Inkjet Printing of Narrow Conductive Tracks on Untreated Polymeric Substrates**

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In the last two decades inkjet printing has grown to a major topic in scientific research, especially drop-on-demand (DOD) inkjet printing systems.[1–3] DOD inkjet printing has progressed from printing text and graphics, where it started originally, to a tool for (rapid) manufacturing technology.

During the last years, the fabrication of narrow conductive tracks by methods of inkjet printing has been investigated extensively.[4–7] Printing of flexible electronics and minimizing their feature size dramatically lowers the production costs of electronic devices, because material can be positioned on-demand, which reduces the amount of necessary material. The main bottleneck in inkjet-printed features on flexible (polymeric) substrates is the low softening point ($T_g$) of the substrate, which limits the processing temperature. The $T_g$ of commonly used polymeric substrates, like poly(ethylene terephthalate) (PET) or polycarbonate (PC), is below 150 °C. Typically, colloidal suspensions of conductive materials need a sintering temperature of > 200 °C, which is, hence, not compatible with most polymeric substrates. Feasible products of flexible electronics include, for example, interconnections for circuitry on a printed-circuit board (PCB),[8] electrodes for thin-film transistor (TFT) circuits,[9] organic light-emitting diodes (OLEDs),[10] or disposable displays and radio frequency identification (RFID) tags.[11,12] Furthermore, printing large-area displays is also a possibility.[13]

The typical dimensions of inkjet-printed features depend on the nozzle diameter, and are usually not below 100 µm.[14,15] The most obvious way to minimize the feature size, that is, line width, is by reducing the nozzle diameter.[16,17] However, this introduces a narrow window with respect to surface tension and viscosity of the inks, and thereby limits the choice of inks that can be printed.[18,19] Furthermore, when printing suspensions the particles should be sufficiently smaller than the nozzle diameter; otherwise nozzle clogging occurs.[20] When using piezoelectric-based DOD inkjet printers, smaller droplets can also be produced by modifying the waveform.[21]

Much research has been done to predefined (surface energy) patterns on a substrate that forces material to remain in a preferred area on the surface.[22–24] These techniques rely on the use of expensive masks and conventional photolithography, which increases production costs.

Here we present a method to produce narrow conductive silver tracks without prepatterning or modifying the surface energy of the substrate. Preferably, the surface energy should not be too low, because printing on such foils introduces bulges into the printed features,[25,26] for example with poly(tetrafluoroethylene) (PTFE) foils. Line-bulging is an unwanted mechanism that locally broadens the printed structures, as can be seen on the left-hand side of Figure 1. Commonly used polymeric substrates like PET or polyimide (PI), have a high surface energy, shown on the right-hand side in Figure 1. Although printing on these substrates leads to continuous and straight lines, broad lines are obtained over the whole printed feature, owing to the relatively good wetting of the solvent with the substrate. Clearly, an optimum between surface ener-

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gy and solvent is necessary. Polyarylate polymeric foils fulfill this need, because they have a surface energy value between that of PTFE and PI.

In order to print conductive nanoparticles, we have used a commercially available ink from Cabot with particle sizes below 50 nm that need a typical sintering temperature of 200 °C. Although the Cabot silver nanoparticles do show conductivity at temperatures as low as 150 °C, the resistivity reaches a value of five to six times the value of bulk silver only when sintering temperatures of 200 °C–or higher–are used. Because of this preferred sintering temperature, the polymeric foils need a high glass transition temperature. Cabot nanoparticle suspensions were inkjet-printed by using a commercial Dimatix printer, equipped with a special cartridge able to dispense droplets with a volume as small as 1 pL.

Besides a decrease in nozzle size, and thus a higher print resolution, further decrease in line diameter was realized by heating the sample holder of the printer to its maximum temperature (60 °C), which stimulates evaporation of the solvent and prevents broadening of the lines.[14] Figure 2a shows the dependency of line width on dot spacing, that is, the distance between the centers of two adjacent droplets. A decrease in line width is observed when the dot spacing is increased. Obviously, with increased dot spacing less material is deposited per unit length, resulting in smaller structures. Partially continuous lines were formed when a dot spacing larger than 25 μm was used, and further increase led to individual droplets. In the same way, the resistance will increase when the dot spacing is increased, as depicted in Figure 2b. However, the number of layers printed on top of each other strongly influences the dependency. The resistance of lines consisting of three layers strongly increases with dot spacing, whereas the resistance shows a much more gradual increase with dot spacing when five layers are printed on top of each other. This can be explained by the formation of more parallel percolating pathways when more material is deposited per unit length.[5]

Typical dimensions of printed silver tracks onto polyarylate films are shown in Figure 3. Straight lines were obtained after drying, without any defects such as bulges or coffee-stain effects. The silver lines printed on the polymer foil were sintered in an oven at 200 °C for 1 h. Subsequently, the resistance was measured by using the 4-point method. The electrical resistivity $\rho$ of an inkjet-printed line was then calculated from the resistance $R$, the length $l$, and the cross-sectional area $A$ of the line using $\rho = R \cdot A / l$ and subsequently compared to the value of bulk silver ($1.59 \times 10^{-8}$ Ω·m).[11] The cross-sectional area was determined by numerical integration of a measured profile. Compared to bulk silver, the conductivity was 23% for the tracks printed with a dot spacing of 5 μm and 13% when using a dot spacing of 25 μm.

In summary, we have combined methods for the preparation of narrow conductive tracks on a flexible polymer substrate without the need of predefined (surface energy) patterns. The colorless and transparent polyarylate substrate has a surface energy low enough to limit the wetting of the silver nanoparticle suspension, but high enough to prevent line bulging. This resulted in the direct inkjet printing of lines with a diameter of 40 micrometers. The silver tracks were sintered at 200 °C for one hour, which resulted in a conductivity of 13% to 23%, compared to bulk silver. The as-printed narrow silver tracks can be used in, for example, (plastic) electronic applications such as radio frequency identification (RFID) tags or electrodes for thin-film transistor (TFT) circuits.

**Experimental**

A silver nanoparticle suspension in an ethylene glycol/ethanol mixture was purchased from Cabot (Cabot Printing Electronics and Displays, Albuquerque, USA). The silver ink contained 20 wt % of silver nanoparticles, with the particle diameter ranging from 30 to 50 nm. The viscosity and surface tension of the ink were 14.4 mPa s and 31 mN m⁻¹, respectively. Transparent and colorless polyarylate (Arylite A200HC, Ferrania, Italy; 200 μm thickness) film with a glass transition temperature of 330 °C was used as substrate material. The silver ink had a contact angle of 31.8±2.1° with the polyarylate foils. Furthermore, teflon foils (Teflon A and LP, DuPont de Nemours, Mechelen, Belgium), polyimide and PET (Kapton and Melinex, Dr. D. Müller GmbH, Ahlhorn, Germany) were obtained commercially and used for Figure 1. Inkjet printing was performed using a piezoelectric Dimatix DMP 2800 (Dimatix-Fujifilm Inc., Santa Clara, USA), equipped with a 1 pL cartridge (DMCLCP-11601). The print-

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**Figure 2.** a) Line width, and b) resistance as function of dot spacing for three and five layers subsequently printed on top of each other.
head contained 16 parallel squared (8.6 × 8.6 μm²) nozzles with a diameter of 12.1 μm. The suspension was typically printed at 16.0 V, a frequency of 5.0 kHz, and a customized wave form. The substrate holder was set to a temperature of 60 °C.

Surface topography, thickness, and cross-sectional areas of printed silver tracks were measured with an optical profilometer (Fogale Zoomsurf, white light, magnification 5×). Scanning electron microscopy (SEM) images were taken using a FEG E-SEM XL30 (Philips, Eindhoven, The Netherlands). An OCA30 optical contact-angle measuring instrument was used to determine the contact angles of both diiodomethane and ethylene glycol as apolar and polar test liquids, respectively. Surface energies were calculated from the obtained contact angles using the Neumann equation of state [27].

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Figure 3. Cross-sectional image and 3D image of inkjet-printed silver tracks on polyarylate films using a dot spacing of a) 5 μm, and b) 25 μm. The substrate was heated to 60 °C and five layers were printed on top of each other.