HOT-MELT INKJET AS MASKING TECHNOLOGY FOR BACK-CONTACTED CELLS

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ABSTRACT
Two approaches for structuring thin metal layers for seed and growth metallization for back-contacted solar cells using hot-melt inkjet as masking technology are evaluated. The characteristics of a hot-melt printed image relevant for process development are discussed. A metal lift-off process and a metal etching process, both creating an interdigitated grid — based on hot-melt inkjet are established. The process sequences are characterized regarding the shunt resistance between the grids and the contact resistance to an underlying emitter layer on appropriate test structures. The contact resistance is found to be increased on samples fabricated by metal lift-off compared to samples fabricated by metal etching. The lift-off process is found to open lines with a width of around 120 µm reliably, whereas a line opening width in the range of 50 µm is reliably represented with the etching process sequence, whereas a high shunt resistance is considered the criterion for a successful process.

INTRODUCTION
Back-contacted solar cells provide high module efficiencies as has been demonstrated by companies like Sanyo [1] and SunPower [2] in recent years. Typically, several masking steps are required for manufacturing back-contacted solar cells. Industrial fabrication requires low cost and high-throughput masking technologies with high precision. The feature size and layer to layer alignment achieved with a masking technology are important factors determining among others the efficiency of back-contacted solar cells [2,3]. Digital fabrication with molten micro-drops (hot-melt inkjet) combines high precision and high throughput and allows for non-impact printing [4,5]. Hence, the technology is a candidate for manufacturing high-efficiency back-contacted solar cells on thin substrates.

A possible metallization approach for back-contacted silicon solar-cells is the use of metal layers or metal stack layers deposited by sputtering or e-gun physical vapor deposition on the full area of the rear surface. The metal is structured according to the pattern of n+ and p areas on the rear surface of back-contacted solar cells in order to form contact grids for each polarity. The metal stack layers are subsequently thickened by plating [6,7]. This “seed and growth” approach allows for a reduced contact and line resistance with respect to screen-printed contacts and no firing step is required. Furthermore, rear side metal layers combined with dielectric layers can act as excellent mirrors increasing light harvesting.

For high efficiency laboratory cells, typically lift-off processes based on photolithography are used for metal structuring [8]. In literature alternative techniques for this step without using photolithography are proposed [7,9,10]. In this work, two approaches for defining the seed layer geometry using hot-melt inkjet as masking technology are evaluated. The first section addresses the image characteristics of hot-melt inkjet relevant for process development. Afterwards a metal lift-off and metal etching process are investigated regarding image definition and electrical performance on appropriate test structures.

HOT-MELT INKJETTING
We use the inkjet system DoD300 by the company Schmid Technology GmbH [4]. The system features a piezo-electric drop-on-demand technology. A piezoelectric actuator is triggered, thus applying acoustic wave patterns to an ink reservoir with an orifice such that droplets of continuous size leave the orifice. The droplet is deposited on the substrate after a short flight time in the range of 100 µs. The substrate is placed on an x-y-table, which has a fast and a slow axis. The fast axis is referred to as the printing direction. The native resolution of the print-head is 50 dpi. The table moves perpendicular to the printing direction with a minimum step width of 5 µm. The ink consists of an alkali soluble wax, whereas the effective material composed of several components exhibits its melting point at around 70°C. It is jettable at temperatures between 80…95°C and solidifies directly after impact on the substrate (phase change ink) due to the temperature difference. Fig.1 displays scanning electron microscopy (SEM) micrographs of solidified sessile droplets printed on shiny etched silicon with different coatings: silicon dioxide and a thin metal stack layer.

Fig. 1 SEM micrograph of solidified sessile droplets on shiny etched Si-substrate with different coatings: silicon dioxide and a thin metal stack layer.
Fig. 2 Optical micrograph of two solidified lines of hot-melt ink printed on glass. In printing direction the droplets coalesce, whereas perpendicular to the printing direction the structure of the single droplets is still visible.

The droplets adopt the shape of roughly spherical caps with surface diameters of around 55 µm on the metal-coated substrates and around 60 µm on silicon dioxide coated samples, whereas the same printing parameters resulting in a droplet volume of 20 pl were used for both samples. The spreading of the droplets on the substrate depends among other parameters on the substrate temperature [11]. Reheating of the substrate is observed to lead to further spreading on both samples. Consequently, the solidification process stops the spreading of the droplets. This characteristic is expected advantageous for covering texturized surfaces or steps present on damage-etched multi-crystalline surfaces or certain process sequences for back-contacted solar cells.

The topology of lines in printing direction differs from lines perpendicular to the printing direction. Fig. 2 shows an optical micrograph of two lines printed on glass. In printing direction a continuous line is formed whereas perpendicular to the printing direction the structure of the single droplets is visible. The firing frequency was 5 kHz, hence the time between the impact of two adjacent droplets in printing direction is 200 µs. Perpendicular to the printing direction the time between the impact of two adjacent droplets depends on the image dimensions, and exceeded the time between the impact of adjacent droplets by 4 orders of magnitude in this experiment.

Etch resist applications require closed films over large areas. The surface diameter $d_{\text{surface}}$ depends on the printing parameter set including the shape and amplitude of the voltage pulse applied to the piezoelectric actuator and on the characteristics of the substrate including material and surface. In order to achieve sufficient overlap of the solidified sessile droplets the resolution of the printed image must be chosen such that the distance between the centers of two adjacent droplets is lower than $0.5\sqrt{2d_{\text{surface}}}$. Fig. 3 shows optical micrographs of solidified hot-melt ink films on glass substrates fabricated with different printing parameters. On the left hand side the digital image features a line opening. Three particular printing parameter sets at constant resolution are shown for demonstration purposes. Parameter set 1 produces a comparatively high droplet volume at a droplet speed greater than 5 m/s.

Irregular films and poor edge definition at the line opening are observed. The second parameter set produces a smaller droplet volume at roughly the same speed and results in a regular structure and good edge definition at the line opening. In the last parameter set both droplet volume and droplet speed were further reduced, whereas the droplet speed was below 5 m/s. Defects in the film can be observed.

The film thickness results between 15 and 20 µm for parameter set 2, which was found to be a sufficient thickness for the etch resist application discussed in the next section.

**CONTACT SEPARATION**

Two process variants for structuring a metal stack layer consisting of Al/Ti/Ag based on hot-melt ink are investigated. Fig. 4 displays schemes of cross sections of the rear surface of a back-contacted solar cell (in the figure an emitter-wrap-through cell) illustrating both variants. The starting point is a sample with a dielectric layer on the rear surface exhibiting openings for contact formation. The first variant represents a metal lift-off process. The ink is deposited on a small area extending to both sides of the line where the p-n-junction intersects the crystal surface (1a). The metal layer is deposited on the full area (1b). During the stripping process, the metal is lifted and the structure of the seed layer is defined (1c). In Fig. 4 2) a metal etching process sequence is shown starting with the same conditions as in 1). First, the metal stack is deposited on the full area (2a). A hot-melt ink film with openings at the contact separation zone is printed (2b). Subsequently the metal stack layer is etched with appropriate etching solutions (2c). Finally, the hot-melt ink is stripped. The seed layer is subsequently thickened by plating to provide for sufficient line conductivity (not displayed in figure).
Fig. 4 Process flow for lift-off (1) and etching (2) for back-contacted solar cell.

In order to investigate the image definition and effectiveness of the contact separation process sequences based on hot-melt ink, the test structure sketched in Fig. 5 was fabricated. For process 1 (metal lift-off) a positive meander mask is printed on a silicon dioxide layer. For process 2 (metal-etching), a corresponding negative mask is printed on a substrate with silicon dioxide and metal layers. The busbars allow for the measurement of the shunt resistance between the grids. Appropriate digital images for the fabrication of masks with constant line and line opening width were created. The sample size was 2x2 cm² with 10 fingers per polarity. The finger direction was chosen perpendicular to the printing direction.

1) Metal lift-off
As previously mentioned the melting point of the hot-melt ink is around 70°C. Physical vapor deposition comes along with some thermal impact. In order to minimize the thermal impact on the samples a low evaporation rate was chosen. The thickness of the Al-layer was below 1 µm. The line width in finger direction (perpendicular to printing direction) was varied from 1 to 3 pixels corresponding to line widths of 60 µm, 90 µm and 120 µm respectively. Fig. 6 displays optical micrographs of samples on damage etched surfaces with 3 pixels contact separation width in different stages. For lower contact separation width locally remaining contacts reduced the contact separation resistance considerably (see next section). As can be observed comparing the first two images before (1) and after evaporation (2), the geometry is not drastically changing during the PVD-process. After lift-off (3) a thin dark strip caused by metal residuals that were not entirely removed during the stripping process borders the contact separation zone. Consequently, an opening width of equal or greater 120 µm was achieved in printing direction.

Fig. 5 Scheme of top view and cross section of test structures for lift-off mask (left) and etch-mask (right).

2) Metal-etching
The developmental hot-melt ink formulation used in this work was developed to resist against aqueous acids. In order to etch the silver top layer and the titanium buffer layer nitric acid solution at room temperature was used. The aluminum layer was etched with hydrofluoric acid solution.

Fig. 7 displays optical micrographs of samples with the test structure on Cz-material with damage etched surfaces in two stages: after printing and after stripping. The digital image was designed such that the opening width was two pixels in the print image corresponding to about 40±4 µm. One pixel openings could not be reliably represented for the given droplet volume, printing resolution and substrate characteristics. Perpendicular to the printing
direction the line width is somewhat increased in the printed image. After etching and stripping, the opening width in printing direction in the metal layer is found to be 50±5 µm. The undercut is about 5 µm per side. Furthermore, the metal layer is intact in the respective areas. Consequently, the adhesion of the hot-melt-ink on metal is excellent and the film is dense to the etching solutions. The edges perpendicular to printing direction exhibit the structure of the single droplets creating a wavy edge, whereas parallel to the printing direction the edges are smooth. Furthermore, openings with 3 and 4 pixels in the printed image were realized. For opened lines with three or four pixels opening width the resulting contact separation width in the metal layer was determined to be 85±5 µm and 115±5 µm respectively.

![Fig. 7](image_url)

**ELECTRICAL CHARACTERIZATION**

The previously described test structures allow for the measurement of the resistance between the metal grids. In order to omit diffusion steps and to distinguish between misalignment and insufficient contact separation resistance, a dielectric layer is required that largely suppresses parasitic currents through the substrate. To this end, a wet thermal oxide of 250 nm thickness was grown (see Fig. 5). A comparatively wide bar surrounds the test structure in order to safely isolate the grids. In so doing the resistance of the oxide can be measured between one of the grids and a fixed point outside the bars in order to verify the isolating effect of the dielectric layer.

The resistance between the busbars of the test structures - denoted \( R_{p,1} \) for process 1 and \( R_{p,2} \) for process 2 - was measured in a four point measurement set up. The results are listed in table 1 along with the resulting geometrical data. Process 1 leads to poor results for one pixel and two pixel line width, which could be attributed to local shunt paths due to locally insufficient lift-off. As a result the smallest contact separation width is 120 µm. For process 2 all resistance values are found to be in the MΩ-range. The smallest contact separation width that was reached was 50 µm.

A second test structure was fabricated for transmission line measurements (TLM) according to Schroder et al.[12] to determine the contact resistance of the metal stack layer to a heavy n+ diffusion after forming gas anneal. The contact resistance of the samples fabricated with process 1 exhibited an elevated contact resistance by a factor of about 5 compared to the samples fabricated with process 2, whereas the same metal deposition process was applied in both cases. Possibly the thermal stability of the hot-melt ink is not sufficient for the PVD-process. The origin of the increased contact resistance is subject to ongoing investigations.

**Table 1 Results of measurement of parallel resistance and contact separation width.**

<table>
<thead>
<tr>
<th>no of pixel</th>
<th>lift-off</th>
<th>metal-etching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_{p,1} ) [Ω]</td>
<td>( w_1 ) [µm]</td>
</tr>
<tr>
<td>1</td>
<td>0.2…0.3</td>
<td>60±5</td>
</tr>
<tr>
<td>2</td>
<td>0.2…0.3</td>
<td>90±5</td>
</tr>
<tr>
<td>3</td>
<td>&gt;10⁶</td>
<td>120±5</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
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</tr>
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</table>

**SUMMARY**

A hot-melt inkjet process to fabricate lines and closed uniform films with openings with feature sizes in the range of 50 µm was established. Test structures for the evaluation of metal structuring processes for back-contacted solar cells were designed, exhibiting meander-shaped openings in a metal layer and an isolating dielectric layer, consisting of 250 nm thermal oxide. The test structures allow for the measurement of the shunt resistance of the grids, serving as one criterion for the qualification of a contact separation process. A lift-off process and a metal-etching process based on hot-melt inkjet were investigated.

A lift-off process was possible if a certain line width was exceeded, whereas the minimum opening width resulted in around 120 µm. The contact resistance of the lift-off process was increased with regard to the metal-etching process. Future work will address the origin of the elevated contact resistance. Furthermore, a metal-etching process compatible with the hot-melt ink was established. The hot-melt inkjet films were found to be dense against the etching solution. The image definition was excellent, resulting in a minimum opening line width of around 50 µm.

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REFERENCES


