Controlling Film Formation of Functional Organic Materials in Gravure Printing by Using Temperature-Controlled Substrate Carriers

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1. Introduction and background

The gravure printing process is used for the production of high-quality graphical products in large quantities and at high speeds. Examples are colored magazines, bank notes and cardboard packaging. This process, however, is also particularly suited for functional printing, especially for the printing of organic electronics devices. [1] Typical functional materials are solutions of a polymer or an organic semiconductor in a volatile organic solvent. Compared to inkjet or flexographic printing gravure printing provides some major advantages: gravure printing forms have an inert chromium surface and are stable against mechanical stress and chemically aggressive solvents, leading to a good long-term usability and high throughput as well as minimizing the risk of ink contamination. The printing resolution reaches the 10 µm scale, providing high edge quality of the printed pattern. Modern laser engraving techniques have further pushed this feature and gravure printing seems to become one of the candidates for the solution-based production of very fine conductive grids and electrodes, as e.g. for optically transparent displays and OLED front electrodes, or for the interdigital source and drain electrodes of organic thin film transistors.

In gravure printing the typically cylindrical printing form is covered with micrometer-sized engraved cells which together build up the screened image to be printed and determine the volume of ink that is transferred to the substrate. The process of a sheet-to-sheet based gravure printing machine is schematically depicted in Figure 1. The cells are filled with ink by typically rotating the printing form in an ink reservoir. On the laboratory scale, ink is often applied directly onto the printing form in order to use the expensive materials sparingly. A doctor blade wipes off the excess ink on the non-engraved areas. The substrate on the shuttle is now brought in contact with the rotating cylinder by moving it into the gap between the rotating printing form and the so-called impression roller, which applies the necessary force. In the moment when the substrate lifts off the surface of the printing form a part of the ink is transferred to it.

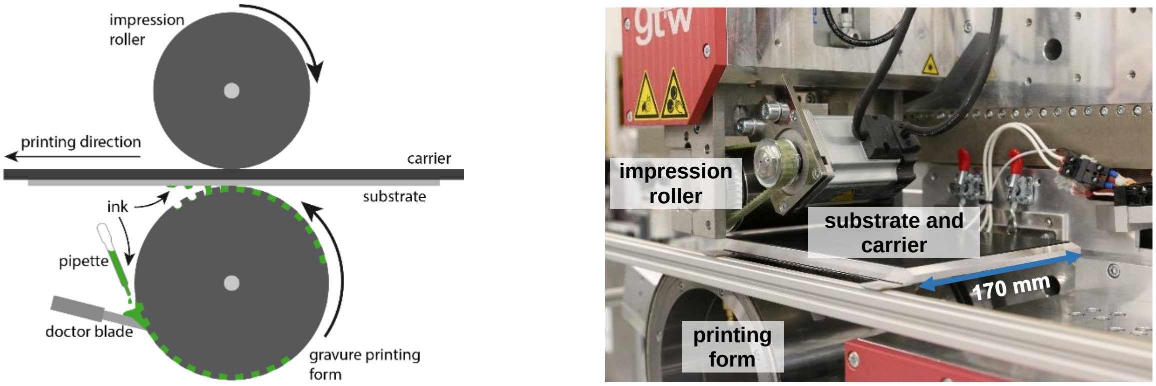


Figure 1: *Left*: Schematic of a laboratory gravure printing machine. *Right*: The laboratory gravure printing machine Superproofer 220 by GT+W which was used in our experiments.

Despite the fact that already working devices can be printed, the gravure printing process is particularly sensitive to specific defects and pattern formation phenomena, which are critical in functional printing where ultra-thin closed layers in the nanometer range with high surface homogeneity are crucial for the performance of the devices [2]. In functional printing often critical ink formulations with low viscosities and very low boiling points are used, leading to unwanted defects in the dry films. Namely, ink dewetting, viscous finger formation and ink agglomeration may occur as displayed in fFigure 2. The defects and artifacts are also influenced by the printing machine parameters, e.g. printing speed and pressure. The strongest impact, however, is caused by the fluid and substrate properties [3,4]. This gives rise to the so-called Marangoni drag [5], caused by temperature and surface tension gradients, and the coffee ring effect based on the conservation of the contact angle [6]. In the case of the already mentioned viscous fingering, also known as Saffman-Taylor instability [7], the dominant wavelength of a surface perturbation in the printing gap, usually of order of few 100 µm, is directly related to the ratio of the viscosity and the surface tension. Since these parameters are highly temperature-dependent, enforcing substrate temperature in the period where the transferred ink is still in the liquid state could improve layer formation drastically. An increase in temperature decreases viscosity and surface tension of fluids and thus improves wetting and spreading of the deposited dots. The leveling of the liquid film is accelerated as well. A higher temperature also leads to a change of the solvent evaporation rate from the printed layer. Consequently, the drying and leveling time can be manipulated. This also enables an enforced and permanent wetting when the film is dried immediately so that no more dewetting can occur.

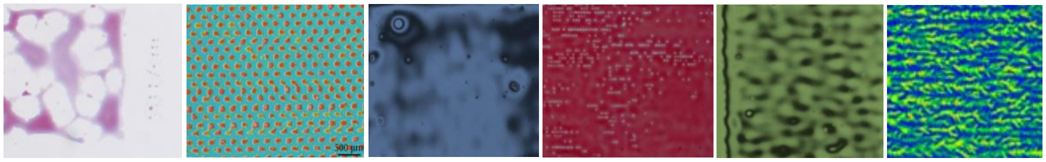
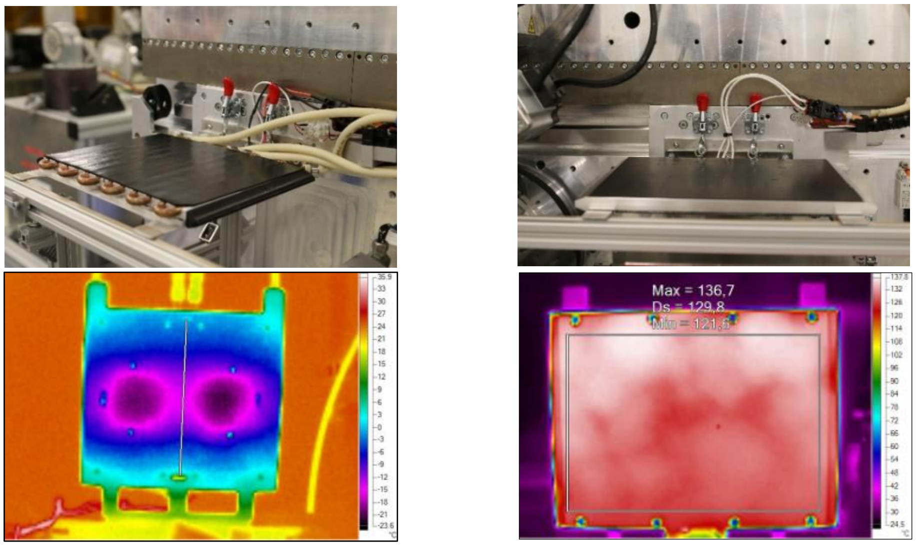

(a) (b) (c) (d) (e) (f)

Figure 2: A selection of film formation defects in functional gravure printing: (a) dewetting, (b) insufficient wetting and drop spreading on the substrate, (c) formation of agglomerates/aggregates, (d) ’missing dots’, (e) Marangoni-inhibited levelling and coffee stain defect at the printing rim, (f) viscous fingering

Obtaining continuous and direct influence on solvent evaporation, viscosity, surface tension and Marangoni drag of functional fluids means a further development of the gravure printing process from a dot-based printing technique towards a technology for the manufacturing of finely structured but dense and uninterrupted thin-film-patterns as is required in printed electronics. Temperature-controllable substrate carriers, capable for heating as well as cooling of the substrates, offer many benefits.

2. Construction and Setup

The sheet-to-sheet laboratory gravure printing machine used for the experiments is a Superproofer 220 manufactured by GT+W. We developed two types of substrate carriers, see Figure 3, which were able to set temperatures from - 20 °C to 180 °C. One carrier is based on Peltier elements with 60 W each and hence requires an active cooling to conduct away the heat. The possible temperatures range from -20 °C to 150 °C. The other substrate carrier makes use of a silicone heating element with a power of 500 W. It can adjust temperatures between the surrounding temperature and 180 °C. Unlike the Peltier carrier, an active cooling is not possible in this construction. Both controllers make it possible to achieve fast temperature changes so that one can directly dry or freeze the printed layer after the ink transfer. The carriers were constructed in a way to realize a homogenous temperature distribution on the surface where they get in direct contact with the substrate. The substrates itself also lead to an even more homogeneous temperature distribution. Only at the maximum and minimum temperature, stronger temperature gradients emerge, as can be seen in Figure 3. In the middle of the carrier where the substrate is placed, the difference between a set temperature of 100 °C and the measured temperature is less than 5 K.



(a) (b)

Figure 3: (a) Peltier-based substrate carrier and temperature distribution for a set temperature of -20 °C. (b) Silicone heater-based substrate carrier and temperature distribution for a set temperature of 120 °C.

Active temperature control is feasible even under rapid motion and acceleration of the sample carrier in the sheet-fed gravure machine. Temperature ramps can also be realized between the subsequent process steps. With both carrier types it is possible to print on a variety of substrates, ranging from thin PET or PEN foil to glass or silicon wafers with a maximum size of 150 mm x 150 mm. Due to the enhanced mass of the carriers the printing speed is limited to 3 m/s.

3. Experiments and Results

In the following, some examples with different materials are presented. All printing runs were performed at a printing speed of 0.5 m/s. As a substrate, we used ITO covered glass sheets. The experiments were conducted under clean room conditions at a temperature of 23 °C and a humidity of 50 %. In order to analyze the surface texture of the printed samples, Imaging Color Reflectometry (ICR) was used to determine the layer thickness of the whole sample in one short measurement step [8,9].

PEDOT:PSS dispersion

Printing this fluid without any modifications typically leads to very disturbed layers, as mentioned in literature [9]. Hence, this material system was chosen in order to see how the defects are changing with a change in the substrate temperature. The dispersion was printed at different substrate temperatures. After the printing, the samples were dried on a hotplate.

Figure 4 shows cut-outs of the same field for each sample. The upper row shows the images of the samples taken with a DSLR camera under blue illumination. The lower row shows the height information, which was calculated using the above-mentioned ICR method. This way the developed structures of the whole samples can be visualized easily.

It is clearly visible that with higher temperatures the formation of viscous fingering increases. At lower temperatures, the wet film has more time to level the disturbances before it solidifies. High temperatures ‘freeze’ the initial state of the viscous fingering that is present in the printing gap due to the fast evaporation of the solvent. Looking at the film thickness, it is also evident that the higher the temperature the less fluid is transferred to the substrate leading to a lower dry film thickness. A reason might be that the fluid is already drying on the printing form when it gets in contact with the substrate.

PEDOT:PSS dispersion diluted with isopropanol

Figure 5 shows the direct comparison of samples printed with a PEDOT:PSS dispersion diluted with IPA at a ratio of 4:1 and pure PEDOT:PSS dispersion. At a temperature of 12 °C, the evaporation rate is lowered. Due to the low surface tension of the IPA, the fluid is spreading stronger and the longer drying time leads to smeared out edges. The particle aggregation is also increased. At 30 °C, the viscous fingering still strong compared to the lower temperature, but the layer is closed and the edges are much sharper.

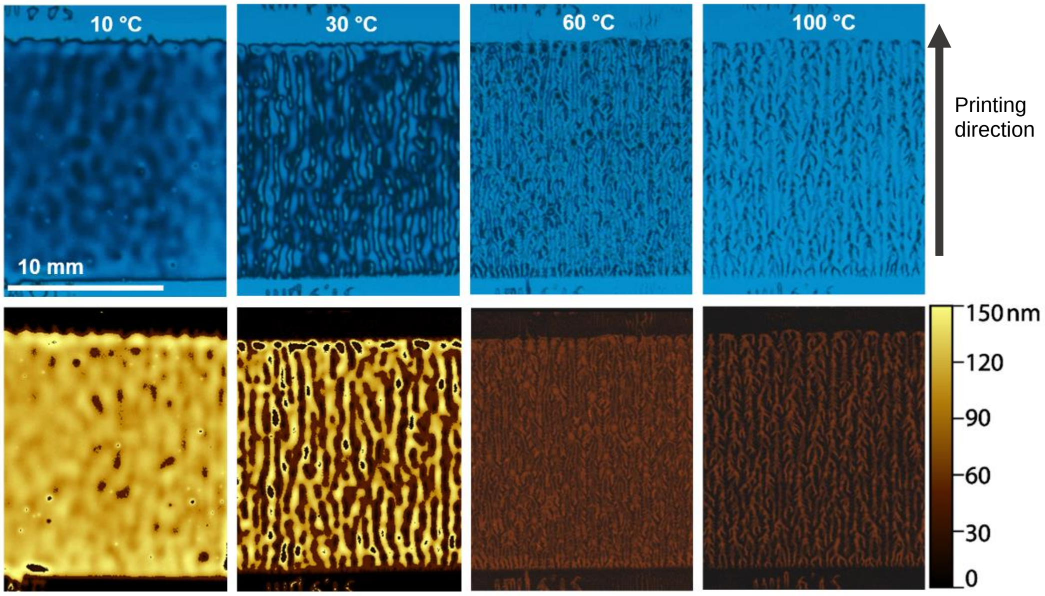


Figure 4: Images of samples printed with PEDOT:PSS dispersion at different temperatures. Upper row: images taken under blue illumination. Lower row: Calculated thickness profile using the ICR method. The influence of the substrate temperature on the formation of viscous fingering and the fluid transfer is clearly visible.

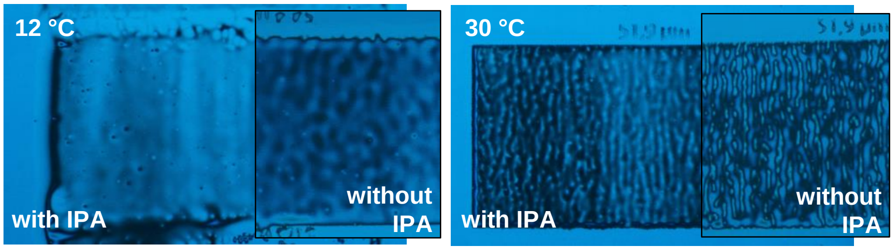
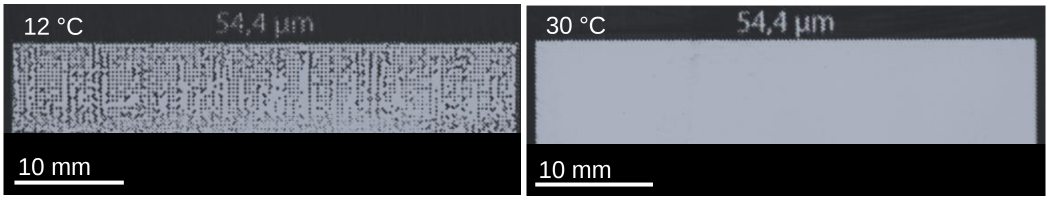


Figure 5: Images of samples printed with a mixture of PEDOT:PSS dispersion with IPA for a substrate temperature of 12 °C and 30 °C. For a comparison, the samples printed with non-diluted PEDOT:PSS are embedded.

Conductive silver ink for flexographic printing

In order to see if a dewetting of the transferred fluid can be effectively prevented in a short time slot after the substrate left the printing gap, we printed a conductive silver ink, which is optimized for flexographic printing on PET foil. Hence, this ink has a higher viscosity and typically dewets on glass substrates. The two images in Figure 6 show samples printed with the same engraved field. One was printed at a temperature of 12 °C, the other at 30 °C. Both samples were heated on a hotplate directly after printing. The images do not show any height information nor detailed surface topography, but this way the difference between the two temperatures is visible at a glance since parts not covered with material appear black. As can be seen, at a temperature of 12 °C the ink has not formed a closed layer. Directly after the transfer to the substrate the film started to dewet leading to points not covered with ink. Likely, the ink was also not transferred as a closed layer due to the high viscosity. At a temperature of 30 °C the ink formed a completely closed layer. The increase in temperature lead to a lower viscosity enabling a better spreading of the ink. Due to the faster evaporation of the solvent a dewetting could be efficiently prevented. Other samples and measurements could show that the ink volume transferred to the substrate is larger for higher temperatures.



(a) (b)

Figure 6: Images of the printed silver ink samples. (a) Layer started to dewet at 12 °C before it was dry. (b) At 30 °C, the layer was already dry before it could start to dewet.

4. Conclusion

In order to better control the film formation of the ink formulations used in functional printing, we developed a possibility to tune the temperature of a variety of possible substrates in the sheet-to-sheet based gravure printing process. With this, the viscosity, surface tension and evaporation rate of the material can be influenced, which in turn strongly effects the defects and pattern formation, like viscous fingering, in ultra-thin layers. Experiments show that controlling the substrate temperature not only highly affects appearance of fluid dynamical effects but also determines the spreading, wetting and leveling as well as the amount of transferred ink.

Acknowledgements

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