Micro-Three-Dimensional Patterning by Inkjet Printing of UV Curable Inks

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Abstract

A UV curable ink serves as a model fluid to find a basic description of the formation of micro-three-dimensional patterns by inkjet printing. The ink was deposited on a rigid surface to form solid lines after irradiation with UV light. The dimensions of the resulting patterns were analyzed with regard to the following settings varied: (1) drop spacing; (2) number of active nozzles; (3) orientation of the lines parallel or perpendicular to printing direction; (4) number of layers printed on top of each other. In addition, two different time-modes of the irradiation with UV light were applied to investigate the influence of printing ´wet-in-wet´ or ´wet-in-dry´: either the irradiation was carried out in one step after the complete printing process or in multiple steps during the printing process. The reported results contribute to understand the formation of functional patterns by inkjet printing in general. Furthermore, based on previous works we show examples like microsieves in which UV curable inks can be applied to create functional patterns.

Introduction

We have shown recently that UV curable inks and polymer solutions can be employed to manufacture functional patterns like microsieves and reinforcing patterns [1, 2]. This article addresses a fundamental research on the application of these materials by inkjet printing. The main purpose is to provide fundamental remarks on effects in the patterning process, following these two sections:

- In a preliminary review on inkjet printing we give a general overview on research topics and a classification of inkjet printed functionalities. Furthermore, possible effects and interactions of applied drops on a substrate are considered. This part shows the versatility of inkjet printing in the patterning of micro-three-dimensional elements.

- In fundamental experiments arrays of drops and lines composed of stacked layers are printed employing model fluids. The morphology of the resulting patterns is related to the parameters of the employed digital images, the setup of the printer, and the moment of the post treatment process.

Preliminary Review on Inkjet Printing

Classification and Research Topics

Traditionally, inkjet printing is to be considered as a digital and non-impact printing technology to manufacture graphic applications [3]. However, in recent years further applications like electronic devices are manufactured [4], and therewith inkjet printing can also be classified as a direct writing [5], and microdroplet generation [6] technology.

In graphic printing inkjet technology still is emerging due to the application in reliable high-throughput and high-resolution machines [7, 8]. This opens a new market beside small and home office printers.

Furthermore, in research the number of publications on inkjet printing is growing [5] and their topics focus on a broad range of approaches:

- Fundamental research is e.g. done on the jetability of inks [9, 10], the formation of coffee rings [11, 12], and the understanding of the patterning process [13, 14].
- Inkjet inks are developed with due regard to their jetability and necessary post treatments like sintering [15, 16].
- The inkjet printing technology is further developed, for example to gain advanced printheads [17] or to evaluate existing devices [18].
- Applications with functionalities beyond the traditional one of color are investigated. These can be (a) electronic devices [4], (b) optical applications like microlense arrays [19], (c) functional patterns like microsieves [1, 20], and (d) biological applications [21]. (Notice: Graphic applications have the functionality to address optic readers like the human eye or barcode readers and can therewith be subordinated under optical applications)

This state of research indicates that inkjet printing is mostly well understood and generally employable as a materials deposition technology.

Possible Effects and Interactions of Sessile Drops

The deposition of drops takes part in an additive manner. Subsequently, a post process like sintering, evaporation, or chemical reaction can result in different effects on the underlying material as shown in fig. 1:

- Additive (Fig. 1a): The drop adds material to the surface to form a layer or to modify its chemical properties for example by adding a monolayer of molecules.
- Transforming (Fig. 1b): The components of the ink transform the underlying material. It can be completely or partially etched [22]. Furthermore, deforming can occur when the underlying material is intermediately dissolved, transported (for example due to the coffee ring effect), and deposited as a new pattern [23]. In addition,

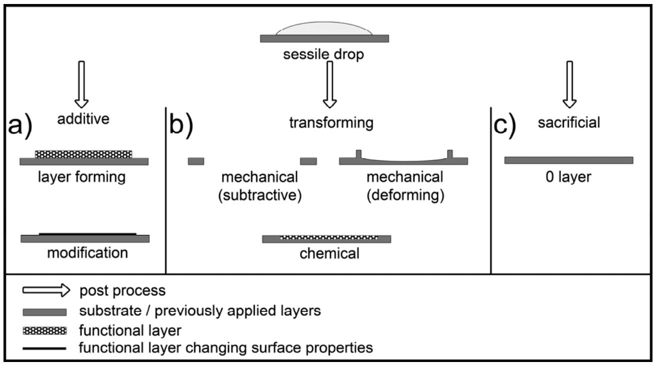

***Figure 1**. Possible effects of a drop on the underlying material: a) additive; b) transforming; c) sacrificial*

a chemical reaction between the ink and the underlying materials can result in changed surface properties.

- Sacrificial (Fig. 1c): An ink is printed on a substrate to fulfill an intermediate sacrificial function, for example to act as a mold [20]. After evaporation of the ink no further material was added by this ink and the underlying material has not been affected.

Moreover, during the printing process a drop being deposited does not only interact with the solid surface of a substrate. The main criterion here is to investigate which surfaces get in contact with a printed drop at the moment of its impact. In fig. 2 we show four types of interactions for an additive effect:

- Liquid-Solid Interaction (L-S type, Fig. 2a): The printed drop only interacts with the substrate or a previous deposited and post treated layer.
- Liquid-Liquid Interaction (L-L type, Fig. 2b): The drop is printed on a previous deposited drop or layer which still is in a liquid state.
- Liquid-Liquid-Solid Interaction (L-L-S type, Fig. 2c): A drop is printed partially on a previous printed liquid drop and partially on a solid material underneath. This type is common to form patterns by overlapping deposited drops.
- Liquid-Solid-Solid Interaction (L-S-S type, Fig. 2d): A drop is partially printed on two different solid materials, for example the substrate and a previous applied solidified layer. This approach can for example result in a morphology of the patterns of stacked coins [13].

The example in fig. 2e shows that during a printing process various types of interaction can occur: Here, first a drop is printed on a solid substrate (L-S); then the adjacent drop is partially printed on the previous printed drop and partially on the substrate (L-L-S); after post treatment of both drops a layer is formed; the next drop is subsequently printed partially on the substrate and partially on the layer (L-S-S).

These remarks on the effects and interactions of inkjet printed drops are however not comprehensive. For example it is conceivable that a drop is dried before it touches the surface. But these few examples elucidate how versatile inkjet printing is employable to manufacture micro-three-dimensional patterns.

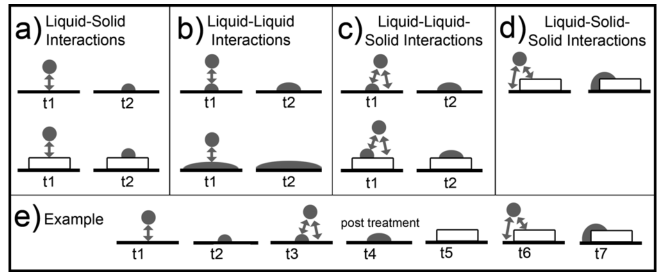

***Figure 2**. Different types of interaction of printed drops; times t indicate a sequential process; a) Liquid-Solid Interactions; b) Liquid-Liquid Interactions; c) Liquid-Liquid-Solid Interactions; d) Liquid-Solid-Solid Interactions*

Experimentals and Results

Experiments were taken out on a Dimatix Materials Printer 2831 (Fujifilm Dimatix Inc.) employing 10 pL printheads with piezoelectric driven nozzles. The drop ejection frequency was set to 1 kHz, all prints were done with one nozzle resulting in a line-by-line printing of the image.

One main important aspect was to investigate the influence of the moment of the post treatment process on resulting patterns. Therefore, two ink systems were chosen, one solidifying upon evaporation, and another one, which is cured by exposure to UV light: a solution of 1 wt% polymethylmethacrylate (PMMA) dissolved in anisole; the UV curable inks UFX7683 (Sunjet), and Hyperion Pro Wet (Tritron). Patterns of single drops and lines were printed on glass substrates (cleaned in ultrasonic baths of toluene, acetone, and isopropanol), and PMMA films.

Contact angle measurements were done on the OCA 20 (DataPhysics Instruments GmbH), microscope images were made using Leica DM4000 (Leica Microsystems). The layer thicknesses were measured using Dektak 150 Surface Profiler (Veeco). For UV curing the BlueWave-50 (Dymax Light Curing Systems) was applied.

Layer Morphology vs. Digital Images

The relation between digital images and resulting patterns was investigated by printing one layer composed of drops which are placed next to each other in the direction of printing, only getting in touch at the contact line.

On glass, the drop diameter of the PMMA solution was 71.35 µm ± 1.3 µm. Therefore, in the first approach the layer was printed from one digital image with a drop spacing of 70 µm in printing direction. Here, most of the drops merge forming short lines, only some single drops arise (fig. 3a). In this case the adjacent drops are deposited at the drop ejection frequency. Thus the previous printed drop still is wet (L-L-S interaction).

To obtain the demanded array of single drops, in the second approach two image separations were employed with a drop spacing of 140 µm, whereas the drops of the second image separation had an offset of 70 µm to the drops of the first image separation (fig. 3b). Both image separations were printed after each other with a time delay of several minutes. Hence, the time between the impacts of adjacent drops was in such a range, that the previous printed drops already solidified before adjacent drops were printed (L-S-S interaction).

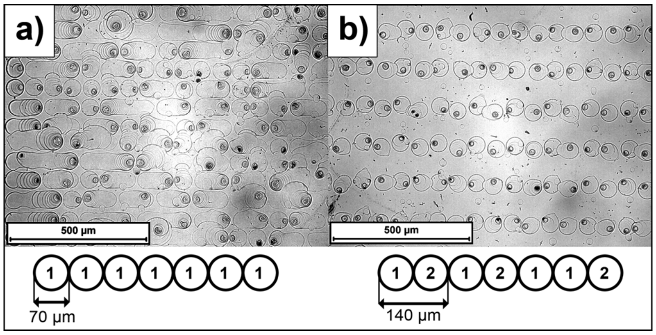

Figure 3. Drops printed next to each other employing a) one digital image with a drop spacing of 70 µm and b) two digital images with a drop spacing of 140 µm applied successively (the contrast of the microscope image was increased)

This experiment reveals that a functional layer can be based on one or several digital image separations leading to a different morphology of the resulting patterns.

Stacked Layers and Post Treatment

Printing of stacked layers can be employed in two modes:

- Intermediate Post Treatment Mode (IPT-Mode): Each deposited layer is post treated before the next is printed on top.
- Post Treatment Mode (PT-Mode): All stacked layers are printed before post treatment takes place.

We already reported on the printing of line patterns composed of stacked layers of the PMMA solution on a PMMA film [2]. Here, the first printed layer spread to a width of about 260 µm, the layers printed on top revealed only a line width of 160 µm. The reason for that are different contact angles: between the ink and the substrate a low contact angle of 6.0° ± 0.7° results in wide spreading. After deposition of the first layer, this solidifies immediately due to evaporation. For further layers on top, an increased contact angle between the ink and the solidified layer of 21.0° ± 0.5° results in narrower lines.

To investigate the difference between the IPT- and PT-mode we now approached employing a UV curable ink which enables to control the post treatment by exposing the layers to UV light. The contact angle on the substrate is 5.2° ± 0.32°, on a printed and UV cured layer 21.1° ± 2.1°. Lines composed of up to five stacked layers were printed at drop spacing of 15 µm, 25 µm, 35 µm, and 50 µm. The measured maximum thicknesses reveal a major difference between the two modes: Lines printed in the IPT-mode are more than twice thicker than lines printed in the PT-mode.

This experiment shows that employing the same ink, printer, and image can result in a very different geometry of the patterns depending on the mode of the post treatment.

Ink – Printer setup – Post Treatment

Lines were printed oriented in and perpendicular to the printing direction at low drop spacing on a glass substrate. For the PMMA solution drops merged to a connected line when deposited in printing direction (L-L-S interaction). However, perpendicular to printing direction the previous printed drop solidifies upon evaporation before the adjacent drop is printed next to it resulting in the line morphology of stacked coins [13] (L-S-S interaction).

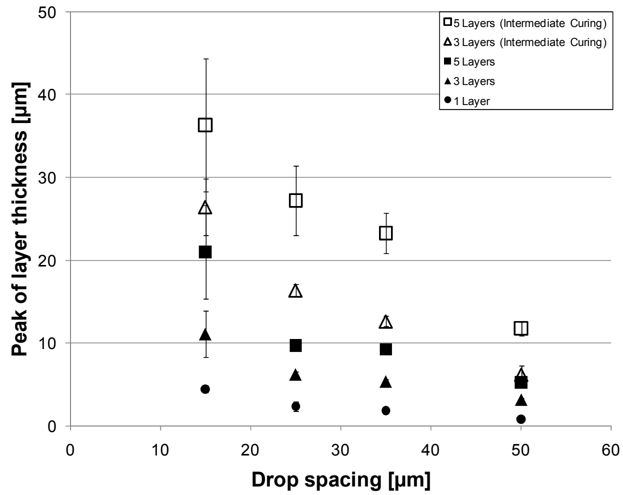

Figure 4. Peaks of the layer thicknesses of lines printed at different drop spacing and two post treatment modes

For the UV curable ink Hyperion Pro Wet the morphology of the lines was independent from printing direction, because the drops are printed wet-on-wet when no solidification takes part on the substrate (L-L-S interaction). However, introducing the post treatment step of UV light curing during the printing process resulted in a line morphology comparable to stacked coins [13]. In contrast to the IPT-mode for stacked layers, here the post treatment was done in-line (Inline-IPT-mode) resulting in a change to L-S-S interaction.

These experiments show that employing the same ink, image, and printing parameters (like drop spacing) can lead to a different line morphology. This occurs from the interaction of the setup of the printer (number of nozzles), the orientation of the image with regard to printing direction, and the moment of post treatment of the ink.

Conclusion

We reported on fundamental remarks on the manufacture of micro-three-dimensional patterns by inkjet printing. Deposited drops can be applied to add material, transform it, or to fulfill an intermediate function. Furthermore, when adding a material, the applied drops can interact with previously printed, liquid patterns, or with solid parts of the substrate or previous deposited and solidified patterns. In basic experiments we have shown that beside ink properties and printing parameters the applied printer setup in combination with the image, the printing direction, and the moment of post treatment, have a great impact on the resulting patterns.

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