Structuring of flexible substrates by the use of an aqueous solution based silver ink

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Abstract

Inkjet printing of conductive tracks is a major research topic for electronic applications. In this context silver is a widely used material. Especially the printing of silver tracks onto flexible substrates is of high interest but is often limited by the temperature applied in the post process. For many silver inks, the required temperatures to obtain metallic silver are much higher than the glass transition temperature of the substrate and thus the substrate is not applicable. Furthermore, nanoparticles in silver inks tend to clog the nozzles of inkjet printheads.

We herein present an ink system, based on water soluble metal-organic molecules with high silver content. The ink transforms rapidly to elemental, conductive silver films at a temperature of 220 °C in only a few minutes. The physical properties of the solution are suitable for the inkjet technology. In addition to ink and printing characteristics, alternative approaches for the conversion of the silver ink with lower temperature induced stress on the substrate are discussed.

Introduction

The use of inkjet printing technology and other printing techniques as alternative deposition methods for functional materials has been generally accepted and applied in the field of production engineering. An important material in the area of printed electronics is silver, as it exhibits high conductivity and reduced influence of corrosion due to the formation of conductive oxides. Two basic concepts for processing silver in a liquid state are established.

Stabilized nanoparticles may be dispersed in organic solvents [1,2] or water [2]. Particles, however, can clog the nozzles when their diameter exceeds 5 % of the nozzle diameter. Relatively high temperatures with respect to the underlying substrate are needed for sintering of the stabilized particles. A second alternative is the synthesis of a silver dye ink, i.e. the solution of a silver-containing molecule in an adequate solvent. For using flexible, low-cost substrates like PET (polyethylene terephthalate) the conversion, or the so-called sintering temperature, is critical for the process. One way to approach this problem is to design inks with low sintering temperatures, but also means to selectively couple energy into the ink may be utilized.

Microwave dielectric heating has been proposed as an alternative and selective way of applying energy to an inkjet-printed pattern and activate sintering. [3] The interaction of a non-magnetic material with an electromagnetic wave is characterized by the complex permittivity ε of the material

$$\varepsilon = \varepsilon' + i\cdot\varepsilon'' = \varepsilon' + i\cdot s / (\omega\cdot\varepsilon_0) \quad (1)$$

where ε´ accounts for energy storage and ε´´ relates to dissipation of energy. s denotes the conductivity of the material, ω the angular frequency and ε_0 the vacuum permittivity. As the complex permittivity is characteristic for any given substance, selective heating may be accomplished by tailoring the loss characteristic as well as the as the incident electromagnetic wave.

Exposure of printed silver structures to ultraviolet radiation (UV) is also an alternative low-temperature sintering method for silver inks. [4] Radiation or light-induced decomposition may be used to trigger the release of the central metal ion of the complex, as the bond strength to the metal is weaker that in the organic framework. Irradiation may furthermore initiate decomposition of the organic moiety or the generation of heat due to the strong absorption of the ink in the ultraviolet region. The energy of the incident radiation has to be greater than the strength of the bond to be decomposed. The energy E is given by

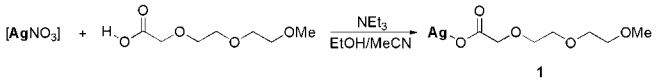
$$E = h\cdot c / \lambda \quad (2)$$

where h is Planck's constant, c is the speed of light and λ is the wavelength of the incident electromagnetic wave. High intensity UV lasers have been widely used for ablative photodecomposition and supply according to Equation (2) reasonable energies. In the here undertaken studies, low intensity UV radiation was investigated as a potential reduction method for the contemplated ink.

We synthesized a silver complex, $[AgO_2C(CH_2OCH_2)_3H]$ (**1**) [5,6], which is soluble in water. After determination of inkjet relevant properties we printed it with a piezo inkjet system onto glass, PET and PI (polyimide), characterized the layer properties and studied the conversion methods of thermal decomposition, microwave sintering and UV exposure.

Silver Ink Synthesis and Properties

A complex $[AgO_2C(CH_2OCH_2)_3H]$ (**1**) [5,6] was used as precursor molecule. This can be synthesized by the reaction of $[AgNO_3]$ with $HO_2C(CH_2OCH_2)_3H$ in presence of triethylamine dissolved in a mixture of ethanol-acetonitrile (20:1, vs/vs) at room temperature (Equation 3). To obtain pure **1** with a 94 % yield the addition of an excess of carboxylic acid is necessary. [6]



(3)

The structure of **1** in the solid state shows a coordination polymer (Fig. 1) in contrast to the low aggregated compound in solution.

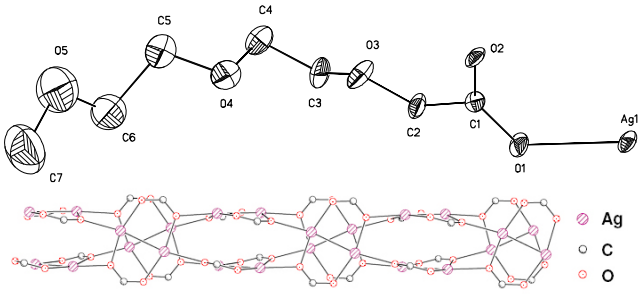


***Figure 1**. Structure of **1** in the solid state (30 % probability level) (top) and the formed D3 network by Ag-O and Ag-Ag interactions (bottom; the atoms C2-C7 and O3-O5 are omitted for clarity) [7]*

The thermal decomposition of **1** was studied by ThermoGravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) to determine the decomposition temperature of the silver salt. The plots are shown in Figures 2 and 3. Experiments were conducted at atmospheric pressure under a nitrogen atmosphere. The thermal degradation starts at 210 °C and is completed above 330 °C. [5] Measurements were carried out under ambient conditions, whereby the decomposition was already finished at 220 °C. Stagnation in weight loss results in a residue of 39.5 % of silver in the TGA pan. This amount is comparable to the theoretical percentage of metallic silver present in the complex.

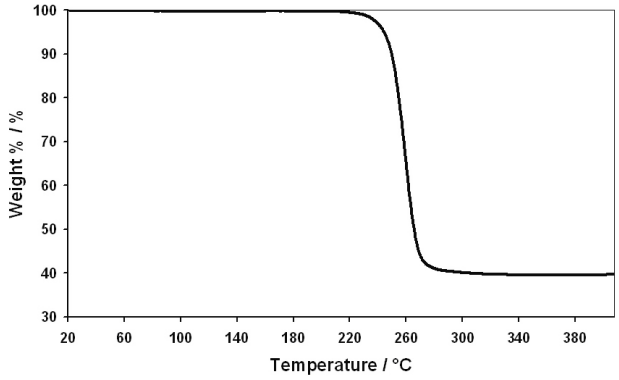


***Figure 2**. TGA of $[AgO_2C(CH_2OCH_2)_3H]$ (heating rate 8 $Kmin^{-1}$, nitrogen atmosphere, 20 $dm^3\ h^{-1}$) [5]*

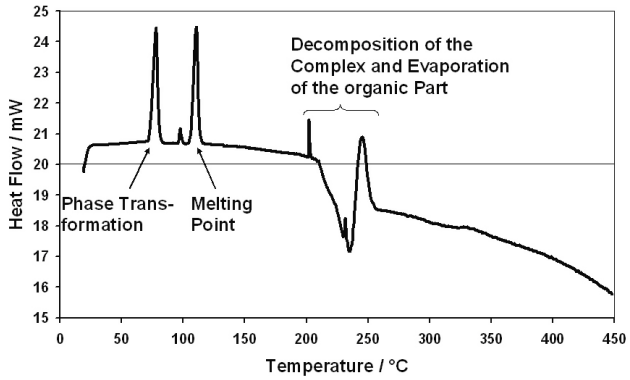


***Figure 3**. DSC traces of $[AgO_2C(CH_2OCH_2)_3H]$ (heating rate 8 $Kmin^{-1}$, nitrogen atmosphere, 20 $dm^3\ h^{-1}$) [5]*

The DSC trace shows the endothermal and exothermal-/ endothermal-overlapping processes in the temperature range of 25 to 450 °C (Fig. 3).

A mass fraction of 23 % of **1** was dissolved in water. This yields an ink with a silver content of 9.1 %. At 20 °C the silver ink has a viscosity of 1.7 mPas and a surface tension of 59.9 mN/m. The solution of **1** is particle free and is with the aforementioned characteristics suitable for piezo inkjet printing.

Experimental

A Dimatix Materials Printer DMP 2831, equipped with a 10 pL printhead was used for printing experiments. A customized waveform with a maximum voltage of 16 V was applied. Printing was carried out heating neither the printhead nor the substrate. Figure 4 shows the droplet formation at one nozzle. After 45 µs a stable spherical drop is formed.

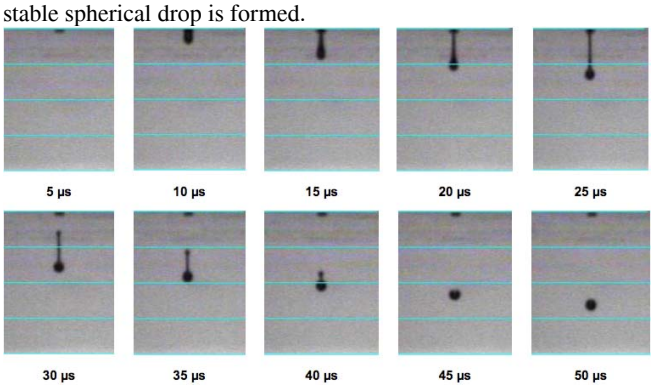


***Figure 4**. Drop formation of the silver ink at the nozzle of the DMP 2831 (pulse width 6.5 µs)*

Thermal decomposition of the printed ink to metallic silver was carried out using a heating plate at 220 °C for 30 s. In contrast to heating under a nitrogen atmosphere a fully conversion could already be accomplished at this temperature.

Initial experiments on microwave processing have been carried out using a commercially available microwave chemistry system (*Biotage Initiator*). Forwarded power could be controlled within 50 to 300 W. The samples were placed in a reaction vial designed for 5 mL of fluid.

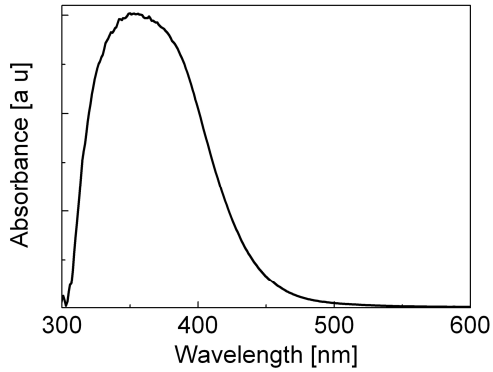


***Figure 5**. Absorption spectrum of $[AgO_2C(CH_2OCH_2)_3H]$*

The UV-Vis spectrum of the ink, depicted in Figure 5, shows high absorbance in the UV region. We irradiated printed structures

with a UV lamp *Delolux 06* (emission spectrum 325 to 600 nm) with a lamp to sample distance of 20 cm. To promote the decompostion the sample was additionally heated by a heating plate to 135 °C.

To evaluate the adhesive strength to the silver layers to the substrate tape tests of the thermally treated deposits on glass and PI and alternatively sintered samples on PET have been carried out.

The printed structures were laminated thrice with commercial adhesive tape (*Tesa Film*) and peeled off after a few seconds. The area coverage of the residual silver layer is an indication of the degree of adhesion strength of the converted silver salt on the substrate.

Results and Discussion

Figure 6 shows a dried silver ink droplet on a glass surface. It has a diameter of 50 µm and appears with a distinct donut shape due to the coffee ring effect. i.e. evaporation mediated deposition of the silver salt in the outer region. [8] This effect is critical for the fabrication of functional layers by means of inkjet technology. [9,10]

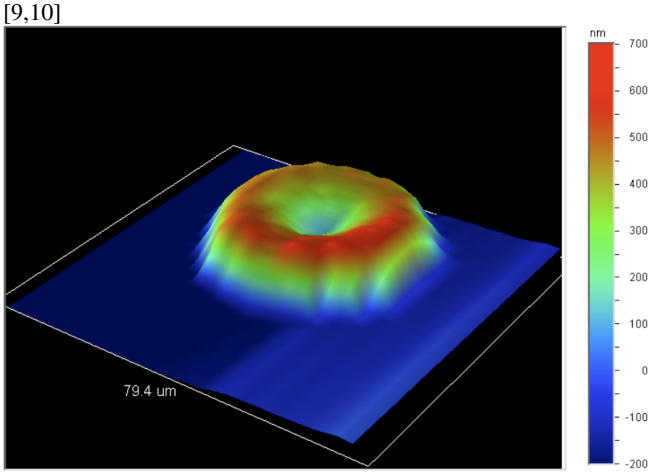


***Figure 6**. 3D image of an inkjet printed and dried droplet of [AgO2C(CH2OCH2)3H] (taken by a profilometer Veeco Dektak 8)*

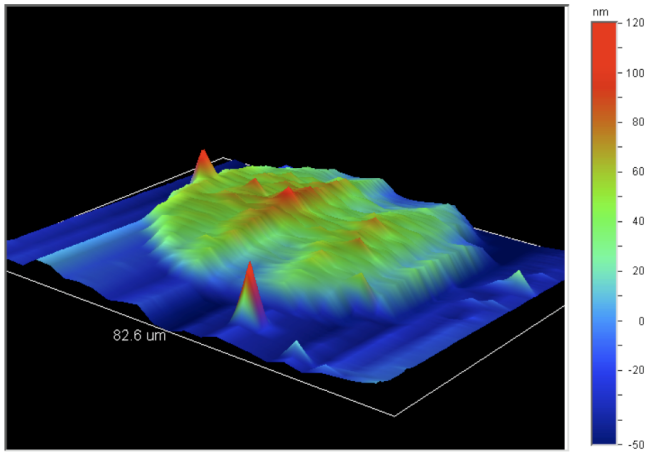


***Figure 7**. 3D image of a thermally converted inkjet printed drop (taken by a profilometer Veeco Dektak 8)*

Compared to non-treated drops the coffee ring effect was not observable at the converted drops (cf. Fig. 7). A single silver drop has a homogenous height of 100 nm. The diameter increases to 63 µm.

For solid areas of silver a drop spacing was adjusted to be 20 µm. Single sintered silver layers exhibit an average thickness of 190 nm varying between 100 and 250 nm on glass and between 0 and 300 nm on polymer substrates.

The electrical conductivity of thermally treated silver structures was at $19 \cdot 10^6$ Sm^{-1} on glass and $13 \cdot 10^6$ Sm^{-1} on PI. Compared to the conductivity of bulk silver ($67.1 \cdot 10^6$ Sm^{-1} [11]), these are 27.7 % (glass) and 19.3 % (PI), respectively. According to literature, acceptable conductivity values reached using inkjet printed silver structures are 5 % [3], 23 % [12] and 80 % [13].

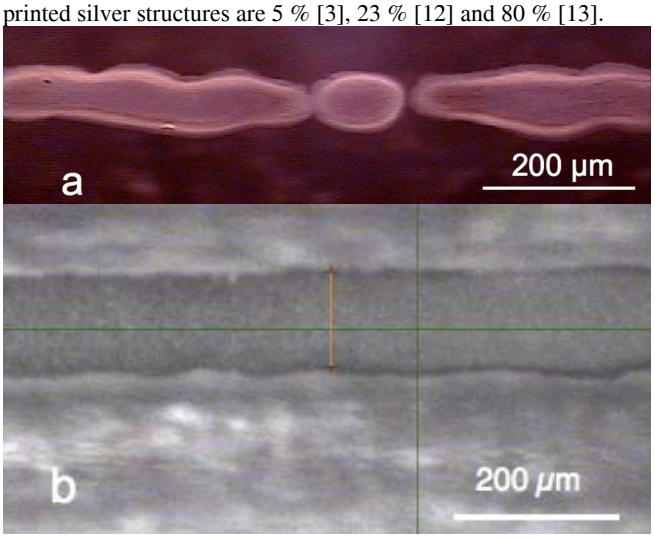


***Figure 8**. a) Disconnected track consisting of a single row of drops on glass, b) track consisting of 5 drops in line width (on glass)*

Tracks were printed in order to achieve structures, as narrow as possible, without any pre-structuring of the substrate. A line consisting of single drops has at least the width of the drop diameter, i.e. 63 µm. However, due to the high surface tension of the ink drops tend to merge as a result of dewetting into each other and thereby depart from their targeted position. This discontinuity interrupts the conductivity of the track (cf. Fig. 8a). It was found that tracks need to consist of at least 5 droplets in a row, in order to be connected safely and to show a constant line width. Figure 8b shows a light microscope image of such a track with a width of 150 ±5 µm. A reduction of the ink's surface tension could possibly lead to better results, concerning minimum width of conductive tracks. On the other hand, the necessary addition of surfactants may negatively influence the conductivity of the converted silver, with respect to the stability of the metal-organic complex, chemical degradation and absorption spectra. Investigations on the improvement of the surface tension will be subject of future research activities.

Microwave experiments were conducted on ink samples deposited on PET and glass substrates, which were allowed to dry on air. The forwarded powers as well as processing time were systematically altered within 150 W to 300 W and 60 s to 1,800 s, respectively. No conductivity was achieved on samples processed

at low power (< 250 W) or short processing times (≤ 240 s at 300 W). Visual inspection of the deposit after the treatment revealed a bluish appearance, which is characteristic for the presence of nanoparticles, indicating the reduction of the metal from the complex and thermodynamically driven growth into larger agglomerates (*Ostwald* ripening). Processing times greater than 300 s at 300 W showed a clear change in the visual impression from a transparent deposit into a silvery colored track of the deposit on glass, suggesting the sintering of the material. The highest conductivity achieved was 3.5 % of the value of bulk silver. The application of high power and long sintering times on PET samples, resulted in the deformation and melting of the foil. As the silver salt reduces to metallic silver and larger conductive structures emerge, microwave power increases as a consequence of the rise of conductivity (cf. Eq. 1). This enhanced power dissipation generates high temperatures that locally exceed the glass transition temperature of the foil and thereby contort the sample.

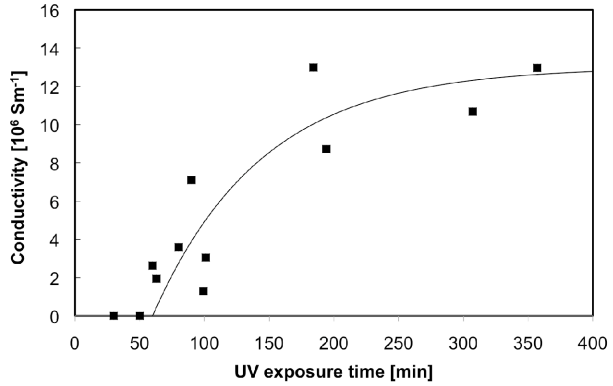


***Figure 9**. Electrical conductivity vs. UV exposure time with exponential fitting curve*

Printed samples on glass and PET were exposed to UV radiation. Figure 9 shows a plot of the conductivity vs. UV exposure time with an exponential fitting. On PET samples a relative conductivity of $2.6 \cdot 10^6$ Sm^{-1} is detectable after a sintering time of 60 minutes. The maximum conductivity was reached after 180 minutes and amounts $13 \cdot 10^6$ Sm^{-1} (21 % of bulk silver conductivity). It seems to be necessary to induce a certain amount of energy into the material to initiate the decomposition process. After an initial conductivity is reached it increases with increasing time and yields in a saturation conductivity. Therefore we assume an exponential correlation between conductivity s and UV exposure time t (valid for $t > t_i$)

$$s(t) = s_0 \, (1 - \exp \, [(t_i - t) / C]) \qquad (4)$$

where s_0 is the saturation conductivity, t_i the initial UV exposure time and C is a constant. For our experimental setup s_0 is $13 \cdot 10^6$ Sm^{-1}, t_i amounts 60 min and C is 84 min^{-1}.

The conversion method yielding the highest conductivities leads on glass to 27.7 % bulk silver conductivity within 1 minute. If a flexible substrate is desired, thermally sintered silver on PI results in high conductivity (19.3 %) on a short time scale (< 1 min). Thermal treatment as well as microwave sintering destroys the PET substrate. Even on glass microwave sintering only leads to low conductivities. Exposure to UV radiation also initiates the conversion process but does not harm the substrate like the aforementioned methods. Achievable conductivities are in the same range as thermal sintering for PI samples (21 %). However, a process duration of at least 3 hours is necessary to reach these values which is not applicable in industrial processes. Shorter conversion times could be most likely realized by application of more intense radiation.

The results of the tape tests are depicted in Figure 10. Samples on glass and PI were sintered thermally, while deposits on PET were converted via UV radiation. The sintered silver structures show poor adhesion to glass (23.3 %). After the first lift-off, approximately 70 % of the silver is attached to the tape. On the contemplated polymer substrates almost no material was removed by the tape and the structures were still conductive after the third lift-off, which is very advantageous for practical applications.

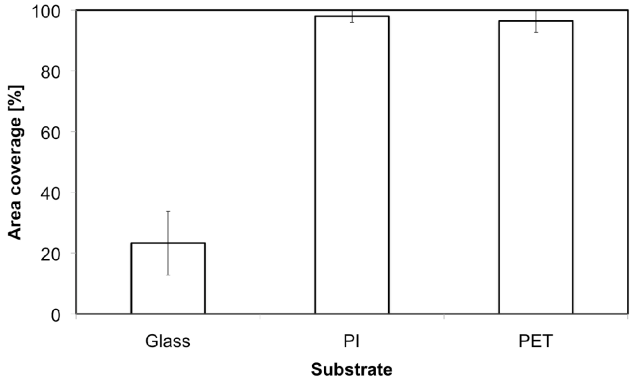


***Figure 10**. Area coverage after tape test*

Conclusion

We synthesized an aqueous silver ink based on metal-organic molecules with a silver content of 9.1 %. We proved the printability in an inkjet process with a Dimatix Materials Printer 2831. The prepared silver ink was printed onto glass, PI and PET and reduced to metallic silver by thermal decomposition, microwave sintering and UV exposure.

Printing tests have shown that we can generate conductive silver structures with a thickness of 190 nm and connected lines with a width of 150 µm.

With respect to sintering time and conductivity, thermal treatment shows the best results but it is not applicable for flexible low-cost substrates like PET. We found that UV exposure provides similar conductivities but at much lower temperatures but with much longer conversion times. Microwave sintering generally leads to conductivity within some minutes but is a very critical process due to the heat generation of already converted silver structures.

The tape tests showed very good adhesive strengths of the silver on polymer substrates like PI and PET.

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