Microwave Flash Sintering of Inkjet-Printed Silver Tracks on Polymer Substrates

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Within the last few decades inkjet printing has grown into a mature noncontact patterning method, since it can produce large-area patterns with high resolution at relatively high speeds while using only small amounts of functional materials.[1–3] The main fields of interest where inkjet printing can be applied include the manufacturing of radio-frequency identification (RFID) tags,[4–6] organic thin-film transistors (OTFTs)[7–9] and electrochromic devices (ECDs)[10,11] and are focused on the future of plastic electronics.[12]

In this contribution, we present a study on antenna-supported microwave sintering of conducted features on polymer foils. We show that it is possible to create conductive printed features with microwave radiation within 3–4 min.[21] However, the main reasons for successful heating of metallic particles through microwave radiation, i.e., inductive coupling, is mainly based on Maxwell–Wagner polarization, which results from the accumulation of charge at the materials interfaces, electric conduction, and eddy currents.[25] However, the main reasons for successful heating of metallic particles through microwave radiation are not yet fully understood.

In contrast to the relatively strong microwave absorption by the conductive particles, the polarization of dipoles in thermoplastic polymers below the $T_g$ is limited, which makes the polymer foil’s skin depth almost infinite, hence transparent, to microwave radiation. Therefore, only the conductive particles absorb the microwaves and can be sintered selectively. Recently, it has been shown that it is possible to create conductive printed features with microwave radiation within 3–4 min.[21] The resulting conductivity, however, is only approximately 5% of the bulk silver value.

In this contribution, we present a study on antenna-supported microwave sintering of conducted features on polymer foils. We...
inkjet printed antenna structures using a colloidal dispersion of silver nanoparticles onto a flexible polyethylene naphthalate (PEN) foil (see Fig. 1a for the template). The template consists of four metal areas, each having a surface area of 11 mm².

Subsequently, curing of the antenna structures was performed at 110 °C for 60 min. These antennae were used both to measure the resistance of the single ink line and to capture electromagnetic waves. After this, a single silver ink line was printed over the metallic probes (black line in Fig. 1a) and quickly cured in an oven for 1–5 min at a temperature of 110 °C. This relatively short time was chosen to stimulate solvent evaporation, but to minimize thermal curing. After this treatment, the single line had a relatively high resistance in the order of 10² to 10⁴ Ω. The sample was subsequently exposed to microwave radiation for at least 1 s, while applying the lowest set-power of 1 W. This resulted in a pronounced decrease of the resistance of which the exact outcome depends on the initial resistance.

The antenna effect, which reflects the capability to absorb microwaves into the material, was studied systematically by altering the surface area of the electrodes of the template. When increasing the size of the electrodes a rapid decrease of the resistance after microwave exposure was revealed, as is shown in Figure 1b and c for pre-dried samples. This may be explained by the improved absorption of the microwaves due to an increased surface area of the electrodes.

The antenna effect, however, is larger when the initial line resistance is small (Fig. 1b), which is likely due to enhanced heat conduction from the electrodes to the ink line. For ink lines with an initially large resistance (Fig. 1c), the energy transfer is still very effective, although the total antenna area has less impact on the final resistance. The data obtained in the absence of antennas (A = 0 mm²) clearly demonstrate that the energy absorption by the printed line is negligibly small. The absorption of microwave radiation may be improved by the presence of antennae due to a subsequently smaller impedance mismatch between air and sample. According to Zuckerman et al. the intrinsic impedance Z of a circuit relative to free space is given by

\[ Z = Z_0 \sqrt{\varepsilon_r} \]  

where \( Z_0 \) is the impedance of the free space (\( Z_0 = 377 \, \Omega \)) and \( \varepsilon_r \) is the complex permittivity of the circuit relative to free space. The complex permittivity is related to the dielectric constant and loss factor according to

\[ \varepsilon_r = \varepsilon' + i\varepsilon'' = \varepsilon' + i\frac{\sigma}{\omega \varepsilon_0} \]  

where the real part \( \varepsilon' \) is the ability of the material to store energy and where the imaginary part \( \varepsilon'' \) accounts for the losses via energy dissipation. The reflection, i.e., impedance mismatch \( Z/Z_0 \), scales with the square root of the complex permittivity \( \varepsilon_r \) and thus, in our experiments, with the resistance of the electrodes, which depends on their total surface area.[27]

Figure 2 depicts the effect of the initial resistance of the printed line on the final resistance after microwave exposure for different times. When the flashing time is equal to 1 s, the resistance can be decreased to a few Ohms per line, only if the initial resistance is within a range of \( 10^2 \) to \( 10^4 \, \Omega \). Above a threshold if \( 10^5 \, \Omega \), the microwave coupling and transfer at the antenna-line interface is insufficient to accomplish pronounced sintering of the nanoparticles and to form a percolating network through the line.

Figure 1. Schematic representation of the printed template (a) with four silver electrodes/antennae in gray and a single silver line inkjet printed on top of the antennae in black. The total length of the line is 1.6 cm. Influence of the total surface of the four electrodes on the template for an initial line resistance of 100 Ω (b) and 1 kΩ (c) on microwave flash exposure for 1–60 s.
Therefore, longer sintering times are necessary for lowering the resistance. As shown in Figure 2, an exposure of 60 s increases the initial threshold resistance from $10^5 \Omega$ up to $10^7 \Omega$. Moreover, higher power settings and/or longer exposure times would even further increase this threshold value.

To highlight the effect of the surface area of the ink line on the final resistance, lines were inkjet printed onto the foil with modified surface wetting properties, while using equal print settings to dispense the same volume of material. On the one hand, the surface wetting was decreased by increasing the platen temperature to 60 °C, which stimulates solvent evaporation and therefore results in a different line geometry.\cite{3,28} On the other hand, a plasma surface treatment was applied to increase the surface energy, which improves the wetting behavior of the ink, and consequently gives broader lines. The line width was measured to be 172 and 161 μm for lines printed at room temperature and 60 °C, respectively, while after plasma treatment the lines were 353 μm in width. Figure 3 shows the effect of the line width on the resistance after microwave flash exposure. It can be inferred that a narrow line shows a three times higher resistance than a broad line for sintering times shorter than 10 s. This suggests that there is a positive correlation between surface area of the line, which is directly linked to the line width, and the amount of energy absorbed. However, this surface effect diminishes after 30 s of microwave exposure. This indicates that the surface area of the electrodes mainly determines the effective sintering time.

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 $\rho = R \cdot A/l$. The maximum conductivity ($1/\rho$) for the maximum surface area (44 mm$^2$) of the antennae was found to be 34% when compared to the theoretical value of bulk silver. The lowest revealed conductivity was 10% for the antennae with a surface area of 20 mm$^2$. This value, however, is significantly larger than the 5% that was reported previously for microwave sintering.\cite{23}

Scanning electron microscopy (SEM) images of the printed silver tracks in Figure 4 show the morphology and particle packing within the line before and after sintering. In Figure 4a, a close-up of the unsintered but pre-cured track is depicted, where the silver nanoparticles with a typical diameter of 30–50 nm can still be distinguished individually. Upon drying, the particles probably have lost a part of their organic protecting shell, which causes the particles to form a percolating pathway for the electrons in an early stage.\cite{16} After microwave flash exposure most of the organic material has been removed and the particles...
have merged, i.e., sintered, into larger agglomerates – as shown by the cross-section in Figure 4b. In Figure 4b, the bottom part is the polymer foil and the top layer is the as-printed silver line, which is depicted in more detail in the inset. It can also be seen that the agglomerates form a relatively dense packed layer of silver, which increases the amount of percolating pathways for the electrons through the line. This also explains the relatively high conductance values of 34%.

Since it is mainly the antenna that directs the electromagnetic microwaves to the target structure, sintering should also take place when the antennae are in the vicinity of the target structure, instead of in direct contact. Therefore, additional experiments were performed where a single line was inkjet printed between the antennae without making contact to the antenna structures. After exposure to microwave radiation for one second the line showed pronounced sintering, but the conductance was found to be lower than when a direct contact mode was used. Again, the total surface of the antennae determines the amount of sintering that takes place, where larger antennae structures lead to an enhanced effect.

In conclusion, we have shown that flash microwave sintering of inkjet printed colloidal dispersions on thin polymer substrates strongly depends on the total antenna area, the pre-curing time, and the geometry of the line. The presence of conductive antennae unambiguously promotes nanoparticle sintering in pre-cured ink lines, to an extent that depends on the total area of the antennae. This antenna effect is more pronounced if the ink line already exhibits conductivity. We believe this is due to the decreased mismatch between the impedance of air and sample. Using metal antennae, we have found that 1 s is sufficient to obtain pronounced sintering by microwave heating. The degree of sintering for these short exposure periods, however, strongly depends on the total resistance of the pre-cured ink lines. Furthermore, increasing the width of the lines enhances the initial conductivity raise due to improved energy absorption as a result of the increased surface area.

After microwave flash sintering, the tracks revealed conductance values of 10 to 34% when compared to the theoretical value of bulk silver, which is significantly higher compared to conventional heating methods. The procedure of printing and subsequently microwave flash sintering can be used in production of conductive features with low materials usage on common polymer substrates in printed electronics, such as large area fabrication of RFID tags or solar cells. Its major advantage pertains to both the high process speed and the low processing temperature, which reduce processing costs, as common polymer foils like PEN can be used.

**Experimental**

A silver nanoparticle dispersion in an ethylene glycol/ethanol mixture was purchased from Cabot (Cabot Printing Electronics and Displays, USA). The silver ink contains 20 wt% of silver nanoparticles, with the particle diameter ranging from 30–50 nm. The viscosity and surface tension of the ink were 14.4 mPa s and 31 mN m \(^{-1}\), respectively. Transparent, colorless polyethylene naphthalate (PEN, DuPont Teijin, The Netherlands, 125 μm thickness) film with a glass transition temperature of 120 °C was used as substrate material. Prior to printing, the foils were cleaned with ethanol. A template for four-probe resistance measurements was printed onto the foil, as displayed in Figure 1a, and heated in an oven for 60 min at 110 °C.

Plasma treatment was performed using a Branson IPC S2100/11220 apparatus with a 2000 Ti controller, operating at a frequency of 13.56 MHz. The power and time were set to 600 W and 1 min, respectively, and nitrogen was used as carrier gas (500 mL min \(^{-1}\)).

Inkjet printing was performed using a piezoelectric Dimatix DMP 2800 system (Dimatix-Fujifilm Inc., USA), equipped with a 10 μL cartridge (DMC-11610). The print head contains 16 parallel squared nozzles with a diameter of 30 μm. The dispersion was printed at a voltage of 28 V, using a frequency of 20 kHz and a customized waveform. The printing height was set to 0.5 mm, while using a dot spacing of 20 μm.

The as-printed structures were sintered in capped reaction vials using the Biotage Initiator monomodal microwave system, operating at frequency of 2.45 GHz, which corresponds to a wavelength of 12.2 cm. The used monomodal microwave did not show an influence on the vertical rotation of the sample. However, there is a dependency of the vertical placement within the microwave chamber to the absorption of the microwaves. Therefore, all samples were placed exactly in the center of microwave chamber. The power was set to its minimum of 1 W. Surface topography, thickness and cross-sectional areas of the printed silver tracks were measured with an optical profilometer (Fogale Zoonsurf, France). Scanning electron microscopy (SEM) images were taken using a FEG E-SEM XL30 (Philips, The Netherlands).

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