# Inkjet Printing of Phase-Change Materials

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## Abstract

*Inkjet printing of hybrid phase-change inks from Rohm and Haas with Xaar 126/50pl binary piezoelectric printheads was investigated. These inks consist of a wax-like phase-change component and a UV-curable component that enable to produce thermally stable resist pattern after curing. These properties make the hybrid phase-change inks well suitable for printing of masks for a variety of plating or etching processes.*

*The print parameters for the hybrid inks were evaluated, and an operational window for best performance regarding drop formation and satellites was identified. With these print parameters it was possible to produce smooth lines and gaps as they are needed for resist masks. The width of the printed lines was 84µm at 470dpi printing resolution, while gaps of 47µm width were obtained at 527dpi. Furthermore, it was demonstrated that 2.5-dimensional free formed structures could be produced with multi-pass printing and intermittent UV-curing, with the capability to obtain single-pixel columns of 70µm diameter and up to 2mm in height.*

## Introduction

The fabrication of solar cells, PCBs and large-area electronics (such as backplanes for TFT displays) requires a number of patterning steps for conductive or functional materials, where usually resist layers are used to define the appropriate pattern for etching or plating processes. Conventional lithography processes with photoresist masks have the disadvantages of being more costly, requiring a considerable number of process steps and producing chemical waste. Inkjet technologies on the other hand offer the possibility to deposit a variety of materials in a direct digital printing process, and large substrate areas and complicated geometries like non-flat surfaces or distorted pattern don't set limits for deposition by inkjet printing processes.

One possibility for inkjet deposition is the direct additive printing of materials like metal-nanoparticle dispersions or conductive and functional polymers [1, 2, 3]. The complication of that approach, however, is in the strong dependence of the pattern formation and line width on properties like the surface energy of the substrates or the composition of the ink. This leads often to reduced resolution due to spreading of the inks on the substrate. To overcome this, the inkjet printing of resist masks for subtractive processing like etching or for deposition processes is an alternative approach for the patterning process of metals and other functional materials. This approach also allows the processing of materials that are difficult to deposit in a fluid-based additive process. Plain UV-curable resist inks have been employed for that purpose [4], as they result in good hardness and chemical resistance, but they are also very sensitive to the surface conditions, which can result in strong spreading before they are fixated by UV-curing. To limit these spreading effects, hot-melt or phase-change inks have been developed and e.g. already utilized for the production of thin-film transistors for TFT devices [5]. These types of wax-like inks are jetted above the melting point, and solidify almost immediately after impact on the colder surface. The drawback of these wax inks is the low softening and melting temperatures of typically in the range between 40 and 70ºC, which makes it not suitable for certain etching processes that require higher processing temperatures than this range.

In a new approach, inks were designed that combine the desirable attributes of both UV-curable and phase-change inks. The hybrid LithoJet™ inks from Rohm and Haas consist of a phase change component, which allows the printed ink to be pinned with very little spreading, while a second, UV-curable component facilitates the achievement of mechanically and thermally stable resist pattern after curing [6]. Furthermore, these inks consist of 100% solid materials, giving minimum shrinkage and eliminating volatile organics during processing.

In this paper, the application processes and parameters for printing of wax-like and hybrid phase-change materials in Xaar-type printheads are evaluated, and achievable pattern formations and structure dimensions are presented. Furthermore, the production of 2.5-dimensional free formed structures by inkjet printing of hybrid phase-change materials is demonstrated.

## Experimental

The inkjet printing with a range of phase-change materials was evaluated using Xaar's piezoelectric drop-on-demand printheads. These printheads have the advantage of offering a high intrinsic printing resolution, like 180dpi or 360dpi (for printheads with two actuator rows), as their operation is based on a shear-mode/shared-wall principle [7], and the number of active nozzles ranges from 126 up to 1000 for different printhead models. The combination of a high number of nozzles and high intrinsic resolution is an inherent advantage for printing of masks or functional materials, as the material can be laid down in a single-pass printing process. Multi-pass printing with several consecutive printing passes perpendicular to the printing direction would increase the risk of non-continuous lines or rugged structure edges.

The tests reported here were conducted with Xaar 126/50 printheads, supplying a drop volume of 50pl. This printhead model has 126 active channels with the nozzles aligned in a single straight line with 137.14µm spacing, thus providing an intrinsic linear resolution of 185dpi. Different resolutions across the print direction can be obtained by rotating the printhead against printing direction. However, only certain rotation angles provide the printing of the dots onto a square grid with an identical dot spacing in printing direction and across the printhead when the Xaar 126 printhead is operated in its typical three phase firing mode. The channels are sequentially assigned to A, B and C phases, which can be fired in two different phase orders, either in A-B-C or in the reverse order A-C-B.

Figure 1a shows one example of printing onto a square grid of pitch *d* for the case of firing order A-B-C. The printhead is rotated at an angle $\alpha$, and the y-axis indicates the printing direction. The location of the nozzles is shown as open circles. In this example the position of the nozzles of the B-channel and the C-channel are 1/3 *d* and 2/3 *d* displaced from the targeted grid positions, respectively. These displacements are precisely compensated in this example since the paper has moved the distances 1/3 *d* and 2/3 *d* when channels B and C fire due to their phase delays. As a consequence the dots land on the positions indicated as solid circles in Figure 1a, and thus all dots land on the square grid.

All angles $\alpha$, which result in printing onto a square grid, can be calculated according to formula (1), when printing in A-B-C phase order. In formula (1) *x* and *y* are the projections of the line between two consecutive A nozzle positions onto the x and y axis respectively. Table 1 compiles the first four results from formula (1) including the angle $\alpha$, the pitch of the square grid, as well as the corresponding dpi.

$$\frac{y}{x} = \left(N + \frac{1}{3}\right);\ N = 0, 1, 2,.. \quad (1)$$

Formula (2) applies to the calculation of the rotation for the reverse firing order A-C-B, and Table 2 compiles the results for the four lowest rotation angles. Figure 1b depicts the example for the case *y*/*x*=2/3 and A-C-B firing order.

$$\frac{y}{x} = \left(N - \frac{1}{3}\right);\ N = 1, 2,.. \quad (2)$$

**Table 1. Possible resolutions and printhead angles for A-B-C phase order (Equation 1)**

| N | y/x | angle α | pitch [µm] | dpi |
|---|---|---|---|---|
| 0 | 1/3 | 18.43 | 130.1 | 195 |
| 1 | 4/3 | 53.13 | 82.3 | 309 |
| 2 | 7/3 | 66.8 | 54 | 470 |
| 3 | 10/3 | 73.3 | 39.4 | 645 |

**Table 2. Possible resolutions and printhead angles for A-C-B phase order (Equation 2)**

| N | y/x | angle α | pitch [µm] | dpi |
|---|---|---|---|---|
| 1 | 2/3 | 33.69 | 114.1 | 223 |
| 2 | 5/3 | 59.04 | 70.6 | 360 |
| 3 | 8/3 | 69.44 | 48.1 | 527 |
| 4 | 11/3 | 74.74 | 36.1 | 704 |

It is obvious from Figure 1 that printing with an angled printhead results in a skewed printout, with the dots from neighboring nozzles landing at different grid positions. This can is compensated by angling the print bitmap prior to printing with the help of a suitable algorithm.

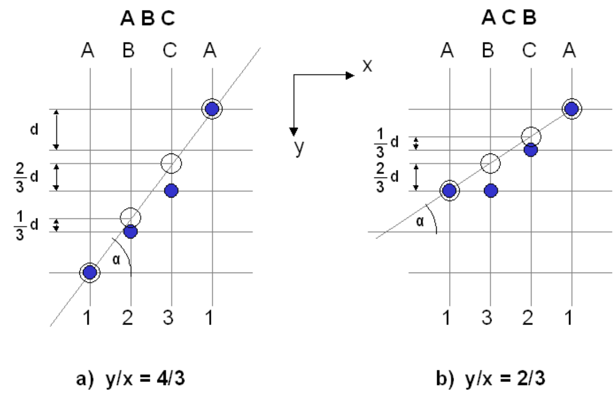


***Figure 1.*** *Principle of printing onto a square grid at higher resolutions with an angled Xaar 126 printhead, for examples with A-B-C phase order (a) and with A-C-B phase order (b); open circles indicate the nozzle position and solid circles the position of the printed dot on the substrate; printing direction is in y-direction*

Phase-change materials investigated for the inkjet printing process in Xaar 126 printheads included both wax-like materials, which solidify instantaneously when jetted onto a cold substrate, but which are not thermally stable above process temperatures of above approx. 50ºC, and 'hybrid waxes' which consist of a phase-change material combined with a UV-curable component. The hybrid inks used in this work were inkjet resists from the LithoJet™ series developed by Rohm and Haas. These inks are converted to 100% solid materials during curing, and no volatile organics evaporate in the processing of these materials, which makes them to an environmentally friendly choice as well. The hybrid inks don't settle on the substrate in a true phase-change reaction, but they thicken in viscosity significantly within a very short time after printing, allowing them to be pinned with very little spreading regardless of the surface conditions. The final UV-cure of the printed materials ensures mechanically stable structures, with a thermal stability up to 150-200ºC.

The following table lists the major physical and chemical properties of the LithoJet™ inks:

**Table 3. Physical and chemical properties of LithoJet™ inks:**

| | |
|---|---|
| Form | Semi-solid paste to solid at 25°C |
| pH | Neutral |
| Melting point | 50-60°C range |
| UV-curing dose | 300-1500 mJ/cm$^2$ @ 365nm |
| Hardness after cure | 3H to 6H depending on cure level |

The main part of the present work has been performed with two different versions of the LithoJet™ ink, *'Version A'* and *'Version B'*. In Figure 2 the viscosity curves for both ink versions above the melting point are given.

The recommended viscosity range of the Xaar 126 binary printheads is in the order of 8–12cP. The printhead was heated to the operational range of the phase-change materials (between 70 and 90ºC) with a special printhead fixture with resistor heaters and temperature control, and the temperature set points during the printing experiments were calibrated to the actual temperature inside the printhead. The ink supply consisted of a heated aluminum ink container, which was fitted to the printheads ink inlet, and heated to the same temperature as the printhead fixture.

The printing runs were either performed on a custom-built XY flatbed printing station, or on an 'XY Materials Deposition System' from iTi Corporation. Both stations were equipped with suitable UV-curing systems.

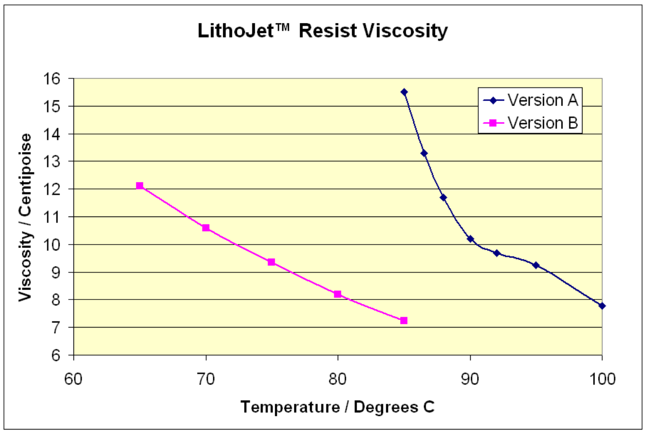


***Figure 2.*** *Viscosity curves for the LithoJet™ hybrid inks Version A and B*

Typical recommended drop speed for the production of uniform printouts is in the order of 5-6m/s, but higher or lower drop velocities could be beneficial for improving the print quality. Using the drop watcher system, the required actuator driving voltage for achieving different drop speeds in the temperature range between 73 and 86ºC was analyzed, as depicted in Figure 4.

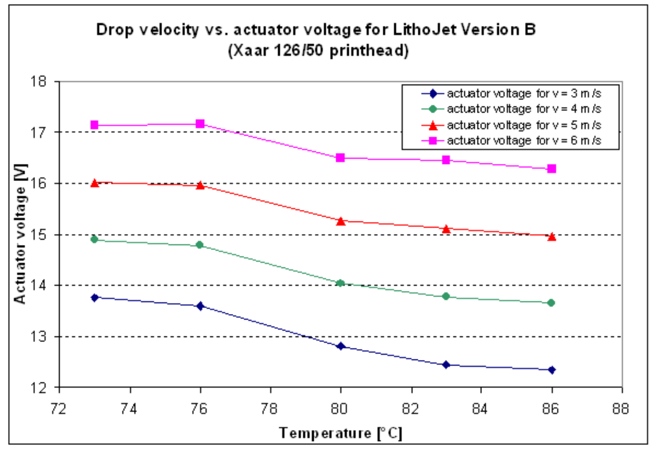


***Figure 4.*** *Actuator voltages required to obtain different ink drop velocities at a temperature range between 73 and 86ºC*

## Jetting Performance and Operation Window

### *Drop formation investigation*

The jetting performance of the LithoJet™ Version B hybrid ink in a Xaar 126/50 printhead was investigated using a stroboscopic drop watcher system. Figure 3 shows an image of the drops in flight, formed at 81ºC printhead temperature and 3kHz jetting frequency, with a drop speed of 5m/s. Maximum jetting frequencies of 5kHz were found to be feasible. Some satellite drops were formed, but for optimized printing conditions these satellites were expected to land at the same position as the main drop, as they follow it in a straight trajectory. It was also possible to achieve a slight reduction in satellite drops by further modifications of the printhead driving waveform.

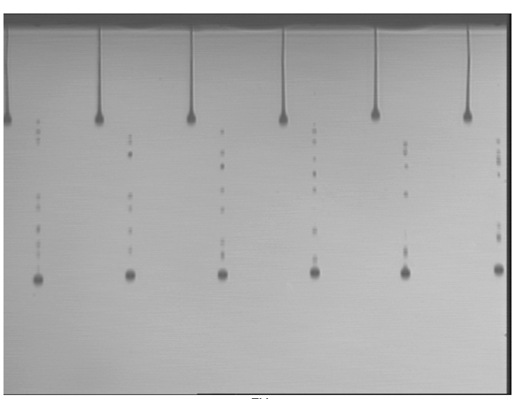

***Figure 3.*** *Drop formation with LithoJet™ Version B in a Xaar 126/50 printhead, 3 kHz jetting frequency, drop speed = 5m/s, T = 81°C*

### *Evaluation of the operation window at printing conditions*

To evaluate the operation window for the best printing quality, test patterns were printed at different operation conditions onto polyimide substrates, and analyzed according to following parameters:

- Observed angle deviation of jets
- Straightness and continuity of lines in printing direction
- Straightness and continuity of lines across printing direction
- Appearance of satellite drops
- Quality of printed compact areas

The operation conditions that have been varied for this analysis were temperature (between and 69 and 85ºC) and the actuator voltage (between 15 and 17V). Printing resolution for all samples was 360dpi, and the printing speed was 0.1m/s.

The print quality for each of these parameters was classified in ratings between 1 (best) and 5 (worst) by observing the printed test patterns under the microscope. Figure 5 and Figure 6 show the results of this investigation for the parameters '*straightness and continuity of lines across printing direction*' and '*appearance of satellite drops*', respectively. As it can be seen from the figures, the best results for both of these parameters were obtained at a printhead temperature of 85ºC and an actuator voltage of 15V, and the combination of these conditions resulted in best ratings for the other parameters as well. Consequently, print parameters around this sweet spot were used for the printing experiments, which are presented in the next chapter. The move to even higher temperatures would lower the viscosity of the hybrid ink too much and might even have negative effects on the stability of the ink, and lower voltages would result in too low drop speed.

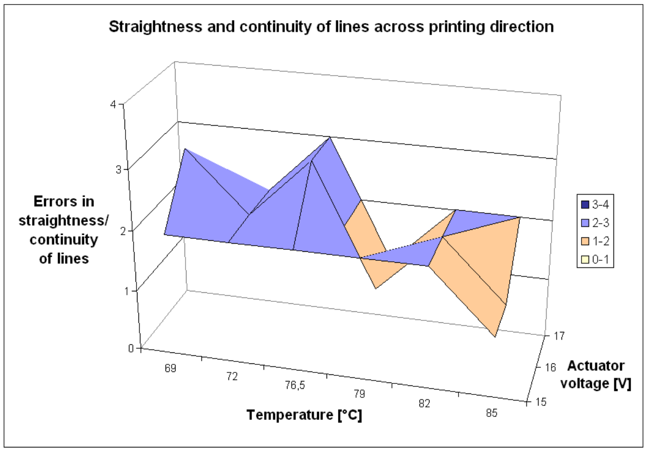


***Figure 5.*** *Straightness and continuity of lines across printing direction within the evaluated process window (1=best, 5=worst)*

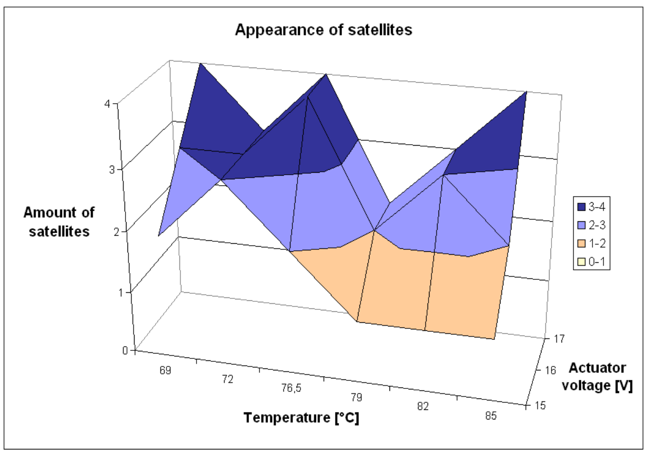


***Figure 6.*** *Appearance of satellite drops within the evaluated process window (1=best, 5=worst)*

## Printing of Resist Mask Pattern

The most important parameters for the deposition of resist mask pattern are the minimal line and gap widths, and the quality of the produced masked areas (e.g. edges roughness and straightness, continuity of lines and areas). In this chapter structures achievable with the Xaar 126/50 printhead and LithoJet™ Version B are discussed, and the analysis of these parameters for different printing resolutions is presented. The operation conditions for the printhead were chosen at 85ºC printhead temperature and 15V actuator voltage (giving a drop speed of about 5m/s), based on the sweet spot in the operation window that was shown in the previous chapter.

Figure 7 and Figure 8 show optical photographs of 1-pixel lines jetted in printing direction, at 360dpi and 470dpi resolution, respectively. The resolution perpendicular to the printing direction was fixed at 527dpi in this case. It can be seen that a printing resolution of 360dpi was not fully sufficient to achieve straight line edges, as there was only some minor overlap of the individual dots, which was not sufficient to let surface tension effects form high quality lines before the phase change reaction took place. At 470dpi, however, continuous lines with well-defined edges could be accomplished. The average line width was 80µm at 360dpi, and 95µm at 470dpi.

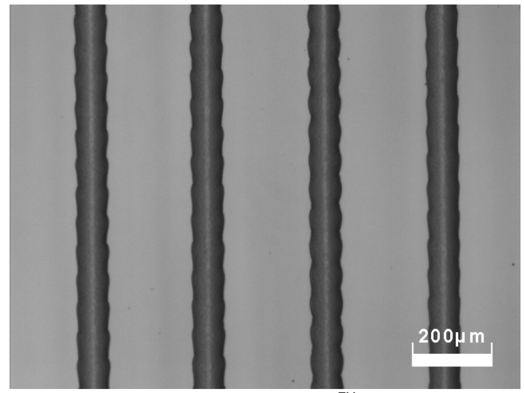


***Figure 7.*** *Single-pixel lines printed with LithoJet™ Version B onto a glass substrate, resolution in printing direction was 360dpi*

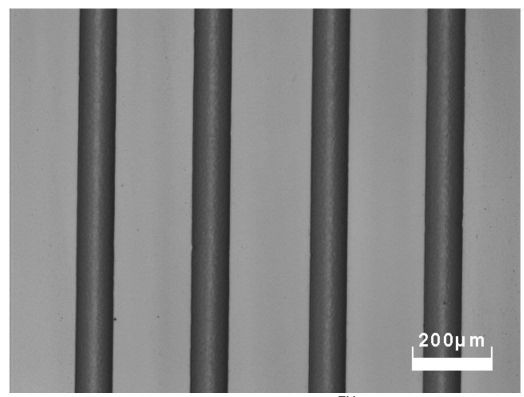


***Figure 8.*** *Single-pixel lines printed with LithoJet™ Version B onto a glass substrate, resolution in printing direction was 470dpi*

In another test series the obtainable line width before UV-curing was measured for smaller variations in printing resolution in a range between 360dpi to 470dpi. These results are summarized in Table 4. In that case the substrate was pretreated in a different way, resulting in slightly smaller line dimensions.

**Table 4. Line width for 1-pixel lines printed with Xaar 126/50**

| Resolution [dpi] | 360 | 400 | 440 | 470 |
|---|---|---|---|---|
| Line width [µm] | 74 | 79 | 83 | 84 |

Further reduction of the line width with phase-change materials was accomplished by using a proto-type model Xaar 126 printhead with 15pl drop volume. In that case a width of 60µm for a single-pixel line printed at 600dpi was feasible.

In case the hybrid phase-change materials are applied for plating or deposition processes, the quality of small openings and gaps in the mask layer is the more relevant parameter. In Figures 9 and 10 such gaps are shown for 360dpi and 527dpi resolution in printing direction, respectively. The resolution across printing direction was 527dpi for both cases. These gaps were achieved by printing a blank opening of 2 pixels in the printing bitmap, as a one-pixel opening in the bitmap did not result in the reliable formation of gaps on the substrate at this resolution.

Again, it can be seen that the 360dpi resolution in printing direction produced wavy edges from the individual drops. However, in this case this behavior occurred only on one side of a printed solid area. The reason for this is still not fully understood and will be investigated further, but it could be assumed that it is related to the time dependent positioning of the drops with an angled printhead.

The pattern produced with a printing resolution of 527dpi in both directions (Figure 10) produced regular lines and gaps with good edge definition. In Table 5 the achievable gap width for the different printing resolutions are summarized.

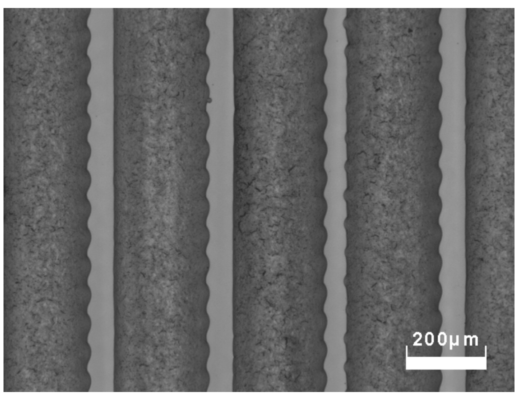


***Figure 9.*** *Gaps printed on a glass substrate, 360 dpi in printing direction*

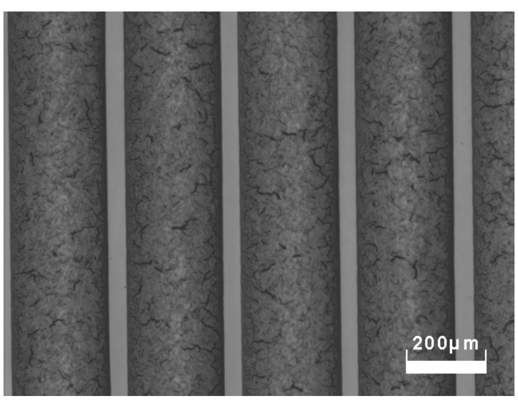


***Figure 10.*** *Gaps printed on a glass substrate, 527dpi in printing direction*

**Table 5. Obtained gap width on glass substrates printed with the Xaar 126/50 printhead**

| Resolution [dpi] | 360 | 470 | 527 |
|---|---|---|---|
| Gap width [µm] | 59 | 56 | 47 |

In a further test sequence the LithoJet™ ink was printed onto copper-coated silicon substrates. It was possible to accomplish similar line- and pattern formation as on the glass substrates, however, the resist pattern edges were more irregular due to the grain-like surface structure of the Cu layer. An example of such an inkjet printed mask pattern on Cu with a finger-like structure is shown in Figure 11, printed in a single pass at 527×527dpi.

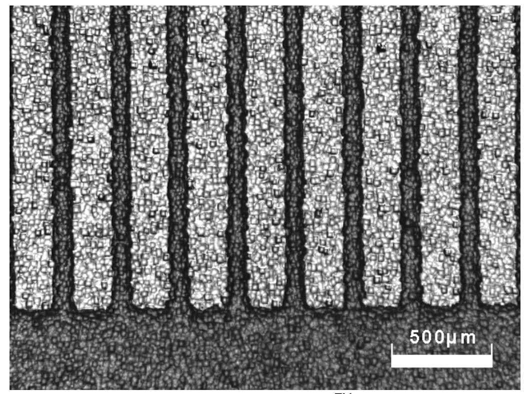


***Figure 11.*** *Test pattern printed with LithoJet™ Version B onto a Cu-coated silicon substrate at 527dpi*

Further evaluation of printing resolution and best printing conditions, including heating of the substrate, the printing with inkjet printheads supplying smaller drop volumes, and the production of more complex mask pattern is currently under investigation.

## Production of Free Formed Structures (2.5D)

As a further potential application area, the production of 2.5-dimensional (2.5D) free formed structures by inkjet printing has been evaluated. The term 2.5D refers in this case to 'pseudo 3-dimensional' structures, which can be obtained by projecting a 2-dimensional pattern into the third dimension. This was obtained in our case by inkjet printing an identical pattern in a large number of printing passes, to build up the desired 2.5D object in a layer-by-layer approach.

Several simple test objects of such 2.5D structures were produced with the LithoJet™ hybrid ink Version A. The ink was again printed with a Xaar 126/50 printhead model, at 470dpi resolution, printhead temperature of 90ºC and actuator voltage of 18V.

Figure 12 shows an SEM image of an array of rod-shaped structures that were obtained by printing single pixel dots on top of each other in 40 consecutive passes, with UV-curing performed after each printing pass. The resulting structures were almost perfectly arranged, demonstrating the good reproducibility of the printing process. The misplacement of one single dot at the bottom of each structure, as visible in the image, was caused by an error in the controller software that shifted the first printed layer by one pixel (which could only be corrected later on). Figure 13 depicts another test pattern, which consists of an array of squares with different dimensions. As can be seen in the SEM image, well shaped straight structure edges with a high aspect ratio were achieved, however the top edges were considerable rounded.  The height of these squares, produced in 40 printing passes, was measured as 700-800µm. It was furthermore possible to demonstrate the printing of these structures composed of 100 or more layers, which yielded about 2mm high single-pixel columns and 2.5D structures.

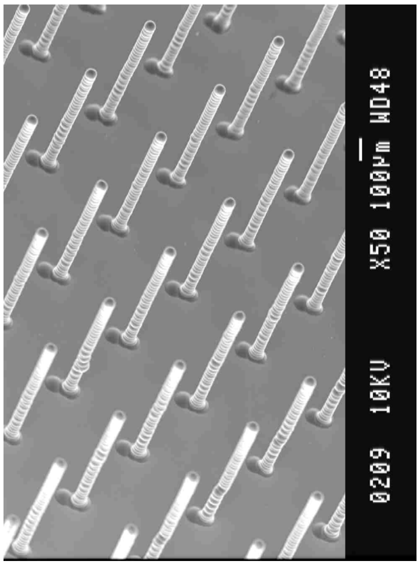


***Figure 12.*** *Rod-shaped 2.5D structures obtained by printing single pixel dots in 40 consecutive passes*

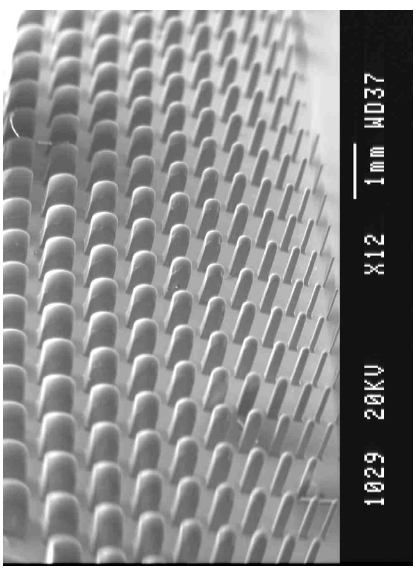


***Figure 13.*** *Free formed test structure consisting of an array of squares with different dimensions; the structures were produced in 40 printing passes, yielding a structure height of 700-800 µm*

## Summary

Lithojet™ hybrid inks from Rohm and Haas were inkjet printed with Xaar 126/50pl binary piezoelectric printheads. A special waveform was developed and print parameters were evaluated to obtain well controlled jetting in the temperature range from 70 to 90ºC. Print quality regarding dot placement and satellites was investigated and a sweet spot providing best performance was found for 15V driving voltage and 85ºC printhead temperature. With these print parameters it was possible to print smooth lines and gaps as they are needed for etch masks e.g. in solar cell manufacturing. Smooth lines of 84µm width could be printed at 470dpi resolution, while gaps of 56µm and 47µm width were obtained with 470dpi and 527dpi, respectively. Both these printing resolutions allow printing on a square grid with the printhead rotated at the appropriate angle.

Free formed 2.5-dimensional structures of different geometries could be produced with multi-pass printing and intermittent UV-curing. The capability and process reliability was demonstrated by multi-pass inkjet printing a single pixel pattern, which resulted in straight columns of 70µm diameter and up to 2mm in height.

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## Author Biography

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