The Influence of Post-Treatment Strategies in Inkjet Printing on the Morphology of Layers and the Functional Performances of Electronic Devices

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Abstract

A UV curable ink is deposited on substrates by inkjet technology with constant jetting parameters and identical digital images. As the ink is composed of non evaporating liquids the patterns stay wet until being exposed to UV light. This enables the precise control of the transition from the liquid to the solid phase. By adjusting the time scales and energy levels of the post-treatment processes diverse pattern morphologies with different three-dimensional profiles are generated. We investigate the influence of the employed post-treatment strategies on 3D-functionalities. In addition, different treated UV ink layers are used in simple electronic devices and characterized by their performance. The results reveal exemplarily the significance of the process steps after the deposition of each single drop.

Introduction

Inkjet-Technology: State-of-the-Art

In *graphic printing* inkjet has become a state-of-the-art-technology for Small Office/Home Office-, Coding/Marking-, Proof-, Photo-, Wide Format-, and Label-Printing. Moreover, manufacturers of printheads like HP, Xaar, Fujifilm Dimatix, or Konica Minolta, develop sophisticated printheads for high resolution printing at high velocities and on wide formats. These are utilized in productive machines addressing traditional mass markets like newspapers or books printing. For this purpose, various companies like MGI, Konica Minolta, Screen, Landa, Fujifilm, Kodak, HP, or Océ/Canon supply sheet fed as well as web fed machines. These advancing developments will in future contribute not only to manufacture graphic application by inkjet printing, but also layers with certain functionalities beyond color [1].

In this field of *functional printing*, the inkjet technology has attracted a great interest in research. In the period from 1990 to 1999 only 256 scientific articles with the terms “inkjet” or “ink-jet” in the title, the abstract, and the keywords were published, from 2000 to 2009 the number of publications was already 1620 (research was done on Web of Knowledge/Web of Science, Thomson Reuter, 05.06.2012). This growing interest is to be explained by unique characteristics of the inkjet technology: the non-contact process is digital, the drops are deposited with high accuracy, and the material consumption is low. Recent examples for inkjet printed functional patterns are the deposition of graphene-based inks for thin-film transistors [2], the formation of active layers for solar cells [3], or the development of an inkjet printed humidity sensor [4]. Beside such applications for printed electronics, there are further fields being addressed like tissue engineering [5] or three-dimensional patterning [5, 6]. It is apparent, that inkjet printing is used for diverse approaches and applications, and the technology has become a versatile tool for “inkjet-based micromanufacturing” [7].

Workflow for Inkjet Printed Functionalities

With the prospective implementation of inkjet printing for the high-through put manufacture of functionalities, it will be necessary to develop workflows. In graphic printing the general workflow is divided in the three main parts of *prepress*, *press*, and *post-press*. This approach can be adapted to the inkjet printing of functional layers. However, depending on the application it also has to be reconsidered.

In this report, we focus on such considerations and show the influence of different applied workflows for a model process, where three-dimensional patterns in the range of micrometers are built. In the section for the prepress we introduce theoretical aspects and practical results of influencing parameters like the substrate, the ink, the environment, the setup of the printer, and the digital image. In the section about press we investigate the influence of the relation between the printing and post treatment of the ink. The experiments reveal that different patterns result only by changing the workflow, although the applied ink, printer, environment, and substrate is kept constant.

Experimental Setup

The experiments were done on a Dimatix Materials Printer 2831 (Fujifilm Dimatix Inc.) employing printheads ejecting a nominal drop volume of 10 pL and 1 pL. The nozzles are driven by piezoelectric elements. The drop ejection frequency was 10 kHz, all prints were done with one nozzle. The UV curable ink Hyperion Pro Wet (Tritron) was printed at a nozzle temperature of 40°C. Digital images were prepared to print single drops, lines, and regular hexagons. All samples were printed on glass substrates (VWR), cleaned for 3 minutes in acetone in an ultrasonic bath.

The manufactured capacitors consist of two electrodes printed with a silver-nanoparticle ink (EMD5603, SunChemical) and an insulating layer composed of the UV curable ink. Sintering of the silver ink was done on a heating plate at 120°C for 10 min. To ensure wetting of the stacked layers, a corona treatment was applied after solidification of the insulating layer.

Microscope images were taken using Leica DM4000 (Leica Microsystems). The layer thicknesses were measured using Dektak 150 Surface Profiler (Veeco). For UV curing the BlueWave-75 (Dymax Light Curing Systems) was applied. The measurement for the capacitances was done with a LCR meter (Agilent E4980A precision LCR meter).

Results and Discussion

Prepress

The main objective of the prepress is to set all parameters enabling a reliable manufacture of a printout with specific characteristics. Among others, the settings determine…

(1) …the formation of drops, which characteristics should be constant and reproducible over the complete printing time (drop volume, jetting straightness, and drop shape).

(2) …the information about the time for the ejection and the place for the deposition of each single drop during the printing step.

(3) …the post treatment of the drops in terms of the time of the treatment after deposition, and the resulting effect (drying, solidification, pinning, etc.).

The influencing parameters are numerous, they comprise aspects of:

- the environment (temperature, humidity, gas),
- the substrate and its pretreatment,
- the ink (composition, viscosity, surface tension, density, vapor pressure),
- the digital image (drop arrangement, image size, drop spacing),
- and the printing device, its working principle (pixel or vector based, 1-bit or greyscale, motion system), the applied printhead (number of nozzles, temperature, working principle), substrate temperature, and the printhead settings (waveform, drop ejection frequency).

It is important to note that each parameter can interact with others and this interaction can have an impact on the resulting pattern. One example of such a prepress parameter is the setting of the driving waveform, which defines the voltage being applied to the piezo element over time. It has been shown, that the design of the waveforms can be used to optimize and change the drop ejection properties in a wide range [8].

We studied the drop formation of the UV curable ink applying a standard waveform as given in fig. 1a. The results are in accordance to literature [8, 9]:

By increasing the maximum voltage, the drop volume increases proportionally (fig. 1b). However, the energy introduced to the ink chamber is not high enough to eject the nominal given volume of 10 pL. In addition, the velocity of the head of the drop increases by increasing the voltage. In contrast, the pinch off time for the tail end (break off of the drop from the nozzle orifice) stays constant at 37 µs. This results in longer tails at higher voltages (fig. 1c, d).

When printing line patterns at different drop spacing, the change in the maximum voltage has an influence on the resulting line widths. A difference of 4 V resulted in the changes of line widths as given in fig. 1e and is to be explained by the change in the volume of the drops. The same waveform was also applied for printheads ejection a nominal volume of 1 pL. Here, the introduced energy was too high and drops with a higher volume than the nominal one were formed.

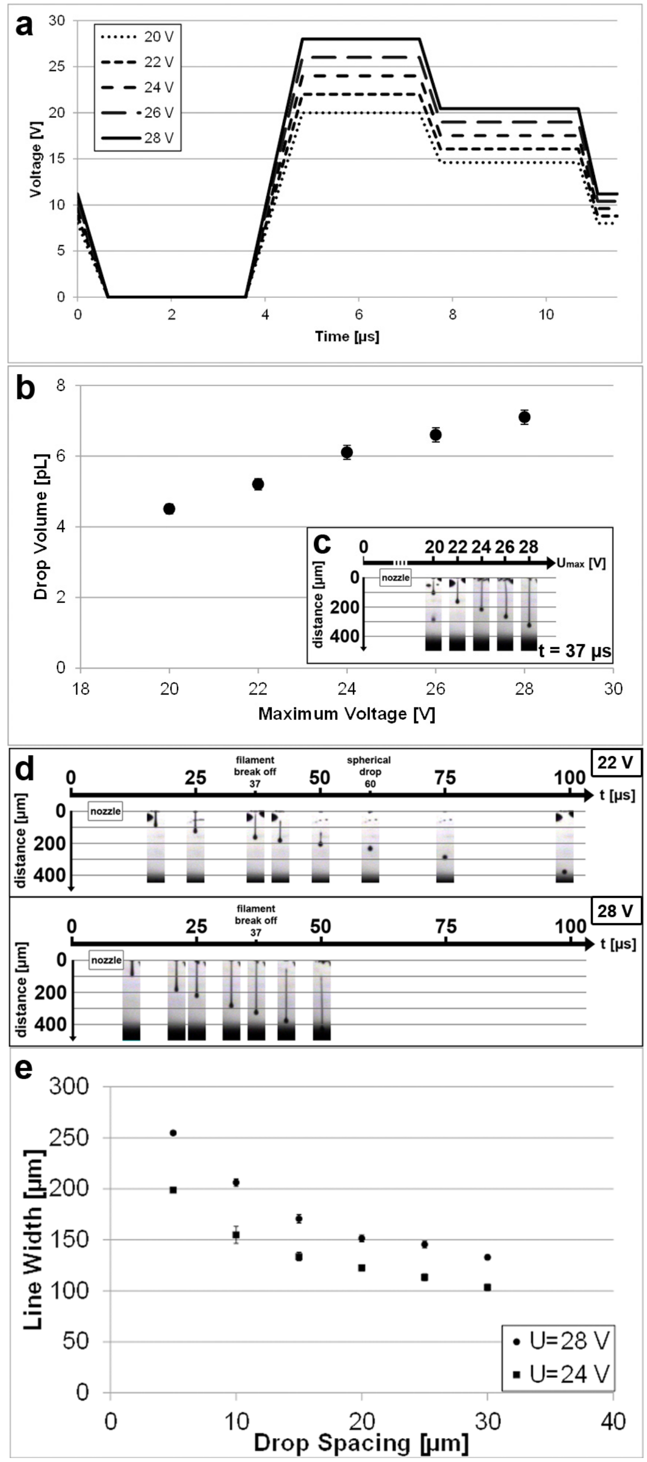

Figure 1. *Prepress Parameters: a) Applied Waveform, changing the maximum voltage between 20 V and 28 V; b) Increasing drop volume with increasing maximum voltage (for each measurement point the mass of 1 million drops was determined three times); c) Drop ejection at drop pinch off time of 37 µs, with increasing maximum voltage, the tail becomes longer, and the velocity of the drop is faster; d) Examples for the drop ejection at maximum voltages of 22 V and 28 V, the pinch off time (filament break off) is constant, at low voltages the drop becomes spherical, at high voltage the drop forms a long tail; e) Resulting widths of lines for 24 V and 28 V depending on drop spacing and max. voltage*

Press (Printing and Post-Treatment)

Line Patterns

In first experiments it was observed, that single drops spread after deposition until being solidified by exposure to UV light. Therefore, we introduced a spreading time t_{spread}. At t_{spread} = 3s the drops showed a diameter d of 92 µm ± 2 µm, at t_{spread} = 15s the diameter d was 115 µm ± 3 µm. Several experiments revealed that this spreading takes part with a dependency of $d \sim t_{spread}^{1/6}$ to $d \sim t_{spread}^{1/10}$. These deviations in the results are mainly due to the manual procedure of the time measurements of t_{spread}. However, the relations which were found correspond to other results and follow roughly Tanner´s law of spreading [10, 11, 12].

As already shown, the drop volume can be changed to adjust the width of inkjet printed lines (fig. 1e). In addition, it is well known that the drop spacing has a major influence on the width and thickness of printed lines [13, 14].

In additional experiments we combined the drop spacing and the spreading of the ink to adjust the morphology of the line patterns: the maximum voltage of the driving waveform was kept constant at 26 V (corresponding to a volume of 6.6 pL ± 0.2 pL). Lines were printed in printing direction by changing the drop spacing between 5 µm and 30 µm and by changing t_{spread} between 3s and 20s. The line patterns, widths and line thickness peaks are given in fig. 2a-d.

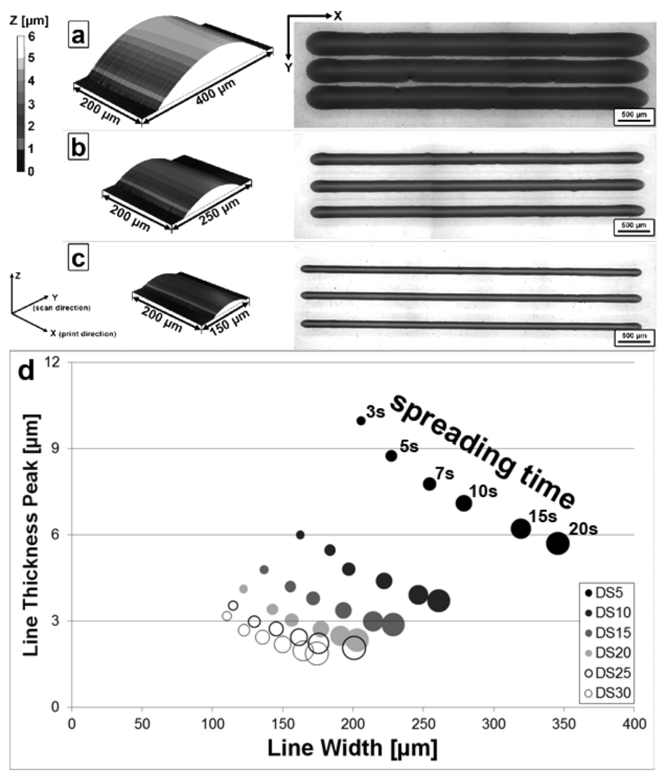

Figure 2. Line Formation depending on Drop Spacing (DS [µm]) and time between deposition and UV curing (t_{spread} [s]): a, b, c) Examples, Microscope images and 3D Profiles of segments of lines; a) DS = 5 µm, t_{spread} = 20s; b) DS = 15 µm, t_{spread} = 7s; c) DS = 30 µm, t_{spread} = 3s; d) Graph showing the influence of drop spacing and t_{spread} on line width and thicknesses of inkjet printed lines (deviations in the line widths and thicknesses are up to 5 %)

These results show that the morphologies of patterns can be adjusted in a wide range only by changing two workflow parameters (drop spacing and t_{spread}). It is obvious, that the widest lines form when printing at the lowest drop spacing of 5 µm and the longest spreading time of 20 s (fig. 2a), and the thinnest lines in diameter result from printing at the highest applied drop spacing of 30 µm and the shortest spreading time of 3 s (fig. 2c).

Regular hexagons

In further experiments regular hexagons were printed. The digital image given in fig. 3a was used and three workflows were applied with following results:

(1) The complete pattern was printed and then cured by exposure to UV light (fig. 3b): As printing was done with only one nozzle, the printing time was about 10 min. During this time, the ink spread over the substrate and the final shape of the hexagons became irregular.

(2) Each drop was deposited and subsequently pinned by an exposure to UV light for only 0.01 s before the adjacent one was printed (fig. 3c). This post-treatment prevents the ink from spreading, whereby the drop stays liquid. The resulting hexagon shows a much more regular morphology with continuous lines.

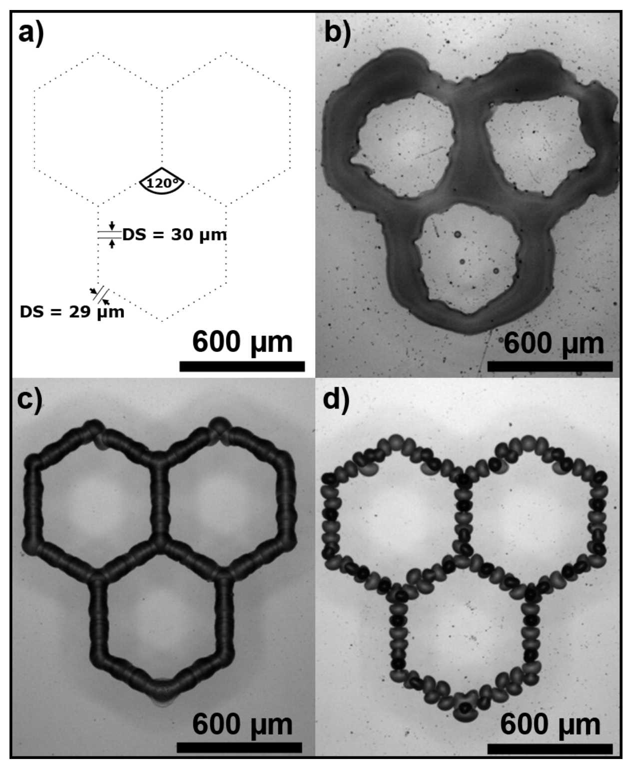

Figure 3. Resulting patterns of regular hexagons: a) Digital image adapted for regular hexagons with a homogeneous distribution of material in each line of the hexagon; b) The complete image was printed and then UV cured; c) Each drop was pinned by a short exposure to UV light (0.01 µs) before the adjacent drop was printed; d) Each drop was solidified by long exposure to UV light (3s) before the adjacent drop was printed

(3) Each drop was deposited and subsequently solidified by an exposure to UV light for 3 s before the adjacent drop was printed (fig. 3d). In this case the previous drops form a new surface for the following ones. The ink shows a better wettability for the glass substrate compared to the surface of the solidified drops. This results in a pattern where individual drops are visible.

We already reported on the application of such hexagons for the mechanical stabilization of fragile membranes [15]. In this application continuous lines with a low width are required. Therefore, the second workflow with a pinning of each single drop should be implemented for the manufacture.

Capacitors

For printed electronic devices it is important to build layers with a good defined morphology. The UV curable ink was applied as insulating layer in fully inkjet printed capacitors. The drop spacing was varied between 20 µm and 40 µm resulting in capacitors with poor capacitances between 0.2 nF/cm² and 0.8 nF/cm² at 40 Hz.

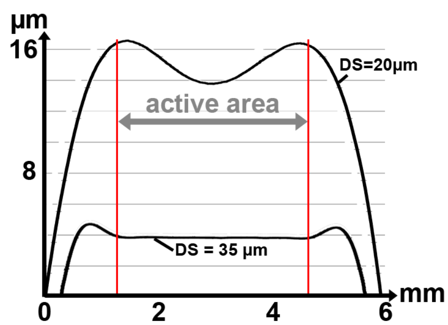

Figure 4. Line scan of profiles of insulating layers for capacitors, printed at different drop spacing

One major result was the morphology of the insulating layers (fig. 4). It is obvious, that with increasing the drop spacing, the layer thickness is reduced, and the capacitors show a better performance. In addition, the profiles of the layers show very different morphologies: For a drop spacing of 20 µm the layer is not flat, but curved. When the top electrode is printed, the thickness in the active area varies in a range of 14 µm and 16 µm. In contrast, the layer thickness at a drop spacing of 35 µm is constant (4 µm) within the active area.

Conclusion

A model process for the manufacture of three-dimensional patterns in the range of micrometers was applied to describe a selection of workflow parameters influencing the resulting layer morphologies.

For printed functional layers, in prepress parameters like the environment, the substrates, the inks, the digital images, and the setup of the printer with related parameters (like its principal of work, the motion system, and) have to be considered. We have shown exemplarily the influence of the applied waveform settings on the drop formation and line morphologies.

In the press step we found for the applied ink-substrate-interaction, that the spreading of the ink can be controlled to adjust the layer morphology. The time between the deposition and UV curing of the pattern becomes an important parameter for the workflow. In addition, we applied three different workflows for printing patterns composed of continuous lines. Each single drop which was deposited can be pinned, solidified, or still being wet before the adjacent one is printed. This changes the morphology of the resulting pattern. These examples reveal that an inkjet process can be applied versatile, and the workflow has to be adapted carefully to the particular requirements.

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Author Biography

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Acknowledgment

We thank Khushbeen Kasania for the experiments.