Inkjet Printing Silver-containing Inks

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Abstract

The fabrication of conductive silver tracks using Drop-on-Demand inkjet printing has been the focus of much research in the first decade of the 21st century. The appeal lies in inkjet's ability to produce patterns without using masks on a variety of substrates, with the goal being to produce highly conductive silver tracks on flexible, polymeric substrates. In order to achieve this, inks have been printed using silver nanoparticle suspensions, which require low curing temperatures. Inks that have been prepared from silver solutions have also been printed. This type of ink gives good conductivities (50% of bulk silver and higher) and can be chemically converted at room temperature, which allows low T_g *polymeric substrates such as PET (*T_g *75°C) to be used. This paper primarily discusses the obtained morphologies from the thermal, laser-assisted or chemical conversion of an inkjet printed silver solution ink.*

Introduction

An organometallic 'ink' has been prepared that can be better described as a solution since it is composed of a silver carboxylate dissolved into a simple organic solvent [1, 2]. However, it is frequently referred to as an ink on account of this being the common appellation applied to the liquid media that are used in inkjet printing. This ink has been used, in an inkjet printer, to draw patterns or circuits that have potential for use in electronic applications after processing is complete. The concluding step, in the fabrication of these patterns, is to convert the ink into metallic silver, which is usually achieved thermally.

The advantage of inkjet printing is the ability to place pre-determined amounts of a specified substance at desired locations. In essence, it allows one to put what one wishes, where one wishes, when one wishes. Inkjet printing is recognised as a direct-write technology that has eliminated the need for masks and has furthermore, enabled advances in the fields of rapid prototyping and layered manufacture, amongst others [3, 4].

The inkjet printer that was used for this study employs the drop-on-demand (DOD) technique; whereby droplet formation is initiated by applying a pressure pulse by actuation of a piezoelectric crystal to an ink-filled chamber, which has a small opening. This action results in the ejection of a column of ink from the orifice, which subsequently forms into a droplet due to the ink's surface tension. Inks must be formulated to fit the physical and rheological requirements of fluid flow in an inkjet printhead, especially when extending inkjet printing to other applications, with viscosity being the key factor. If the ink is too viscous then a large pressure pulse is needed to generate a droplet; whereas if the surface tension is too low the printhead generates satellites as well as the desired droplet [5]. These satellites drastically reduce the quality of printed feature resolution.

The goal of producing electrically conductive patterns, via the inkjet route, is predominantly driven by the desire to lower the processing temperature. This subsequently enables the use of a wider range of printable substrates [6]. Other reported research has described the use of silver nano-particles suspended in an organic carrier. These were thermally converted to conductive silver at temperatures of 300 °C [7, 8]. This thermal conversion temperature was significantly reduced to values as low as 150 °C by using a solution instead of a suspension [1]. Silver-based inks are frequently used because the resistivity of bulk silver is the lowest of all the elements [9]. Silver is more reactive than gold in that it forms a wider range of compounds for dispersion in organic solvents and unlike copper a careful control of the oxygen content in the processing atmosphere is not needed [10].

An issue, however, with thermal conversion is that in order to enable full metallic conversion it is necessary to subject the entire substrate to the thermal regime, regardless of whether a solution or a suspension was used. This seems a somewhat redundant approach since ideally one would prefer a far more localised heating of only the deposited ink and not of the entire substrate. Just such an approach has been undertaken in the fabrication of copper and gold interconnects using a diode laser [11]. Another approach would be to use a conversion process that avoids a heating step, allowing low T_g substrates, such as amorphous PET or PE, to be used. This paper reports on the thermal, laser-assisted and chemical conversion of an organometallic ink to produce conductive metallic silver, and the subsequent characterisation of the microstructures that resulted from the three different processing techniques.

Results and Discussion

Figure 1 shows the typical microstructure that occurs for a silver solution ink that has been thermally processed at 150 °C. It can be seen that the crystals are clustered together in a manner that forms structures that can be described as resembling millet sprays or ropes. This rope-like structure is seen to result as a consequence of thermal conversion. Since the ink is actually a solution it is thought that the silver-organic solute used undergoes a degree of dissociation in the solvent. After deposition the track is subjected to a heat treatment in order to enable conversion to silver. This causes the solution to lose solvent until the saturation concentration is exceeded and precipitation of the dissolved organometallic begins. This precipitate eventually forms a large interconnected structure. It is thought that some of the solvent remains attached to the precipitate as a liquid of crystallisation. With further heat and time, the organic component is removed via dissolution in the evaporating solvent and also as a result of decomposition.

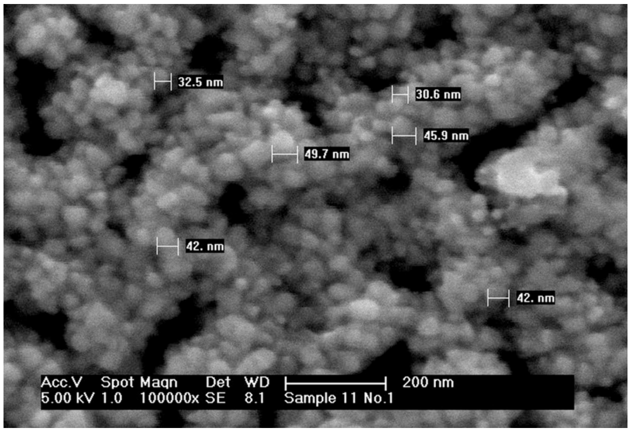

Figure 1. *A high-resolution micrograph of a track thermally converted at 150°C.*

A study of the TGA data can be seen in Figure 2 for both the salt and the solution. The mass loss has been normalised to allow for a more meaningful comparison. The plot for the salt shows the onset of mass loss occurring after 150 °C and being complete by 225 °C, whereas the plot for the solution begins much earlier at 100 °C and is complete by 200 °C. The plot for the solution shows a gradual loss of mass rather than a sudden loss of mass that would accompany decomposition and supports the idea that a significant amount of the organic component is removed via evaporation. These data also suggest that the millet-spray structures observed at 150 °C are a result of kinetics since the loss of mass is not over until 200 °C.

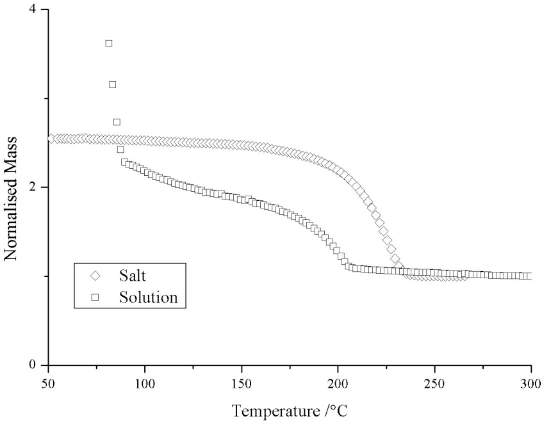

Figure 2. *A comparison of the thermal behaviour of the silver carboxylate salt and its solution.*

The remaining silver crystallites that are left behind form a structure that closely resembles the one that had previously been formed as a result of precipitation. In thermal conversion, the main factors that are thought to contribute to the observed structure are time and the fact the material is converted at a specific temperature. Time is an important factor since not only is the time the deposit spends at conversion temperature a factor but the time taken to reach conversion temperature and return to room temperature afterwards also need to be taken into account. The thermal conversion process takes much longer than the laser conversion, which is almost instantaneous.

The microstructure observed in Figure 3 is a high-resolution image of a laser-converted track. Whereas the particle sizes for the thermally converted track are between 30 to 50 nm, the particles shown in Figure 3, the laser converted track, have sizes between 40 and 70 nm, and larger particles can be seen. It is suggested that the microstructure evidenced by laser curing is a result of the high temperatures achieved by the laser and are therefore a result of thermodynamic processes. Crystallite formation also appears to have been more chaotic.

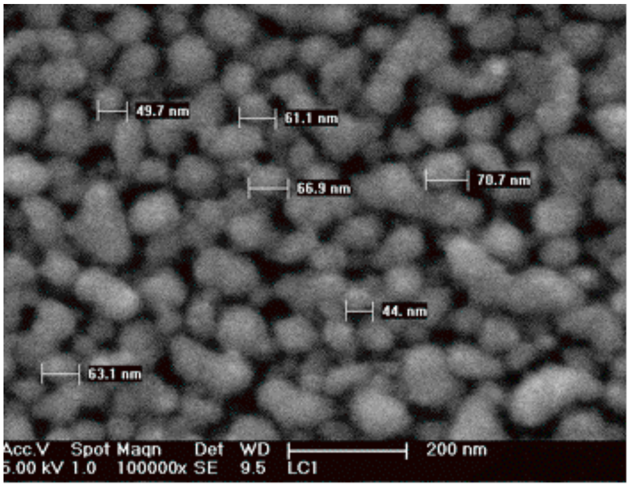

Figure 3. *A high-resolution micrograph of a laser-converted track.*

The image shown in Figure 4 is of a chemically converted silver track. The substrate used was PET, unlike the two previous conversions, which used glass as the substrate. The uniformity of crystal size is similar to the thermally converted tracks. It can also been seen that the particles are not as closely packed compared to those in Figure 1.

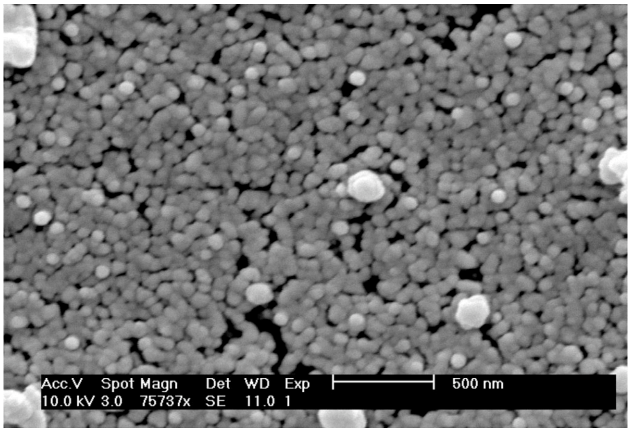

Figure 4. *A high-resolution micrograph of a chemically converted track.*

The particle sizes of the thermally converted tracks, the laser-converted tracks and the chemically converted tracks were measured and a graph of their average particle size is shown in Figure 5.

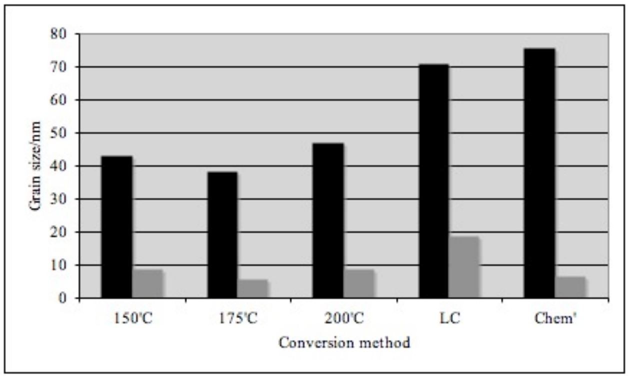

Figure 5. A graph comparing the average size, in nm, of the silver particles of tracks thermally converted at 150, 175 and 200 °C, tracks that were converted by laser (LC) and chemically converted tracks (Chem'). The smaller columns, which are coloured in grey, represented the standard deviation.

It can be seen, from the graph, that the particles in the laser-converted tracks are much bigger than those found in the thermally converted tracks. Furthermore, there appears to be no influence of conversion temperature on average particle size for the thermally converted tracks. However, it is worth noting that many of the particles in the track which was thermally converted at 200 °C display a needle-shaped morphology. The range of particle sizes for the thermally converted tracks was narrower than that seen for the laser-converted track. With a value of ± 8 nm being recorded for the standard deviation for the tracks that were thermally converted at 150 and 200 °C, ± 6 nm for the tracks at 175 °C and a value of ± 19 nm for the laser converted track. Remarkably, the particle sizes for the chemically converted tracks are the largest of the five samples, with an average size of 76 nm. The high level of uniformity of the crystal sizes is demonstrated by the low standard deviation of ± 6 nm.

Clearly the processing method used to convert the organometallic ink to silver influences not only crystal size but the distribution of the crystals as well. The conversion time used in laser processing is much shorter than that used in thermal processing. Also with the thermal processing route the substrate is also at temperature and this will take time to return to room temperature once it is removed from the oven. A further comment is that with thermal conversion the temperature experienced by organometallic ink can be known with a large degree of certainty. With the chemically converted tracks, the process takes under one minute yet produces larger crystals than for thermal conversion but which have a narrower size distribution.

When one considers the conductivities for the three methods, the values of the thermally converted tracks are the highest with measurements between 33 – 50 % bulk silver [1]. The chemically converted tracks have a conductivity of 10 % bulk silver [12]. The value of conductivity for the laser-converted tracks could not be determined with a great level of accuracy, although it has been estimated to be lower than the thermally converted tracks.

When one considers the microstructure of the thermally converted tracks it is not surprising that they are the most conductive given how tightly connected the particles are to each other. The microstructures for the other two methods are much "looser" in terms of packing.

Conclusion

An organometallic silver salt that was dissolved into xylene was inkjet printed onto glass substrates or PET substrates. These deposits were then converted to silver via one of three methods: thermally, via the application of a laser or chemically. The tracks' microstructures were then examined by scanning electron microscope and a difference was observed. The microstructure in the thermally converted tracks has a rope-like structure, with the crystals that make up the structure being tightly packed. The size of the crystals was about 40 nm and there was little variance in distribution of size. The crystals sizes in the laser-converted tracks were larger and their distribution was more uniform than for the thermally converted tracks. However, the crystals were packed more loosely. Similar loose packing was seen for the chemically converted tracks. However, the standard deviation of particle size for the chemically converted tracks was as narrow as for the thermally converted tracks. The values of standard deviation suggest that crystal formation for both the thermally and chemically converted tracks is less chaotic than for the laser-converted tracks.

Experimental

The silver ink used in this study was prepared by dissolving a synthesised silver carboxylate into a non-polar organic solvent, in this case xylene. The silver salt was synthesised following a procedure that was modified from that which was first described by Vest [13] and is described in further detail elsewhere [1]. The ink used in this study was analysed by thermal gravimetric analysis (STA 449C, Netzsch-Gerätebau, Selb, Germany) and found to contain a final silver content of 10 weight %. The ink's dynamic viscosity was measured under Couette flow using a concentric cylinder rheometer (Brookfield Rheometer, DV-III+, Brookfield Engineering, Middleboro, MA, USA) at shear rates from 60 to 250 s^{-1}, using a temperature controlled small sample adapter, set to 25 °C; and found to be 4.04 mPa·s, (standard deviation = 0.21). Surface tension was determined by the pendant drop method using conventional CCD imaging and dedicated image analysis software (Camtel FTA 200, Royston, UK) and found to be 0.028 $N \cdot m^{-1}$ (standard deviation = 0.0013). Both of these values fell within the parameters specified by MicroFab and the ink was therefore deemed to be printable [14].

The silver ink was printed using a 60-micron diameter piezoelectric printhead (MJ-AB-01-60, MicroFab Technologies Inc., Plano, TX, USA). The inkjet driving parameters, such as frequency, voltage and the pulse duration of the trapezoidal electrical pulses, which were used to excite the piezoelectric transducer, were chosen as a result of previous optimisation studies [1, 5, 6]. Printing experiments were performed using a single fixed printhead that could only move in the Z direction and a platform that moved in the X and Y direction, (Jetlab, MicroFab Technologies Inc., Plano, TX, USA). The tracks were obtained by synchronous drop ejection and translational movement, which is called vector drawing or plotting. All printing was performed at room temperature on glass substrates that had been cleaned with acetone.

The printed tracks intended for thermal conversion were placed into a temperature-controlled muffle furnace at either 150, 175 or 200°C, for 20 minutes in order to reduce the ink to silver. The tracks that were converted by laser were passed under a 200 mW Argon laser (Stabilite 2017, Spectra-Physics, Mountain View, CA, USA) using a manually-driven micrometer screw to move the substrate. The laser employed a 1 mm diameter, focused spot size set at a wavelength of 514 nm. The conversion occurred within less than a second. The tracks that were prepared at room temperature were processed following the procedure described elsewhere [12]. All samples were then characterised by scanning electron microscopy - SEM (6300 SEM, JEOL, Tokyo, Japan) to determine their morphology.

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Author Biography

After obtaining his Ph.D. from Cambridge University in 2001, Patrick Smith worked as a post-doctoral researcher for Brian Derby at Manchester University. In November 2005, he joined the group of Ulrich Schubert at Eindhoven as a project leader. In May 2007, he moved to the University of Freiburg to become an Assistant Professor in the group of Jan Korvink. His current research areas are rapid prototyping, silver-containing inks, droplet behaviour on the substrate and other inkjet-related research.