Breaking the Limits of Line Width and Aspect Ratio for Inkjet Printed Conductive Lines by Controlling Post-Deposition Ink Contraction

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Abstract

Electrically conductive structures comprising both narrow line widths and high aspect ratios are indispensable components of many electronic devices. Producing them reliably on an industrial scale by inkjet printing of metal-based inks is a serious challenge. Firstly, due to spreading of the ink on the substrate, widths of 30 microns are currently the limit of any standard industrial inkjet technology. Secondly, the solid loads of conductive inkjet fluids are usually confined to a low volume fraction. Consequently, fine and high conductive structures are difficult to reach with single pass printing approaches.

Here we report on a method which circumvents these limits by employing specific changes in the ink-substrate interactions during solvent evaporation. Freshly printed lines have widths in the order of 100 microns. Upon drying, these structures reproducibly shrink to very narrow (< 25 micron), though still continuous and highly conductive lines with heights of several microns. This results in aspect ratios of up to 0.3, which are unprecedented for single pass inkjet printing.

We propose a mechanism for this process which involves the sequential evaporation of the ink's solvents according to their vapour pressures. Since their volatilities correspond inversely with their respective polarities, the effective polarity of the material remaining on the substrate will continuously increase. A continuous movement out of the wetting envelope of the substrate is the logical consequence, resulting in ever poorer wetting, increasing contact angles and line shrinkage.

Introduction

Precise control over ink-substrate interactions is a critical prerequisite to produce well-defined inkjet printed functional patterns [1]. This is especially relevant in the area of printed electronics, where even small irregularities can result in a significantly decreased device performance. A striking example is the manufacturing of electrically conductive structures using metal based inks for e. g. OLEDs, OPV cells and RFID tags [2,3]. In these applications, any short circuit or missing connection increases the risk of declining efficiency or even device failure.

Although the printed electronics industry cannot compete with traditional semiconductor technologies in terms of miniaturisation, producing ever narrower metallic lines is nevertheless an important objective. On the other hand, in order to guarantee a specified current transporting capacity, a certain cross-sectional area is necessary, which can only be achieved by compensating for the decreased width by means of increasing the height. Usually, single-pass inkjet printing of metallic conductive inks is limited to line dimensions below 1 micron height and widths above 40 micron [1,4]. As a consequence, inkjet printing usually produces structures with very low aspect ratios.

Here, we present an approach where we exploit the changing interactions during drying of a silver nanoparticle ink with a moisture barrier coating to produce extremely narrow lines with unprecedentedly high aspect ratios. Sequential evaporation of solvents in the ink gives rise to a continuous increase in polarity and a steady decrease in favourable ink-substrate interactions. As a consequence, controlled dewetting is observed, but without breaking of the lines into isolated droplets. Instead, the lines contract in a well-behaved manner to form conductive structures with high aspect ratios (width below 20 micron, heights up to 8 micron) without the need for multiple layer printing.

Experimental Part

Materials

Conductive ink (Suntronic U5714) was obtained from Sun Chemicals, UK. It is a concentrated dispersion (solid content 40 wt%) of silver nanoparticles (average diameter 30 - 50 nm) stabilized with a polymeric shell in a mixture of ethanol, 2-isopropoxyethanol, ethylene glycol and glycerol. The ink was filtered prior to printing using polypropylene syringe filters (Whatman GD/X) with a pore size of 450 nm. Glass plates were homogenously covered by inkjet printing with a 20 micron thick layer of an acrylate based organic coplanarization (OCP) coating provided by Huntsman, Cambridge, UK, which was cured by UV illumination and serves as a barrier material for organic light emitting diodes. Borosilicate glass (Eagle XG) was obtained from Corning Display Technologies, USA. Silicon nitride was supplied by Philips Research, The Netherlands, as a sputtered layer on PET foil. Poly(ethylene naphthalate) (PEN) foil (Teonex Q65FA) was purchased from DuPont Teijing Films, The Netherlands, all other polymer foils were obtained from Goodfellow Cambridge Ltd., U.K.

Processing

The ink was deposited on the substrates using a piezoelectric DMP-2800 materials printer from Dimatix-Fujifilm Inc., USA, equipped with a 10 pL cartridge (DMC-11610). The print head contains 16 parallel squared nozzles with a diameter of 30 μm. The dispersions were printed at a voltage of 20 V, a print head temperature of 30 °C, a frequency of 10 kHz and with a customized waveform. The printing height was set to 1 mm, while using a dot spacing of 20 µm and a substrate temperature of 22 °C. Line widths were set from 20 to 200 µm (corresponding to 1 to 10 pixels). After printing, the samples were thermally sintered in a Memmert hot air oven set to a predefined temperature.

Sample characterisation

Surface topography, thickness and cross-sectional areas of the printed silver lines were measured with an optical profilometer (Wyko NT9100, Veeco, Mannheim, Germany) and optical micrographs were taken using an optical microscope (DM 2500M, Leika, Wetzlar, Germany). Total surface free energies (SFE) of liquid samples and its polar and dispersive components were determined at room temperature using a Data Physics OCA20 apparatus. Fitting of the drop shape was carried out following the Laplace-Young method. Liquid densities were provided by the supplier. Surface characterization of OCP coated glass was carried out using a drop shape analysis system (DSA 100, Krüss, Hamburg, Germany), equipped with a hot stage (THMS 600, Linkam Scientific Instruments, Guildford, UK) and a calibrated temperature probe. Distilled water and diiodomethane were used as reference liquids. For room temperature measurements, a 5 µl drop was placed on the substrate and expanded with additional 5 µl on three spots on the sample. At elevated temperatures, the volume of the drop volume was increased frequently in order to compensate for evaporation. The data obtained were processed according to the method of Owens, Wendt and Kaelble, yielding the SFE components of the OCP. All other substrates were characterized at room temperature in a similar manner, using a Krüss Easydrop surface tension meter.

Results and Discussion

Line shrinkage phenomenon

When the silver nanoparticle ink Suntronic U5714 is printed on OCP-coated substrates, it wets the surface, forming well-defined lines which are about 2 – 3 times wider than the predetermined nominal widths from the printing pattern. This behaviour is typical for many conductive inkjet inks on plastic foils. Upon drying at elevated temperatures, however, a very uncommon effect is observed, namely the shrinkage of the lines by a factor of up to 8 compared to the original wet widths (Fig. 1). Depending on the temperature, this process can occur within a time of less than one minute. This contraction in the lateral dimension is compensated for by the formation of unusually high line profiles, compared to the structures formed under the same conditions on other types of substrates.

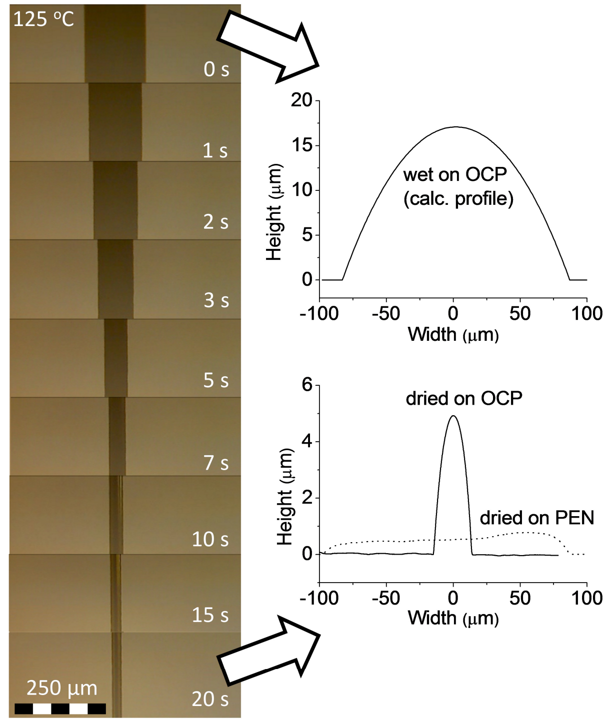

***Figure 1**. Lateral shrinkage of a silver ink line on an OCP surface in time. The graphic at right show the height profiles of the wet line (calculated based on the known wetting angle and ink volume) and of the dried and sintered line. For comparison, also a profile of the same ink on another substrate is shown.*

Investigating this effect in more detail, it was found that the contraction process is stable up to a certain nominal line width (up to 7 pixels). Up to that value, a linear dependence of both the wet and dry line widths on the nominal widths was observed (Fig. 2). For broader lines, irregular patterns were formed instead of well-defined straight lines.

Additional experiments revealed that the shrinkage process is highly dependent on temperature, proceeding faster and to a larger extent when going from 22 to 125 °C. On even hotter substrates, the speed further increases, but the degree of shrinkage achieved is less pronounced.

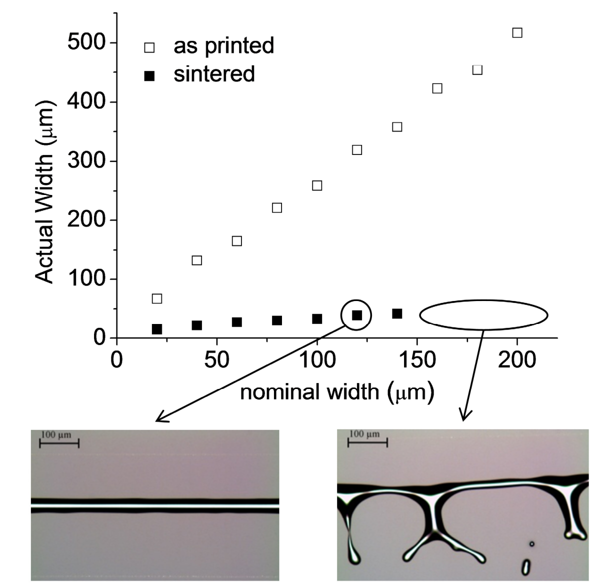

Figure 2. Dependence of the actual measured line widths for silver ink on OPC prior to and after drying. The images show well-defined and irregular structures, which are formed depending on the nominal line width of the printing pattern.

Proposed mechanism

The observed phenomenon of line shrinkage suggests a significant changes in ink-substrate interactions during the drying process. The wetting behaviour of an ink on a surface can be described by its position with respect to the wetting envelope of the substrate. When characterising the OCP substrate, it turned out that its wetting envelope was rather small compared to other types of common substrates, with the notable exception of PTFE (Fig. 3). When printing on these materials, no phenomenon comparable to the line shrinkage on OCP was observed. Upon drying, the lines kept their original widths; on PTFE, break-up into isolated droplets already occurred in the wet state.

The extraordinary behaviour of the silver ink on the OCP substrate hinted at a very particular interaction, the strength of which changed during the drying process. This suggested that the shrinkage process was linked to the evaporation of the volatile ink components. Analysing the ink composition it turned out that the silver nanoparticles are dispersed in a mixture of four solvents. Interestingly, their polarities increase in parallel with their boiling points and vaporisation enthalpies (Table 1).

As the solvents are expected to evaporate sequentially according to their respective volatilities, this will naturally lead to an ever increasing polarity of the liquid remaining on the substrate. As a consequence, a continuous movement from inside the wetting envelope out of it can be assumed (Fig. 4). This in turn will give rise to continuously less favourable ink-substrate interactions, increasing wetting angles and thus line contraction.

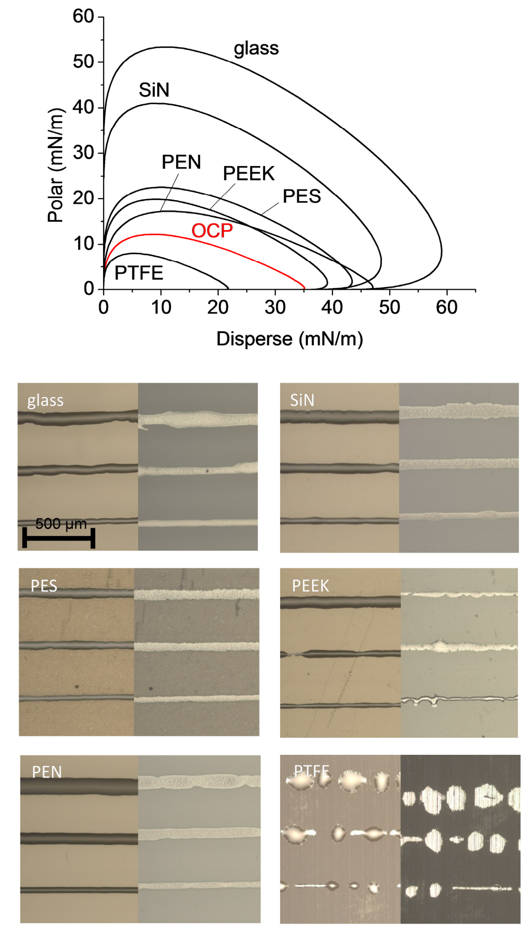

Figure 3. Wetting envelopes of various types of substrates (top). Optical micrographs of silver ink lines prior to (left) and after (right) drying at 125 °C on these substrates (bottom). The scale is identical for all images.

Table 1. Boiling points, vaporisation enthalpies and surface free energy (SFE) components of the four solvents present in the silver ink.

	T_b (°C)	ΔH_{vap} (kJ/mol)	Disp. SFE (mN/m)	Polar SFE (mN/m)
EtOH	78	42.4	17.5	4.6
2-IPE	142	50.1	23.6	5.0
ethylene glycol	197	65.6	30.9	16.8
glycerol	289	91.7	37.0	26.0

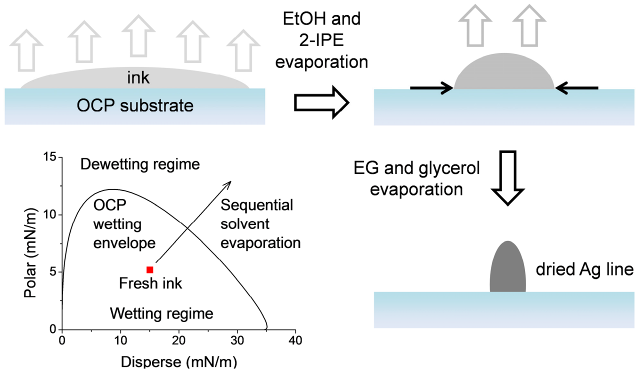

Figure 4*. Illustration of the proposed mechanism for line shrinkage of silver ink on OCP.*

Conclusions

A process is reported to produce very narrow inkjet printed line structures with high aspect ratios by exploiting the specific interactions between a particular type of silver nanoparticle ink and a barrier coating. Upon heating, sequential evaporation of the solvents in the ink occurs in the order of their respective volatilities. As a consequence, the polarity and surface free energy of the liquid remainder on the substrate continuously increase, inducing ever worse wetting and shrinkage of the lines in the lateral dimension. This is accompanied by a corresponding increase in height compared to lines where no contraction occurs. Additional research is necessary to determine whether this phenomenon can be used for the production of functional structures which can be applied in printed electronic devices.

References

[1] B. Derby, "Inkjet Printing of Functional and Structural Materials: Fluid Property Requirements, Feature Stability, and Resolution", Ann. Rev. Mater. Res., 40, 395 (2010).

[2] A. Kamyshny, J. Steinke, S. Magdassi, "Metal-Based Inkjet Inks for Printed Electronics", Open Appl. Phys. Journ., 4, 19 (2011).

[3] G. Cummins, M. P. Y. Desmulliez, "Inkjet printing of conductive materials: a review", Circuit World, 38, 193 (2012).

[4] T. H. J. van Osch, J. Perelaer, A. W. M. de Laat, U. S.Schubert, "Inkjet Printing of Narrow Conductive Tracks on Untreated Polymeric Substrates", Adv. Mater., 20, 343 (2008).

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