paper and PET foil depending on applied quantity

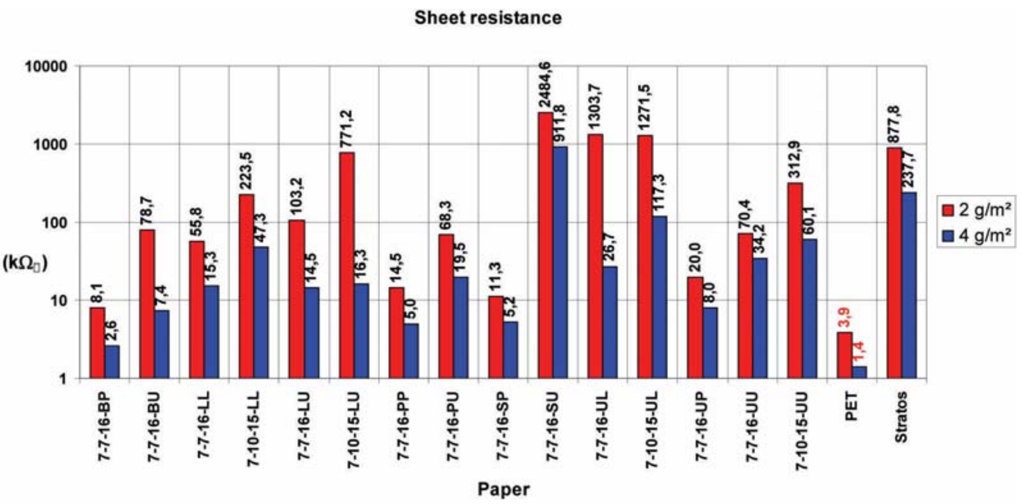

Fig. 6 Sheet resistance of the offset printed PEDOT:PSS layers on paper in the fourth coating test (the numbers on x-axis symbolise different component concentrations of the coatings)

Fourth test: The lack of kaolin in the top coating possibly has a negative influence on the roughness of the coated paper surface. The best value was $R_a = 0.53$ µm, which is significantly higher than the roughness values of papers with kaolin-based top coatings. The sheet resistance values at 4 g/m² *(Fig. 6)* are between 2.6 kΩ□ (BP) and 5/5.2 kΩ□ (PP/SP), and are, thus, almost as good as those of PET foil (barrier dispersion with talcum-B, latex-L, PVOH-P, starch-S). In the beginning, plasma treatment was necessary before printing because of the low surface energy SE = 38 mN/m.

Fifth test: Although roughness has improved significantly ($R_a = 0.31$ µm) in comparison to the manually coated samples, sheet resistance increased to 27 kΩ□.

Discussion

To evaluate the basic applicability of a substrate for printed electronics, it is best to assess if the functionality of the printed polymers on paper is still guaranteed.

Due to the absorbency of paper, the PEDOT:PSS entered the paper's volume, which might have been the cause for the measured decrease in conductivity. It is assumed that the increase of sheet resistance results from the partial absorption of the conducting layers [15] and the partial loss of the PEDOT:PSS doping and from the chemical interaction between printing material and substrate (Fig. 5 and *Fig. 7*). Research is still being done to determining the influence that penetration and loss of doping have on the sheet resistance. That is the reason for choosing sheet resistance of PEDOT:PSS as the main evaluation criterion.

The sheet resistances of the paper samples of test 1 to 3 were too high to prepare transistors with parameters, that meet the requirements of even simple circuits.

Additionally, the surface tension of the papers plays an important role, because the wetting behaviour of the printing material PEDOT:PSS influences the homogeneity of the conducting layers and, thus, also their conductivity (Fig. 7 and *Fig. 8*) [15]. The non-linear behaviour of the sheet resistance (Fig. 7) is caused by so-called "viscous fingering". The effect becomes even more pronounced when higher quantities are applied.

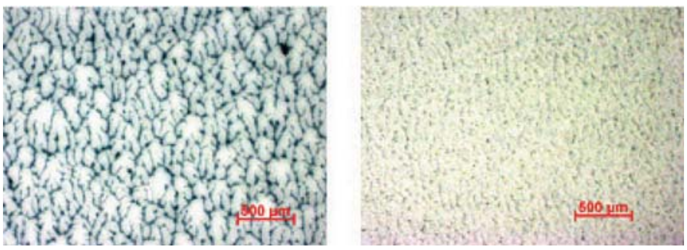

Fig. 8: Light optical microscope image of offset printed PEDOT:PSS layers on PET foil (left) and Stratos (right)

The smoothness of the substrate is also significant to ensure the homogeneity of thin layers on the surface *(Fig. 9)* [15].

The lowest sheet resistances could be achieved with samples that had a smooth precoat and a separate pigment-free top coating.

The coated paper 7-7-16-BP has the best sheet resistance and could, thus, be suitable as starting point for further optimisations. The roughness should be decreased to at least 0.05 µm [9].

The efficiency of printed transistors on paper is by far lower than that

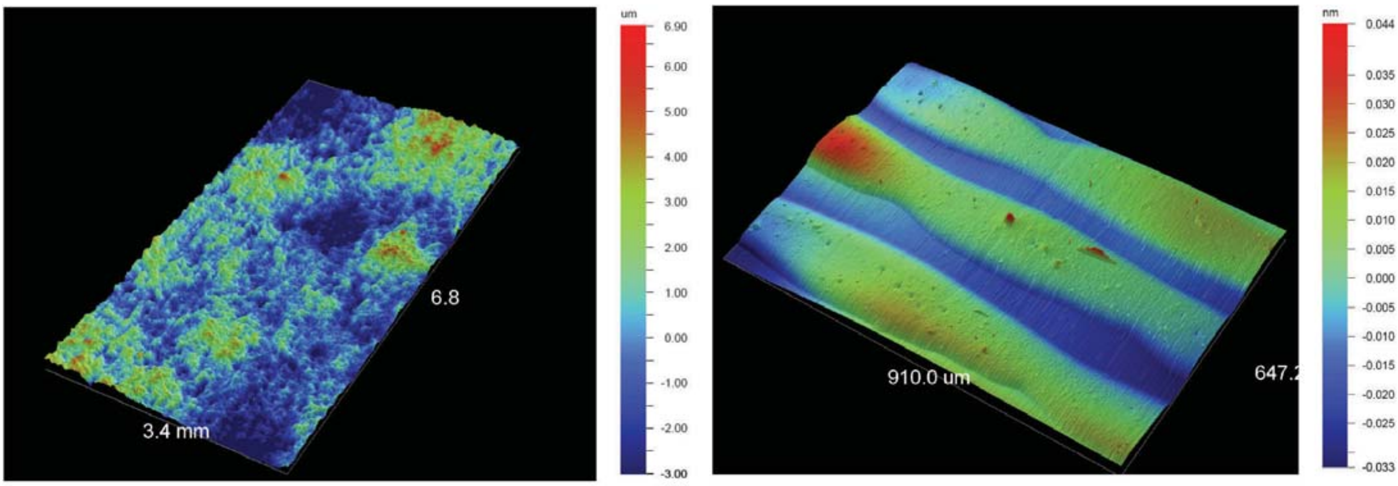

Fig. 9: Profile of a paper sample (D2- final coating contains hollow sphere pigment, $CaCO_3$ and kaolin) with gravure printed source/drain structures (left) and PET foil with gravure printed source/drain structures (right)

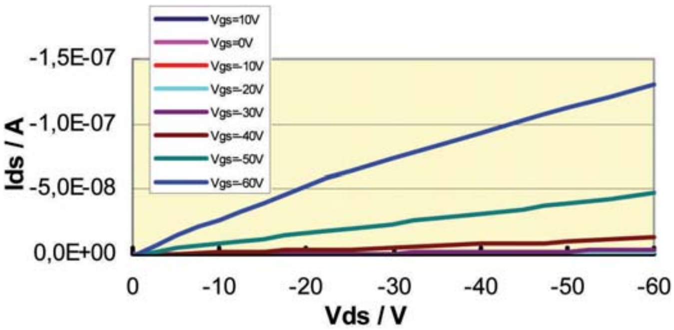

Fig. 10: Transistor curve of an OFET on paper; S/D and gate electrodes: PEDOT:PSS, semiconductor: F8T2, low-k: Cytop, high-k: Luxprint; S/D structure was gravure printed

of printed transistors on PET foil (on/off ratio (0V–60V) = 230 paper; approx. 15 000 PET foil) *(Fig. 10)*.

Conclusion

It was possible to modify the paper surface by coating, so that sheet resistances of printed conductive polymers are now similar to sheet resistances on PET foil (factor 2) at the same layer thickness. There are narrow confines for the chemical and physical properties of paper for the application in printed electronics. Compared to image printing, the printing material must not be absorbed (even if sometimes desired), because absorption of the "ink" influences the functionality of the printed PEDOT:PSS layers. The doping in PEDOT:PSS requires a chemically inert surface to maintain its functionality. The average roughness of paper was still very high for these applications (the reached value was Ra = 0,26 µm), because the layer thicknesses for transistor printing are between 20–300 nm.

Nevertheless, the results provide the basis for future research in the optimisation of paper for printed electronics.

Acknowledgement

The collaborative project IGF 199 ZGB, carried out by the PTS and Forschungsgesellschaft Druckmaschinen e. V., was supported by the Federal Ministry of Economics and Technology and AiF within the programme "Industrielle Gemeinschaftsforschung (IGF)" (Joint Industry Research). Sincere thanks.

Special thanks also go to cooperating companies of the paper and suppliers industry for providing support for our research project.

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**In this paper, the layer thickness refers to wet layers