Inkjet Printing of Phase-Change Materials With Xaar1001 Printheads

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Abstract

Inkjet printing of phase-change or hot melt materials allows to produce etch masks by digital and additive processing, thus enabling highly efficient fabrication of printed circuit boards, solar cells etc. Previously the binary inkjet printing with drop volumes of 50 pL was demonstrated with Xaar126 end-shooter printheads.^[1] The present work describes new results on printing with Xaar1001 printheads. These printheads offer both, grayscale printing with a subdrop volume of 6 pL and excellent reliability by way of their unique 'true throughflow' capability, respectively.

While the advantage of grayscale printing for high-resolution patterning is obvious and straight forward, the complexity lies in the recirculating ink systems that provide the constant ink flow through the printhead channels. A narrow temperature range has to be established throughout the total ink path, which avoids hot spots that would damage the inks as well as cold spots that counteract the ink flow rate. Print results with Sunjet Crystal HEP9520, operating between 80 °C and 90 °C, clearly show good droplet formation for 7 distinct gray levels spanning a range from 5 to 37 pL with increments of 5.3 pL at a frequency of 5 kHz.

Introduction

Inkjet printing has lately proven to be a viable alternative to some subtractive patterning techniques. For specific applications inkjet printing provides sufficient resolution, volume control and positioning accuracy, where the advantage of the versatility of fluids to be used is of major interest to researchers and industrial users. While common inkjet ink formulations typically exhibit viscosities in the range less than 20 mPas with low contact angles, phase-change inks have drawn the attention due to the high contact angles,^[2] resulting in high aspect ratio structures as a result if increased viscosity through cooling of the ink during flight. These inks may be used as etch masks in printed circuit board manufacturing or as barriers in diffusion processes for solar cell manufacturing, where the direct application of the resist material reduces process steps and waste.

As phase-change materials are characterized by relatively high viscosities at room temperature, the ink system needed for handling these kinds of fluids in the Through-Flow Technology TM unique to Xaar 1001 printheads, requires careful system design in order to allow for constant low viscosities, the prevention of hot and cold spots as well as high flow rates for the removal of ingested air or debris.

Early experiments

The thermal impact of the ink and ink system on the actuator is of major importance for the final application. While the piezoelectric materials exhibits minor fatigue due to the their thermal stability lying distinctly beyond 100 °C, material combinations present in the assembly may not withstand differential thermal expansion and result failure of the actuator. A proof of concept for the handling of fluids in the temperature range for 70 - 100 °C, which is clearly outside the standard operating range of room temperature to 60 °C, was conducted utilizing an industrial lubricant (Statoil, Glideway 68) as an experimental equivalent due to its rheological behavior at the anticipated temperature.

As a first approach, our proprietary Evaluation Low Volume Ink System (ELVIS), which allows for simultaneous control of the flow, i.e. the differential pressure, and meniscus pressure solely through the interplay of hydrostatic overpressure and applied negative pressure, was modified to enable heating up to 100 °C. This was accomplished by introduction of resistively heated reservoirs, supply and return tubes as well as the printhead itself, which allowed for the control of temperature of the inward flowing liquid to 100 ± 5 °C, providing a suitable viscosity of 10-11 mPas. This system was jetting up to 42 pL droplets at frequencies up to 6 kHz and a duty cycle of about 15 % for the duration of multiple days, which proved basic feasibility.

Further experiments were performed using Dow Enlight[™] 1310 phase-change material. This highlighted many weak spots in the setup, including solidification of the material in the peristaltic pump used for recirculation, cold spots omitting continuous flow through the printhead as well as pressure drops throughout the system.

The following sections give an overview on the measures taken to minimize the impact of the Phase-Change Evaluation Low Volume Ink System (HELVIS) on the jetting performance of the Xaar 1001 printhead.

Heated Evaluation Low Volume Ink System (HELVIS)

Figure 1 shows a schematic of the final assembly of the developed ink system for phase-change materials in conjunction with throughflow inkjet printheads, achieving temperatures up to 120 °C.

It is essential to generate a constant temperature profile throughout the complete ink path, where excessive heating may disintegrate the ink and cold spots inhibit high flow rates necessary for the efficient removal of air bubbles and other ingestions.

The fluid tanks, as can be seen in Figure 1, are positioned above the printhead to generate a hydrostatic overpressure. In order to generate flow and prevent the fluid from leaking through the nozzles, negative pressure is applied to the outlet cavity, establishing a pressure gradient between in- and out tank alongside with a constant average meniscus pressure. For convenience and larger operational windows, negative pressure as well as overpressure may be attached to both tanks. Recirculation is ensured through a diaphragm pump (KNF NF 10).



Figure 1: Schematic overview of the assembled ink system with a cut-out revealing the interior of the outlet tank

The tank assembly is wire-eroded from a solid aluminum block, which then comprises the inlet and outlet tank, the recirculation path of the fluid between the tanks, jackets for the resistive heaters as well as the collet for the pump. Bottom and top lids were optimized to minimize the dead volume, accommodate the fittings for pressure application as well as floating sensors included for flow and fluid level control.

The heating time t of this assembly, neglecting the thermal conductivity and capacity of the fluid may be estimated by

$$t = \frac{Q}{P} = \frac{m_t \cdot \Delta T \cdot c_{th} \cdot R_G}{U^2 \cdot 60} \tag{1}$$

where m_t is the mass of the aluminum tank, ΔT is the temperature difference to overcome, c_{th} specific thermal capacity of aluminum, R_G resistance of the heaters and U the supplied voltage. For a temperature difference of 70 °C this results in a heating time of approximately 5 minutes.

A major temperature drop was expected due to the strong temperature gradient between the fluid temperature and the outside of the PTFE tubing connecting the tanks and the printhead. To reduce the gradient and therefore the need for superheating of the fluid within the tanks, resistive heating using Kanthal D wires was realized. Neglecting convective and conductive evacuation, the power needed may be estimated using

$$\Delta T = \frac{I^2 \cdot t}{\kappa \cdot A^2 \cdot \rho \cdot c_{th}}$$

$$P = R \cdot I^2 = \frac{l}{\kappa \cdot A} \cdot I^2$$
(2)
(3)

where I is the current, t is the time, κ is the electrical conductivity of the wire, A is the cross-sectional area of the wire, ρ is the density of the wire, c_{th} is the specific thermal capacity of the wire and ΔT the anticipated temperature difference.

The printhead itself poses the most critical component of the system, as it on the one hand represents the highest flow resistance due to the micron sized geometry of the channel and at the same time poses the least accessible building block. Additional proportionally controlled heaters (MINCO HK5575) were installed on two distinct locations within the printhead. A first heating element was located on top of the stiffener providing mechanical

strength to the actuator assembly. Its thermal mass occurs to be sufficient to enable homogeneous spreading of the temperature supplied by the heaters as well as the power dissipated from the internal electronics. A second heater was introduced close to the inlet and outlet connections as these are exposed to convective heat transfer from the surrounding air.

The pump head was faced against the outside of the heating tanks. Hence, viscosities were sufficiently low for the pump to operate but have been insufficient to cover the full flow rate spectrum of the system. In the current experiments flow rates are limited to the maximum of approximately 90-100 mL/min. Though diaphragm pumps are prone to creating rather large pressure pulses as a result of their mode of operation, no influence on the stability of jetting was observed during strobe analysis or printing.

Operation of the system described was verified by a comparative study of flow rates of a analog printing ink (MIT Ink Analog 106), which exhibits a viscosity of 11 mPas at room temperature and HEP9520 from Sunjet's Crystal Hotmelt Etch & Plating resist family which exhibits an equivalent viscosity at 85 °C.

Flow rates were recorded for different combinations of positive and negative pressure supplied to the in- and out tank, maintaining a constant average negative meniscus pressure. The results are displayed in Figure 2.



Figure 2: Flow rate as function of applied differential pressure for MIT Ink Analog 106 (25 °C) and Sunjet HEP (85 °C) exhibiting a viscosity of 11 mPas

As can be clearly discerned from coinciding measurements in the embodiment, flow rates are equal for both fluids and therefore, no obstructions or cold spots are present in the system.

Waveform development

Driving waveforms for the piezoelectric actuator were developed using a stroboscopic setup allowing for triggered illumination of droplets at various frequencies and duty cycles. Using Xaar's multipulse binary technology for grayscale droplet generation, 7 distinct dpd (drops per dot) levels could be generated, allowing for the modulation of drop volume from 5 to 37 pL.

For the anticipated applications in digital fabrication it is essential to omit satellite generation during droplet formation, which is on the one hand attributed to the characteristics of the fluid^[3] but may also be influenced using advanced acoustic patterns for firing. The latter make use of out-of-phase wavefronts arriving at the nozzle to determine the point of break-off and thereby control the forward movement of the droplet and the retracting motion of the meniscus.

As can be seen from Figure 3, stable and satellite free droplets could be generated at full duty cycle and a frequency of 5 kHz, which translates into 0.35 m/s production speed at 360 dpi in printing direction. The characteristic 3 cycle pattern, stemming from the shared-wall operation^[4] furthermore gives an indication of the velocity consistency between different cycles, i.e. neighboring channels, as well as deviation between differing velocities between the gray levels. The velocity characteristic for this waveform is depicted in Figure 4. The difference in droplet speed is about 1.5 m/s as worst case between 1 dpd and 7 dpd for this particular waveform, which would result in a deviation of 31.2 μ m on the substrate.



Figure 3: Depictions of jetting performance for Sunjet HEP9520 for 1, 3, 5 and 7 dpd [5 kHz, 95 °C, 100% duty cycle]

Volume was calculated from gravimetric analysis assuming a density of 1 g/cm³. The results are presented in Figure 4 show good linearity with increments of 5.3 pL.

Printing results

Test prints were produced with an engineering-type printhead on a custom-built x-y print rig at a resolution of 360 x 360 dpi and print velocity of 0.35 m/s, in order to characterize the printhead at the maximum frequency of the waveform produced. The experiments were performed using PMC02C (Hifi Industrial Film) as substrate, which was kept at room temperature.

Figure 5 visualizes the optically measured deviations from optimal placement for two actuator rows. As can be seen, variations are well within a confidence band of 20 μ m, exhibiting a σ of 4.95 μ m across the printhead and 7.4 μ m in printing direction.

The performance of the generated gray levels was evaluated by printing different structures at the standard resolution of the printhead. These patterns included straight lines along and across the printhead, differently angled lines, dot patterns, text as well as printed circuit layouts. A selection of the results is summarized in Figure 6. Feature sizes clearly differ and are attributed to the changing amounts of liquids, impact speeds (cf. Figure 4) as well as cooling conditions of the droplets during flight. While 1 through 4 dpd show insufficient coverage of the substrate and would therefore result in perforated etch masks, droplet volumes of the higher gray levels allow for continuous features at 360 x 360 dpi.



Figure 4: Velocity and volume characteristic for Sunjet HEP9520 [5 kHz, 85 $^{\circ}$ C]



Figure 5: Dot placement deviation from optimal 180 dpi at 6 dpd using Sunjet HEP9629 [0.35 m/s, 5 kHz, 85 °C, substrate at room temperature, x – across printhead, y – print direction, measured using Mitutoyo, QuickVision Elf]

In order to exploit the full potential of the gray level printhead, resolution should be improved across the printhead as well as in machine direction. Higher resolutions call for the application of multiple interleaved printheads in order to overcome the physical limit perpendicular to the machine direction and decrease of machine speed due to the frequency barrier of the waveform. An alternative approach is multipass printing, where single printheads or the stage are moved in order to interleave the previously printed patterns and therefore enable better coverage.



Figure 6: Print results of Sunjet HE9520 on PMX02C for 1 dpd, 3 dpd, 5 dpd and 7 dpd [0.35 m/s, 5 kHz, 360 x 360 dpi, 85 °C, substrate at room temperature]

Conclusion and outlook

In the presented experiments we have shown the basic applicability of Xaar 1001 with its grayscale and unique 'true throughflow' capabilities to the field of phase-change materials. The latter allows for higher reliability due to self recovery of channels after air or debris ingestion into the ink channel and better thermal consistency due constant supply of fresh ink and evacuation of excessive heat generated during piezoelectric actuation.

A proprietary recirculation ink system, based on the interaction of hydrostatic as well as externally applied positive and negative pressure, was designed to allow for consistent heating of the phase-change material and thereby replicating the flow behavior of conventional inks exhibiting viscosities of approximately 10 mPas.

A waveform, generating droplets of 5 to 37 pL with an average increment of 5.3 pL was proven to perform well up to 5000 Hz. This corresponds to a production speed of 0.35 m/s at the printhead's natural resolution of 70.05 μ m.

Print tests verified the anticipated operation of the printhead. Patterns printed on PMX02C at the determined maximum frequency of the present waveform showed dot placement accuracy of $4.95 \ \mu m$ across the printhead and $7.4 \ \mu m$ in printing direction at a substrate velocity of $0.35 \ m/s$. Continuous features

were found to form above a droplet volume of 26 pL using the contemplated combination of temperature, substrate and resolution. This, however, is strongly dependent on the kinetic energy introduced from the droplet during impact^[5] and may therefore be influenced by appropriate waveform development towards higher droplet velocities.

Future work will include acoustic preconditioning of the ink channel in order to optimize the droplet velocity profile, lifetime tests as well as closer study of the influence on the different cooling rates on the various droplet sizes generated.

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Acknowledgements

The authors would like to thank Tom Sutter from Dow Electronic Materials as well as Peter Walshe and Mike Pickrell from SunJet for kind support of the project.

Author Biography

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