Inkjet Printing of conductive silver tracks in high resolution and the (alternative) sintering thereof

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Abstract

We present different methods to improve the resolution of inkjet printed lines. The first is a direct method without surface treatment. Small droplets of a single picoliter have been inkjet printed directly onto a polymeric foil that has a surface energy smaller than that of common polymer foils. On the other hand the surface energy was high enough to form continuous tracks, which is usually the case when printing, for example, onto Teflon foil. The second method uses a combination of inkjet printing and hot-embossing. The latter technique is used to create microchannels in a polymer foil by pressing a master into the substrate, which is held above its glass transition temperature, after which an inkjet printer is used to dispense single droplets of a silver nano-particulate ink over these as-formed channels. Subsequently, the channels will fill by means of capillary forces and afterwards sintering resulted not only in narrow tracks smaller than 10 µm, but also gave higher conductivity values than the conventional inkjet printed lines. Typically, conductivities up to 20% were revealed, which can be explained by a higher packing due to the capillary forces used for filling the channels.

Moreover, we present an alternative technique to sinter in a selective method inkjet printed silver tracks on common polymer foils, by microwave radiation. This alternative technique is capable of a low temperature decomposition of the organic binding material that is around each metal nanoparticle. This results in the formation of conductive tracks. After applying this selective sintering technique, the features have a conductivity similar to conventional convection-radiation sintering, which is the most commonly used sintering technique at the moment.

Introduction

The basis for inkjet printing was established already in the 18th century by Lord Rayleigh, who discovered that a stream of liquid could break up into separate droplets.[1] The break-up of a liquid jet takes place because the surface tension of a liquid sphere is smaller than that of a cylinder and, while having the same volume, is energetically favorable. Subsequently, the drop-formation process is synchronized by the forced mechanical vibration and therefore ink drops of uniform mass are produced. This was seen as the basis for continuous inkjet printing. However, in the late 1940s the impulse inkjet printers were invented, where droplets are created on demand, hence drop-on-demand (DoD).

Although inkjet printers are widely used for graphical applications, it was only within the last decades that inkjet printing has grown to a mature patterning technique. As a consequence, it has gained specific attention in scientific research because of its high precision and its additive nature: only the necessary amount of functional material is dispensed.[2] Furthermore, the absence of physical contact between print head and substrate allows many potential applications, such as inkjet printing of labels onto rough curved surfaces, or surfaces that are sensitive to pressure.

Inkjet printing of microelectronic devices has been shown to be applicable as a low-cost alternative in the production of microelectronic devices, such as thin-film transistors, and radio frequency identification tags.[3-5] Moreover, during the last years, there has been a growing interest in inkjet printing of conductive materials, such as metals or (semi-)conductive polymers. The latter polymers, with PEDOT being the most used example, have been frequently used due to it relatively low costs, but typically lack a high conductivity.[6] Besides the conductive polymers, metal nanoparticles, which are highly conductive and have a diameter between 1 and 50 nm, have been used to create microstructures onto polymer substrates.[3,4] The resolution of these structures is comparable to the nozzle diameter, and is typically between 70 and 100 µm. While decreasing the nozzle diameter improves resolution, it also creates a smaller window of inks that can be used for printing, with respect to their viscosity and surface tension.[7] Printability of an ink can be formulated by Fromm's *Z*-number, which is the inverse of the Ohnesorge number (*Oh*): $Z = \eta^{-1}(\rho D \sigma)^{1/2} = \mathrm{Oh}^{-1}$, where ρ, σ and η are the inks density, surface tension and viscosity, respectively. D is a characteristic length, which in the case of inkjet printing is the nozzle diameter. Fromm predicted that drop formation in DoD systems was possible only when the *Z*-number is greater than 2.[8]

Results and discussion

In order to improve inkjet printing resolution, other methods are required. Recent literature describes the controlled minimization of the printed droplet by changing the waveform over the piezoelectric ceramic,[7] by fluid-assisted dewetting effects, [9] or by increasing the substrate's temperature, which will stimulate solvent evaporation and leave smaller droplets on the substrate.[10] Furthermore, dot spacing, that is the center to center distance between two adjacent droplets, should be chosen carefully:[11] if the dot spacing is chosen too large, separate droplets will be dispensed onto the substrate and lead to discontinuous features, whereas too small dot spacing causes too much material dispensed per unit of area, which leads to line or film bleeding, hence irreproducible structures. Figure 1 shows the line width and height as function of dot spacing for printed silver nanoparticles onto glass substrates. With an increase of 1.5× in dot spacing a line width and height reduction of approximately 37% and almost 50% was revealed.

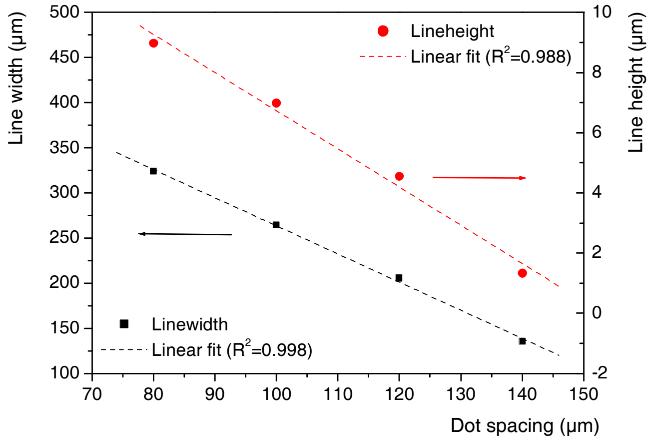

Figure 1. Line width and height as function of dot spacing.

Obviously, the substrate is not passive during printing and it was found that the surface energy is an important factor for droplet spreading of the impinging droplet. Droplets that are printed onto a low surface energy substrate, for example Teflon foils, have a hemispherical or almost spherical shape, in order to minimize their surface overlap. In this extreme case, inkjet printing is difficult, since droplet merging does not take place and dewetted droplets of ink form non-continuous features. Moreover, on these low surface energy, hence hydrophobic, substrates line-bulging can take place, which results in inhomogeneous line morphologies, as shown in Figure 2.[12]

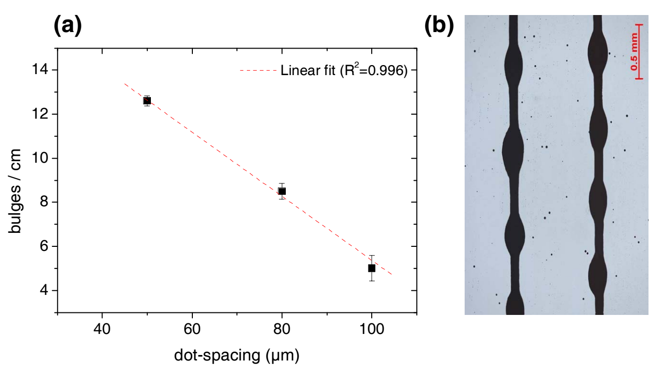

Figure 2. Correlation between dot-spacing and the number of bulges per cm (a) appearing in a printed line of aqueous suspension of TiO_2 nanoparticles at 25 °C on OTS-treated glass (b).

On the other hand, hydrophilic substrates enhance surface wetting of the ink and, therefore, do not favor the formation of narrow feature sizes. Therefore, the surface energy and ink's surface energy should match and an optimum between the two needs to be found. Figure 3a shows the surface energy of various commercially available polymeric foils.

By carefully tuning the surface tension of the ink to the substrates surface energy, we have created the up to now smallest conductive inkjet-printed tracks by direct inkjet printing. Hereto, a silver nanoparticle suspension was dispensed onto untreated and heated polymeric substrates using a commercial inkjet printer equipped with a cartridge, able to produce droplets with a volume as low as 1 pL.[13] The flexible and transparent polyarylate foils have a surface energy of 36 mN m^{-1}, which is, according to Figure 3, slightly lower than for PET or polyimide. This resulted in lines with a diameter as narrow as 40 microns, as depicted in Figure 3b.

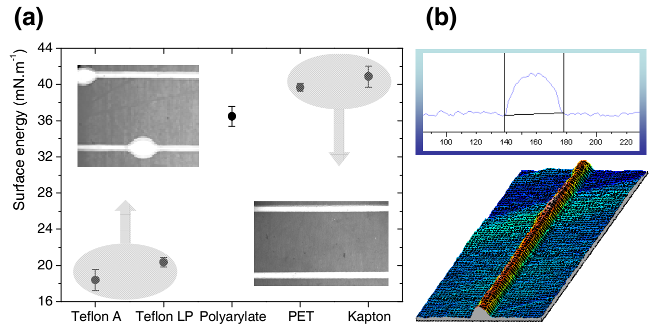

Figure 3. Surface energy of five commercially available polymer substrates. Cross-sectional image and 3D image of inkjet printed silver tracks on polyarylate films.

Another approach to improve the resolution is to pre-pattern the substrate, either by modifying its surface energy, *e.g.* by micro-contact printing, or by creating variations in topography. Both techniques direct the printed ink into preferred regions. Hendriks *et al.* have prepared recessed topography structures by means of hot-embossing, which were subsequently filled with silver nanoparticle inks using capillary forces.[14] Hereby, a master is pushed into a polymer foil, which is kept above its glass transition temperature (Tg), that creates microchannels. After this, droplets of a silver nanoparticle ink are dispensed over one of these as-formed grooves using an inkjet printer. The ink fills the grooves as a consequence of capillary forces and is observed to form tracks with a uniform width. A single droplet with a volume of 113 pL is capable of filling a channel over a length of 4 mm. The tracks are described as 'invisible' on account of having widths ranging from 5 to 15 µm. Figure 4 shows the uniformity of such formed lines, where the line width is as small as 7 to 8 µm. Wider tracks could be produced by dispensing more droplets and tracks with different morphologies could be produced by using different masters.

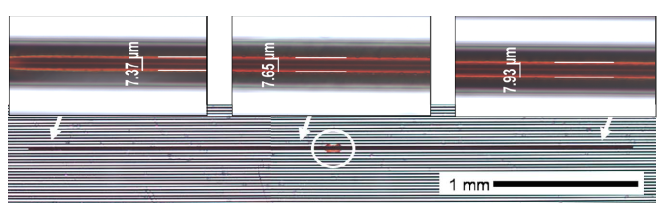

Figure 4. Optical microscopy image of a single silver nanoparticle track on a hot-embossed polystyrene structure.

After printing the tracks, a sintering processing step is necessary in order to remove the organic binding and stabilizing material that is present around each nanoparticle, after which the particles form a percolating pathway for the electrons. There are two reasons for the presence of organic materials in a nanoparticle ink. Firstly, a dispersant is required to prevent agglomeration of the particles in the ink. In non-polar solvents usually long alkyl chains with a polar head, like thiols or carboxylic acids, are used to stabilize the nanoparticles. These molecules provide a larger steric hindrance and the adsorption of the polar group on the surface of the nanoparticle reduces the surface energy. Secondly, organic binders are often used to assure mechanical integrity and adhesion to the substrate after drying.[15]

After removal of the organic material, the particles start sintering as a result of neck formation between. The driving force for sintering is the release of the high surface energy related to the small radius of curvature of the particle's surface. Sintering at lower temperatures can be realized by using very small particles. Upon formation of large agglomerates, the conductivity builds up due to an increased amount of parallel percolating pathways throughout the track. The lowest temperature at which printed features become conductive is mainly determined by the amount and type of organic additives in the ink.[15]

Figure 5 shows the resistance as function of temperature for inkjet printed tracks consisting of Cabot silver nanoparticles. Heating was performed at a constant rate of 10 °C min^{-1}. The resistance decreases rapidly when heated above a critical temperature of 194 °C. Around the same temperature, the thermo-gravimetric analysis (TGA) shows a sharp decrease in mass and the mass decreases to approximately 30%, which is, according to its supplier, the silver load of the ink. Apparently, all organics have to be removed before the sintering of the silver nanoparticles can proceed in a fast way.

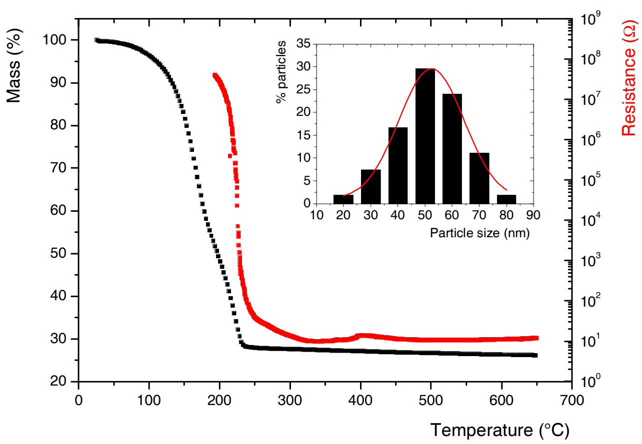

Figure 5. Resistance as function of temperature and thermogravimetric analysis (TGA) of Cabot silver ink. The inset shows the particle size distribution of Cabot silver nanoparticles.

In addition to the dynamic heating, some experiments were performed at a constant temperature. When heating takes place at a constant temperature, much lower temperatures can be used to sinter the silver nanoparticles, as shown in Figure 6. It can be seen that sintering takes already place at temperature as low as 100 °C, although longer times are necessary to reach lower resistance. Longer times also initiates decomposition of binder, but a minimum temperature is still necessary.

If inkjet printing of conductive nanoparticles is used for the fabrication of microelectronic structures on polymeric substrates, for example for plastic electronics, the features should be rendered conductive at a temperature that is compatible with the substrate. Therefore, when using polymeric materials the sintering temperatures should be below its glass transition temperature (Tg), in order not to deform the underlying substrate upon further processing. As shown in Figure 6, a sintering temperature between 100 and 120 °C is below the Tg of typical engineering polymer foils, like polycarbonate (PC), but is still above that of common used foils, like polyethylene terephthalate (PET). Therefore, other techniques have to be used in order to render the features conductive and, preferably, in a selective method.

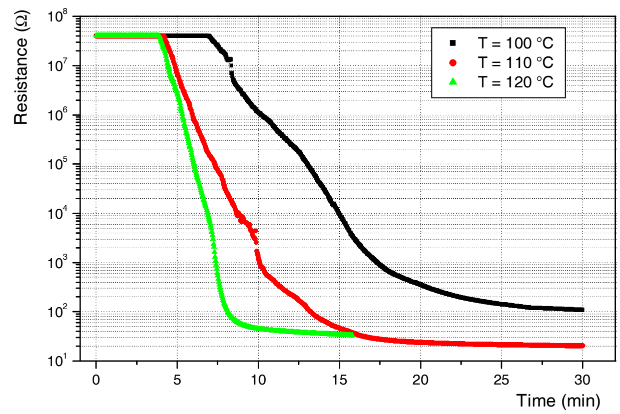

Figure 6. Resistance as function of time over inkjet printed tracks consisting of Cabot silver nanoparticles, while heating at a constant temperature.

A few alternative techniques have been described in literature. In the first technique that is reported by Grigoropoulos and Poulikakos,[16] an Argon ion LASER beam follows the as-printed feature and selectively sinters the central region, without affecting the substrate. This results in features that have a line width as narrow as 10 µm.[17] However, the large overall thermal energy impact together with the write speed of the translational stage is a limiting factor with speeds of 0.2 mm s^{-1} being reported as resulting in the best conductivities.

A second technique that has been reported as a selective alternative sintering technique uses microwave radiation.[10] According to the Maxwell equations, microwaves are better absorbed by highly conductive materials than by isolators. The penetration depth (d_p) can be expressed as: $d_p = 1/(\pi f \mu \sigma)^{1/2}$, where f is the frequency of the microwave radiation, μ the permeability of the material, and σ the conductance. Highly conductive materials, *e.g.* metals, have a very small penetration depth: the penetration depth for microwaves with a frequency of 2.54 GHz for silver, gold and copper is 1.3 to 1.6 µm, respectively. Microwave sintering of metals is, therefore, non-trivial and can only be successful if the dimension of the object perpendicular to the plane of incidence is of the order of the penetration depth. Inkjet printed tracks of silver nanoparticles fulfill this requirement. When comparing the conductance of the nanoparticles to the underlying thermoplastic polymer foil, the substrate is virtually transparent to microwaves and, therefore, the microwaves are only absorbed by the conductive nanoparticles. The inkjet printed silver tracks were treated in a single mode microwave reactor and their sintering times were dramatically shortened, from 60 minutes or more down to less than 240 seconds. Longer sintering times did not increase the conductivity, but sometimes resulted in deformation or decomposition of the substrate at the edges of the silver lines and the substrate.

Figure 7 shows the typical conductance build-up upon exposure to microwave radiation, with a rapid increase in conductance between 120 and 200 seconds. The conductivity values after 3 minutes were comparable to those obtained from conventional radiation-conduction-convection heating.

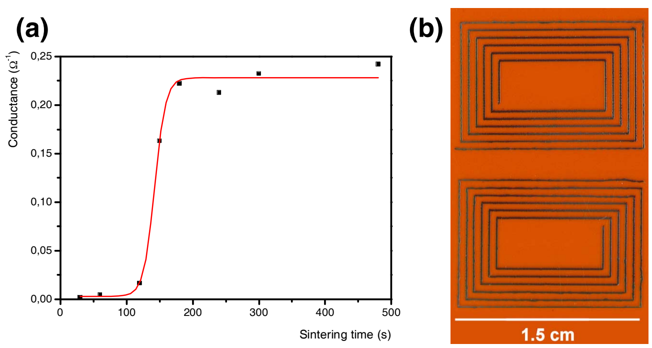

Figure 7. Conductance as function of time for the microwave sintering of silver tracks (a) printed onto a polyimide substrate (b).

Figure 8 displays typical Scanning Electron Microscopy (SEM) images of inkjet printed silver tracks consisting of nanoparticles. The image depicted on the left was taken before sintering, where the individual nanoparticles with a diameter between 20 and 50 nm are visible. The image on the right hand side shows the track after microwave sintering and it can be seen that the particles have merged into larger clusters, indicating a percolating and conductive pathway throughout the track. Moreover, the presence of voids explains the rather low conductivity of the tracks after sintering.

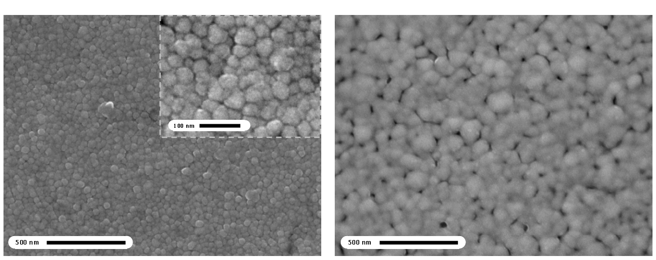

Figure 8. Scanning electron microscopy (SEM) images of inkjet printed silver nanoparticles before (left) and after (right) microwave sintering.

Conclusions

It was shown that inkjet printing can be used for the precise deposition of silver nanoparticle into three dimensional lines in a high resolution, either directly printed or by combination of a substrate that was patterned prior to printing by hot-embossing. After inkjet printing, the structures need a sintering step in order to render the particles conductive. Various techniques were discussed, including sintering by LASER beam and by microwave radiation.

By a combination of inkjet printing conductive nanoparticulate inks and microwave sintering, patterns of conductive features can be realized in a reduced amount of steps, reducing both time and waste, when comparing to standard and expensive lithography methods. Moreover, this combination introduces the possibility for the production of flexible electronics in a roll-to-roll (R2R) manner.

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Author Biography

Jolke Perelaer received his MS in chemistry from the Utrecht University (the Netherlands, 2004), with a major in organometallic chemistry and minors in physics and NMR-spectroscopy. In 2005 he started a PhD within the group of Professor Dr. Ulrich S. Schubert (Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology). His research focuses on inkjet printing of conductive materials, such as silver nanoparticles, onto polymeric substrates. Furthermore, he investigated selective and alternative methods to sinter these materials.